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ABOUT THE EDITOR



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After completing BSc (1985) and MSc (1987) in Physics at Ataturk University (AU), he completed his PhD (1993) on the characterization of defect centers based on microwave technologies, at the University of Manchester (UMIST-Electrical Engineering and Electronics). He won the UK's ORS awards (1991/92) due to his capacitance spectroscopy (C2-DLTS) experiments. He returned to Turkey in 1993 and became a faculty member as Associate Professor at AU (1994). He pursued post-doctorate studies on positron annihilation at the Center of Atomic Energy of Saclay-Paris. After he was appointed to full professorship position at AU (1999), he worked as a Fulbright Professor at the Ultra-Fast Spectroscopy Labs in the USA. He has been in the administration of AU as respectively Head of High Energy and Plasma Physics, Vice Dean, Dean, Vice Rector and Director of Techno-park, and also established the Eurasian Silk Road Universities Consortium (ESRUC) as the Secretary General, involving institutions from China and India to Italy and France. He was the Editor-in-Chief of Turk J Phys (2010-15). He is still the Editor-in-Chief of Asian Journal of Research and Reviews. While he is currently working at AU as a faculty member of solid state physics, he is the author of several Turkish translation books. Book Publisher International series and "The Quantum and Cosmic Codes of the Universe" published by Cambridge Scholars Publishing (2020). Along with his current studies on solar cells and gas sensors, he is presently conducting studies such as "quantum gravitation models" and "electronic behaviors in high gravity" in theoretical physics.

PREFACE

This book covers key areas of Physical Science. The contributions by the authors include nanopowder, metallic nanoparticles, magnetic field, ferromagnetic resonance, electrical conductivity, magnetic permeability, Transverse Electric Magnetic, raw cotton, pneumatic installation, aerodynamic force. static pressure, dynamic pressure, power consumption, pneumatic transport, non-baryonic dark matter, negative R p-parity, neutralino, electon-positron experiment, bulk metallic glass, MD simulations, MEAM potential, radial distribution function, glass forming ability, voronoi tessellation analysis, optoelectronic, XRD, XPS, dynamic SIMS, thermo-elasticity, polyurethane aerogels, scattering mechanisms, rayleigh scattering, mie scattering, thermal conductivities, long-term electricity consumption forecasting, kernel principal component analysis, inhomogeneity, schottky diode, Mo/n-type4H-SiC, field effect transistors, bipolar Junction Transistor, TiO₂ nanoparticles, visible-light photocatalytic activity, hydrothermal synthesis, photocatalytic activity, long-chain alcohols, interaction dipole moment, induced polarization, h-bonded complex, constant velocity, complex variable boundary element method, finite volume method, ideal fluid flow, computational fluid dynamics. This book contains various materials suitable for students, researchers and academicians in the field of Physical Science.

Extraction of Microwave Properties Using a Single Transmission Line: Application to Carbon Nanopowders Decorated with Magnetic Nanoparticles

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ABSTRACT

The microwave properties of carbon-based nanopowders, whether or not they are coated with magnetic nanoparticles, are characterized using a unique approach in this chapter. The microwave characterization of materials is of prime interest for several applications. Dielectric constant, electrical conductivity, and complex magnetic permeability, which are its microwave properties, are derived from tests with a single transmission line acting as the test cell. Successful tests were conducted on two different transmission line geometries. A phenomenological model is used to evaluate the measurement data and fit the conductivity and dielectric constant measurements, giving insight into the powder sample's compacity quality. Additionally, the discovery of a ferromagnetic resonance with a linear dependence on the external DC magnetic field supports the extraction of the permeability.

Keywords: Nanopowder; graphene; metallic nanoparticles; microwaves; magnetic field; ferromagnetic resonance.

1. INTRODUCTION

Materials are crucial components of microwave systems and proper and accurate measurement of their dielectric properties is important to aid a high level of accuracy in design. A material that has the capability of storing energy when there is an external electric field applied is classified as dielectric [1-3]. For many

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applications, the microwave characterisation of materials is of utmost importance. When designing various microwave devices, such as electromagnetic absorbers, attenuators, and resistors, electromagnetic constitutive parameters (complex permittivity and associated electrical conductivity, magnetic permeability) must be known. Different methods using various topologies have been proposed over the vears. The most commonly measured quantities are the reflection and/or transmission coefficient of the microwave signal in free space in presence of the material acting as a screen or a reflector; the resonant frequency and the loaded 0-factor of a resonator containing a sample of the material under scope; and the measurement of reflection and transmission coefficients at the end of a transmission line in which the material acts as a discontinuity. Waveguides, coaxial lines, and planar topologies are all possible test cells [4]. The microwave and millimetre-wave frequency range spans from approximately 300 MHz to 300 GHz, corresponding to wavelengths of 1 m and 1 mm, respectively [5,6]. At microwaves and millimeter waves, the permittivity is derived from the measured variation of the reflection coefficient [7] at the input of a shortened waveguide [8] or a resonant cavity [9] loaded by a solid sample. For liquids or powders, transmission lines combining reflection and transmission measurements are preferred: they use waveguides or TEM (Transverse Electric Magnetic) transmission lines, coaxial [10] or not [11,12]. Transmission line methods suffer from strong uncertainties when their length is multiples of halve-wavelengths since transmission and reflection measurements [13] or reflection measurements only [14], are used for extracting permittivity and permeability.

The various techniques listed above are nevertheless still used for powders beyond the '2000. In [15], a biochar powder dispersed in epoxy was molded into rectangular plates for measurement in a rectangular waveguide between 8 and 12GHz. In [16] the microwave characterization of lanthanum iron garnet-filled PVDF-polymer composite using rectangular waveguide was performed at X-band frequency. In [17], the dielectric properties of powders of PbTiO₃, dispersed in paraffin, were measured from 1MHz to 18GHz in coaxial mode using toroidal paraffin sample composites. A similar topology was used in [18] for characterizing barium-ferrite-coated fly-ash cenospheres. And in [19], the complex permittivity and permeability of rubber composites filled with carbonyl iron powder were measured at frequencies from 2-18 GHz using a free-space arch method. In [20], α -lactose monohydrate powder samples were inserted in rectangular sections ended by irises. Resonances observed in the measured transmission are exploited to extract the dielectric constant of the powder in the 8-10 GHz frequency range. In [21] a planar single circular ring resonator and a 4 coupled square rings resonator were measured in transmission in order to exploit their resonance for the extraction of the permittivity of food powder samples in the 1-3 GHz range. In [22], the microwave complex permittivity of activated carbon powder was measured using two different techniques, microwave cavity perturbation at 2.5 GHz and broadband coaxial probe in the frequency range between 10MHz and 10GHz.

A lot of work has been done previously by our team on the characterization of (nano)materials, but embedded in alumina [23,24] or polymer [25-27] template.

We recently extended our studies to the characterization of nanopowders themselves [28,29] and developed subsequently an efficient single-line method for their direct characterization, which is presented in this chapter.

To achieve a broadband characterization, we exploit here a property of the Line-Return-Line (LRL) method [30] that provides, as a by-product, the propagation constant of the line from which the permittivity ε_r is extracted [31]. Our formulation does not include reflection measurements and hence does not suffer from half-wave uncertainties. However, the propagation constant cannot discriminate between permittivity ε_r and permeability μ_r since it involves only their product. Permittivity ε_r can be extracted for non-magnetic materials only. Hence we propose to use a single line, successively measured twice: once empty and once filled with the material of interest. This combination enables to retrieve the sample's ε_r and μ_r parameters simultaneously, requiring the fabrication of a single line only.

The main originality of our work is that it allows us to extract the parameters of the sole nanopowder. In the literature, nanostructures are usually dispersed in an insulating polymer [32-36] or wax [37-39] matrix, and only the microwave properties of the whole nanocomposite mixture are retrieved. We study here decorated carbon-based nanopowders preferably to other powders precisely because there are no methods reported for their characterization in the microwave frequency range, and as part of a research project "Nano4waves" [40] aiming at developing carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) decorated with magnetic nanoparticles (MNPs) for the design of devices enabling the control of electromagnetic (EM) waves propagation.

Another originality of our method is to make the retrieval of ε_r and μ_r possible by exploiting two different features. Firstly, the permittivity ε_r is extracted by combining the empty line measurement with the measurement of the filled line under a high DC magnetic field. This ensures that the permeability of the material is equal to unity during the measurement. Secondly, the permeability μ_r is extracted from the combination of the measurement of the filled line under zero DC magnetic field and the prior measurement of the empty line.

Section 2 "Materials and methods" presents the synthesis of the nanopowders, the fabrication of the two transmission lines used for their microwave measurement, the characterization tools, and the extraction procedure for permittivity and permeability based on measurements of the empty and filled lines. Section 3 "Results" presents the phenomenological model for obtaining the complex permittivity of the nanopowder proposed in [25], which provides information on the compacity of the powder, and the permittivity and permeability extracted from the measurement of the empty and filled lines. Measured permittivity ε_r is assessed by the phenomenological model. Measured permeability μ_r is assessed by the detection of ferromagnetic resonance (FMR) following a linear dependence on an externally applied DC magnetic field and by a phenomenological model of the permeability. Section 4 concludes with the main features of this work.

2. MATERIALS AND METHODS

2.1 Synthesis of Nanopowders

This section describes the preparation of the nanocomposite powders under scope.

2.1.1 Pristine nanocarbon supports (NCS)

Three types of graphenic nanocarbon supports (NCS) were employed: graphene oxide (GO) and reduced graphene oxide (rGO) (both from Nanoinnova Technologies SL, Spain), and graphene nanoplatelets (GNPs, TIMCAL, Switzerland). These NCS were microwave characterized as received.

2.1.2 Decoration of graphene oxide (GO) with magnetic nanoparticles (MNPs)

Metallic zero-valent iron (ZVI) and nickel (Ni) nanoparticles (NPs) were deposited onto graphene oxide (GO). The synthetic methodologies employed will be briefly described below. In both cases, the engaged quantities aimed at a 50% metal/GO weight loading rate (LR). Corresponding TEM pictures are given in Figs. 1,2.



Fig. 1. TEM images of graphene oxide decorated with zero-valent iron nanoparticles (ZVI@GO) at different magnifications

2.1.3 Synthesis of ZVI@GO nanocomposite

The preparation of ZVI nanoparticles supported on GO was performed using a Pechini-type solgel method. In a typical synthesis, 50 mg of graphene oxide (GO), 180.8mg of iron (III) nitrate nonahydrate ((FeNO₃ • 9H₂O)99 + %, Across), 516mg of citric acid (CA, Analytical grade, Merck) and a magnetic stir bar were introduced in a small round-bottom flask. 3.3ml of ethanol (Technisolv, VWR) were added, the flask was closed with a septum and the mixture was stirred until

complete dissolution of the reactants. The suspension was then sonicated at 80 W for 1 hour (VWR ultrasound cleaner USC 1200-THD) in order to disperse GO. 112μ L of ethylene glycol (EG, Spectrophotometric grade, Alfa Aesar) were added and the suspension was heated with a reflux condenser in an oil bath at 90°C for 3 hours. The suspension was then poured in a porcelain combustion boat and placed in a drying oven under vacuum at 30°C for 2 hours. The obtained gel-covered ceramic plate was introduced in a tubular furnace (Carbolite Gero STF16, United Kingdom) and heated to 750°C for 2h under Ar/H₂95/5 atmosphere. The temperature was increased and decreased at a rate of 1.7 °C/min. The recovered powder was stored in air.



Fig. 2. TEM images of graphene oxide decorated with nickel nanoparticles (Ni@GO) at different magnifications

2.1.4 Synthesis of Ni@GO nanocomposite

GO was decorated with nickel nanoparticles using a one-pot solvothermal method. In a typical synthesis, 50mg of GO were dispersed in 40 mL of ethylene glycol (EG) and sonicated for 120 minutes in a VWR ultrasound cleaner USC 1200-THD at 80 W sonication power. 110mg of nickel (II) acetylacetonate (Ni(acac)₂, 95%, Sigma Aldrich) were then added to the above suspension under vigorous stirring. Subsequently, an aqueous 1MNaOH (Normapur, VWR) solution was added dropwise, under vigorous stirring, until a pH value of 10.5 was reached. After stirring for 45 minutes, the mixture was transferred into a 300 mL stainless steel autoclave vessel with a Teflon lining and heated at 190°C for 24 hours. The autoclave temperature was automatically regulated by a Parr 4836 temperature controller (Parr Instrument Company, USA) having an average heating rate of 4 °C/ min. The autoclave inner atmosphere was never purged nor modified in any manner during the synthesis, while the system pressure was left to build up during heating without any type of external control. Reaction solutions were continuously stirred at 300rpm while heating. When the reaction time was completed, the autoclave was immediately immersed in an ice bath and cooled down to ambient temperature. Reaction products were separated from the

reaction media by magnetic decantation and then recovered by filtration over a PVDF filter (Millipore GVWP02500, 0.22μ m pore size). Afterward, they were purified by rinsing six times, alternating Milli-Q water and ethanol. Finally, they were dried under vacuum at room temperature for 12 hours.

2.2 Characterization

2.2.1 Transmission electron microscopy (TEM)

Samples were dispersed in hexane by sonication. Three drops of the supernatant were then deposited onto a holey carbon film supported on a copper grid (C-flat, Protochips, USA), and left to dry, overnight, at room temperature under vacuum. TEM images were obtained on a LEO 922 OMEGA Energy Filter Transmission Electron Microscope operating at 120kV.

2.2.2 Fabrication of the transmission line test cells

Two geometries of transmission lines (TL) were tested: a coplanar waveguide (CPW) and a microstrip. The CPW device consisted of a 0.762 mm thick Teflon substrate of type Ro4350B onto which a $17\mu m$ thick copper layer was deposited. By using an Oxford J-1064/355 pulsed laser system, two parallel lines were etched lengthwise on the copper substrate, exposing the Teflon substrate. For this etching procedure, the 355 nm laser was chosen, operated at 0.5 W, a speed of 200 mm/s, and a frequency of 200kHz, pulsing every 10ps for 11 cycles. Leaving the extremities of the line untouched, their central section was fully etched through the thickness of the substrate by using the 1064 nm laser at 1.6 W during four cycles, while the speed, frequency, and pulse length were kept constant. More details about the dimensions of the obtained device can be found in Fig. 3. The same procedure applies to the microstrip. However, a twosubstrate configuration was used: cavities were drilled in the top Ro3010 substrate, and stripped of its copper layers, in order to prevent a short circuit between microstrip and ground in case of highly conductive nanopowders. The bottom layer was machined out of a Ro4003 substrate for which only the bottom $17\mu m$ thick copper layer was conserved (see Fig. 4).

In both cases, the same method was employed to fill the TL. The nanopowders were mixed with ethanol to form a slurry that could be introduced into the TL's rectangular cavities. A Teflon spatula was then used to compact the samples. The procedure was repeated thrice in order to compactly fill the cavities. Afterward, the as-filled TLs were dried overnight under vacuum, at ambient temperature, to eliminate the solvent. Finally, nanopowder leftovers were removed with a thin cotton swab impregnated with ethanol in order to clean the TL surface. After filling, a piece of cellotape was placed on top of the microstrip substrate in order to maintain the low-density nanopowders in the cavities. In the case of the CPW substrate, cellotape was placed before and after filling on the bottom and top sides, respectively. Tests were performed to verify that the cellotape did not affect the TL line electromagnetic characteristics. It has to be emphasized that the same microstrip (or CPW) line was used for all nanopowders characterized in this paper. Cavities were simply carefully cleaned using ethanol before moving from one powder sample to another.



Fig. 3. Dimensions of the coplanar waveguide (CPW) line for measurements (not in scale). Top: top view; and bottom: side view. The Teflon substrate is represented in light grey whereas the top copper layer is colored in dark pink and nanopowder is black



Fig. 4. Geometry of the microstrip line for measurements (not in scale). Top: top view; and bottom: side view. The Teflon substrates are represented in light grey and grey white whereas the strip and ground copper layers are colored in dark pink, cellotape in light blue and nanopowder in black

2.2.3 Scattering matrix (S-parameters) measurements

The microwave response of the empty and sample-filled microstrip and coplanar waveguide lines (CPW) was measured under DC magnetic field applied perpendicularly to the substrate using a NTM 10400M-260 electromagnet supplying magnetic field values ranging from 0 to 9 kOersteds (kOe). The samples were placed in the gap of the electromagnet and connected to one end of a set of long coaxial cables using a pair of Anritsu 36801 K right-angle launchers. The other coaxial cable ends were connected to the ports of a 12-term calibrated Agilent N5245A PNA-X 70GHz vector network analyzer (VNA), placed away from the electromagnet's intense DC magnetic field. Data acquisition of the transmission S-parameters was performed using Labview.

2.3 Extraction Procedure for Permittivity and Permeability

In this section, we will present the extraction procedure for the characterization of nanopowders. It is important to stress here that the extraction of permittivity and permeability is based on the propagation constant that takes into account the whole cross-section of the TL used, including the surrounding air visible on Figs. 3,4. As a consequence the section will first present the extraction method for the so-called effective permeability and permittivity of each sample, denoted by subscript "e", taking into account surrounding air. Afterwards, the formulas for the retrieval of relative parameters of the characterized nanopowders themselves, denoted by subscript "r", will be presented.

Fig. 5 shows a schematic view of the measurement configuration, adapted from [24]. Boxes *A* and *B* hold for the transmission of a signal between the source of VNA and the input of transmission line (*A*) and from the output of the transmission line to the detector of VNA (B), respectively. They include cables from the source to connectors and connectors from cables to transmission lines. Their transmission factors are noted S_{21A} and S_{21B} , respectively. The transmission factor of the transmission line having length *L* is expressed as $e^{-\gamma L}$, where γ is the propagation constant of the line. The extraction of permittivity and permeability is based on the successive measurement of the filled line under zero DC magnetic field, of the filled line under high DC magnetic field, and of the empty line. The transmission factor from the source to the detector for a filled line under zero DC magnetic field can be expressed as the product of the three transmission factors as

$$S_{21filled} = S_{21A} e^{-\gamma_{filled}L} S_{21B} \tag{1}$$

and for empty lines, it writes

$$S_{21empty} = S_{21A} e^{-\gamma_{empty} L} S_{21B} \tag{2}$$

where

$$\gamma_m = j 2\pi f \sqrt{\varepsilon_{em} \mu_{em}} / c_o \tag{3}$$

with m = filled, empty, *L* is the length of the line, c_o is the light velocity in air and *f* is the frequency of the signal.

The material contribution to the measurement is thus included in the propagation constant γ_m via μ_e and ε_e . Using these equations we can derive from the ratio $S_{21\text{filled}}/S_{21\text{empty}}$

$$\frac{\gamma_{filled} - \gamma_{empty}}{2\pi f L/c_o} = -\ln \frac{S_{21filled}}{S_{21empty}} / (2\pi f L/c_o)$$

$$= J\left(\sqrt{\varepsilon_{efilled} \times \mu_{efilled}} - \sqrt{\varepsilon_{eempty} \times \mu_{eempty}}\right)$$
(4)



Fig. 5. Schematic of the measurement configuration

As:

$$\varepsilon_{\text{eempty}} = \mu_{\text{eempty}} = 1$$
 (5)

since the empty line is filled with air, we use another measurement performed on the filled line in order to extract ε_e . A high magnetic field is applied during the frequency measurement of the filled line in order to move any magnetic effect above the frequency range under scope resulting into $\mu_{efilled} \rightarrow 1$, yielding

$$\frac{\gamma_{\text{field}} - \gamma_{\text{empty}}}{2\pi f L/c_o} = -\ln \frac{S_{21\text{field}}}{S_{21\text{empty}}} / (2\pi f L/c_o) = J \sqrt{\varepsilon_{\text{efilled}}} - 1$$
(6)

since

$$\gamma_{\text{field}} = \sqrt{\varepsilon_{\text{efilled}} (2\pi f L/c_o)} \tag{7}$$

The high magnetic field considered in this work is equal to 9 kOersteds. As will be shown later, in Fig. 16, this value ensures that the permeability tends to 1 for the magnetic nanopowders studied in this paper. It corresponds also to the magnetic saturation of the samples as measured in [41,42]. From these last two

equations the permittivity and the permeability of the material are extracted. The permittivity ε_e , defined as the permittivity extracted from the filled line $\varepsilon_{efilled}$, is obtained from (6), using the measurement under high magnetic field ensuring that $\mu_{efilled} = 1$ so that only ε_e is involved and can be retrieved. Then the permeability μ_e defined as the permeability $\mu_{efilled}$ extracted from the filled line is obtained by introducing the permittivity ε_e in (4). The procedure is also applied in this paper for measuring permeabilites as a function of an applied DC magnetic field of a given value H. In this case, three measurements are considered: empty line, filled line under H field, and filled line under 9k0e field.

For the microstrip topology of Fig. 4 the permittivity ε_s of the substrate supporting the microstrip and hosting the filled cavities is retrieved from the effective one ε_e using the following expression derived from [43]:

$$\varepsilon_s = 2 \times \frac{\varepsilon_{e^{-1+F}}}{1+F} \tag{8}$$

with

$$F = \frac{1}{\sqrt{1 + 12H/W_s}} + 0.04\{1 - (W_s/T)^2\}$$
(9)

where *T* is the total thickness of the substrate and W_s the width of the microstrip. For the topology of Fig. 4, F = 0.231.

The relative permeability of the whole substrate including filled cavities is obtained from the following chart in Fig. 6 derived from expressions in [44]. The relative values that will be presented in section 3.2.2, are close to 1. This is due firstly to the low density and dusty nature of the material under scope and secondly to the low loading rate of MNPs on GO nanoplatelets. As a consequence, the intrinsic permeability of the powder grains is diluted in the surrounding air inside the cavity of the test cell. Thus, in the current experiment, effective permeability values obtained from (4-6) are close to 1.02. Using Fig. 6, it can be found that the corrected substrate permeability value would thus be 1.011. This slight difference represents less than a 2% correction.

For the CPW line topology of Fig. 3 the derivation of substrate values from effective ones is much simpler since the following well-known assumption holds [45]:

$$\varepsilon_s = 2\varepsilon_e - 1 \tag{10}$$

and

$$\mu_s = 2\mu_e - 1 \tag{11}$$



Fig. 6. Ratio of relative by effective permeability μ_r/μ_e for the microstrip topology of Fig. 3, calculated from equation in [44] with T = 1.53 mm and $W_s = 1.00$ mm

Finally, we can retrieve the contribution of the sole nanopowder by using a simple volumetric factor taking into account the volume occupied by the nanopowder in the cavities as compared to the total volume present around the central strip conductor. If the width of each cavity is noted W, and the width of the central strip is noted W_s , the parameters of the sole nanopowder are obtained from those extrblackacted from (4-6) using the multiplicative factor V:

$$V = \frac{2W + Ws}{2W} \tag{12}$$

Factor V compensates for the volumetric dilution of the powder in the whole substrate.

To summarize, the full procedure for the retrieval of the parameters ε_r and μ_r of the nanopowder follows three steps:

- The effective parameters ε_e and μ_e of the transmission line whose cavities are filled with the nanopowder are obtained from measured S-parameters of the lines empty, filled, and filled under 9 kOe DC magnetic field, using equations (4-6).
- The parameters ε_s and μ_s of the inhomogeneous substrate are obtained from ε_e and μ_e using equation (8) and Fig. 6 in case of microstrip line, and equations (10-11) for the case of CPW line.
- The parameters ε_r and μ_r of the nanopowder are obtained by multiplying the substrate parameters by the factor *V*, i.e :

 $\varepsilon_r = V \varepsilon_s$ and $\mu_r = V \mu_s$

(13)

3. RESULTS AND DISCUSSION

3.1 Phenomenological Model for Complex Permittivity

To assess the efficiency of the method, extracted permittivity ε_r will be compared to a model previously developed for conductive inclusions dispersed in an insulating matrix [25], illustrated in Fig. 7. In the present paper, conductive inclusions are the grains of the powder, surrounded by insulating air, the whole forming the nanopowder. According to the model in [25] the random distribution of NPs is approximated by a network of grains, separated by air. Each grain is assumed to be conductive, having an equivalent resistor, and strongly coupled to its neighbors by a capacitor. The resulting model is a 2-layered transmission line. The equivalent complex permittivity ε_p of the nanopowder has the following expression :

$$\frac{1/\varepsilon_p}{\varepsilon_p} \stackrel{\Delta}{=} \frac{1}{(\varepsilon_r + \sigma/J\omega\varepsilon_o)}$$

$$= (T_2 + T_1/[\varepsilon_{NPS} + \sigma_{NPS}/J\omega\varepsilon_o])/T_1 + T_2)$$
(14)

where ε_{NPs} is the dielectric constant of the NPs and σ_{NPs} their conductivity while ε_o is the permittivity of vacuum and T_i the different layer thicknesses.

The inputs for the phenomenological model (14) are: the dielectric constant of the nanoparticles under scope, and their intrinsic conductivity, while fill represents the filling factor defined as the ratio: $fill = T_2/(T_1 + T_2)$, which models the proximity between NPs inducing capacitive coupling responsible for the variation in frequency of the dielectric constant and conductivity of the nanocomposite agglomerate. When the phenomenological model is used to fit the measurements, values of *fill* give an insight on the compacity of the nanopowder, hence on the reproducibility of the filling method of the cavities.



Fig. 7. Schematic representation of model. Left: topology of a nanocomposite; center: equivalent circuit; and right: two-layered equivalent transmission line

3.2 Microwave Properties of Nanopowders

In this section, we present the extraction of parameters for nonmagnetic and magnetic conductive nanopowders characterized with the techniques described

in Sections 2.2.3 and 2.3. Figs. 8-11 show the results obtained for the pristine non-decorated nanocarbon supports (NCS), reduced graphene oxide (rGO) and graphene nanoplatelets (GNPs), as well as for the ZVI@GO and Ni@GO synthesized nanocomposites. These results are discussed hereafter.

3.2.1 Pristine NCS powders

Fig. 8 shows the dielectric constant and conductivity extracted from the measurement of reduced graphene oxide (rGO) filling the microstrip line, and of the same microstrip kept empty. Fig. 9 shows the same for graphene nanoplatelets (GNPs). The conductivity reached at high frequency for rGO is lower than that for GNPs, as expected for such oxidized and defective nanocarbon supports. The filling factor is similar for the two kinds of nanoparticles (0.35). Since typical volumetric densities of GNPs and GO are reported to be similar (1.85 g/cm³ versus 1.9 g/cm³, [46,47], this result suggests that the same amount of nanopowders are introduced in the cavities and that the filling of the cavities is thus reproducible.



Fig. 8. Dielectric constant and conductivity extracted from (4-6) and (8) for rGO nanopowder. The solid line shows extraction from measurement, dashed line shows phenomenological prediction from (14)

It is worth mentioning here that oscillation ripple observed in the experimental curves is due to residual mismatch between the 50Ω reference impedance of the VNA measuring equipment and the characteristic impedance of the MS and CPW lines used for the characterization [48]. The value of the latter impedance depends on the dielectric constant and permeability of the supporting substrate, hence also on the parameters ε_r and μ_r of the included nanopowder. As they are

a priori unknown, the best possible strategy is to design the geometry of the line kept empty, in order to achieve 50Ω . When filled lines are measured, their mismatch against 50Ω induced by the filling powder creates the well-known ripple phenomenon [48] on the S-parameters, and so on ε_r and μ_r , as they are deduced from S-parameters using (4-6). Despite this ripple, the trend behavior of ε_r and μ_r is clearly retrieved from their mean value, and further assessed by the phenomenological model (14).

Also, we have checked the reproducibility of our procedure by making 5 measurements spread over 8 months on a same sample. The observed variation on the extracted permittivity is less than 3%. This illustrates the good repeatability of the extraction procedure and the excellent stability of our samples over time.

As stated in the introduction, no other method is published in the scientific literature that allows to directly characterize the EM properties of nanopowders without prior sample preparation. The closest-matching methodology loads the nanopowder into a paraffin matrix and a toroidal-shape test sample is produced from this mixture [37-39]. Reported amounts of loaded nanopowders typically range from 130 to 220mg. While with our methodology, the CPW and microstrip line cavities require approximately 1.1 and 1.9mg to be filled, respectively. The reported amounts, almost 100 -fold superior to those used in our test cells, give an indication on the acute sensitivity of our methodology.

3.2.2 Ferromagnetic conductive nanopowders

Figs. 10,11 show the conductivity and dielectric constant extracted from the measurement of the two ferromagnetic samples, nickel (Ni) and zero-valent iron (ZVI) nanoparticles deposited onto graphene oxide (GO). As previously mentioned, the method implies using two sets of measurements: one in which the CPW line is filled with each nanopowder and the other in which it is kept empty. As can be observed in both figures, the phenomenological model successfully fits the extracted conductivity and dielectric constant over the whole frequency range.

Figs. 12,13 show the extracted complex permeability μ_r . The measurement is made for several values of DC magnetic field applied perpendicularly to the line substrate. The imaginary part shows a minimum (marked 'o') depending on the DC field which is responsible for the so-called Ferromagnetic Resonance (FMR) [49] absorption. For each sample, the validity of the extraction of μ_r can be assessed by drawing the dispersion relation showing the FMR frequency (where the minimum of $\Im(\mu_r)$ occurs) as a function of applied DC magnetic field. Figs. 14,15 show for each sample a linear relation in accordance with the theoretical law for FMR:

$$f_{FMR} = g\{H_{DC} + H_a\} \tag{15}$$

where g is the gyromagnetic factor equal to 2.8MHz/Oe, and H_a is the effective anisotropy field proportional to the saturation magnetization of the ferromagnetic nanoparticles.

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Fig. 9. Dielectric constant and conductivity extracted from (4-6) and (8) for GNP nanopowder. The solid line shows extraction from measurement, dashed line shows phenomenological prediction from (14)

As another assessment, the permeability of our ferromagnetic material can be modeled by an FMR formalism derived from [49]. Its expressions are:

$$\mu_r = 1 + \frac{\alpha 4\pi M_S g f_r}{(f_r + J/\tau)^2 - f^2} \tag{16}$$

In equation (16) $f_r = g[H_a + H_{DC}]$ is the ferromagnetic resonance (FMR) frequency, τ is the relaxation time associated to the damping factor, f is the sweeping frequency, α holds for the dilution of magnetic nanoparticles in the nanopowder, and M_s and g are the saturation magnetization and the gyromagnetic ratio, respectively. Fig. 16 shows the simulation of the permeability for different values of applied DC magnetic field. It is observed that at 9kOe the complex permeability tends towards unity since the FMR resonance vanishes. This means that for this value equation (6) holds. The simulation shows a good agreement with measurements of ZVI@GO shown in Fig. 13.



Fig. 10. Dielectric constant and conductivity extracted from (4-6) and (10) for Ni@GO nanopowder. The solid line shows extraction from measurement, dashed line shows phenomenological prediction from (14)







Fig. 12. Permeability extracted from (4-6) and (11) for Ni@GO nanopowder. Circles indicate the location of minima corresponding to FMR frequency.



Fig. 13. Permeability extracted from (4-6) and (11) for ZVI@GO nanopowder. Circles indicate the location of minima corresponding to FMR frequency



Fig. 14. FMR dispersion relation for Ni@GO nanopowder, extracted from Fig. 12 (solid) and calculated according to (15) (dashed) with $H_a = 24.40e$



Fig. 15. FMR dispersion relation for ZVI@GO nanopowder, extracted from Fig. 13 (solid) and calculated according to (15) (dashed) with $H_a = 7200e$.

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Fig. 16. Permeability calculated according to (16) with $\alpha = 0.082, 4\pi M_s = 720$ Oe, $\tau = 8 \cdot 10^{-11}$ s

4. CONCLUSION

In this chapter we have demonstrated the efficiency of a method based on a single transmission line reusable for all samples to extract both complex permittivity and magnetic permeability of lowdensity nanocomposite powders. The extraction of dielectric constant and conductivity is successfully validated by implementing a phenomenological model including as input parameters the dielectric constant and conductivity of nanoparticles, and a filling factor modeling the distance between particles and enabling to assess the quality of the filling of cavities with nanopowders. The magnetic permeability is also extracted and modeled successfully, and further assessed by an accurate retrieval of the FMR frequency that closely follows the linear theoretical law. This highlights that the procedure is efficient for this kind of low-density samples. Although the proposed extraction method is used here for nanopowders, it can also be applied to other topologies of lines and other materials such as ferrites, liquids, or ferrofluids, provided they can easily be inserted in the cavities.

This is of prime interest for the design of numerous microwave devices such as absorbers, filters, and metamaterials.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Studies on Energy Consumption in Pneumatic Conveying of Raw Cotton

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ABSTRACT

The findings of experiments on energy consumption during the pneumatic transport of raw cotton to gineries are presented in the article. Increased power consumption for inclusion in the composition of raw cotton environmental obvious and objectively. Based on the findings of theoretical and empirical research, it offers suggestions and opinions for managing the cotton pneumatic transport process effectively and lowering energy expenditures. Obtained from the power consumption dependency of flow characteristics, specifically average speed, line pressure, and pipe length and diameter. It advised using 355 mm diameter pipe and 315 mm diameter pipe instead of 400 mm diameter pipe at a moderate rate of flow to lower the power consumption of the pneumatic installation.

Keywords: Raw cotton; pneumatic installation; aerodynamic force; static pressure; dynamic pressure; power consumption.

1. THE AIR PRESSURE IN THE PNEUMATIC PIPELINE AND ITS CHANGE

Pneumatic conveying installation, is primarily the aerodynamic unit, which pumps air from one place to another. The difference is that pneumatic conveying installation serves the material, which captures the moving air and throws it at the destination [1-3]. Wind power is viewed as a function of the square of airflow or speed in the established theories of pneumatic transport [4-6]. This indicates that it is only dependent on dynamic pressure, which does not fluctuate along the length of the tube when a complete seal is present and the pipeline system element is present. Experience demonstrates that the strength of the aerodynamic force is not constant, but rather depends on the length of the tube, with the fan's maximum value increasing toward the pipeline's beginning and progressively decreasing thereafter, much like static pressure [7-9]. Based on these considerations, we must determine the effect of static pressure on the value of wind power.

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To analyze the use Fig. 1, where: 1 suction pipe, 2-fan (pump) 3 -forcing pipeline. In operation the fan 2 draws air from the conduit 1 and provides the pipe 2. Subsequently, the pipeline 1 is formed in the negative pressure (vacuum) - the vacuum, and in the 2 nd positive (gauge) pressure. In this case, the fan creates a pressure value called nominal being passport fan pressure. Moreover, the total pressure consists of P_p2 terms, P_d is the dynamic pressure and static P_{ct} :

$$P_p = P_d + P_{ct}$$

Where P_{p} , P_{d} and P_{ct} is the pressure of the dimension of Pa.



Fig. 1. Simplified diagram of the pneumatic installation

The dynamic pressure Pd is, the kinematic energy of the flow, and depends only on its parameters - medium density ρ and speed v:

$$P_{\rm d} = 0.5\rho v^2$$

Static pressure is the potential energy of the medium position. it is mathematically well described for a fixed environment, but for a moving medium is difficult to describe. Our studies show that we have proposed semiempirical laws describing the change in the static pressure on the transportation lines are well supported with experimental data [10,11]:

$$P_{\rm ct} = P_{\rm H} - P_{\mu} = P_{\rm H} - 0.5\rho v^2 \lambda L/d,$$

Here, $P_u = 0.5\rho v^2 \lambda L/d$ - static pressure required to overcome the frictional force of the medium on the inner wall of the pipeline, Pa; P_H-rated pressure developed by the fan during normal operation, Pa; ρ - density of the fluid kg/m³; v - of the medium speed, m/s; λ - drag coefficient, L- length, d - diameter of the pipeline, *m*.
According to (1) the force applied to overcome the frictional force must be directed against it and the direction of motion of the medium. Based on this, change the sign between the terms in the (+) in the equation (3):

$$P_{\rm cT} = P_{\rm H} + 0.5\rho v^2 \lambda L/d$$

The total pressure is defined as $P_p = P_{st} + P_d$. with this in mind (2) comes after some transformation to the form:

$$P_{\rm p} = P_{\rm H} + 0.5\rho v^2 (\lambda L/d + 1)$$

2. FORMATION OF WIND POWER AND POWER CONSUMPTION FOR PNEUMATIC TRANSPORT

Move medium in the pipeline produces aerodynamic force $F_a(N)$, and the force of friction $F_u(N)$ seeks to stop the move [12,13]. A motion carried to as indicated above, should be accompanied by a force equal to F_u but against its direction. Moreover, the aerodynamic force F_a produce dynamic and static pressure and friction force F_u - static. The resultant force \mp contributing to the movement of the medium is equal to the multiplication of the total pressure on the crosssectional area of the pipeline:

$$F_{a} = P_{p} \cdot f = 0.25\pi d^{2} \cdot (P_{cH} + 0.5\rho v^{2}(\lambda L/d + 1))$$

Where *f* - the cross section of the tube, m^2 ; P_{cH} - nominalstatic pressure generated by the fan; ρ - the density of the medium; *L*-length, d -diameter of the tube; λ -drag coefficient of 1 m pipe the movement of the flow.

If you pay attention to the last equation force F increases with increasing length L and the drag coefficient decreases with increasing diameter of the pipeline and it is logical, because the greater the transport distance, the more energy it will take. If this power depended on the dynamic pressure, the tightness of the system at full strength would be constant over the entire length of the pipeline. However, according to (4) the value of the aerodynamic force is not constant. After simple transformations, we finally obtain:

$$F = 0.125\pi d^2 \cdot (\rho U^2 (1 + \lambda L/d) + 2P_{cH})$$

This force does the work of A(J - joul), equal When the system operation:

$$A = F_a \cdot L$$

Through the work done within the time device power consumption N(kWt) is as follows:

$$N = A/t = FL/t$$

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The ratio of the distance on time is the average flow rate:

$$U_p = L/t$$

Where U_p -average speed, m/s; t - time of transport, s.

In view of the latter, we obtain the dependence of the power expended in moving the environment from the set parameters and flow:

 $N = 0.125\pi d^{2} \cdot (\rho U^{2}(1 + \lambda L/d) + 2P_{cH})U_{p}$

This formula shows that the power expended in transporting the medium depends largely on the average flow rate, then the parameters from the (inner surface resistance, length and diameter) of the pipeline.

3. POWER CONSUMPTION IN PNEUMATIC CONVEYING AND ITS CHANGE

Let us analyze the dependence (11). Here, *d* indicator not only of the pipeline, and the index of the medium, too, because it determines the size of the cross-flow and is equal to the inner diameter of the pipe: d = 0.315; 0.355; 0.4 m. The air density $\rho = 1.2 \text{ kg/m}^3$, fuel mixture $\rho = 1.65 \text{ kg/m}^3$.

The length of the pipeline will take equal to L = 100 m.

 λ - friction coefficient of the medium on the inner surface of the pipeline is:

- When air flows:

 $d = 0.315 \text{M} - \lambda = 0.068$ $d = 0.355 \text{M} - \lambda = 0.066$ $d = 0.4 \text{M} - \lambda = 0.064$

-With Movement aeromixture:

 $\begin{aligned} d &= 0.315M - \lambda = 0.134; \\ d &= 0.355\mathcal{M} - \lambda = 0.133; \\ d &= 0.4M - \lambda = 0.132. \end{aligned}$

(Accepted as the average value of clean air friction coefficients ($\lambda = 0.064 - 0.068$), and cotton ($\lambda = 0.2$) of the inner surface of the steel pipe).

The analysis is performed on a computer with standard programs, the results of which are presented in graph form in Fig. 2, which show that they correctly describe the process: with increasing the flow rate of power consumption increases significantly.

In graphs: 1 - d = 0.315 m, $\rho = 1.2 \text{ kg/m}^3$; 2 - d = 0.355 m, $\rho = 1.2 \text{ kg/m}^3$; 3 - d = 0.4 m, $\rho = 1.2 \text{ kg/m}^3$; 4 - d = 0.315 m, $\rho = 1,65 \text{ kg/m}^3$; 5 - d = 0.355 m, $\rho = 1,65 \text{ kg/m}^3$; 6 - d = 0.4 m, $\rho = 1,65 \text{ kg/m}^3$. Thus: 1.2 and 3 - with air movement of 4.5 and 6 - fuel mixture during the motion.



Fig. 2. Power consumption depending on the type, flow rate, and pipeline parameters

The graphs show that a significant portion of the power consumed for air transportation. Thus, when pipe diameter 0.315 m, a flow rate of 20 m/s is required to move the medium 16kWt of power, and when the raw cotton in the medium increases to the power consumption of 25kWt. Thus, 64% of the power consumed for air transportation.

At a speed of 30 m/s is required to move the air 40kWt, and the mixture of air and raw cotton 85kWt, or 48% corresponds to the air flow. With a diameter of 0.4 m, flow rate of 20 m/s is required to move the air 20kWt, and the mixture of air and raw cotton 40kWt. At a speed of 30 m/s is required to move the air 50 kW, and the mixture of air and raw cotton 110kWt. Moreover, the power consumption is 50% and 46% of the total power consumption.

Increased power consumption for inclusion in the composition of raw cotton environmental obvious and objectively. The absolute increase in consumption can be estimated as: $\Delta N = Na - Nx$. Here, Na - consumption (kWt) when driving fuel mixture; Nx - consumption for air movement. Fig. 3 is a graph showing changes in the absolute increase in power consumption of the flow velocity in the pipe diameter 0.315 m and 0.4. The results also evident that at high speeds and at high conveying pipe sizes power costs will be considerably larger.

To determine the proportion of the power costs of air transportation and fuel mixture we use the formula:

$$\Delta N_{\rm H} = (\rm Na - \rm Nx)/(0.01\rm Na)$$

Analysis of relationship (12) at flow rates (20 - 30 m/s) is shown in Fig. 4, which show that during the pneumatic transport of seed cotton over half power setting to move the spent air. At the same time, the share of power consumption for air transport at high flow rates is less than the lower, which is also obvious - to give

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the environment a large proportion of high speeds requires more effort than giving it a lower rate.

From the above we can conclude that the relationship (11) correctly describes the power consumption of the process of change of the flow parameters and the pneumatic installation as a whole and may be offered for use in the design of pneumatic conveying systems.



Fig. 3. The dependence of the absolute increase consumption the power of the flow velocity





4. CONCLUSIONS

- (A) Research has established that the aerodynamic force that contributes to the displacement of the medium through the pipeline pneumatic transport installation depends on the total pressure of the flow, ie, the sum of the dynamic and static pressures.
- (B) It was also found that the power expended in transporting the medium depends largely on the average flow rate, then the parameters from the (inner surface resistance, length and diameter) of the pipeline.

- (C) Analysis of the results of studies power expended in transporting the medium indicates that an increase in power consumption flow rate increases markedly, with a considerable portion of the power consumed for air transportation.
- (D) It was also found that the diameter of the pipe and the flow rate significantly affect the power consumption of the transportation environment, which leads to the conclusion that the use of smaller diameter pipes at moderate flow rates, thereby reducing power consumption and thus reduce production costs ginneries
- (E) Research results can be recommended to reduce the energy consumption used pipe diameters of 355 mm and 315 mm, instead of pipes of 400 mm diameter at a moderate rate of flow.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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Evidence for Non-Baryonic Dark Matter in High Energy Regions above 10 GeV

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ABSTRACT

At an infinite sublayer level, there exists an infinite number of quarks $u(\infty)$ with the flavors f = u, d, s, c, b and anti-quarks $u(\infty)$ having all one-half electric charge $Q=\pm 1/2$. These particles are considered as the ultimate building blocks of the universe, since they are structure-less and absolutely stable. These particles are also regarded as the non-baryonic dark matter, since the baryon number is zero and the R_p -parity is -1. It is emphasized that supersymmetric particle, neutralino has also the R_p -parity of -1 and well known good cold dark matter candidate. In modern particle physics, all ordinary particles have the R_p -parity of +1, while both the ultimate quarks $u(\infty)$ and neutralino have the R_p -parity of -1 This means that these particles can only be created or annihilated in pairs in reactions of ordinary particles. From electron-positron annihilation experiments at high energies, it is shown that the prediction value from the ultimate quark $u(\infty)$ is in good agreement with many ring-storage collider experiments.

Keywords: Non-baryonic dark matter; negative R p-parity; neutralino; electonpositron experiment.

1. INTRODUCTION

Our universe is made up of many different hierarchical clusters, such as quarks, nucleons (protons and neutrons), nuclei, atoms, molecules, gas clouds, planets, stars, galaxies, meta-galaxies, ad infinitum. As we move to the lower side on the hierarchy of such clusters, we hit the bottom of the hierarchy and find the smallest particles that exist, the ultimate building blocks of the universe. In some previous papers [1-6], the present author showed that there exists an infinite number of quark $u(\infty)$ and its anti-quark $u(\infty)$ as the ultimate building blocks of the universe. Recently, there has been great interest in gravitational waves, dark matter and dark energy. The dark matter effects were discussed within the framework of the extended gravity theories [7]. The dark matter. leptons, quarks, gauge bosons and Higgs bosons are also composed of $u(\infty)$ and $u(\infty)$

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The $u(\infty)$ and $u(\infty)$ quarks are good candidates for non-baryonic dark matter, since baryon number is zero and the R_p -parity is negative, that is, -1. The recent astronomical observations imply that the universe consists of 0.5% luminous matter like stars and galaxies, $4\% \pm 0.4\%$ baryonic dark matter, $23\% \pm 3\%$ non-baryonic dark matter and $73\% \pm 3\%$ dark energy [8-13]. As a result, non-baryonic matter, not baryonic dark matter, makes up the universe as it is today. There are a few dark matter models [14]. For example, the candidate of baryonic dark matter, neutrino, axion and neutralino are considered [15-16]. Neutralino is derived from supersymmetric counterpart of neutrino [17]. The lightest neutralino is the leading cold dark matter candidate, since it is absolutely stable and R_p -parity [18] is conserved. R_p -parity is defined with baryon number *B*, lepton number *L* and spin *S*, as

$$R_{\rm p} = (-1)^{3B+L+2S} \equiv (-1)^{3(B-L)+2S} \tag{1}$$

Supersymmetic particle has the R_p -parity of -1. The ultimate quark u (∞) has also the R_p -parity of -1, since B = 0, L = 0, S = 1/2 and the standard quark u has the R_p -parity of +1, because of B = 1/3, L = 0 and S = 1/2.

Thus all ordinary particles of the standard model have the R_p -parity of +1, while neutralino, superpartner of neutrino in supersymmetry has the negative R_p -parity of -1.

 $R_{\rm p}$ -parity is a conserved multiplicative quantum number, therefore, the particle can only appear quadratically in the Lagrangian. This means the supersymmetric particles can only be produced in pairs. This particle is absolutely stable and there is no charged particle into which it can decay.

This fact is what makes the supersymmetric particle a good dark matter candidate.

Now, consider the ultimate quark $u(\infty)$ and its anti-quark $\overline{u(\infty)}$ as non-baryonic dark matter candidates, since they are absolutely stable, similar to neutralino and the non-baryonic particles with the baryon number 0. A pair of an infinite number of $u(\infty)$ and $\overline{u(\infty)}$ quarks would be produced in the early universe of the Big Bang and leave the right relic abundance to explain the observed dark matter. In the following, we will construct the infinite sub-layer quark model.

2. AN INFINITE SUB-LAYER QUARK MODEL

This is derived as follows: The proton (p) and the neutron (n) are made up of u(1) and d(1) quarks, so that p = u(1)u(1)d(1) and n = u(1)d(1)d(1). Furthermore, u(1) and d(1) quarks are made up of u(1) = u(2)u(2)d(2) and d(1) = u(2) d(2)d(2), etc. In summary, u(N) and d(N) quarks at level N are made up of u(N + 1) and d(N + 1) quarks at level N + 1, such as u(N) = (u(N + 1)) 1), u(N + 1), d(N + 1)) and d(N) = (u(N + 1), d(N + 1), d(N + 1)) where $N = 1,2,3,\dots,\infty$.

Here, the u(N) and d(N) quarks have quantum numbers of spin S = 1/2, isospin I = 1/2, third component of isospin $I_3 = \pm 1/2$, fractional electric charge $Q = [(1 \pm 3^N)/(2 \times 3^N)]|e|$, and baryon number $B = 1/3^N$. This is shown in Table 1.

3. SIX QUARKS AT AN INFINITE SUB-LAYER QUARK MODEL

In the standard qurk model, there are six quarks, that is, up(u), down(d), strange(s), charm(c), bottom(b) and top(t). Standard 6 quark quantum numbers are shown in Table 2.

Quantum numbers at an infinite sub-layer level are shown in Table 3.

In Table 2, it is shown that baryon number B = 1/3, R_p -parity = +1, electric charge Q = -1/3 or 2/3, while, in Table 3, B = 0, R_p -parity = -1 and $Q = \pm 1/2$. Thus, at an infinite sub-layer level, all quantum numbers are just one-half.

Level (N)	Symbol	Combination		B	Ι	I_3	Q
0	p(proton)	u(1) u(1) d(1)		1	$\frac{1}{2}$	$\frac{1}{2}$	+ e
	n(neutron)	u(1) d(1) d(1)	$\frac{1}{2}$	1	$\frac{1}{2}$	$-\frac{1}{2}$	0
1	u(1)	u(2) u(2) d(2)	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3} e $
	d(1)	u(2) d(2) d(2)	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{3} e $
:	u(<i>N</i>)	u(N+1) u(N+1) d(N+1)	$\frac{1}{2}$	$\frac{1}{3^N}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1+3^N}{2\times 3^N} e $
N	d(<i>N</i>)	u(N+1) d(N+1) d(N+1)	$\frac{1}{2}$	$\frac{1}{3^N}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1\!-\!3^N}{2\!\times\!3^N} e $
÷	u(∞)	Structure-less	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2} e $
∞	$d(\infty) = \overline{u(\infty)}$	Structure-less	$\frac{1}{2}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2} e $

Table 1. Infinite sub-layer quark quantum numbers from N = 0 to $N = \infty$

	First family		Second family		Third family	
Flavors	d	u	S	с	b	t
$R_{\rm p}$ -parity	+1	+1	+1	+1	+1	+1
Baryon number B	1/3	1/3	1/3	1/3	1/3	1/3
Electric charge Q	-1/3	2/3	-1/3	2/3	-1/3	2/3
Isospin I	1/2	1/2	0	0	0	0
Third component of isospin	-1/2	1/2	0	0	0	0
I_3						
Strangeness number S	0	0	-1	0	0	0
Charm number C	0	0	0	1	0	0
Bottomness number \mathcal{B}	0	0	0	0	-1	0
Topness number T	0	0	0	0	0	1
Thirdcomponentof	-1/2	1/2	-1/2	1/2	-1/2	1/2
weakisospin $(t_3)_L$						

Table 2. Additive quantum numbers of the quarks in the standard model. The subscript "L" indicates the left-handed particle

 Table 3. Additive quantum numbers at an infinite sublayer level. All quantum number is just one-half

	First family		Second family		Third family	
Flavorsataninfinitesublayer	d(∞)	u(∞)	<i>s</i> (∞)	<i>c</i> (∞)	b(∞)	<i>t</i> (∞)
$level N \rightarrow \infty$						
R _p -parity	-1	-1	-1	-1	-1	-1
Baryon number B	0	0	0	0	0	0
Electric charge Q	-1/2	1/2	-1/2	1/2	-1/2	1/2
Isospin I	1/2	1/2	0	0	0	0
Third component of	-1/2	1/2	0	0	0	0
isospin I_3	•					
Strangeness number spin	0	0	-1/2	0	0	0
<i>S</i> /2						
Charm number spin $C/2$	0	0	0	1/2	0	0
Bottomness number spin	0	0	0	0	-1/2	0
· · · · · · · · · · · · · · · · · · ·					,	
Topness number spin $T/2$	0	0	0	0	0	1/2
Thirdcomponentof	-1/2	1/2	-1/2	1/2	-1/2	1/2
weakisospin $(t_3)_L$,		,		,	•

4. ELECTRON-POSITRON ANNIHILATION INTO MUON PAIRS AND QUARK PAIRS

Now consider electron-positron annihilation via a virtual photon (γ).

This Feynman diagram is shown in Fig. 1.

The lowest order QED differential cross-section for the process via a virtual photon (γ)

$$e^{+}e^{-} \rightarrow \gamma \rightarrow \mu^{+}\mu^{-}\text{gives}$$

$$d\sigma = \frac{\pi\alpha^{2}}{2(\sqrt{s})^{2}}(1 + \cos^{2}\theta)d(\cos\theta)$$
(2)

where θ is the angle of emission of muons in the CMS(center of mass) system, α is the fine structure constant, and \sqrt{s} is the center-of-mass energy [19].

The total cross-section is written as

$$\sigma = \frac{4\pi\alpha^2}{3(\sqrt{s})^2} \tag{3}$$

We neglected the lepton masses. An e^+e^- annihilation can produce hadrons through a virtual photon (γ) and $e^+e^- \rightarrow \gamma \rightarrow q_f(\infty)\overline{q_f}(\infty) \rightarrow$ hadrons. We obtain the total cross-section

$$\sigma = \frac{4\pi\alpha^2}{3(\sqrt{s})^2} Q_f^2 N_c \tag{4}$$

Here Q_f are quark charges for the flavors f = u, d, s, c, b and t. N_c are the color charges c = red, green and blue and $N_c = 3$.



Fig. 1. Electron-positron annihilation into quark pairs $(e^+e^- \rightarrow \gamma \rightarrow qf(\omega)qf(\omega))$ and muon pairs $e^+e^-\rightarrow\gamma\rightarrow\mu+\mu-\gamma$ via virtual photon γ

The cross-section ratio R is written as

$$R = \frac{\sigma(e^+e^- \to q_f(\infty)\overline{q_f(\infty)})}{\sigma(e^+e^- \to \mu^+\mu^-)} = 3\sum_{q_f(\infty)} Q_{q_f(\infty)}^2$$
(5)

We consider the following generalized Gell-Mann-Nishijima formula [20],

$$Q = I_3 + \frac{1}{2}(B + S + C + B + T)$$
(6)

From the standard quark model in Table 2, we obtain the following crosssection ratio R for u, d, s, c and b quarks:

$$R = 3 \times [Q_u^2 + Q_d^2 + Q_s^2 + Q_c^2 + Q_b^2]$$

= $3 \times \left[\left(\frac{2}{3}\right)^2 + \left(-\frac{1}{3}\right)^2 + \left(-\frac{1}{3}\right)^2 + \left(\frac{2}{3}\right)^2 + \left(-\frac{1}{3}\right)^2 \right]$
= $\frac{11}{3}$

for u, d, s, c, b quarks.

The prediction value R = 11/3 was already compared with various experiments [21-25].

Now consider $u(\infty), d(\infty), s(\infty), c(\infty)$ and $t(\infty)$ quarks at an infinite sub-layer level.

From Table 3, we obtain the following theoretical branching ratio R = 15/4 = 3.75.

$$R = 3 \times \left[Q_u^2 + Q_d^2 + Q_s^2 + Q_c^2 + Q_b^2\right]$$

= $3 \times \left[\left(\frac{1}{2}\right)^2 + \left(-\frac{1}{2}\right)^2 + \left(-\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2 + \left(-\frac{1}{2}\right)^2\right]$
= $\frac{15}{4} = 3.75$

This prediction value is compared with various storage-ring collider experiments from the CELLO [26-27], CLEO [28-29], JADE [30-31], MARK J [32], PLUTO [33] and TASSO [34-35] Collaborations. This is shown in Fig. 2.

For clarity, all data in the references are not appearing in the figure.

Thus, the prediction value from the ultimate quark $u(\infty)$ agrees well with many ring-storage collider experiments.

The third order QCD radiation correction formula is written as

$$R = 3\sum_{q_f} Q_{q_f}^2 \left[1 + \left(\frac{\alpha_s(s)}{\pi}\right) + 1.4092 \left(\frac{\alpha_s(s)}{\pi}\right)^2 - 12.8046 \left(\frac{\alpha_s(s)}{\pi}\right)^3 \right]$$
(7)

and gives

R(34GeV) = $11/3(1.056 \pm 0.008) = 3.87 \pm 0.03$, thus the QCD (Quantum Chromodynamics) correction increases the predicted value by 5% [36] which agrees with our predicated value R = 15/4 = 3.75 better than the naïve 5 quark value R = 11/3 = 3.67.



Fig. 2. Various experimental values *R* from 10.49GeV to 43.46GeV versus prediction value R = 15/4 = 3.75

5. DISCUSSION AND CONCLUSIONS

As the ultimate building blocks of the universe, there exists an infinite number of structure-less quarks $u(\infty)$ and anti-quarks $u(\infty)$ at an infinite sub-layer level. These particles have the R_p -parity of -1, since the baryon number is zero. Similarly, supersymmetric particles have also R_p -parity of -1. They are created and annihilated in pairs. For all ordinary particles, the R_p -parity is $\pm 1. u(\infty)$ and $u(\infty)$ quarks and the lightest supersymmetric particle, especially, neutralino are good candidates for non-baryonic dark matter, since they are absolutely stable.

The ultimate $u(\infty)$ and $\overline{u(\infty)}$ quarks are regarded as partons [37-38] and non-baryonic dark matter [3].

To validate our model, we examined electron-positron annihilation into muon pairs and quark pairs in high-energy physics. As shown in Fig. 1, the prediction value is in good agreement with the experiments. A pair of $u(\infty)$ and $\overline{u(\infty)}$ quarks would be produced in the first and early universe after the Big Bang and then remains abundantly as the non-baryonic dark matter for all time , stable against decay. It is emphasized that CP is violated in the hot early universe of the Big

Bang to account for the asymmetry of the number of particles and anti-particles [30]. This is explained by an SU(2) non-commutative geometry [39-41]. As shown in Table 2 and Table 3, there are three families. In a previous paper, we showed that there are just four families [42]. This is derived from Charge, Parity and Time(CPT) transformation and the SU(2)_LxU(1) gauge theoty. We assumed that the second, third and fourth families are the excited states of the first family. Therefore, the $u(\infty)$ and $\overline{u(\infty)}$ quarks are the ultimate particles in the universe. It is interesting to note that in Table 3, all quntum nmbers are just one-half including the electric charge. Thus, "Nature is simple and beautiful. The truth lies in its beauty". CP violation in β decay and preon model was also discussed in the references [43-46]. We showd that gauge bosons, leptons and Higgs bosons are composed of the $u(\infty)$ and $\overline{u(\infty)}$ [4]. Especially, if the electron is made up of the $u(\infty)$ and $\overline{u(\infty)}$ quarks and CP is violated, then the self-energy of the electron is removed. It is not necessary to consider renormalization theory [47].

Higgs bosons are also made of the ultimate quarks, and we replace the Higgs potential with the gravitational potential. It was shown that the masses are produced and Einstein's cosmological constant was derived [48]. By considering the n-th order T product Green's function in the path-integral representation, we can construct a quantization theory including the cosmological constant without the gravitational field [49-50].

Recently, there has been great interest in gravitational waves, dark matter and dark energy [51-54]. The dark matter effects were discussed within the framework of the extended gravity theories [7].

The problem of future gravitational waves in astronomy was also discussed [52]. We proposed theoretically the possibility of gravitational wave lasers [53].

Finally, it is concluded that an infinite number of $u(\infty)$ and $\overline{u(\infty)}$ quarks was created in the early universe after the Big Bang, and leaves the right relic abundance to account for the observed non-baryonic dark matter. We compared it with high-energy experimental results to obtain validation of our model.

As can be seen from Fig. 2, the existence of non-baryonic dark matter has been confirmed.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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Fundamental Research and Application of Physical Science Vol. 6 Evidence for Non-Baryonic Dark Matter in High Energy Regions above 10 GeV

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Molecular Dynamics Simulation Studies on Structural Evolution and Glass Forming Ability of Zr₅₀Ag₅₀ Alloy

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ABSTRACT

Bulk metallic glasses are amorphous alloys with interesting structures and mechanical characteristics in comparison to the crystal metallic structures and have attracted the interest of material researchers. In the present work, molecular dynamics simulations with modified embedded atom method force field parameters have been conducted to study the structural evolution and glass forming ability of Zr₅₀Ag₅₀ alloy during solidification process. The structural analyses are carried out through different techniques, such as the radial distribution function, coordination number distribution and Voronoi tessellation analysis. The reduced glass transition temperature of the Zr₅₀Ag₅₀ alloy is determined from the glass transition temperature and melting point temperature of the alloy. The estimated reduced glass transition temperature indicates good glass forming ability of the alloy. The Voronoi tessellation analysis reveals that most of the Voronoi polyhedrons are <0,2,8,4>, <0,3,6,4>, <0,1,10,2>, <0,2,8,2> and <0,0,12.0> structures in this system, which are icosahedral structures. Hence, this observation of larger population of icosahedral structures confirms the formation of bulk metallic glass in this alloy.

Keywords: Bulk metallic glass; MD simulations; MEAM potential; radial distribution function; Glass forming ability; Voronoi tessellation analysis.

1. INTRODUCTION

Bulk metallic glasses (BMGs) are prepared by rapid cooling of melted liquid alloys [1]. As advanced metallic alloys, BMGs have attracted much attention in materials science and engineering. Due to their amorphous atomic structures (presence of both long-range disorder and short-range order), BMGs show unique mechanical and physical properties like- high strength, excellent wear, high corrosion resistance, and low elastic modulus as compared to conventional

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crystalline materials. These unique properties make BMGs promising candidates for many applications [2-5].

Zirconium (Zr) based metallic alloys show excellent glass forming ability (GFA) amongst various glass forming alloys. The application of Zr-based alloys for the making of cladding tubes in nuclear reactors makes them superior materials and detailed analysis on the structure-property relationship are hence required. Löffler and group developed a series of nickel-free Zr-based BMGs possessing high GFA and showed that Zr58Cu22Fe8Al12 did not exhibit cytotoxicity [6,7]. More recently, Li and co-workers [8] and Jiang et al. [9] have developed a series of Zr-based BMGs that exhibit low elastic modulus, good GFA, and higher strength. J. H. Na et al. demonstrated the GFA of Zr-Ni-Nb-Al metal alloys and found that the replacement of Nb with Zr improved the GFA of the metal alloy [10]. Moreover, corrosion behavior of Zr-based BMGs in different chemical solutions has been investigated and it is found that the BMGs exhibit higher corrosion resistance compared to conventional crystalline Zr and Zr-based alloys [11,12]. Hua et al. studied the metallic Zr-Al-Co-Ag glasses and observed increase in the corrosion resistance upon addition of silver (Ag) [13]. Most of the BMG's mechanical and thermodynamic properties are investigated from its atomic structure. However, characterization of the structural states of BMGs is a very important and challenging issue because of the complex nature of their amorphous phase. In this perspective, molecular dynamics (MD) simulation becomes an efficient technique to analyze atomic structural configurations during the formation of metallic glasses. For the structural analysis of the short-range order, radial distribution function, Voronoi tessellation analysis, coordination number analyses techniques are effectively used to determine the GFA and local atomic arrangement in amorphous metallic systems [14-16]. Very recently, few groups have performed MD simulation studies to investigate on the structural evolutions, dynamics and GFA of various Zr-based alloys [17-20] and found that BMGs are formed with good GFA in these alloys.

Keeping in mind the potential applications of Zr-based alloys and the scarcity of research on Zr-Ag alloy, a $Zr_{50}Ag_{50}$ alloy has been prepared with equal concentration of both the elements in the present work and its atomic structural configuration as well as GFA are investigated by classical MD simulations with the use of MEAM potentials. To calculate GFA, the reduced glass transition temperature (T_{rg}) has been calculated from the liquidus temperature (T_{l}) and the glass transition temperature (T_{g}). In addition, radial distribution function, Voronoi tessellation analysis, coordination number calculation has been employed to determine the atomic structure and GFA of the Zr-Ag BMG. This simulation work showed that $Zr_{50}Ag_{50}$ has good glass forming ability and forms bulk metallic glass.

2. METHODOLOGY

The initial configuration of the simulation cell representing the $Zr_{50}Ag_{50}$ is constructed by randomly distributing 6912 number of atoms (Zr and Ag) in a three-dimensional cubical box of box length 12 Å in an HCP crystal. Periodic

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boundary conditions are applied along all three dimensions to simulate the bulk properties. First, the simulation cell is heated under the statistical ensemble of isothermal isobaric conditions (NPT) with a heating rate 10¹² K/s from 300 K to 2500 K, which is significantly higher than the melting point of both the components (Zr and Ag) in order to achieve liquid state. Then, the simulation box is relaxed at 2500 K for 1 ns in the constant volume canonical ensemble (NVT) to completely avoid the crystalline structure. Finally, we used a high cooling rate of 10¹² K/s to cool the alloy back to 300 K in a statistical NPT ensemble. The system is again relaxed at 300 K for 1 ns in an NVT ensemble to achieve equilibrium state. MD simulations are carried out by using the open-source software, Large Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [21]. Visualization of structures and some analyses are done by using the Open Visualization tool (OVITO). Equations of motions are integrated with 1 fs time step and Nose-Hoover thermostat/barostat are used to control the temperature. Fig. 1 shows the snapshot of the initial $Zr_{50}Ag_{50}$ alloy along with the snapshots after heating (melted) and cooling (solidified) process.



Fig. 1. Snapshot of atomic distribution in Zr₅₀Ag₅₀. (a) Initial structure (b) at 2500K (after heating) (c) at 300K (after cooling). Blue and red balls represent zirconium and silver atoms, respectively

Interatomic potentials play a crucial role in determining properties in classical simulations. The modified embedded atomic model (MEAM) potential with the second nearest neighbor (2NN) developed by K. H. Kang et al. [22] is chosen to describe the interatomic interactions. MEAM is a semi-empirical force field method based on density functional formalism. The total energy E for a system is described as follows

$$E = \sum_{i=1}^{n} \left[F(\rho_i) + \frac{1}{2} \sum_{i \neq j} S_{ij} \left(\varphi_{ij} \right) (r_{ij}) \right]$$
(1)

Where F is the embedding function for embedding the ith atom into the electron density ρ_i , S_{ij} is the screening function and $\phi_{ij}(r_{ij})$ represents the pair interaction term between atoms i and j, separated by a distance rij.

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3. RESULTS AND DISCUSSIONS

3.1 Glass Transition Temperature

To study the structural transitions in $Zr_{50}Ag_{50}$ alloy, the variation of volume with temperature during the heating and cooling process is investigated, as shown in Fig. 2. It is observed that during the heating process, initially the volume rises monotonically with the temperature, then shows a sharp jump indicating the occurrence of solid-liquid phase transition and then again, a smooth increase in volume is observed. The temperature at which the sharp jump in volume is observed, marks the melting point temperature of the alloy. The heating curve bends upward as the melting starts and overlaps with the cooling curve at the completely melted structure representing the liquidus temperature (T₁). The calculated value of T₁ is 1530K.



Fig. 2. Variation of volume with respect to temperature during the process of heating and cooling of $Zr_{50}Ag_{50}$ amorphous alloy

During the rapid cooling of the molten alloy, the volume decreases continuously and smoothly with decrease in temperature without showing any prominent discontinuity as seen in the heating process. The difference in volume between the molten alloy and the solidified alloy is known as the free volume. This free volume suggest that crystallization has not occurred and the solidified alloy acquired an amorphous or glassy structure [23]. Finally, the glass transition temperature (T_g) was calculated from the cooling curve. At glass transition temperature, the melted alloy becomes rigid and acts as a solid with an amorphous atomic structure. In this instance, the glass transition temperature can be calculated by determining the cross-over of two straight lines with differing slopes in the volume-temperature curve (shown in the inset of Fig. 2). The estimated T_g is 896K for the alloy.

3.2 Radial Distribution Functions (RDFs)

The method described in the previous section to estimate the glass transition temperature is very effective when a discontinuity is observed in the cooling curves. But, due to the smooth and continuous nature of the observed cooling curve in this work, to confirm the glass transition temperature, it is again calculated by using the radial distribution functions (RDFs). RDF demonstrates the probability of finding a particle at a distance of r from a reference particle and is given by the following expression,

$$g_{\alpha\beta}(r) = \frac{v}{N_{\alpha}N_{\beta}} \left(\sum_{r=1}^{N} \frac{n_i^{\alpha\beta}(r)}{4\Pi r^2 \Delta r} \right)$$
(2)

Here, V denotes volume of the system, N_{α} and N_{β} are the numbers of atoms of α type and β type respectively. $n_i^{\alpha\beta}(r)$ is the number of atoms located in the shell from r to r+ Δr . Fig. 3 shows the RDF curves of $Zr_{50}Ag_{50}$ alloy at different temperatures during the cooling process. It is found that the RDF curves at the higher temperature have smooth, diffused first and second peaks, indicating the liquid structure. While cooling till a temperature of 963 K, the melted structure is still present, but below this temperature, an increase in the height and decrease in the width of the first peak are observed in the RDF curves, indicating the enhancement of the short-range order (SRO) during the cooling process. Furthermore, the splitting of the second peak in the RDF curves into two sub-peaks represents the initiation of the formation of metallic glasses [24-26].

To evaluate the glass transition temperature, the well-known Wendt-Abraham parameter (WA= gmin/gmax) has been used. Here, g_{min} and g_{max} represents the first minima and the maxima of the RDF curve respectively. The inset in Fig. 3 shows the variation of the WA-parameter with respect to temperature during the rapid cooling of $Zr_{50}Ag_{50}$ alloy and the glass transition temperature is determined from the linear fit curve. The reduced glass transition temperature T_{rg} can be easily derived from the ratio between T_g and T_i ($T_{rg} = T_g/T_i$), which is an important criterion to quantify the GFA. The evaluated value of T_{rg} for the alloy is 0.58. The result shows that the $Zr_{50}Ag_{50}$ alloy forms BMG upon solidification at room temperature since its calculated value is greater than 0.5 [27].

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Fig. 3. RDF of $Zr_{50}Ag_{50}$ metallic alloy during the cooling process at the rate of 1012 K/s. The insets show the estimation of glass transition temperature Tg



Fig. 4. Distributions of the coordination numbers in Zr₅₀Ag₅₀ BMG at 300K

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3.3 Coordination Numbers (CNs)

To determine the local atomic structure in more detail, the coordination numbers, which give the number of nearest neighbor atoms of a reference atom have been calculated. The CNs for each atom can be obtained by a mathematical expression given as follows,

$$N_i = \sum_{j=1}^n \int_0^{r_{min}} 4\pi r^2 \rho_j g_{ij}(r) dr$$
(3)

Fig. 4 shows the fraction percentage of CNs of $Zr_{50}Ag_{50}$ BMG at 300 K. The population fraction of atoms with CNs from 10 to 18 are shown in the figure. It is observed that icosahedral-like clusters with CN = 14 are dominant in the $Zr_{50}Ag_{50}$ alloy, which confirms the formation of BMG.

3.4 Voronoi Tessellation Analysis (VTA)

In this work, to study the evolution of different local atomic configurations of liquid and amorphous material, we have used another important method, Voronoi tessellation analysis (VTA). This method characterizes each atom by a Voronoi index (<n3, n4, n5, n6>), where n3 is the number of triangles, n4 is the number of quadrangles, n5 is the number of pentagons and n6 is the number of hexagons in the Voronoi polyhedron (VP). In BMGs, the most prominent VPs are indexed as <0, 0, 12, 0 >, <0, 1, 10, x>, <0, 2, 8, x>, <0, 3, 6, x>, <0, 4, 4, x>, <0, 5, 2, x>, where the value of x is in the range of 0 and 6. Further these VPs are regrouped into three main group. The Voronoi indices of the type <0, 0, 12, x>, <0, 1, 10, x> and <0, 2, 8, x> represent the icosahedral-like VPs, whereas <0, 4, 4, x> and <0, 5, 2, x> represent the crystal-like VPs and the <0, 3, 6, x> represents mixed group VPs.



Fig. 5. Population fraction of dominant VPs at 300 K for Zr₅₀Ag₅₀ BMG

The calculated population fraction of all the VPs in the BMG state of the alloy is shown in Fig. 5. It is clear from the results that the crystal-like VPs are the least in number as compared to the mixed-state VPs and the icosahedral-like VPs. Moreover, icosahedral-like VPs are formed in abundance at 300K. This analysis suggests that the icosahedral-like VPs with Voronoi indices <0,2,8,4>, <0,1,10,2>, <0,2,8,2>, mixed-state VPs with <0,3,6,4> and perfect icosahedral VPs with <0,0,12,0> indices are predominantly responsible for the formation of the glassy structure of the $Zr_{50}Ag_{50}$ alloy.

4. CONCLUSION

In summary, the glass-forming ability and local atomic structure of the $Zr_{50}Ag_{50}$ alloy are investigated by using MD simulations in conjunction with 2NN-MEAM interatomic potentials. The reduced glass transition temperature (Trg) is estimated and is used to examine the glass forming ability of the alloy. The estimated value of T_{rq} for the $Zr_{50}Ag_{50}$ alloy is 0.58, which indicates that it is a potential bulk metallic glass. Moreover, the radial distribution function, Coordination number and Voronoi tessellation analysis are employed to study the local atomic structure. We found that RDFs exhibit splitting in their second peaks at temperatures below 896 K, which is known as the characteristic behavior of metallic glasses. This splitting becomes deeper and more distinct with decreasing temperature. Furthermore, the Voronoi analysis shows that <0,2,8,4>, <0,1,10,2>, <0,2,8,2>, <0,3,6,4> and <0,0,12,0> are the top dominant VPs in the system. This indicates that after solidification, these icosahedral-like clusters arranged in large amounts act as barriers to crystalline growth and help in the formation of short-range order BMG. The work will further be extended to study the dependency of GFA and structures of Zr-Ag BMGs on concentration of Ag and cooling rate.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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XRD, XPS and Dynamic SIMS Analyses of p-Type Zinc Oxynitride Thin Films Deposited on Silicon Wafers by MOCVD

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ABSTRACT

The present study aimed to determine the XRD, XPS and Dynamic SIMS analyses of p-Type Zinc Oxynitride Thin Films Deposited on Silicon Wafers by MOCVD. Zinc oxide thin film is a handy material for several solid state applications due to its many favourable properties. Bis(glycinato-N,O) zinc precursor was synthesized and used to deposit zinc oxynitride thin films on SiO2 substrates at 390°C and 420°C respectively, using the metalorganic chemical vapour deposition (MOCVD) technique. The thin films produced were characterized with hot probe, x-ray diffractometry (XRD), x-ray photoelectron spectroscopy (XPS) and dynamic secondary ion mass spectroscopy (SIMS). Thin-film technology plays an important role that allows deposition of very thin layers (from a few nanometres down to the angstrom level) of semiconductor material on a supporting substrate. The resulting material exhibits novel mechanical, chemical, optical and electrical properties with the reduction in size to the nanometre scale, which is the result of surface and quantum confinement effects. The hot probe tests showed that the thin films had p-type conductivity. XRD spectra of the films gave poorly defined peaks, signifying blurred crystallinity. The XPS analyses revealed the presence of Zn, O and N peaks, with the thin films deposited at 390°C having higher N-doping level than those deposited at 420°C. Results of destructive layer analyses conducted during dynamic SIMS tests on the films were inconclusive. The results show that lower deposition temperatures using the precursor may be preferred to higher temperatures even though the thin films were very thin. Optics and solid state electronics could both use the p-type zinc oxynitride.

Keywords: Zinc oxynitride; thin films; p-Type; precursor; XRD; XPS; dynamic SIMS.

1. INTRODUCTION

Investigations conducted severally over the years show that zinc oxide is the second most abundant metal oxide after iron. ZnO nanoparticles have recently

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attracted attention owing to their unique features. There are numerous promising applications of ZnO nanoparticles in veterinary science due to their wound healing, antibacterial, antineoplastic and antigenic properties [1]. Zinc oxide thin film is a handy material for several solid state applications due to its many favourable properties. The progressive development of thin-film technology has resulted in its extensive use in fields of optics, electronics, aircraft, defence, space science and other industries. The categories in which thin-film technology finds applications are mechanical, chemical, thermal, electrical, magnetic, electronic, chemical, optical and optoelectronic [2]. Such properties include high optical transparency, wide bandgap of about 3.4 eV, large exciton binging energy of 60 meV, high crystallinity, hexagonal wurtzite structure, high chemical and thermal stability, ease of handling and fabrication and high piezoelectric coefficient. Various electronic and optoelectronic devices which exploit these properties have been in use for long [3-6]. There are also now the added discovery of applicability in surface acoustic wave devices and high electromechanical coupling coefficient suitable for applications in nanoelectromechanical (NEM) and microelectromechanical (MEM) devices [7,8]. The thin films can be deposited using a variety of methods, including physical, chemical, and sputtering methods and their combinations. Which of the highlighted properties predominates in the deposited thin film is significantly influenced by the deposition method [9,10].

Zinc oxide as a key semiconductor element is native n-type. Realizing a p-type version of the material is an up-hill task because of the asymmetric nature of its lattice structure. The possibility is there, however, and among several options the N atom is believed to be a very suitable substitute for O in the lattice to effect a significant p-type doping.

We have previously used the metalorganic chemical vapour deposition (MOCVD) method to realize N-doping, by adopting a special precursor combination technique [11]. The result was saturated N-combinations with the ZnO, as was then reported. The desire to achieve minority N-doping which will furnish an effective p-type material led to the consideration of a different single solid source precursor complex, the bis(glycinato-N,O) zinc (or glycine zinc complex), to deposit N-doped ZnO (zinc oxynitride) thin films, by metalorganic chemical vapour deposition (MOCVD) technique. The present work is centred on this concept.

2. METHODS

The precursor used was prepared with zinc chloride, 2-aminoacetic acid (glycine) and sodium hydroxide. Stoichiometric amounts of the three substances were reacted according to the equation

$$ZnCl_2 + 2C_2H_5O_2N + 2NaOH \rightarrow C_4H_8N_2O_4Zn + 2NaCl + 2H_2O$$

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The bis(glycinato-N,O) zinc or glycine zinc complex ($C_4H_8N_2O_4Zn$) was thereafter separated and dried for use as a single solid source precursor for the work. Its structural formula is of the form (Fig. 1).



Fig. 1. Bis(glycinato-N,O) zinc structure.

The precursor was placed in the receptacle of metalorganic chemical vapour deposition (MOCVD) unit, and its vapour was passed through the cracking chamber of the unit to deposit the zinc oxynitride thin film. Oxidized silicon wafers (SiO₂) were used as the substrates while the flow rate of the precursor vapour was maintained at $2.5 \text{ dm}^3 \text{m}^{-1}$, with air as the carrier gas. Two different sets of deposition were carried out, one at 390°C, and the other at 420°C, for two hours each at atmospheric pressure. The thin films emanating from the depositions were respectively labeled as Sample A and Sample B.

The samples were characterized by using Hot probe, X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS) and Dynamic secondary ion mass spectroscopy (SIMS). The Hot probe was done by placing two droplets of silver paste side by side each other about 1 mm apart on the surface of the test sample. Then the cold electrode was placed on one of the drops at room temperature while the hot probe (soldering iron) was set to be placed on the other drop, without letting the two probes touch each other. The probe terminals were connected through a nanocurrent amplifier to a null deflection microammeter. As soon as the hot probe was placed on the drop, the meter was monitored for deflection to the left (indicating n-type) or the right (indicating p-type). An uncoated substrate, and samples A and B were tested for carrier types using this technique.

In the XRD analyses the samples A and B were scanned through $2\theta = 20^{\circ}$ to 65°. Also scanned was a sputtered 15nm ZnO thin film on Si substrate (MIT test standard) to act as comparison. The XPS examination of samples A and B were carried out along with the sputtered 15nm ZnO thin film. The XPS charts were correlated with standards and the doping levels of samples A and B compared. The dynamic SIMS analyses were done on samples A and B by destructive layer by layer analyses for elemental compositions and stoichiometry.

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3. RESULTS AND DISCUSSION

In the hot probe examination, the uncoated SiO₂ substrate gave deflection to the left, indicating n-type conductivity, while the coated samples A and B gave deflections to the right, each indicating p-type conductivities. These results show that p-doping was realized in the thin films. The deflection due to sample A was greater than that due to sample B. With further investigation and confirmation of the p-type doping results through the glycine zinc precursor in the MOCVD method, it is possible to build whole solid state devices and touch-sensitive display panels using zinc oxide alone, say by applying the undoped material for the n-type, and the N-doped material for the p-type.

Strong peaks were not obtained from the XRD scans of the samples, as the results in Fig. 2 show. Fig. 2(a) is for sample A, Fig. 2(b) is for sample B, Fig. 2(c) is the combined spectra of samples A and B, and Fig. 2(d) is the spectrum for the MIT standard ZnO test sample. The results of the samples A and B did closely match each other, as can be seen from the combined Fig. 2(c). When compared with the XRD result for the MIT standard in Fig. 2(d), one can testify that though the peaks for the samples were stunted, they did occur similarly as for the standard peaks, save for slight shifts in their 20 angles. The stunted appearance of the sample peaks is strongly believed to be as a result of the films being too thin, or from the calibration of the XRD machine, the latter possibility being plausible if one considers the fact that the peaks for the MIT standard, though better defined than for the samples, are equally not prominently sharp.



(a) XRD spectrum for sample A with ZnO library peaks overlay

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(b) XRD spectrum for sample B with ZnO library peaks overlay



(c) Combined XRD spectra of samples A and B with ZnO library peaks overlay: Teal-Sample A; Black- Sample B

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(d) XRD spectrum of sputtered 15 nm thick ZnO thin film on Si substrate (MIT test standard)

Fig. 2. XRD spectra of samples A and B and MIT standard ZnO test sample.

Also, some workers had previously reported poor crystallinity of their ZnO thin films and attributed it to different reasons [11-14], but one significant tally with the present work is that of Tan et al. [15], in which diminished crystallinity was attributed to the introduction of a N-dopant to realize p-type conductivity. So the diminution of prominent peaks in these XRD results is also attributable to the p-type nature of the thin films.

In Fig. 3 are displayed the XPS spectra of the thin films. Fig. 3(a) contains the spectra of samples A and B, Fig. 3(b) is the combined spectra of samples A and B and the MIT test standard, Fig. 3(c) and Fig. 3(d) are portions of the spectra for samples A and B, rescanned at 2 eV to respectively highlight the Zn 2p peaks and the N 1s peaks. The XPS spectra of samples A and B in Fig. 3(a) are seen to match each other, and reveal the presence of the key elements, viz, Zn, O and N. In Fig. 3(b) the samples spectra perfectly match the spectrum of the MIT test standard sample with respect to the elemental peaks, save for their relative intensities which are less prominent for samples A and B.

Compared with the 15 nm thick standard sample, the dwarfed intensities of samples A and B indicate that the coatings are very thin, possibly less than 5 nm thick. Some stray elements (Na, Cl, C and K) were also detected. They may have originated from the substrates cleaning process or wrong handling. The O peaks are sufficiently prominent in the spectra. The rescanned spectra of Fig. 3(c) and Fig. 3(d) show that while the Zn level in sample B is higher than that in sample A, the N-doping level in sample A is higher than that in sample B.
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(a) Combined XPS spectra of samples A and B: Red – Sample A; Green – Sample B



(b) Combined spectra of samples A, B and MIT test standard for comparison: Green - Sample A; Blue - Sample B; Red - MIT test standard

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(c) Zn 2p peaks of samples A and B rescanned at 0.2eV per step for higher resolution and comparison: Red – Sample A; Green – Sample B



(d) N 1s peaks for samples A and B, rescanned at 0.2 eV per step for higher resolution and comparison: Red – Sample A; Green – Sample B



This latter development may be the reason behind sample A having higher current flow than sample B in the hot probe tests. Looking back at the samples deposition parameters, it seems quite cogent that the lower deposition temperature of sample A (390°C) as against that of sample B (420°C) allowed the ZnO matrixes in sample A to accommodate more N atoms than those of sample B. Lower deposition temperatures, down to about 300°C, are hence advocated in future work with the bis(glycinato-N,O) zinc precursor (boiling point = 250°C). Perfecting the production sets the stage for cheap electronics using the doped and undoped ZnO materials for components [16].

Dynamic SIMS analyses were carried out on samples A and B by destructive layer analysis to establish the compositions and stoichiometry of the elements present. Because of the very low thinness of the thin films however, no conclusive results were obtained from the SIMS analyses [17].

4. CONCLUSION

In this work, the rare precursor, bis(glycinato-N,O) zinc (or glycine zinc) complex was utilized to deposit p-type zinc oxynitride thin films by metalorganic chemical vapour deposition (MOCVD) technique, on n-type silicon wafer. The thin films obtained were thin, possibly less than 5 nm thick. XRD scannings gave spectra with poor crystallinity due to the p-type nature and small thickness of the films. XPS spectra showed that films deposited at 390°C had higher doping level than films deposited at 420°C, indicating that lower deposition temperature may be preferable for higher doping levels and thicker films. Dynamic SIMS analyses of the samples were inconclusive owing to the thinness of the thin films. Applications of the new materials are possible in transparent and solid state electronics [18,19].

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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A Study on Two-Temperature Generalized Thermoelasticity and Its Applications

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ABSTRACT

Youssef theory serves as the foundation for the two-temperature Generalized Thermo-elasticity (GT) theory. With no energy dissipation, it is utilized to solve border line value issues in two-dimensional half-space for homogeneous and isotropic bodies. The Lord-Shulman (LS) theory-based GT equations in an isotropic elastic material depend on the reference temperature. The classical dynamical coupled theory (CD) is combined with LS theory at this point. Here is lot more work on two-temperature Thermo-elasticity is scrutinized. The time required for the heat flow to accelerate is included in the equation specifically because it is crucial to a general dynamical explanation of Thermo-elasticity. The coupled equations that come from the theory's contemplation of the coupling among heat and strain rate are both hyperbolic. Hence, the main issue of an inestimable propagation velocity is addressed in the related hypothesis of Thermo-elasticity. The basic formulations of two-temperature Thermo-elasticity are discussed in this chapter along with applications of the two-temperature Thermo-elasticity in various scientific fields of research.

Keywords: Elasticity; two-temperature; generalized thermo-elasticity (GT); basic formulations.

1. INTRODUCTION

The vibrant systems interact with their surroundings through transfer of heat, mechanical work, and external work, Thermo-elasticity is concerned. Temperature changes are the cause of thermal damage to materials. It has the ability to produce heat strain, deformation, and stress. A material expands as its "thermal" energy (and temperature) rises, along with the vibration of its atoms and molecules, which is what thermal warp essentially means. As a result, the

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molecular bonds might be thought of as being stretched. While Material's thermal energy (as temperature) drop off, the substance will deal in size or indentation. As a result, temperature change caused by the expansion and compression of the test part is necessary for Thermo-elasticity. To show how objects change in shape when temperatures change, certain procedures are used in the study of Thermo-elasticity.

Thermo-elasticity comes in three flavors: coupled, uncoupled, and generalized. Two occurrences predicted by the traditional uncoupled thermo-elasticity hypothesis are at odds with the known physical data. Second, despite the fact that elastic changes result in heat effects, no elastic variables are included in the equation for heat conduction in this theory. Second, the parabolic nature of the heat equation indicates that heat waves will flow at essentially limitless speed.

The aim of Thermo-elasticity theory is therefore to calculate the thermomechanical activities of elastic matter. This has led to widespread use of the elasticity conjecture and the premise of heat transfer in solids. The hypothesis of Thermo-elasticity was established in 1838 by Duhamel [1], who provided the equations for the strain in a flexible body by way of temperature gradients. In 1841, Neumann achieved indistinguishable consequences [2]. On the other hand, the thought was stand on the disjointing of mechanical and thermal practice. By combining the thermal extension lead to the temperature giving out unaided and the expanding pull. The whole strain was intentional. As a result, the theory did not include the activity related to the thermal state, the communication among components, or temperature dispersion. Due to this, reasons based on thermodynamic principles were necessary, and Thomson [3] was the first to present one in 1857. Various other researchers have proposed several research works on generalized Thermo-elasticity [4-21] which are found in published literatures. In this chapter a study on two-temperature generalized Thermoelasticity and its applications have been discussed.

The organization of this chapter is as follows: literature survey related to Two-Temperature Generalized Thermo-elasticity has been done in section 2. The Principles of Generalized Two-Temperature Thermo-elasticity has been discussed throughly in section 3. Section 4 discusses the recent day's applications of Generalized Two-Temperature Thermo-elasticity and in the conclusion of this study has been given in section 5.

2. LITERATURE REVIEW

In their study, Kh. Lotfy, et al. [22] used the theory of two-temperature generalized Thermo-elasticity, which is based on the theory of Youssef, to solve boundary value problems in two-dimensional half-space. The Lord-Hulman (LS) and classical dynamical coupled theory (CD) are used to resolve the governing equations by using the normal mode method. The general answer is applied to the specific problem of a half-space that has been heated using one method, the thermal shock sort. They examine how rotation impacts the total deformation of thermo-elastic half-space and their interactions under the influence of two

temperature hypotheses. The material is flexible, homogeneous, and isotropic. They solved the resulting no dimensional coupled field equations for the two theories by using normal mode analysis techniques. Graphics were used to present and discuss the numerical results for the temperature distribution, force stresses, and displacement components. The distributions of the conductive temperature, dynamical temperature, stress, and strain were all shown visually with some comparisons.

By incorporating the theory of heat conduction in deformable bodies, M. Youssef [23] established a new theory of generalized Thermo-elasticity. According to this theory, the difference between the conductive temperature and the thermodynamic temperature—which is proportional to the heat source—determines how much heat may be transferred through deformable bodies. The uniqueness theorem for equations of two-temperature generalized linear Thermo-elasticity for a homogeneous and isotropic body is obtained by them in their work.

S. Mukhopadhyay, et al. [24] investigated thermo-elastic interactions in an infinite medium with a cylindrical cavity using a theory of generalized Thermo-elasticity in which the theory of heat conduction in deformable bodies depends on two different temperatures—conductive temperature and dynamic temperature. The hollow surface, which is ostensibly stress-free, receives thermal shock. In order to compare the two-temperature generalized thermo-elastic model with the onetemperature generalized thermo-elastic model, the problem is formulated on the basis of two distinct Thermo-elasticity models, namely the Lord-Shulman model and the two-temperature Lord-Shulman model. The solutions for field variables in the physical domain are then obtained by inverting the Laplace transform using a numerical method. The solution in the transform domain is generated using the Laplace transform technique and coupled differential equations that are realm, decoupled. In the physical analytically generated short-time approximations are also obtained, and they are contrasted with the earlier findings. In their research to clarify the problem, physical quantities' numerical values for the copper material are computed, and the results from several models are graphically displayed.

When the surface of the cavity is exposed to a laser heating pulse, Al-Lehaibi, E. [24,25] presents two-temperature generalized Thermo-elasticity without energy loss in an infinite medium with a spherical cavity. The three distributions of temperature, strain, and stress resulting from the time exponential decay of the laser pulse have closed-form solutions. The Laplace transformation method is used to create the governing equations. The inversion of the Laplace transform will be computed using the Riemann-sum approximation method. Figures that indicate how the two temperature parameters and the time exponentially dropping laser pulse effect each of the fields that were being studied are used to present the study's conclusions.

Abouelregal, A. E, et al. provided a two-temperature theory to examine the thermally insulated stress-free surface of a thermo-elastic solid half-space

brought on by an angled load in an article they published in 2016 [26]. The inclined load is created by linearly combining a normal load and a tangential load. A normal mode analysis has been used to solve the current problem. Variations in conductive and thermodynamic temperatures, displacements, and stress distributions have been visually shown with regard to the horizontal distance. A few comparisons have also been made as part of the study effort to determine the effects of the two-temperature parameter and the inclination angle on the field values. From this investigation, specific instances from prior research have also been identified.

Hamdy M. Youssef, et al. [27] created a new theory of generalized Thermoelasticity by taking into account the theory of heat conduction in deformable bodies, which depends on two separate temperatures: the conductive temperature and the thermo-dynamic temperature. This study comes to the twotemperature generalized Thermo-elasticity model's variation theorem for the homogeneous and isotropic body.

An unbounded isotropic thermo-elastic media with a spherical cavity was the subject of Md Abul Kashim Molla, et al. [28] inquiry into the impact of fractional and two-temperature factors on the distribution of stresses. This was accomplished within the parameters of the Green-Naghdi model III-based theory of two-temperature generalized thermo-elasticity. The surface of the cavity, which is supposed to be free from traction, undergoes a slow heating effect that changes over time. In order to define the problem, the governing equations are solved in the Laplace transform domain using a spherical polar coordinate system. The numerical Laplace transform inversion method was then used to get the stresses in the time domain. The stress distributions are numerically estimated and graphically represented to study the effects of fractional and two-temperature factors.

3. THE PRINCIPLES OF GENERALIZED TWO-TEMPERATURE THERMO-ELASTICITY

The fundamental equations of two-temperature anisotropic Thermo-elasticity according to Mandal, Middya and Pal [29] within the framework of Lord and Shulman [30] theory are

The stress-strain temperature relations:

$$\Gamma_{ij} = C_{ijkl} E_{kl} - \gamma_{ij} (\mathbb{T} - \Theta_0)$$
⁽¹⁾

The displacement-strain relation:

$$E_{ij} = \frac{1}{2} (U_{i,j} + U_{j,i}) \qquad \dots \qquad (2)$$

The equation of motion:

$$\rho \ddot{U}_{i} = \Gamma_{ji,j} + \rho \mathcal{F}_{i} \tag{3}$$

The energy equation:

$$-\mathbb{Q}_{ii} = \rho \, \mathbb{T}_0 \mathbb{S} \qquad \dots \qquad (4)$$

The modified Fourier's law:

$$-\mathbb{K}_{ii}\Theta_{j} = \mathbb{Q}_{i} + \mathsf{T}_{0}\mathbb{Q}_{i} \qquad \dots \qquad (5)$$

According to the context of the Lord and Shulman theory, equations (1) through (5) give the fundamental equations of isotropic two-temperature Thermo-elasticity as follows:

$$\mathbb{K}\Theta_{,jj} = \rho C_{E}(\bigoplus +\tau_{0} \stackrel{.}{\bigoplus}) + \gamma \mathbb{T}_{0}(E_{kk} + \tau_{0}E_{kk})$$
(6)

$$\rho \ddot{U}_{i} = (\lambda + \mu) U_{j,ij} + \mu U_{i,jj} - \gamma \bigoplus_{i} + \rho \mathcal{F}_{i}$$
(7)

$$\Gamma_{ii} = 2\mu E_{ii} + (\lambda E_{kk} - \gamma \bigoplus) \delta_{ii}$$
(8)

Within the context of Green and Naghdi's [31] theory, the basic mathematical formulations for isotropic two-temperature Thermo-elasticity are as follows:

$$\mathbb{T}_{0} \gamma \,\delta_{ij} \,\ddot{E}_{i} + \rho C_{E} \,\ddot{\mathbb{T}} = \mathbb{K}^{*} \Theta_{,ii} \tag{9}$$

$$\Gamma_{ij} = 2\mu E_{ij} + (\lambda E_{kk} - \gamma \bigoplus) \delta_{ij}$$
⁽¹⁰⁾

$$\rho \ddot{U}_{i} = (\lambda + \mu)U_{j,ij} + \mu U_{i,jj} - \gamma \bigoplus_{i} + \rho \mathcal{F}_{i}$$
(11)

Here, \mathbb{T} denotes mechanical temperature, $\Theta_0 = \mathbb{T}_0$, denotes reference temperature, where $\bigoplus = |\mathbb{T} - \mathbb{T}_0|$ and $\bigoplus_{\mathbb{T}_0} \ll 1$, $\Gamma_{\underline{i}\underline{i}}$ denotes stress tensor, E_{ij} denotes strain tensor, C_{ijkl} denotes tensor of elastic constants, is γ_{ij} stress-temperature tensor, \mathcal{F}_i denotes external forces per unit mass, ρ denotes mass density, \mathbb{Q}_i denotes heat conduction vector, \mathbb{K}_{ij} denotes thermal conductivity tensor, C_E denotes specific heat at constant strain, U_i denotes components of the displacement vector, \mathbb{S} denotes entropy per unit mass, τ_0 denotes thermal relaxation time (which will ensure that the heat conduction equation will predict finite speeds of heat propagation), $\gamma = (3\lambda + 2\mu)\alpha_t$, and α_t denotes thermal expansion coefficient, λ and μ denotes Lame's elastic constants, δ_{ij} denotes Kronecker delta symbol, Θ denotes conductive temperature and satisfying the relation $\Theta - \mathbb{T} = b^*\Theta_{,ii}$, where $b^* > 0$, denotes two-temperature parameter and \mathbb{K} , \mathbb{K}^* denotes material characteristic constants.

4. APPLICATIONS AREAS

4.1 Dual Composite Bar

The dual composite bar is utilized in many electrical products, including microwave ovens, air conditioners, and refrigerators.

4.2 Expansion of Solids

Rail lines need to have enough space between them because they expand as a train passes over them. This is another application of thermo elasticity that can be seen in the wheel of the Bullock cart. In such a situation, a lot of heat is produced, and the line is extended.

4.3 Geothermal Energy

Geothermal energy is a component of Thermo-elasticity that, depending on the temperature and fluid flow (steam), can be used to produce electricity. There are numerous ways geothermal power plants can generate electricity.

4.4 Drilling Process

The process of proper drilling to find shell oil, is another use of Thermo-elasticity.

4.5 Fluid Injection and Hydraulic Systems

Fluid injection and hydraulic systems are another example of Thermo-elasticity.

4.6 Aerodynamic Heating

In the discipline of aeronautics, it has been discovered that the high velocity of contemporary aircraft leads to aerodynamic heating, which in turn causes significant thermal stresses and lowers the elastic limit, weakening the aircraft structure.

4.7 Nuclear Field

The extraordinarily elevated temperatures and heat gradients generated by nuclear reactors have an impact on the construction and operation of these systems as well.

4.8 Propulsive Systems

Similar to this, undesired thermal stresses originate from combustion processes' high temperatures in modern propulsion systems like jet and rocket engines.

4.9 Space Vehicles and Missiles

Similar phenomena are seen in the physics of big steam turbines, in the design of spacecraft and missiles, and even, strangely enough, in shipbuilding. Thermal stresses of modest intensities are frequently implicated in ship fractures.

5. CONCLUSION

The governing equations of nonlinear Thermo-elasticity were presented. They provided the same physical behavior of linear Thermo-elasticity's thermal and

mechanical waves passing through thermoplastic materials. The distributions of stress, displacement, and strain are significantly impacted by the nonlinear term's parameter. Based on the nonlinear Thermo-elasticity theory rather than the linear Thermo-elasticity theorem, the speeds of thermal and mechanical wave propagation are less. The basic formulations of two-temperature thermo-elasticity are discussed in this chapter along with applications of the two-temperature Thermo-elasticity in various scientific fields of research.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Fundamental Research and Application of Physical Science Vol. 6 A Study on Two-Temperature Generalized Thermoelasticity and Its Applications

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Studying the Scattering Mechanisms on Highly Transparent Polyisocyanurate-**Polyurethane Aerogels**

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ABSTRACT

Polyurethane-based aerogels have been synthesized and their optical properties studied in detail. The strong and direct relationship between the structural features of the produced materials with the final light transmittance allowed to analyze the scattering mechanisms. Thus, through the modification of the initial polyurethane formulations tunable structures were obtained and, consequently, their final optical properties were tailored. In this way, for aerogels with networks formed by small particles and pores, the highest transmittances were reached (85% at 650 nm). However, these values were progressively reduced with the enlarging of the structural features owing to the light scattering that they produce. Then, the transition through Rayleigh scattering to Mie scattering was determined by measuring the light transmittance at a wide range of light wavelengths (UV-Vis). Additionally, the Beer-Lambert law was verified for all the aerogels under study through the effect of the sample thickness on the final transmittance. Therefore, the optical properties of polyurethane aerogels were studied in detail, obtaining aerogels with tunable transmittances which opens a wide range of applications in building and energy sectors such as glazing windows.

Keywords: Polyurethane aerogels; transparency; scattering mechanisms; rayleigh scattering; mie scattering.

1. INTRODUCTION

Aerogels are open-porous materials formed when the liquid solvent that fills the gel pores is replaced by air while the porous structure remains nearly intact. These materials are gaining popularity due to their extraordinary features, such

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as high porosities (80–99%), ultralow densities (3–500 kg/m³), low thermal conductivities (10–100 mW/mK), and high specific surface areas, among others [1]. Aerogels are sometimes also known by different names such as frozen smoke, solid smoke, solid air, or blue smoke owing to translucent nature and the way light scatters in the material [2-4].

The combination of these exceptional properties has awakened a great level of interest in the production of aerogels from a great variety of materials used in several fields such as automotive [5], aerospace [6], buildings [7], cosmetics and even biomedical sector [8,9]. Some of these aerogels, in particular, exhibit a large transmittance to visible light, with some applications based on the combination of two of the most exciting features, namely their low heat conductivity and high light transmittance [10-14]. As a result, transparency is becoming a more desirable feature for aerogels. Transparency in aerogels is usually linked to silica matrices, and in fact, silica aerogels commonly present high transmittances [15–17]. The fundamental explanation of this high transparency is, on the one hand, the negligible light absorption of the silica matrix, unlike carbon- or metal-based aerogels [18,19]. On the other hand, these structures slightly scatter visible light. The size of the particles forming the silica aerogel is smaller than a tenth of the visible wavelength, which leads to a small amount of scattered light and, therefore, to a high transmittance. This behavior can be described through Rayleigh's scattering [20], which states an inverse relationship between the transmitted intensity and the fourth power of the wavelength, which explains the characteristic bluish color of some aerogels [21]. Nevertheless, when the size of the scatterers is similar to the wavelength of light, Mie scattering takes place, and the transmitted intensity varies with the first power of the light wavelength [22]. The Rayleigh-like behavior has been widely studied in the literature. For example, Mandal et al. [23] analyzed the haze of silica wet gels and aerogels presenting low densities (0.017 g cm $^{-3}$), which were attributed to Rayleigh scattering from secondary particles rather than from pores. They explained how scattered light also depended on the initial sol concentration and, therefore, on the final density. Zhao et al. [24] developed a theoretical model for the optical performance of aerogels. This model, based on the radiative transfer equation, demonstrates that the radiative properties depend only on the aerogel microstructure. Experimental data were used to validate this proposal. With this purpose, absorption and scattering were separately quantified, obtaining for the latter a dependence on a wavelength of λ^{-4} (typical of Rayleigh scattering).

Additionally, different features affecting the final light transmittance have been widely studied in the literature. Using ultra-small angle X-ray scattering measurements, Emmerling et al. [25] explained how the scattered light depends on nanostructural parameters of the gel network, such as the average particle size, interparticle voids, pore size, and an ordering factor related to the monomer concentration. Twej et al. [26] studied the relationship between the pH during the synthesis of silica aerogels, their morphology, and their final optical properties. In this way, a strong dependence was found of the light transmittance on the wavelength, which was governed by the microstructure features.

Although silica aerogels have high transparency, it is highly interesting to produce organic aerogels with high transparency due to their potential improved mechanical performance [e.g., higher toughness) than inorganic aerogels [27]. The possibility of increasing the hydrophobicity and the ease of achieving a more controlled and predictable nanostructure [28] are other features favoring organic aerogels. There are several examples of polymeric aerogels showing high light transmittances such as melamine-formaldehyde aerogels [29], chitosan-based aerogels [30], nanocellulose aerogels [31], polyimide aerogels [32], or even composites based on cellulose-nanofiber–polysiloxane aerogels.

particular, the of based In use transparent aerogels on polyurethane/polyisocyanurate could lead to the combination of a transparent material showing a very low thermal conductivity and a cost-effective solution based on a well-known polymer matrix in the building sector. Recently, the first transparent PUR-PIR aerogels were synthesized by obtaining high values of light transmittance [33]. These aerogels were employed also as an additional matrix in reticulated polyurethane foams by filling their inner pores. This strategy thus led to a significantly lower thermal conductivity in comparison with the initial non-filled foams [34]. Herein, we present a detailed and systematic study of the optical properties, as well as the effect of different factors (aerogel thickness, porous structure, and incident light wavelength) on the optical transmittance of these PUR-PIR aerogels. In addition, the scattering mechanisms in these aerogels were analyzed.

Therefore, the microstructure–properties relationship is assessed through the analysis of the structure and morphology, as well as the study of nanoscale physics phenomena, for these ultralightweight aerogels.

1.1 Objectives

Evaluating the effect of the porous structure on the optical properties of polyurethane-based aerogels could determine the optimum structural features (pore and particle size) for obtaining highly transparent aerogels.

The determination of the scattering mechanisms acting as light attenuators provides an interesting information to analyze the effect of the light wavelength on the final transmittance. In addition, finding the transition from Rayleigh to Mie scattering could explain the influence that the scatterer centers present on these mechanisms.

2. METHODOLOGY

2.1 Sol-gel Chemistry and Drying

Sol-gel technology was employed for the synthesis of the polyisocyanuratepolyurethane aerogels in one step. The whole procedure has been described in detailed by the authors [33] and can be summarized in the following steps: Studying the Scattering Mechanisms on Highly Transparent Polyisocyanurate–Polyurethane Aerogels

- A solution of isocyanate (IsoPMDI 92140, BASF Polyurethane) (44 g/L in CH₃CN:THF at 65:35%vol.) was poured into a plastic cup, and then the corresponding amount of the pentaerythritol (PTOL) solution (Alfa Aesar) (100 g/L in DMSO) was added to obtain a molar relationship of PTOL/p-MDI of 0.43.
- The sol-gel process is promoted by the addition of the corresponding amount of catalyst (Kosmos 75 MEG, Evonik) (2–18 wt.% of the total of PTOL and p-MDI mass) and the solution was stirred at 500 rpm for 20 s at room temperature (controlled temperature at 22 °C).
- The obtained sol was poured into a plastic syringe (2 mm in diameter) until reaching the gelation time. A transition from yellowish transparent to whitish translucent was observed when the gelation point was reached. Syringes were tightly sealed with a plastic film in order to avoid solvent evaporation and premature drying of gels.
- Ageing of the produced gels was performed by adding acetonitrile until completely covering the gels (24 h).
- Two washings (24 h each) with acetonitrile were applied to remove nonattached chemicals.
- Finally, gels were dried by supercritical drying (40 °C, 100 bar).

The developed formulations were based on the same proportions of polyol and isocyanate but changing the reaction kinetics through the catalyst amount, which ranges from 2 to 18 wt.%. The obtained cylinders (ca. 16 mm in diameter and 10 mm in height) were cut in different thicknesses with a metal blade.

2.2 Characterization of the Produced Aerogels

• Geometrical density, relative density and porosity were measured following the ASTM D1622/ D1622M-14 [35]. The outer skin (ca. 2 mm) of the produced specimens was removed for those measurements. Porosity was calculated as described by equation 1:

$$\Pi = (1 - \rho_r) * 100 \tag{1}$$

where p_r is the relative density, defined as:

$$\rho_{\rm r} = \frac{\rho}{\rho_{\rm s}} \tag{2}$$

where ρ is the geometric density of the aerogel and ρ_s is the solid density of the polymeric matrix, i.e., 1.17 g/cm³, determined by helium pycnometry [33].

 Scanning electron microscopy (ESEM Scanning Electron Microscope QUANTA 200 FEG, Hillsboro, OR, USA) was applied after iridium metallization by a sputter coater (EMITECH K575X Sputter Coater, Fall River, MA, USA).

- Specific surface areas were determined by nitrogen sorption through a Micromeritics (Norcross, GA, USA) ASAP 2020 instrument at the University of Málaga (Spain). The experiments were run at – 196 °C in the range P/P0 = 0.05 – 0.30, and the Brunauer-Emmett-Teller (BET) method [36] was employed for the calculations.
- **Particle size** was determined using software based on Image J(2.0-1.52q, 2019)/FIJI [37] and SEM micrographs. The visualized particles were drawn, and their diameter was estimated. The particle size is the mean value of at least 50 particles. The standard deviation and particle size distribution were also measured for each formulation.
- **Pore size** was measured through the Barrett–Joyner–Halenda (BJH) method by nitrogen sorption [36]. The pore volume employed for these calculations was estimated by equation 3.

$$V_p = \frac{1}{\rho} - \frac{1}{\rho_s} \tag{3}$$

where ρ is the geometric density of the aerogel and ρ_s is the solid density of the polymeric matrix. Considering the specific surface area and the total pore volume, the average pore size can be determined assuming cylindric pores:

$$\Phi_{\rm p} = \frac{4V_{\rm p}}{S_{\rm BET}} \tag{4}$$

- Light transmittance was calculated as the ratio between the intensity passing through the aerogel (I) and the intensity without sample (I0). The setup consists of a laser as light source (red laser 650 nm, a green laser 532 nm, blue laser 450 nm) and a photodiode joined to an integrating sphere with 12.5 mm window (PRW0505, Gigahertz-Optik) connected to a photometer (X94, Gigahertz-Optik, Türkenfeld, Germany) as a light detector (detector–laser distance fixed at 133 mm). In order to collect the maximum scattered light, samples were placed directly in the window of the integrating sphere. Different thicknesses have been measured for each sample by cutting plane-parallel slices with a metal blade (from 0.4 mm to 12 mm).
- UV-Vis (UV-2102 PC, Shimadzu, Kyoto, Japan) was used for measuring the light transmittance on a wide range of light wavelengths (400 900 nm). The experiments were performed with an aperture of the slit of 1 nm. A back-ground spectrum without any sample was made to take this intensity as 100% of transmittance. According to the UV–Vis assembly, samples were placed 2 cm from the detector, thus, some of the transmitted light did not reach the detector. For this reason, UV–Vis transmittance values were taken as relative values by comparison between samples and as a strategy to determine the dependence of the wavelength on the transmitted intensity.

3. RESULTS AND DISCUSSION

3.1 Density, Porosity and Structural Features

The produced aerogels were characterized in terms of their density, porosity and porous structure. Table 1 gathers the collected information for all the formulations. The aerogels are labeled with numbers that correspond to the amount of catalyst used during their synthesis (wt.%).

The modification of the catalyst concentration and, therefore, of the polymerization rate leads to different density values, ranging from 0.079 g/cm³, for the material produced using the highest catalyst content (aerogel 18), to 0.128 g/cm³, for the material produced using a catalyst content of 3 wt.%. Porosity values are in a narrow range, from 89 to 93%, indicating that a large gas volume fraction is contained in these aerogel samples. The values for the structural parameters obtained by nitrogen sorption (pore volume and specific surface areas) are also included in Table 1. As expected, pore volume increases with porosity, reaching a maximum value of 9.04 cm³/g.

The results obtained for the specific surface areas are in agreement with the particle size measurements, since the larger the particles the lower the surface area. Surface areas increase from 49 m^2/g when particles present a size value of 78.6 nm (aerogel 18) and increases until 294.11 m^2/g when the particle size is reduced to 24.6 nm (aerogel 2).

SEM micrographs are displayed in Fig. 1 showing the porous structures of the samples under study. On the one hand, it can be seen that the obtained aerogels present a homogeneous nanostructure, which is relevant for obtaining high transparency values. On the other hand, the aerogel nanostructures vary with different amounts of catalyst, showing significantly different particle and pore sizes. The images indicate that increasing the catalyst content leads to larger particle and pore sizes. This effect was quantified by analyzing the particle size distribution and the mean particle size (Table 1).

Particle size ranges from 23 to 78 nm and show a clear increase with the catalyst amount, as previously discussed. Values above 40 nm, a tenth of the wavelength of the visible light, were only reached for the two samples with higher amounts of catalyst: aerogels 15 and 18. Regarding the mean pore sizes, the same tendency is observed with the catalyst content with pore sizes that increase from 85 to 141 nm for the samples with catalyst contents ranging from 2 to 10 wt.%. A sharp increase in the average pore size was obtained for the samples with the highest catalyst content, reaching a maximum value of 722 nm. The explanation of these differences is related to the reaction kinetics that control the polycondensation reaction in which the polymeric skeleton is formed [33]. Therefore, when the catalyst amount is increased, promoting a faster skeleton formation, particles form aggregates that give rise to larger secondary particles.

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Aerogel	Density (g/cm ³)	Porosity	Particle Size	Average Pore	Pore volume	Specific surface
		(%)	(nm)	Size (nm)	(cm³/g)	area (m²/g)
2	0.097 ± 0.001	91.68	24.6 ± 5.4	85.0	6.25	294.11
3	0.128 ± 0.023	89.08	23.0 ± 6.0	72.1	5.19	288.15
4	0.108 ± 0.015	90.77	25.6 ± 6.4	93.1	5.63	242.09
6	0.109 ± 0.011	90.73	32.0 ± 6.9	91.1	6.24	274.12
8	0.089 ± 0.001	92.38	34.1 ± 7.8	137.9	6.79	197.10
10	0.109 ± 0.001	90.72	32.6 ± 6.9	140.6	7.88	224.28
15	0.081 ± 0.001	93.03	45.7 ± 12.3	249.1	9.04	145.21
18	0.079 ± 0.003	93.23	78.6 ± 16.0	722.0	8.97	49.70

Table 1. Main characteristics of the PU aerogels

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Studying the Scattering Mechanisms on Highly Transparent Polyisocyanurate-Polyurethane Aerogels



Fig. 1. SEM micrographs and the corresponding particle size distribution for the aerogel samples with different catalyst contents

Fig. 1 also includes the particle size distribution obtained from the scanning electron micrographs. The particle size distribution of each sample affects the efficiency of the scattering mechanism. Narrow distributions are obtained for those aerogels with a low catalyst content in their formulation (2, 3, 4, and 6 samples), which are formed by particles with a homogeneous size. In fact, almost all particles have sizes below 40 nm in these aerogels. Nevertheless, for samples containing higher catalyst amounts (8, 10, 15, and 18 wt.%), the size of the polymeric particles is more heterogeneous, covering a wider range of the nanometric scale, with a significant number of particles larger than 40 nm that are expected to reduce the final transmittance.

These distributions affect the scattering mechanisms, as it will be studied in the following section.

3.2 Light Transmittance

3.2.1 Laser measurements: Bee-Lambert law

Transmittance gives account for the amount of light that is able to pass through a material in comparison with the incident light. However, far from the simple

appearance of this definition, many factors and parameters affect the light transmitted by aerogels. In the following sections, these key parameters are discussed.

Samples were cut at different thicknesses to study its effect on the final transmittance and verify the Beer-Lambert law. Additionally, the effect of the light wavelength was studied by using lasers at three different wavelengths: 450, 532, and 650 nm. Fig. 2 displays these measurements.

a) Catalyst content effect

Transmittance shows the same behavior for the three laser wavelengths measured: the lowest catalyst contents lead to aerogels with higher transmittance values. This trend was expected since the samples with lower catalyst showed the structures with the smallest particles and pores, as well as the narrower particle size distributions. The samples produced with larger catalyst contents show very low values of transmittance, below 7%, even for very low thicknesses.



Fig. 2. Transmittances obtained for materials produced with different catalyst concentrations at different thicknesses and different light wavelengths

b) Thickness effect

The trend between the final transmittance and the sample thickness follows the Beer-Lambert law [38]:

$$T = \frac{I}{I_0} = e^{-\mu \cdot L}$$
(5)

Where μ is the attenuation coefficient and L the sample thickness.

As observed in Fig. 2, transmittance follows an exponential decay for samples between 2 and 10 wt.%, which follows the Beer–Lambert law. High transmittances are still obtained for aerogels under 4 mm in thickness, tending to 1 when thickness tend to 0. However, transmittances are clearly smaller for thicker aerogels.

By representing $-\ln T$ as a function of the aerogel thickness, a straight line should be obtained whose slope corresponds to the attenuation coefficient μ [39].

c) Light wavelength effect

The highest values, above 85% of transmittance, were reached for 650 nm (red color); around 78% for 532 nm; 65% for 450 nm: the absolute value clearly decreased when the light wavelength was reduced for each sample and each thickness. The main reason behind this observation is that for smaller wavelengths, a higher amount of light will be scattered by the scatterer centers (particles forming the skeleton).

In order to compare in a separate way the light wavelength effect on the final transmittance, transmittance was calculated for a normalized value of sample thickness (1 mm). Equation 6 was employed for these calculations, being a derivation of the Beer-Lambert law.

$$T = T_0^{\frac{L}{L_0}}$$
(6)

where T_0 corresponds to a reference transmittance value, L_0 is the real sample thickness, and L is the selected thickness to calculate the transmittance.

Fig. 3a represents the decrease on the final transmittance for larger catalyst amounts and for smaller wavelengths, as explained before. Three different regions can be observed that are correlated with the particle size as it will be explained in the following section.



Fig. 3. a) Transmittance values of aerogels with different catalyst content for a thickness of 1 mm. b) Dependence of normalized transmittance on the particle size of the final aerogels (1 mm thickness)

d) Particle size effect

The obtained transmittance results and the observed tendencies can be explained by considering the light interaction with the aerogel internal structure. When light passes through an aerogel, two processes can contribute to attenuating the radiation: scattering and absorption. Thus, part of the incident radiation may be transformed into thermal energy, corresponding to an absorption process that, although it depends on the scattering mechanisms [20], will be neglected in this work since all the aerogels present the same polymer matrix and a similar relative density. Additionally, the scattering mechanism deviates the incident light with a certain angle depending on the characteristic features of the scatterer centers.

Aerogels are open-porous materials formed by interconnected voids and a network of polymeric nanoparticles, i.e., a continuous air phase in which interconnected particles are dispersed. Therefore, in terms of its light transmission, the aerogel can be considered a continuum air medium through which the light can pass through, being scattered by the presence of nanometric particles. Moreover, the aerogel presents a refractive index slightly different from air, so the transmitted light would be slightly reduced by the refraction caused by the air–aerogel interface.

Aerogels' transparency mainly depends on the size of the structural inhomogeneities (i.e., particles forming the solid skeleton), the particle size distribution, and the packaging of these inhomogeneities, i.e., the aerogel density [9]. Particles act as nanometric scattering centers for the incident radiation by radiating electromagnetic energy in all directions. Therefore, the size of the structural elements forming the solid 3D network plays an essential role in the amount of scattered light, as well as in the direction the light is scattered. When the incident wavelength is similar to the scatter size, Mie scattering takes place [22,40]. In this case, most of the light is scattered in the forward direction. When the scatter size is reduced up to a tenth of the incident light, scattering turns into Rayleigh scattering [41]. In this case, the amount of scattered light is reduced, leading to a higher transmittance, whereas the wavelength dependence becomes stronger.

The aerogels' density depends on the packaging of the spherical particles and the shrinkage experimented by the samples during the supercritical drying step. Thus, this factor must be considered in order to normalize the final transmittance, thus compensating for the potential deviations associated with different densities. The normalized transmittance (T/ρ) allows the effect of particle size to be analyzed more independently and enables a reliable comparison between different samples. The relationship between the normalized transmittance (for aerogels with 1 mm thickness) and the sizes of the scattering centers are displayed in Fig. 3b.

The normalized transmittance shows a strong dependence on particle size, even for a narrow range of particle sizes (23–78 nm). The normalized transmittance is sharply reduced when the particle size increases from 23 to 30 nm (from region 1 to region 2). For particle sizes above 30 nm (region 2), the increase in the particle size leads to small variations in transparency. When the heterogeneities size is above one tenth of the visible light wavelength (400–700 nm), i.e.

above 40 nm (region 3) transparency sharply decreases [42] because a strong scattering is induced by these particles.

Thus, a slight increase in the final particle sizes leads to a significant loss in visible-light transparency. Hence, careful control of the reaction kinetics during the sol-gel process and an optimized supercritical drying method that avoids huge shrinkages and structural damage are crucial in the synthesis of transparent aerogels. PUR–PIR aerogels containing a low catalyst percentage, with particle and pore size values of a few nanometers, therefore display the highest transmittances.

e) Refraction index effect

Due to the different refractive index between the polymeric matrix and the air, there is an inhomogeneous interaction between light and the aerogel [14]. Since more than 89% of the aerogel (Table 1) is air, its refractive index is expected to be very close to 1, meaning that light will only be slightly refracted by the PUR–PIR aerogels. Although the refractive index depends on the bulk density of the samples, these density values are within a narrow range (0.079–0.128 g/cm³), so we can assume that the refraction index will be similar for all the aerogels under study. The refraction index value can be calculated for each sample by the Clausius–Mosotti formula (Equation (7)) [43]:

$$n - 1 = \frac{3 \rho}{2 \rho_s} \left(\frac{n_s^2 - 1}{n_s^2 + 2} \right)$$
(7)

where the solid density (ρ_s) for polyurethane is 1.160 g/cm³ and the refractive index for solid polyurethane (n_s) is 1.67.

The refraction indexes thus obtained for our samples range between 1.038 and 1.062 (Table 2), and thus, since they are close to 1, there is no significant refraction in the interface.

Aerogel	Refraction index	
2	1.047	
3	1.062	
4	1.052	
6	1.052	
8	1.043	
10	1.052	
15	1.039	
18	1.038	

 Table 2. Refraction index for the aerogel samples calculated by the

 Clausius-Mosotti equation

3.2.2 UV-Vis measurements: Determination of the scattering mechanisms

As previously discussed, the incident wavelength strongly affects the transmittance. Three different regions could be distinguished in the graphs of Fig. 3 regarding the effect of wavelength: the transmittance dependence on wavelength is less noticeable for samples with a high catalyst content (15 and 18 wt.%, region 3) since their particle sizes surpass 40 nm, i.e., above a tenth of the wavelength of visible light. The decrease in transmittance observed for the rest of the samples can be explained by the light scattering that those particles produce. In particular, samples with 2, 3, and 4 wt.% (region 1) present a strong dependence on the light wavelength since the diameter of their particles is below 30 nm. The last group is formed by samples with 6, 8, and 10 wt.% (region 2), which are composed of particles with diameters of ca. 30 nm; thus, the dependence on the wavelength is still strong.

This dependence was studied in detail through the results obtained using a UV– Vis spectrometer. This spectroscopic technique has been used to cover a larger range of light wavelengths (400–900 nm) and analyze the dependence of transmittance on the incident wavelength. Fig. 4 shows the transmittance curves for all the samples under study (for 1 mm thickness), except for those with the highest catalyst content (15 and 18 wt.%), since the latter display very small transmittance and poor signal-to-noise ratio.



Fig. 4. UV–Vis transmittance measurements for all the samples under study. Measurement corrected for samples of 1 mm. Optical micrographs of the samples from left to right; catalyst content and particle size increase in the following order: 2 wt.%, 3 wt.%, 4 wt.%, 6 wt.%, 8 wt.%, 10 wt.%, and 18 wt.%

Fig. 4 shows a clear trend between transmittance and the amount of catalyst; this trend is higher for samples with less catalyst, which is in agreement with the results of the previous sections. Moreover, the strong effect of the wavelength on the final transmittance confirms the difficulty for light to travel through the aerogel samples at small wavelengths.

The effect of light wavelength on the optical properties has been previously analyzed for silica aerogels, and their transmittance behavior has been attributed to Rayleigh scattering [44-46]. Rayleigh scattering refers to the elastic scattering of light when interacting with scatterer centers with a diameter smaller than about a tenth of the incident light wavelength [41]. The scattered intensity from Rayleigh scattering, I, that particles produce can be described as follows [47]:

$$I_{\text{scattered}} = \frac{8 \pi^4 d^6}{r^2 \lambda^4} [\frac{n^2 - 1}{n^2 + 2}] (1 + \cos^2 \theta)$$
(8)

where d is the particle diameter, n is the refractive index of the scatterer center, r is the radial distance from the scatterer, and θ is the scattering angle. The dependence of the scattered intensity on the scatterer size is to the sixth power, which explains the notable differences in the final transparency when particles increase in size (Section 3.2.1, d). According to Equation (8) of Rayleigh's law, the scattering intensity varies with the fourth power of the inverse wavelength of the incident light. Therefore, transmission can be expressed as follows [42]:

$$T = A e^{-\frac{BL}{\lambda^4}}$$
(9)

where A and B are constants, and L is the sample thickness.

Nevertheless, the scattering mechanism produced when the scatterer's diameter is larger than about one-tenth of the wavelength is known as Mie scattering [22]. Maxwell's equations must be solved under the scattering conditions [48,49]. For particles with a radius greater than about ten times the wavelength of the light, the scattered intensity is given by:

$$I_{s} = I_{i} \int_{\alpha_{0}}^{\alpha_{1}} |S(\theta, \alpha)|^{2} f(\alpha) d\alpha$$
(10)

where I_i is the total transmission, $S(\theta, \alpha)$ is the scattering function, and $f(\alpha)$ is the distribution for the particle size parameter (α). This parameter can be described as:

$$\alpha = \frac{2 \pi n_m}{\lambda} r \tag{11}$$

where nm is the refractive index, λ the wavelength, and r the particle radius.

The transmittance–wavelength dependence varies, in this case, with the first power of the inverse wavelength of the incident light. In this way, with $-\ln(T)$ representing a function of either L/λ^4 or L/λ in the range of 400–900 nm, and analyzing whether the data fit better, considering one or the other dependence allows us to understand the scattering mechanism in each case [39].

The fit of the average of the adjusted R² values for the fitting is shown in Table 3. The obtained values confirm that there are different scattering mechanisms in the PUR–PIR aerogels described herein. Samples are divided into the three groups discussed above based on their different behaviors (Fig. 3).

Table 3. Average adjusted R^2 values for the fitting of -Ln(T) as a function of L/λ^4 or L/ λ

	Rayleigh (L/λ⁴)	Mie (L/λ)
Aerogel	R ²	R ²
2, 3, 4	0.994	0.962
6, 8	0.994	0.966
10	0.977	0.991

The three samples with the lowest amounts of catalyst (2, 3, and 4), where the particles' diameter is clearly less than a tenth of the visible wavelength, fit significantly better with the relationship L/λ^4 , indicating that the Rayleigh scattering mechanism occurs. This leads to a smaller amount of scattered light, and, therefore, transmittance in these samples is notably high. Samples with 6 and 8 wt.% still show a Rayleigh regime. However, the particle size distribution of the aerogels with 10 wt.% of catalyst content is shifted to higher values, meaning that Mie scattering is the principal scattering mechanism (see the structural parameters shown in Table 1 and particle size distribution shown in Fig. 1. This means that the amount of scattered light increases and, therefore, that transmittance decreases, as demonstrated experimentally.

4. CONCLUSIONS

In this work, the synthesis and a detailed characterization of different polyisocyanurate-polyurethane (PUR-PIR) aerogels have been described. Through the variation of the catalyst concentration tunable porous structure and thus, tunable optical properties were reached.

The scanning electron micrographs showed that really different pore and particle sizes are present when varying the catalyst amount. In this way, small contents led to the minimum particle size of ca. 23 nm and this value is increased until 78 nm for faster reactions. In addition to the particle size values, the particle size distributions indicate that larger particles lead to a more heterogeneous distribution.

The dependence of the light transmittance was studied as a function of different parameters.

Regarding the catalyst content, the reaction kinetics during the formation of aerogels had a significant effect on their optical transmittance, with the samples with the highest transparency being the samples with the lowest catalyst content. On the other hand, aerogels were cut at different thicknesses (from 1 to 14 mm) to evaluate the effect on the final transmittance. These data followed the Beer–Lambert law which allowed to calculate the transmittance for any thickness.

The strong effect of the aerogels structure on the light transmittance was evaluated through the particle size. For particles below 30 nm, the highest transmittances were reached, since this value is smaller than a tenth of the wavelength of the visible light. Nevertheless, when these values surpass that limit, i.e. 40 nm, transmittance was sharply decreased. In this way, PU aerogels ranging from highly transparent to almost opaque were obtained.

In view of the huge effect of particles on the optical properties of these materials, the scattering mechanisms were studied by analyzing the dependence of the transmittance on a wide range of light wavelengths (400 to 750 nm). The transition from Rayleigh scattering to Mie scattering was found when particles presented values larger than 32 nm. Therefore, aerogels presenting the smallest particles followed a wavelength-transmittance dependence of L/ λ^4 while for larger particles this dependence is L/ λ , thus, significantly decreasing their transparency.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Forecasting of Long-term Electricity Consumption in China: A Combined Approach based on KPCA and Linear Regression Model

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ABSTRACT

In this chapter, we demonstrate that the integrated model of Kernel Principal Component Analysis (KPCA) and Linear Regression (LR) outperforms other methods, thereby offering a novel and feasible approach for long-term electricity consumption prediction. We propose a combined model of KPCA and LR for this purpose. Despite a limited sample size, the model can accurately forecast the temporal changes in total electricity consumption, boasting high interpretability and practical utility. We employed KPCA to reduce the complexity of the original data, then input the dimensionally reduced data into a Backpropagation Neural Network (BPNN) and other models, yielding optimal model results. Visualization of the three principal components derived through KPCA revealed that the first principal component represents the long-term growth of electricity consumption, while the other two components represent the long-term fluctuation of electricity consumption. Additionally, population features, price features, and industrial structure features also contribute to the increase in China's electricity consumption, albeit in a more fluctuating manner. Lastly, we predict that China's total societal electricity consumption will reach 1.83 trillion KWH by 2035, a forecast more optimistic than that of Oxford experts and consistent with China's victory in combating COVID-19. The model holds an optimistic view of China's future economic prospects, aligning with China's rapid economic growth and its comprehensive victory in the fight against COVID-19.

Keywords: Long-term electricity consumption forecasting; kernel principal component analysis; linear regression; China.

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1. INTRODUCTION

China is the world's largest and second largest producer of coal and electricity respectively. China is also a major exporter of coal and importer of oil. The energy sector plays an important role in the economy, both in terms of employment and industrial output. Major oil and power enterprises are among the largest state-owned enterprises [1]. The total amount of electricity consumed is rising along with China's economy's rapid growth. Since modern society depends on energy for both production and citizen life, changes in total electricity consumption can be used to measure both the growth of the national economy and the raising of citizens' standards of living. Accurately forecasting long-term total social electricity demand could help the nation develop economic development strategies, transform its industrial structure, and fulfil its obligations to other countries in terms of energy conservation, emission reduction, and low-carbon environmental protection. . Therefore, forecasting the long-term total electricity consumption accurately has been an important topic in the academic and industrial fields. The majority of China's consumption consists of fossil fuels, with renewable energy taking up less than 8%. The combustion of fossil fuels has generated considerable greenhouse gas (GHG) and particulate matter (e.g., black carbon) emissions, which not only contributes to global warming but is the major source of haze. It has been well known for its deleterious health impacts and as an obstacle to sustainable development [2].

There are various methods for long-term electricity consumption prediction, and the main methods can be divided into three categories, namely the econometric model, machine learning model and bottom-up subsector model. To be specific, firstly, econometric models include multivariate linear regression, time series, etc. For example, Bianco et al. forecasted electricity consumption in Italy with linear regression models [3]. Huang et al. applied the AMRA model, a classic time series method, to forecast electricity consumption in Changli County, China [4]. These models are usually based on scenario analysis, that is, assuming that future economic, population, carbon emissions [5] and other economic indicators change at a specific growth rate, then estimating how each major economic variable changes, and finally predicting the future value of electricity consumption based on the estimated variable. The mainstream scenario analysis method is Shared Socioeconomic Pathways (SSPs), which assumes that there are five types of economic growth modes in the future. They are green growth (SSP1) [6], a middle-of-theroad scenario (SSP2) [7], AIM (Asia-Pacific Integrated Assessment) implementation scenario (SSP3) [8], a world deepening inequality (SSP4) [9], and energy and resource-intensive scenario (SSP5) [10] respectively. SSPs have certain reference value, but due to the complexity and variability of the real world (i.e., COVID-19), SSPs may not be able to include all the possibilities of future economic situations, making electricity consumption forecast inaccurate.

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Secondly, the machine learning model is also a common method to predict electricity consumption, such as neural networks [11-14], support vector machine [15], random forests [16], wavelet analysis [12], fussy Bayesian [17], etc. Specifically, Li and Lu [12] established a combined forecasting model using a backpropagation neural network (BPNN) and wavelet analysis. In this model, wavelet analysis identifies important components and extracts critical information, and BPNN is used to fit the model. The authors finally obtained good prediction results. However, even though the machine learning model usually has good fitting performance, it is difficult to guide production in the real world due to its "black box" feature and lack of interpretability. In addition, because many economic data are quarterly or annual, the sample sizes are usually small, which will hinder the machine learning model's predictive performance.

Thirdly, bottom-up subsector models, like LEAP [18] or MARKAL [19], should divide the total social electricity consumption into small parts, to obtain the electricity consumption in each electricity department. By predicting the electricity consumption in different departments one by one, the total electricity consumption of the whole society can be finally obtained. However, this method requires a large amount of basic data for calculation and consumes a huge amount of computing resources, so it is not suitable for the field of private prediction.

Therefore, it is of practical significance to propose a long-term electricity consumption prediction model with high prediction accuracy, strong interpretability and a small sample requirement. Hence, based on the existing electricity forecasting methods, this paper proposed a combined model of Kernel Principal Components Analysis (KPCA) with linear regression (LR) to forecast long-term electricity consumption. KPCA can reduce the sample's dimension nonlinearly, which is used to process linear inseparable data sets. KPCA has the characteristics of a classical statistical model, that is, the model is non-black-box and has a low requirement for data volume (compared with machine learning methods). In addition, KPCA increases the model complexity due to its nonlinearity and adjustable parameter, so it has higher fitting accuracy (compared with the traditional statistical methods).

KPCA is widely used in various forecasting fields. For example, Liu et al. [11] combined KPCA and BPNN to forecast monthly electricity consumption in European countries. The authors used KPCA to reduce the complexity of the original data, then put the data after dimensionality reduction into LR and other models, and the ideal model results were finally obtained. Besides, there were applications of KPCA in face recognition [20], auxiliary driving [21], disease diagnosis [22], and so on.

This study aims to develop an accurate and interpretable long-term electricity consumption forecasting model for China.

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Fig. 1. Research and modeling process

The structure of this paper unfolds as follows: The second chapter introduces the data. The third chapter presents the principal components analysis (PCA) and kernel principal components analysis (KPCA). The fourth chapter applies PCA and KPCA to the original data for dimension reduction, deriving new variables. These variables are then incorporated into the linear regression model and machine learning model. The fifth chapter analyzes and elucidates the optimal model results, while the sixth chapter concludes the paper. The research and modeling process for the entire text is depicted in Fig. 1.

2. DATA

The data utilized in this paper is sourced entirely from the Oxford Economics Database (www.oxfordeconomics.com). This database aggregates data from open and authoritative sources, such as the World Bank, IMF, OECD, and National Statistical Offices of various countries, and integrates them into a comprehensive global economic database. Furthermore, experts at Oxford University annually provide professional forecasts for all indicators in the database. Consequently, the database offers a broad spectrum of economic data spanning from 1980 to 2050, facilitating easy usage and analysis. Based on the research findings of [23,24], this paper gathers nine annual economic variables of China from 1980 to 2035 (data from 1980-2019 represent real values, while data from 2020-2035 are predicted values derived from Oxford exports). These variables include total societal electricity consumption, population growth rate, urban population proportion, nominal GDP, residential electricity price, fuel prices, secondary industry added value proportion, tertiary industry added value proportion, and per capita employment output value. The first variable is the dependent variable, while the remaining variables serve as explanatory variables. All variables are designated as shown in Table 1."

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In Table 1, according to the characteristics of independent variables, they can be divided into five types, namely population feature, economy feature, price feature, industrial structure feature, and production efficiency feature. All of these variables have a certain influence on total electricity consumption. Visualize all the data as shown in Fig. 2.

	Variable	Abbreviation	Note
Dependent	Total electricity	Elec	Electricity feature
Variable	consumption in the whole		
	society)		
Independent	Population growth rate	Popu	Population feature
Variable	The proportion of urban	Urban	Population feature
	population		
	Nominal GDP	GDP	Economy feature
	Residential electricity price	ResiPri	Price feature
	Fuel Price	FuPri	Price feature
	The proportion of added	SecInd	Industrial
	value of secondary industry		structure feature
	The proportion of added	TerInd	Industrial
	value of tertiary industry		structure feature
	Per capita output value of	Output	Production efficiency
	employment		feature

Table 1. Variable explanation



Fig. 2. Visualization of all variables

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	Elec	Popu	Urban	GDP	ResiPri	FuPri	SecInd	TerInd	Output
Mean	4580.16	0.70	46.40	73016.98	0.43	152.76	34.63	43.87	0.07
Median	3362.65	0.60	45.85	29466.85	0.52	182.60	36.00	44.10	0.05
Maximum	12580.20	1.90	76.60	308609.90	0.62	282.30	40.70	57.60	0.20
Minimum	300.60	-0.10	19.40	480.90	0.17	14.20	24.80	28.60	0.00
Std.Dev.	4061.27	0.55	18.02	89004.00	0.16	96.86	5.02	7.38	0.06
Skewness	0.56	0.64	0.09	1.18	-0.71	-0.25	-0.71	-0.05	0.76
Kurtosis	1.87	2.56	1.64	3.21	1.92	1.43	2.19	2.55	2.22
Observations	56	56	56	56	56	56	56	56	56

Table 2. Descriptive statistics of all variables

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Fig. 2 shows that from 1980 to 2035, China's total electricity consumption, the proportion of urban population, GDP, residential electricity price, the proportion of added value of tertiary industry, and per capita output value of employment displayed an upward trend. The first three variables show a steady growth rate, while the latter three variables show some jagged characteristics. The population growth rate has been decreasing over the year since 1990, which is in line with the characteristics of current residents' declining desire to have children. Fuel price is growing but fluctuating over time, which is affected by the supply and demand fluctuations in international energy markets, such as the crude oil market. The proportion of added value of secondary industry presents a trend of increasing first and then decreasing. The turning point came in 2013, which reflects the transformation of China's industrial structure in recent years.

Table 2 displayed the descriptive statistics of all variables.

According to Table 2, the mean value of total electricity consumption and GDP is significantly greater than the median, which is consistent with their exponential growth characteristics. The Skewness and Kurtosis values of most variables are different from those of standard normal distribution (Skewness equals 0 and Kurtosis equals to 3), proving that most variables are not a normal distribution. In fact, according to the Jarque-Bera test, only the proportion of added value of tertiary industry obeys a normal distribution, suggesting that all other variables changed over time.

3. METHODS

3.1 Principal Components Analysis

Principal component analysis, as a statistical method, transforms a group of potentially correlated variables into a group of linearly uncorrelated variables (called principal components, also known as factors) through orthogonal transformation. During transformation, the main information of the original variables will be retained (usually measured by variance maximization).

In all principal components, the first principal component (factor 1, f_1), contains the most information in the original variable and is usually chosen as the representation of the original variable. If f_1 contains insufficient information, factor $2(f_2)$ will be added to jointly represent the original variable, and $Cov(f_1, f_2) = 0$, etc. The calculation process of PCA is shown below.

$$C = \frac{1}{n} X^T X \tag{1}$$

$$Ca_i = \lambda_i a_i \tag{2}$$

Where original independent variables are X_{n*p} , n is the number of observations, p is the dimension of samples, C_{p*p} is the covariance matrix of X_{n*p} , λ_i and a_i are the eigenvalue and the corresponding eigenvectors of C_{p*p} respectively.

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If the first m principal components are taken, the principal component matrix F can be calculated as follows:

$$P = (a_{ij})_{p*m} = (a_1, a_2, \cdots, a_m)$$
(3)

$$F = XP \tag{4}$$

Where P_{p*m} is the matrix formed by the largest first *m* eigenvectors of *C*, F_{n*m} is the principal component with *m* dimensions.

To be specific, the i^{th} principal component F_i is:

$$F_i = Z(X_1) * a_{1i} + Z(X_2) * a_{2i} + \dots + Z(X_p) * a_{pi}$$
(5)

Where Z(X) represents the standardization of *X*, and a_{1i} is the first element of the *i*th eigenvector.

3.2 Kernel Principal Components Analysis

Although PCA is widely used, it cannot handle linear non-fractional dataset, while KPCA can conduct nonlinear dimension reduction on dataset. The general idea of KPCA is to do the nonlinear mapping (also known as kernel function, ϕ) on the original independent variable (*X*), and map it to a higher dimensional space ($\phi(X)$), making the $\phi(X)$ linearly separable, then conduct PCA dimensionality reduction in the $\phi(X)$.

In KPCA, kernel functions play an important role, that is, by inputting two lowdimensional vectors, we can compute the inner product of the vectors in higher dimensions after some transformation. Therefore, even though there are various KPCA methods, the difference between various KPCA methods mainly lies in the different kernel functions selected.

Not all functions can be used as a kernel function. A simple way to judge whether a function satisfies the kernel criterion is Mercer's Condition [25], that is, any semi-positive definite symmetric function can be used as kernel functions.

Common kernel functions mainly include radial basis function kernel (RBF), polynomial kernel (poly), sigmoid kernel, and cosine kernel. Their definitions are as follows.

Radial basis function kernel:

$$k(x, y) = \exp(-\gamma || x - y ||^2)$$
(6)

Polynomial kernel:

$$k(x, y) = (x^{T}y + c)^{d}, d \in N, c \ge 0$$
(7)

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Sigmoid kernel:

$$k(x, y) = \tanh(\alpha x^T y + \gamma)$$
(8)

Cosine kernel:

$$k(x, y) = \frac{x^T y}{\|x\|_2 \|y\|_2}$$
(9)

Among them, *c* and *d* in poly, gamma (γ) in RBF, $alpha(\alpha)$ and $gamma(\gamma)$ in sigmoid are all adjustable parameters.

It can be proved that the above kernel functions all satisfy Mercer's Condition. Since the model parameters of KPCA are tunable, the model effect has a larger space for optimization. This paper will use the above four kernel functions to conduct dimensional reduction on the original data.

4. MODELS AND RESULTS

First, this paper calculated the Pearson correlation coefficients between all variables to analyze the relationships between all variables, and the heat map of the correlation matrix was drawn in Fig. 3.

According to Fig. 3, the relationship among all variables is close. In fact, the average for the absolute value of the correlation coefficient of the whole correlation matrix is as high as 0.81. Among them, the absolute value of the correlation coefficient between Elec and Urban, GDP, TerInd, Output is more than 0.9, and that between Elec and Popu, ResiPri, FuPri is more than 0.8. Therefore, it is necessary to conduct dimensionality reduction on independent variables. Otherwise, the assumption of independent and identical distribution (i.i.d.) of variables in statistical regression cannot be satisfied.

In order to deeply dig the relationship structures inside each variable and to obtain better model fitting effects, PCA and KPCA (RBF, poly, sigmoid, cosine) were respectively conducted in this paper to reduce the sample dimension. Based on multiple experiments, this paper set KPCA's parameters as follows, $\gamma = 0.125$, $\alpha = 1$, c = 1, d = 3. And we retain the first three principal components.

Next, new variables obtained by PCA and KPCA methods were put into different regression models respectively, and data from 1980 to 2009 were taken as training sets, data from 2010 to 2019 as validation sets, and data from 2020-2035 as forecasting sets. The mean squared error (MSE) of the three sets was calculated separately, and the optimal model was selected based on MSE. Two things need to be noted. One is that the value of total electricity consumption from 2020 to 2035 comes from experts' predictions. Therefore, if a model's MSEs in the training set and validation set are both small, but in the forecasting set large, the model is still considered to be ideal. Second, the prediction results of the model should be in line with the practical situation. For example, if a model

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predicts that the total electricity consumption will gradually decrease in 2020-2035, even though the MSE of its training set and validation set is small, we still think that the model is not ideal, because it is generally believed that the total electricity consumption should increase gradually in the future.



Fig. 3. Correlation coefficients of all variables.

Table 3 compared the fitting performances of various dimensional reduction methods combined with different regression models.

In Table 3, we find the optimal model with a small MSE in the training set and validation set, as well as no downward trend in the forecasting set. Therefore, two combinations are selected as the optimal model, that is the combination of polynomial KPCA and LR and cosine KPCA and LR. We respectively assign 50% weights to each combination and add the two together to obtain the final model's forecast result of total electricity consumption in 2020-2035.

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Mean Squ	ared Error	Linear Regression	Random Forest	Neural Network	GBDT	SVM
No PCA	Training	0.0000	0.0000	0.0023	0.0000	0.0069
	Validation	0.0009	0.1124	0.0717	0.0936	0.1942
	Forecasting	0.1538	1.0572	0.4650	0.9805	1.4492
	No downward	No	Yes	Yes	Yes	Yes
	Training	0.0003	0.0001	0.0034	0.0000	0.0059
PCA	Validation	0.0183	0.1996	0.3097	0.1768	0.1569
	Forecasting	0.9034	1.3748	1.6304	1.3715	1.3835
	No downward	Yes	Yes	No	No	Yes
RBF	Training	0.0001	0.0000	0.0061	0.0000	0.0057
KPCA	Validation	0.0218	0.1327	0.2844	0.0996	0.1723
	Forecasting	2.7322	1.4663	1.3966	1.3482	1.4127
	No downward	No	No	Yes	No	No
Poly	Training	0.0001	0.0000	0.0022	0.0000	0.0059
KPĊA	Validation	_0.0078	0.1031	0.1950	0.0885	0.1479
	Forecasting	1.2267	1.2300	1.7098	1.1337	1.3582
	No downward	Yes	No	No	No	No
Sigmoid	Training	0.0035	0.0000	0.0124	0.0000	0.0065
KPČA	Validation	0.0316	0.1043	0.4038	0.0883	0.1359
	Forecasting	0.4828	0.9423	1.6553	0.8984	1.0819
	No downward	Yes	No	No	No	No
Cosine	Training	0.0007	0.0001	0.0059	0.0000	0.0069
KPCA	Validation	0.0084	0.1169	0.2145	0.0920	0.1097
	Forecasting	0.0729	0.9820	1.3422	0.8850	1.0896
	No downward	Yes	No	No	No	No

Table 3. Summary of MSE for all combined regression models

Note: We use multilayer perceptron (MLP) as the neural network method; GBDT is the abbreviation of Gradient Boosting Decision Tree. No downward means the model's forecast value in the forecasting set is not in the downward trend. If a model's No downward is Yes, it means the model's forecast result is in accordance with common sense, because the total electricity consumption should increase gradually in the future



The comparison of the model's forecast value and Oxford expert's forecast value is shown in Fig. 4.

Fig. 4. Comparison between model forecast result and experts forecast result

According to Fig. 4, in 2019, the total electricity consumption in China is 721.24 billion KWH, and in 2035, our model predicts that the total electricity consumption will reach 1827.85 billion KWH. However, experts from Oxford predict that the value is only 1258.02 billion KWH, which shows that the prediction of the model is relatively optimistic. To be specific, cosine KPCA's forecast was lower than that of experts, while poly KPCA's forecast was higher than that of experts. Therefore, these two predictions could be regarded as the lower and upper bounds of China's total electricity consumption in 2035, which is 973.71 billion KWH and 2681.98 billion KWH respectively.

Although the forecast value of the model is much higher than that of the experts, we think the prediction is reasonable to some extent. In effect, the past 40 years of reform and opening up have witnessed China's super-fast economic growth, while experts around the world underestimated China's economic growth rate at that time. At present, with the continuous improvement of China's urbanization and the advancement of RMB internationalization, the future growth rate of China's economy is still immeasurable. Especially in 2020, China has achieved great success in the fight against COVID-19. Therefore, China's future development potential should not be underestimated.

To sum up, the model's optimistic estimate of China's total electricity consumption has a certain realistic basis.

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5. FURTHER INTERPRETATION

To interpret the meaning of KPCA, this paper drew the line chart of three principal components (f_1, f_2, f_3) and the total electricity consumption after standardization (y), as shown in Fig. 5.



Fig. 5. Three principal components and total electricity consumption line diagram

Note: This figure consists of two parts, poly KPCA is the left subfigure and cosine KPCA is the right subfigure. Standardized total electricity consumption is on the right-hand side, and f_1 , f_2 , f_3 are on the left-hand side.

According to Fig. 5, the first principal component of both poly KPCA and cosine KPCA showed a relatively stable growth trend, indicating that the total electricity consumption was continuously increasing. The other two principal components show alternate characteristics of growth and decline, which are used to describe the fluctuation in the evolution of electricity consumption. The above three principal components can better represent the characteristics of electricity consumption spiraling in real life, so a better fitting effect can be achieved. Further, write the regression equation:

$$y = 1.157 + 0.580 * f_1 - 0.578 * f_2 - 0.879 * f_3$$
⁽¹⁰⁾

$$y = 1.157 + 6.055 * f_1 + 5.692 * f_2 + 0.435 * f_3$$
⁽¹¹⁾

Where (10) was the regression equation of poly KPCA, and (11) was about cosine KPCA. All the coefficients in the equations are significant at p < 0.01.

The correlation coefficients between all principal components and all original variables are calculated in Table 4. As can be seen from Table 4, poly KPCA's f_1 has the closest correlation with nominal GDP and per capita output value of employment, and f_2 has the closest correlation with the proportion of added value of secondary industry. And cosine KPCA's f_1 has the closest correlation with population growth rate and residential electricity price, while f_2 still has the closest correlation with nominal GDP and per capita output value of employment. In general, the important features that affect total electricity consumption can be divided into three groups. The first group is the economy feature and production

efficiency feature. The second group is the population feature and price feature. The third group is the industrial structure feature. Among them, the economy feature and production efficiency feature have the most critical impact on China's long-term electricity consumption, which is basically consistent with China's current national conditions.

Moreover, based on the data of the indicators, we can observe that the first group of indicators, the economy feature and production efficiency feature, exhibits a long-term stable growth trend. This explains the reason for the longterm increase in China's future electricity consumption. On the other hand, the second and third groups of indicators, population feature, price feature, and industrial structure feature, present a long-term relatively stable growth with short-term fluctuations. This suggests that although China's electricity consumption will increase in the long run, it may face certain fluctuations and volatility in the short term.

Table 4. Correlation coefficients between principal components and
original variables

Corr. Coef.		Poly KPCA			Cosine KPCA		
		F1	F2	F3	F1	F2	F3
Dep.Var.	Elec	0.94	-0.29	-0.15	0.74	0.67	0.05
Ind.	Popu	-0.77	0.54	-0.20	0.94	-0.24	0.07
Var.	Urban	0.88	-0.47	-0.05	0.86	0.51	0.03
	GDP	0.99	-0.05	-0.09	0.61	0.74	0.09
	ResiPri	0.70	-0.66	0.23	0.97	0.17	-0.14
	FuPri	0.75	-0.63	0.09	0.89	0.33	-0.12
	SecInd	0.16	-0.91	0.36	0.87	-0.39	-0.15
	TerInd	0.89	-0.38	0.04	0.85	0.44	0.24
	Output	0.97	-0.22	-0.13	0.70	_0.69	0.07

6. CONCLUSION

In order to accurately predict long-term electricity consumption under the premise of scarce sample size, a combination model of KPCA and linear regression was proposed in this paper. Empirical results show that the combined models achieve higher fitting accuracy, and the results are consistent with reality. By visualizing the three principal components obtained through KPCA, we found that the first principal component can represent the long-term growth of electricity consumption, while the other two principal components can represent the longterm fluctuation of electricity consumption. Through the correlation analysis between the original variables and principal components, we found that the features that have a significant impact on the total electricity consumption can be divided into three groups, and the first group of features, is the economy feature and production efficiency feature, are of the most importance. What's more, this paper predicted that China's total social electricity consumption will reach 1.83 trillion KWH in 2035, which is higher than the 1.26 trillion KWH predicted by Oxford experts. The model is more optimistic about China's future economic

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prospects, which is consistent with China's rapid economic growth and the fact that China has achieved an overall victory in the fight against COVID-19.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Investigation of the Inhomogeneity Phenomenon in the Metal/Semiconductor Interface: Mo/n-type-4H-SiC Schottky Diode

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ABSTRACT

The inhomogeneities of the metal/semiconductor (M/S) interface have been investigated for many decades and several models have been proposed to explain the physics of the interface state in such contacts. Two important and famous approaches are cited in this chapter book explaining the physics behind the metal/semiconductor (Schottky diode) interface state: the Werner and Guttler's model and the Tung's model. The proposed approaches are based on the temperature dependent of the most important parameter characterizing the M/S interface: the barrier high ϕ_B . Accordingly, the temperature effect on the other parameters, that characterize the current-voltage measurements like the mean barrier high $\phi_{\scriptscriptstyle B0}$, the standard deviation $\sigma_{\rm S}$, the voltage coefficients ρ_2 and ρ_3 for the barrier high and the standard deviation respectively, and the series resistance R_{s_1} is also approving the evidence the inhomogeneity of the interface between the metal and the semiconductor. In the light of this concept, a deep analysis is made on the state of the Mo/n-type-4H-SiC Schottky diode in the range of temperature (298-498) K via its current-voltage measurements. The analysis is based on the simultaneous extraction of the parameters ($\phi_{B0}, \rho_2, \rho_3$, σ_{s_1} , R_s) that define the current-voltage measurements as function of temperature by using the vertical optimization method (VOM). In order to explain the obtained results, we have used the Werner and Guttler's model to approve the inhomogeneity of the Mo/4H-SiC interface in the studied range of temperature. The investigations reported in this book chapter for the Mo/n-type4H-SiC contact confirm the existence of an inhomogeneous interface by the use of the Werner and Guttler's approach.

Keywords: Inhomogeneity; schottky diode; Mo/n-type4H-SiC; temperature.

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1. INTRODUCTION

The semiconductors are the principle materials of the most modern devices processing. Among those devices the electronic (like diodes, Field Effect Transistors (FET), Bipolar Junction Transistor (BJT)) and the optoelectronic (citing: detectors, modulators, laser diodes) ones which drive the electronic technology and the optical networks [1-6]. One of the important diode junctions is the Schottky diode. It is obtained by the deposition of a metal onto a semiconductor forming rectifying junctions or ohmic contacts. To specify the role of the Schottky junction, one could vary the values of the work functions of the metal and the semiconductor and choose the type of the semiconductor (n-type or p-type) [7]. The quality of the Metal/Semiconductor structure (MS) represents a key factor for the different semiconductor devices and the integrated circuit.

The Schottky structures (M/S) could be used to investigate the bulk defects and the interface properties of these contacts. So, it is crucial to understand the fundamental physical and the electrical properties of the M/S structures [8,9]. Different models have been carried out to explain the physics behind the state of the interface in the Schottky diodes [10-13], however they had taken in consideration the homogeneity of the spatial Metal/Semiconductor contacts. When the effect of the temperature is included in the studied Schottky structures, those models are insufficient to explain their current-voltage measurements as function of the temperature. To solve this problem, more researches are done to develop other models that take into account the spatial inhomogeneity of the M/S interface.

This book chapter is aimed to investigate the state of the interface in the Schottky structures by analyzing the basic device physics, the current mechanisms present in and the characterization of such diodes through extracting the different parameters modeling the basic transport properties taking into account the spatially inhomogeneous interface between the metal and the semiconductor.

2. MODELS FOR THE CHARACTERIZATION OF THE INHOMOGENEITY OF THE METAL/SEMICONDUCTOR STRUCTURES

The transport properties or the current-voltage (*I-V*) measurements of the metal/semiconductor contacts are principally produced by the current issued from the majority carriers. There are five main current process present in the Schottky contact for an applied voltage. These current mechanisms are : the thermionic emission (TE) characterized by the electrons flow from the semiconductor into the metal over a barrier high, dominating when the semiconductor is moderately doped (with a dopant concentration $N_D \leq 10^{17}$ cm⁻³, it is to be noted that we restrict our self to describe just the TE emission in the present book chapter because our investigated samples are doped with $N_D \leq 10^{17}$ cm⁻³, one could refer to the section 3), the tunneling current of the electrons through the semiconductor barrier, dominating when the semiconductor is severely doped,

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the recombination current in the space charge region, the diffusion of the electron in the depletion region, the diffusion of the holes from the metal into the semiconductor and the interface current resulting from the traps at the M/S interface [14]. The domination of a current in comparison with another is considered when all the conditions for a specified current cited below are gathered to define a transport mechanism in the Schottky contacts. All these currents are common in the assumption of a spatially homogeneous interface, that's mean that atomically point of view the interface between the metal and the semiconductor is flat. For our knowledge there are two basic models have explained better the interface state of the Schottky structures and make the evidence of its inhomogeneity: the Werner and Guttler's model and the Tung's model.

2.1 Werner and Guttler's model for the Metal/Semiconductor Inhomogeneities

As mentioned above, the dominant current mechanism for a moderately doped semiconductor is the thermionic emission given by the equations (1) [15]. Werner's et al. [16] model demonstrate that the inhomogeneity of the Schottky interface implies that the barrier high ϕ_B between the metal and the semiconductor is not a constant but varies with the temperature. The model demonstrates too that the variation of the ideality factor *n* with the temperature reflects the deformation of the barrier high distribution at the interface. Consequently, the analysis of the current-voltage (*I-V*) measurements of the Schottky diode (*SD*) at room temperature only does not give detailed information about the spatial distribution of barrier at the M/S interface. This is why, the analysis of the (*I-V*) as function of the temperature (*I-V-T*) usually reveals an abnormal decrease in the barrier height ϕ_B and an increase in the ideality factor *n* with a decrease in the temperature.

$$\begin{cases} I = I_s \left(\exp\left(\frac{\beta}{n} (V - R_s I)\right) - 1 \right) \\ I_s = A A^* T^2 \exp\left(-\beta \phi_{B0}\right) \end{cases}$$
(1)

A , A^* , $\beta = \frac{q}{kT}$, k, n, q, R_{s} , T, ϕ_{B0} are the diode area, the effective

Richardson constant of the used semiconductor, the inverse thermal voltage, the Boltzmann constant, the ideality factor, the elementary electric charge, the series resistance, the absolute temperature and the zero-bias barrier height respectively.

Conferring to this model, the inhomogeneity of the metal/semiconductor is represented by a Gaussian distribution of the Schottky barrier height with a mean

value ϕ_B and a standard deviation σ_s as shown in the Eq. (2) [16]:

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$$P(\phi_B) = \frac{1}{\sigma_s \sqrt{2\pi}} \exp\left(\frac{-(\phi_B - \bar{\phi}_B)^2}{2\sigma_s^2}\right)$$
(2)

With
$$I = \int i(V, \phi_B) P(\phi_B) d\phi_B$$
 (3)

 $i(V, \phi_B)$ is the current defined for a given barrier ϕ_B (taken from the gaussian distribution of the barrier high) and a voltage *V*.

As a result of the model, the barrier high and the standard deviation variate both with temperature as indicated by the equations (4) [16] showing ρ_2 as the voltage coefficient of the mean barrier height and ρ_3 as the voltage coefficient for the standard deviation.

$$\begin{cases} \overline{\phi}_B = \rho_2 V + \overline{\phi}_{B0} \\ \sigma_s^2 = \rho_3 V + \sigma_{s0}^2 \end{cases}$$
(4)

Therefore, a new characterized parameter ϕ_{ap} and n_{ap} are defined to model the barrier inhomogeneities at the Schottky interface as given by Eq. (5) [16]:

$$\begin{cases} \phi_{ap} = \overline{\phi}_{B0} - \frac{\beta}{2} \sigma_s^2 \\ n_{ap} = \frac{1}{1 - \rho_2 + \frac{\beta}{2} \rho_3} \end{cases}$$
(5)

Equating Eqs. (1) and (5) thus yields:

$$I = AA^{*}T^{2} \exp\left(-\beta\left(\bar{\phi}_{B0} - \frac{\beta}{2}\sigma_{s}^{2}\right)\right) \times \left\{\exp\left[\beta\left(1 - \rho_{2} + \frac{\beta}{2}\rho_{3}\right)(V - R_{s}I)\right] - 1\right\}$$
(6)

Werner et al. [16] have reported that the parameters $\overline{\phi}_{B0}$, ρ_2 , ρ_3 , σ_s may depend on temperature.

2.2 Tung's Model for the Metal/Semiconductor Inhomogeneities

To explain the inhomogeneities at the metal/semiconductor interface, Tung [17] has proposed a model to take into account the non-uniformity of the interface. The Tung's model is based on the assumption that the conduction path in front of a patch with a low Schottky barrier high (SBH) is *pinched-off* by the presence of high-SBH patches in its close proximity. Once the pinch-off phenomenon

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happens, the potential at a *saddle point* in front of the low-SBH area rules the transport properties. Accordingly, the potential nearby the M/S interface is then defined by a linear combination of the potential due to the uniform SBH noted $\overline{\phi}_{B0}$ (mean Schottky barrier high) and the one due to the dipole layer with a (varying) moment per area noted $2\varepsilon_s \delta(x, y)$, ε_s is the permittivity of the semiconductor. The local values of the SBH at the interface are defined using the Tung's model by the Eq. (7).

$$\phi_B(x, y) = \phi_B^0 + \delta(x, y) \tag{7}$$

The direct implication of the Eq. (7) is that the potential at the interface issued from these barriers have to take in consideration two types of geometries: the circular patch (with a radius of R_0) and the narrow strip (with L_0 as a width and semi-infinite in length). In both geometries the SBH in each patch/strip is defined by the Eq. (8)

$$\phi_{B, patch/strip} = \phi_B^0 - \Delta \tag{8}$$

 \varDelta represents the decrease in barrier at the interface (the local lowering of the barrier high at the *saddle point* in front of a specific geometry of the patch).

In order to measure the strength of the SBH of each patch/strip, Tung modeled it by the parameters (γ , Γ) defined by:

$$\gamma^3 \equiv \frac{27R_0^2\Delta}{4} \equiv 27\Gamma^3\eta V_{bb}^2 \tag{9}$$

 V_{bb} is the total band bending (diffusion potential) potential at a given applied bias *V* for a uniform SB and $\eta = \varepsilon_s/qN_D$.

Accordingly, the Tung's model defines a new effective inhomogeneous barrier from all the patch (strip) ϕ_{eff} as given in the Eq. (10).

$$\phi_{EFF} = \phi_B^0 - \frac{\gamma_0 V_{bb}^{1/3}}{\eta^{1/3}} - \frac{\beta \sigma^2 V_{bb}^{2/3}}{2\eta^{2/3}}$$
(10)

 σ is the standard deviation used in the calculation of the of low-SBH patches distribution and γ_0 is a constant used to calculate the density of the patches.

Several studies had used the Werner and Guttler's model [18-26] and the Tung's model [27-33] to explain the state of the interface in the Schottky diodes. However, for our knowledge, so far there is no clarification on the reasons to why choosing the Werner and Guttler's model and not the Tung's model (or vice versa) to understand the physics of the M/S interface in the Schottky diodes. In

other side, it is noteworthy that several number of new models [34-37] are proposed to explain the inhomogeneities of the SBH in such contacts, that's what will be detailed in the next section.

2.3 Other Metal/Semiconductor Inhomogeneities Models

Many models are reported to explain the anomalies observed at the interface between the metal and the semiconductor and have stated that the inhomogeneities of the barrier could be the principle cause [35,37-39]. In this section we will focus on the model proposed by Reddy et al. [34] because it will be used in the results section to explain the relation between the series resistance R_s and the inhomogeneities of the barrier high at the studied M/S interface. Reddy et al. reported that there is a direct relation between the inhomogeneity of the barrier high ϕ_B characterized by the gaussian distribution and the values of the series resistance that characterize the Schottky contact as shown in the Eq. (11). The new approach of Reddy et al. supposes that the inhomogeneous Schottky diode is modeled as a combination of elementary noninteracting diodes associated in parallel, each one is defined with a barrier height and a series resistance. The ensemble of the barrier heights is modeled by the gaussian distribution ($P(\phi_B)$) and its series resistance $R(\phi_B)$ is also modeled by the inverse of the same gaussian distribution.

$$R(\phi_B) = \frac{R_s}{P(\phi_B)} = R_s \sqrt{2\pi} \sigma_s \exp\left(\frac{\left(\phi_B - \overline{\phi}_{B0}\right)^2}{2\sigma_s^2}\right)$$
(11)

After some calculations details not shown here (for more details one can referred to the Reddy et al. reference [34]), the total current in the through the M/S Schottky diode at the applied voltage V is given by Eq. (12)

$$I = \int_{a}^{b} I_{\phi_B}(\phi_B, V) d\phi_B \tag{12}$$

The limits *a* and *b* represent the range of the barrier high and the $I_{\phi B}$ is the elemental current for a given barrier high in the range between the limits *a* and *b*.

3. DESCRIPTION OF THE MO/4H-SIC STRUCTURE

The Silicon carbide (SiC) is considered as the conventional wide band gap (WBG) semiconductor material with promising properties for the high temperature, the high power and the high frequency technological applications. It is characterized by its remarkable properties citing: high thermal conductivity, high breakdown electric field strength and high saturated drift velocity of electrons. The SiC could be doped to get both *n*-type and *p*-type. Furthermore, it has a stable native oxide (SiO₂) [40,41]. The silicon carbide could exist in

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different types because of the similarity of the carbon and the silicon. This similarity gives the possibility of a huge variety of stacking orders and the elaborated materials are called polytypes. Because they are energetically almost the same and have a very low stacking fault energy, they could with no trouble coexist or transformed to one type to another. The description of the different polytypes is given by the Ramsdell notation followed by the type of the stacking symmetry in the crystalline structure of the SiC material like: H for hexagonal, C for cubic and R for rhombohedral. In general, the cubic SiC material (3C-SiC) is called β -SiC and the other polytypes are called α -SiC [42,43].

In our M/S structures, we have used the *n*-type 4H-SiC (0001) and a Si-face 8° off-oriented toward $< 11\overline{2}0 >$, from Cree Inc, as a substrate. An *n*-type epitaxiallayer with a donor concentration N_D in the range of $[8.0 \times 10^{15} - 1.3 \times 10^{16}]$ cm⁻³ are used as wafers. The oxide with a thickness of 42 nm layer was thermally grown on the epitaxial-layer. It was used as a passivation layer for regions around the Schottky diode and as a sacrificial layer for regions where the contacts were formed. The molybdenum (Mo) is deposited to form the M/S contact. The Mo is known by its compatibility to the standard silicon process technology and for its thermal stability [44]. The current-voltage (*I-V-T*) curves in the range of (298-498) K with a step of 25 K were measured. For more details about the fabricated Schottky diode one could consult the reference [45]. The measured (*I-V-T*) for the fabricated Schottky structures are illustrated in the Fig. 1, first published in the Indian Journal of Physics 93(9), 2019 [45].



Fig. 1. Experimental current-voltage curves of Mo/*n*-type-4H-SiC Schottky contact in the [298-498] K range of temperature: First published in the *Indian Journal of Physics* 93(9), 2019 [45]

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4. CALCULATION ELEMENTS

The characterization of the current mechanism of a given Schottky contact could be done by the determination of all the parameter that define the dominant current emission. As explained above the dominant current in our Schottky contacts is the thermionic current mechanism (because the semiconductor is moderately doped). So, we have to determine the different parameters that define this current taking into account the inhomogeneity of the interface. As reported in most of analysis [46-56] the characterization of such inhomogeneous Schottky diode is realized firstly by the extraction of the ideality factor *n*, the barrier high ϕ_B and the saturation current I_s and secondly by the extraction of the parameters ρ_3 and ρ_2 from the slope and the *y*-intercept of the *n* versus q/2kT plot respectively. But the extraction of ϕ_B and σ_s is realized from the barrier ϕ_{ap} versus q/2kT plot. This type of extraction is known as the graphical method.

The extraction of all the characterized inhomogeneous Schottky diode parameters ($\overline{\phi}_{B0}, \rho_2, \rho_3, \sigma_s, R_s$) simultaneously, without the need to know any parameter previously or extract it from any graphical method, can be made via optimizing the vector of parameters that define the current mechanism. The optimization of the parameters, in our study, is based on fitting the (*I-V-T*) data by minimizing the vertical quadratic error *S* on the axis of the current (vertical axis) [45]. This sort of extraction is called the vertical optimization method (VOM).

The expression of the error S is given by Osvald et al. [57]

$$S = \sum_{i=1}^{m} \left(\frac{I_{imes} - I_{ith}}{I_{ith}} \right)^2$$
(13)

 I_{imes} is the i_{th} measured current, I_{ith} is the i_{th} theoretical fitting value of the current and *m* is the number of measuring points.

To minimize the vertical quadratic error S, we have to solve the equations:

$$\frac{\partial S}{\partial x} = 0 \tag{14}$$

x are all the free parameters used to describe the (*I-V-T*) curves.

When we project the Eq. (14) on our Schottky diode problem, we have to determine simultaneously the five parameters cited by Eq. (6). Accordingly, we have to solve the system of the equations shown in Eq. (15)

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$$\begin{cases} \frac{\partial S}{\partial \sigma_s} = -2\sum_{i=1}^{m} \frac{\partial I_{iih}}{\partial \sigma_s} \frac{I_{iimes}}{(I_{iih})^2} \left(\frac{I_{iimes} - I_{iih}}{I_{iih}} \right) = 0 \\ \frac{\partial S}{\partial \overline{\phi}_{B0}} = -2\sum_{i=1}^{m} \frac{\partial I_{iih}}{\partial \overline{\phi}_{B0}} \frac{I_{iimes}}{(I_{iih})^2} \left(\frac{I_{iimes} - I_{iih}}{I_{iih}} \right) = 0 \\ \frac{\partial S}{\partial \rho_2} = -2\sum_{i=1}^{m} \frac{\partial I_{iih}}{\partial \rho_2} \frac{I_{iimes}}{(I_{iih})^2} \left(\frac{I_{iimes} - I_{iih}}{I_{iih}} \right) = 0 \\ \frac{\partial S}{\partial \rho_3} = -2\sum_{i=1}^{m} \frac{\partial I_{iih}}{\partial \rho_3} \frac{I_{iimes}}{(I_{iih})^2} \left(\frac{I_{iimes} - I_{iih}}{I_{iih}} \right) = 0 \\ \frac{\partial S}{\partial R_s} = -2\sum_{i=1}^{m} \frac{\partial I_{iih}}{\partial R_s} \frac{I_{iimes}}{(I_{iih})^2} \left(\frac{I_{iimes} - I_{iih}}{I_{iih}} \right) = 0 \end{cases}$$

$$(15)$$

A detailed explanation about the application of the VOM can be found in the reference Toumi et al. [45]. In the next section, we represent the different extracted parameters as function of the temperature for the Mo/4H-SiC Schottky structure.

5. RESULTS

In this section, we represent the effect of the temperature on the different extracted parameters that define the thermionic emission in the Mo/*n*-type-4H-SiC contact taking into account the Werner's et al. model to explain the found results. It is to note that all the results cited in this chapter book are first published in the Indian Journal of Physics 93(9), 2019 [45] except the Figs. 9 and 10.

In Figs. 2 and 3, we represent the temperature dependences of the square standard deviation σ_s^2 and the mean Schottky barrier $\overline{\phi}_{B0}$. We remark that both σ_s^2 , $\overline{\phi}_{B0}$ have a linear variation as function of the temperature and they are ruled by the Eqs. (16) and (17) as expected by the model proposed by Werner et al. [16]. The linear fit for the σ_s^2 (7) and $\overline{\phi}_{B0}$ (7) permits us to obtain α_{σ} =-5.22 mV²/K, $\alpha_{\overline{\rho}B0}$ =-0.046 mV/K as slopes and σ_s (T=0)=97.11 mV, $\overline{\phi}_{B0}$ (T=0)=1.18 eV as intersections for the square standard deviation and the mean Schottky barrier respectively.

$$\sigma_s^2(T) = \sigma_s^2(T=0) + \alpha_\sigma T \tag{16}$$

$$\overline{\phi}_{B0}(T) = \overline{\phi}_{B0}(T=0) + \alpha_{\overline{\phi}_{B0}}T$$
 (17)

The variation of the characteristic parameter ρ_2 as function of temperature is illustrated in Fig. 4(a). It is very clear that the $\rho_2(T)$ curve varies linearly. From the linear fit to the data of this figure, one could obtain a slope of $\alpha_{\rho 2}$ =4.80×10⁻⁴ K⁻¹

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and intercept of -0.23 representing the value of ρ_2 at *T*=0 K. In order to determine the value of ρ_2 at very elevated temperature, we have plotted ρ_2 versus the inverse thermal voltage (q/2kT) as shown in Fig. 4(b). It gives the value of ρ_2 =0.13 (at elevated temperature) by means of a slope $\alpha_{\rho 2}$ =-12.33 mV. The temperature effect on the parameter ρ_3 is illustrated in Fig. 5(a). A linear fit is used to model the $\rho_3(T)$ variation. We found that the slope is $\alpha_{\rho 3}$ =0.038 mV/K and the intercept is -19.56 mV giving the value of ρ_3 at *T*=0 K. The plot of the coefficient ρ_3 versus (q/2kT) could give us a slope of $\alpha_{\rho 3}$ =-9.79×10² mV² and a *y*intercept of ρ_3 (at high temperature) =10.54 mV when it is modeled with a linear fit.



Fig. 2. Variation of the square standard deviation σ_s^2 versus temperature of Mo/*n*-type-4H-SiC Schottky contact: first published in the *Indian Journal of Physics* 93(9), 2019 [45]



Fig. 3. Temperature dependences of the mean barrier high $\overline{\phi}_{B0}$ for the studied Schottky contact. The results were first published in the *Indian Journal of Physics* 93(9), 2019 [45]

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Fig. 4. Temperature effect on the values of the coefficient ρ_2 : (a) ρ_2 versus temperature: the linear fit to the data gives $\rho_2(T=0)=-0.2362$, (b) ρ_2 versus the inverse thermal voltage (q/2kT): the linear fit to the data gives $\rho_2(at high$ T)=0.13922. The results were first published in the *Indian Journal of Physics* 93(9), 2019 [45]

In the model of Werner's et al., a very important parameter is included to explain the inhomogeneity of the interface between the metal and the semiconductor, it is the characteristic temperature T_0 called the T_0 -effect. This parameter is a direct measure of the degree of the inhomogeneity of the studied interface measuring the deviation of the ideal factor from the unity. For this modeling approach, the ideality factor *n* of the Schottky contact for an inhomogeneous interface (Eq. (5)) will be defined as shown in the Eq. (18) for the approximation of $(-\rho_2 + \rho_3 q/2kT <<$ 1: this approximation is verified for the studied contact as illustrated in Fig. 6 and the T_0 parameter is then given by Eq. (18). Saxena [58] had reported too an investigation about the inhomogeneity of the Schottky interface and define the idealities as function of the T_0 parameter as expressed in the Eq. (19).

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$$\begin{cases} n(T) \approx 1 + \rho_2 - \frac{\beta}{2} \rho_3 \equiv 1 + \frac{T_0}{T} \\ T_0 \approx -\frac{\rho_3}{2k/q} \end{cases}$$
(18)

$$n(T) \approx 1 + \frac{T_0}{T} \tag{19}$$



Fig. 5. (a) Values of the coefficient of the ρ_3 versus temperature. A linear fit to that data determines the value of ρ_3 at *T*=0, (b) ρ_3 versus the inverse thermal voltage (*q*/2*kT*). A linear fit to the data gives the value of the coefficient at very high temperature. The results were first published in the *Indian Journal of Physics* 93(9), 2019 [45]

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Fig. 6. Variation of the $(-\rho_2 + \rho_3 q/2kT << 1)$ expression as function of temperature for the Mo/*n*-type 4H-SiC Schottky diode. The results were first published in the *Indian Journal of Physics* 93(9), 2019 [45]

Combining the findings of the two models (Eqs. (18) and (19)) we could get the new formula of the T_0 -effect (Eq. (20)) which depend on temperature too contrary what is reported by the Eq. (18) where the T_0 is considered as a constant.

$$T_0(T) = \rho_2 T - \frac{q\rho_3}{2k}$$
(20)

The temperature dependences of the parameter T_0 (calculated with Eqs. (18) and (20)) as function of temperature for the studied Schottky contacts is shown in the Fig. 7. It is noted that for both curves (black filled and empty circles) T_0 vanishes for high temperatures in good agreement with Werner's et al. [16] and Saxena's model [58].

It is noteworthy that at each temperature we have a new value of σ_s , ρ_2 , ρ_3 and ϕ_{B0} describing the Mo/4H-SiC structure. So, at each temperature a new reordering and restructuring of the studied M/S interface is realized as reported by B. Akkal et al. [59] and M. Ozer et al. [60]. The T_0 -effect demonstrates the existence of the inhomogeneity of the interface. Nevertheless, the thermal restructuring and reordering of the interface makes the Mo/4H-SiC contact attains at each temperature a new atomic reorder and reconstruction making it more flat. Accordingly, the decrease of T_0 with the increase of temperature can be well understood (Fig. 7). This result is confirmed by the decrease of the standard deviation σ_s and by tendency to zero of the parameters ρ_2 and ρ_3 with the increase of the temperature. However, at extremely elevated temperature we remark that the parameters ρ_2 and ρ_3 become significant, which might be explicated by the higher inhomogeneity of the interface reached for this order of temperature.

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Fig. 7. T_0 -effect in the Mo/*n*-type 4H-SiC Schottky diode contact. Black filled circles designate the obtained values of T_0 taking into account both the coefficients ρ_2 and ρ_3 to calculate the parameter T_0 . Black circles give the values of T_0 considering just the coefficient ρ_3 for the calculation of the corresponding temperature T_0 . The results were first published in the *Indian Journal of Physics* 93(9), 2019 [45]



Fig. 8. Series resistance *R_s* as function of the temperature. The results were first published in the *Indian Journal of Physics* 93(9), 2019 [45]

The temperature dependences of the series resistance R_s of the Mo/4H-SiC Schottky contact is also investigated. Fig. 8 shows the variation of the extracted values of R_s as function of the temperature. Using the Reddy's et al. model [34] cited in the section 2.2, we have calculated the distribution of the series resistance $R(\phi_B)$ for the Mo/*n*-type-4H-SiC. The results of the obtained distribution as function of the barrier high ϕ_B of the studied contact is illustrated in the Fig. 9. The gaussian distribution of the series resistance in the interface is
perfectly obtained as predicted by the approach of Reddy et al. The temperature dependences of the same distribution $R(\phi_B)$ are shown in the Fig. 10.



Fig. 9. The distribution of the series resistance $R(\phi_B)$ as function of the barrier high ϕ_B for the Mo/*n*-type-4H-SiC



Fig. 10. Temperature dependences of the distribution $R(\phi_B)$ of the Mo/*n*-type-4H-SiC Schottky contact

6. CONCLUSIONS

The investigation of the Mo/*n*-type-4H-SiC Schottky interface in the (298-498) K range of temperature by extracting simultaneously the five parameters ($\overline{\phi}_{B0}, \rho_2, \rho_3, \sigma_s, R_s$) that characterize the current-voltage curves has been detailed in this chapter book. The temperature effect on these parameters could measure the inhomogeneity of the interface by the assumption of a gaussian distribution of the barrier high at the interface with a mean value of $\overline{\phi}_{B0}$ and standard deviation σ_s

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(using the Werner's model). The systematic analysis of the state of the interface using the (I-V-T) measurements has given the following results:1) the mean barrier height increases linearly with temperature by means of a negative slope parameter $\alpha_{\overline{\phi}B0}$ = -0.046 mV/K and y-intercept $\overline{\phi}_{B0}$ = 1.18 eV, 2) the parameters ρ_2 and ρ_3 (that identify the barrier voltage deformation) both show an increase with increasing temperature and their values were found in the intervals of [-0.23, 0.13] and [-19.56, 10.54] mV respectively, 3) the temperature dependence of σ_s^2 illustrates a linear behavior with slope parameter α_{σ} = -5.22 mV²/K and y-intercept parameter σ_s (T=0) = 97.11 mV, 4) the parameter T_0 decreases with increasing temperature and vanished at high temperature, this result is in good agreement with the Werner's et al. model, 5) and the value of series resistance R_s increases with increasing temperature. The distribution of the series resistance $R(\phi_B)$ is found to vary with the barrier high ϕ_B as predicted by the Reddy's et al. model. Accordingly, the values of the series resistance in the Schottky contacts have a direct relation with the degree of the inhomogeneity measured (by the T_0 -effect) as shown in the Figs. 7 and 10.

All the results obtained in this study report the evidence of the inhomogeneity of the studied interface between the metal (Mo in our case) and the semiconductor (*n*-type-4H-SiC).

HIGHLIGHTS

- Models for the characterization of the inhomogeneities of the Metal/Semiconductor interface. The cited approaches are Werner and Guttler's model, Tung's model and Reddy and Kumar's model.
- Investigation of the Thermionic Emission (TE) conduction current mechanism in the Schottky diodes with Wide band gap semiconductor 4H-SiC.
- Current-voltage measurements of the Mo/n-type-4H-SiC Schottky diode in the (298-498) K range of temperature.
- > Simultaneous extraction of the five parameters (ϕ_{B0} , ρ_2 , ρ_3 , σ_s , R_s) characterizing the TE current in the M/S contacts using the Werner and Guttler's model.
- Investigation of the inhomogeneities of the Schottky contacts via the temperature dependence of the parameters describing the inhomogeneities of the M/S interface.
- > The calculation of the series resistance distribution $R(\phi_B)$ as function of the barrier high ϕ_B using the Reddy's et al. model.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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TiO₂ Nanoparticles Acid-assisted Synthesis and the Enhanced Visible-light Photocatalytic Activity

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ABSTRACT

The simple synthesis of TiO₂ and improved visible-light photocatalytic performance of TiO₂ have been the goal of researchers. When compared to pure phase TiO2, mixed-phase TiO2 nanoparticles with oxygen vacancies can aid in lowering the band gap and carrier recombination rate, which improves the performance of visible light photocatalysis. In this study, three different acids were separately applied in the hydrothermal synthesis of TiO₂ nanoparticles without any post-heat treatment. The reaction was carried out at a relatively low temperature not exceeding 140 °C. Under the visible light illumination-assisted photocatalytic degradation of methyl orange in water, the TiO₂ nanoparticles obtained from HCI (H-TiO₂) and CH₃COOH (A-TiO₂) showed stable photocatalysis performance for increasing the cycles up to ten times while only five cycles for TiO_2 nanoparticles obtained by HNO_3 -assisted (N-TiO₂). Compared with efficiencies of N-TiO₂ nanoparticles, H-TiO₂ and A-TiO₂ showed superior efficiencies and have excellent photocatalytic performances when assisting in the degradation of methyl orange in water under visible light illumination. The high visible-light photocatalytic performance and the simple acid-assisted synthesis of the H-TiO₂ and A-TiO₂ nanoparticles will promote the industrial application.

Keywords: TiO₂ nanoparticles; visible-light photocatalytic activity; mixed phase; oxygen vacancies; hydrothermal synthesis.

1. INTRODUCTION

Titanium dioxide (TiO_2) as a photocatalyst has been ubiquitously studied for environmental applications. Though, readily available, nontoxic, and environmentally friendly; lower efficiency, less energy harvesting within the UV– Vis range with the ease of photogenerated charge recombination is still a

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concern for its full-scale deployment as a photocatalyst for environmental remediation applications [1]. It has been one kind of widely investigated widebandgap semiconductor materials because of its environmentally friendly, good chemical stability, good cycling performance and cheap [2-5]. Nowadays. TiO2 has known as an effective photocatalyst under UV light illumination [2,6]. TiO2's photocatalytic activity is created by the electron transition that occurs in the presence of light. The electrons and holes that are being produced have reducing and oxidising abilities, respectively. The relationship between a semiconductor material's conduction band and valence band determines how well it performs as a photocatalyst. Due to the quick carriers' recombination of electrons from the conduction band and holes from the valence band inside of the TiO2, which limits the extensive application of TiO2 in the degradation of pollutants, it has a low efficiency under visible-light illumination [7,8]. Currently, titanium dioxide (TiO2) has gained great attention as a promising photocatalyst due to its beneficial properties among the other photocatalysts, such as excellent optical and electronic properties, high chemical stability, low cost, non-toxicity, and ecofriendliness. However, the photoactivity of TiO2 is still inhibited because it has a wide band gap and a low quantum field [9].

Over the past decade, numerous methods have been proposed to enhance the visible light photocatalytic efficiency of TiO₂ powders [10-15]. The photocatalysis performance of amorphous TiO₂ is always worse than crystallized TiO₂. The amorphous TiO₂ is long-range disorder. Therefore, they are with more bulk defects. The characteristic of amorphous TiO₂ leads to higher recombination rate of carriers than that of crystallized TiO₂ [6]. According to previous works, the crystallized TiO₂ formed by both anatase phase and rutile phase shows much higher photocatalytic efficiency than pure phase TiO₂. The mixed phase TiO₂ with the appropriate band gap exhibits enhancement of charge separation [10,16]. An internal electric field is formed between the phase cross sections [17]. The mixed phase junction plays a decisive role in the effective separation of carriers, thus prolonging charge lifetimes, resulting in greater photocatalytic reactivity [18]. The crystallized TiO₂ need high temperature to construct the phase junction. However, the post-heat calcination treatment will cause the growth of grain, loss of hydroxyl groups and repugnant agglomerations of TiO₂ powders, which is resulting in deteriorating the photocatalytic activity. In addition, defects have been demonstrated to regulate the band gap [19,20]. The defect level and the shallow donor level can help to reduce the band gap inside of the crystalline TiO₂ thus expanded the range of photocatalysis performance [21,22]. Oxygen vacancies are one kinds of defects in crystalline TiO2. In addition, the density of states below the Femi energy level could be produced by the oxygen vacancy defects [23]. Thus, the carriers are significantly promoted efficient separation [24]. Therefore, introducing oxygen vacancies in crystalline TiO₂ is another useful route to promote the visible light photocatalytic efficiency.

In this paper, highly crystallized mixed-phase TiO_2 with oxygen vacancies were synthesized by acid-assisted hydrothermal method without any high temperature calcination. Titanium butoxide (TBT) was used as titanium source, while HCl, CH₃COOH or HNO₃ played an assistant role to promote the formation of the

mixed-phase and introduce the oxygen vacancies. The methyl orange (MO) in water was photodegraded under visible light illumination with the existence of TiO₂ powders. The TiO₂ obtained from HCl (H-TiO₂) or CH₃COOH (A-TiO₂) exhibited a visible light photocatalytic efficiency higher than that of TiO₂ obtained from HNO₃ (N-TiO₂). The visible light photocatalysis performance of the mixed-phase TiO₂ nanoparticles respectively from HCl, CH₃COOH and HNO₃ were indeed investigated, which are given more choice for commercial production of TiO₂ in the future.

2. EXPERIMENTS

2.1 Preparation of TiO₂ Nanoparticles

In a beaker, 7.5 mL titanium butoxide (TBT) was slowly added in sequence to 120 mL ethanol under constant stirring, and then continue stirring for 30 minutes to form a homogeneous solution A. In order to prevent the hydrolysis of TBT due to high air humidity, the beaker was wrapped with plastic wrap. Solution B is either 4 mL 36 wt% hydrochloric acid (HCl) aqueous solution or 12 mL 99.5 wt% acetic acid (CH₃COOH) aqueous solution or 4 mL 98 wt% nitric acid (HNO₃). Dropwise solution B into solution A under constant stirring. After completing dropwise, the solution C is formed by continue stirring for 30 minutes. Afterwards, transfer the mixed solution C to a Teflon-lined autoclave for further hydrothermal reaction at the temperature of 140 °C for time of 4 h to complete the precipitation procedure. The powders were collected by centrifugation at 9000 r/min for 5 min. Then, the samples washed with distilled water for two times and followed ethanol for two times. Finally, the three TiO₂ samples are dried at 80 °C in air for 24 hours for further characterizations and photocatalytic experiments.

2.2 Characterization

The morphology information was obtained by using a field emission scanning electron microscopy (FESEM, Apreo S HiVac). The X-ray diffraction patterns were conducted on Rigaku SmartLab XRD diffractometer with the 0.15406 nm λ value of Cu K α radiation. Fourier infrared spectroscopy experiments were conducted with an IR Prestige-21 spectrometer (Shimadzu). The UV-1900i near-infrared spectrometer (Shimadzu) is used to collect the UV-vis absorption spectra. An Autosorb-IQ2-MP Quantachrome Instruments is using to analysis the specific surface area (SSA) and pore size distribution (PSD). The low-temperature N₂ adsorption/desorption was performed. The Brunauer-Emmette-Teller method was used to calcinate the SSA. On the other side, the Barrett-Joyner-Halenda method was used to recorded the PSD.

2.3 Photocatalytic Activity Evaluations

Both the visible light photocatalytic experiments and the cycling photodegradations were performed in water by photodegrading the original concentration of 0.01 mM methyl orange (MO) under the visible light illumination. The wavelength of light is all more than 420 nm. The visible light source was

offered by a 250 W Xenon lamp with a filter. In a typical procedure, 20 mg catalyst powders were dispersed in 100 mL MO solution. Firstly, the samples were stirred without any light for several hours. The aim of this process is reaching an adsorption–desorption equilibrium before photodegradation. The dye concentration was collected the wavelength of around 465 nm, which was determined by a UV-1900i equipment.

3. RESULTS AND DISCUSSION

Fig. 1 show the morphologies of samples discerned from the FESEM images. TiO₂ nanoparticles respectively obtained by HCI-assisted (H-TiO₂, Fig. 1a), CH₃COOH-assisted (A-TiO₂, Fig. 1b) and HNO₃-assisted (N-TiO₂, Fig. 1c) hydrothermal approach show different morphologies. Compared with the N-TiO₂ nanoparticles, H-TiO₂ and A-TiO₂ show much higher homogeneity. The H-TiO₂ shows the best dispersibility of the three samples. For the other two TiO₂ samples, A-TiO₂ shows less agglomeration than N-TiO₂ powders. In fact, N-TiO₂ nanoparticles show obvious harden in the same magnification. Generally, the more agglomeration and serious harden of the catalyst shows the worse photocatalytic performance [25].

Fig. 2a illustrates the XRD patterns of three samples: $H-TiO_2$, $A-TiO_2$ and $N-TiO_2$ nanoparticles. The peaks of the $A-TiO_2$ can be only indexed to two well crystallized phases without brookite phase: rutile phase (JCPDS No. 21–1276) and anatase phase (JCPDS No. 21–1272). The $H-TiO_2$ and $N-TiO_2$ nanoparticles synthesised by the HCI-assisted and HNO₃-assisted hydrothermal method respectively, show the three-phase mixture of anatase, rutile and brookite phase (JCPDS No. 29–1360).

Fig. 2b shows the FTIR spectra. Obviously, the peaks of -OH stretching bands of the H-TiO₂ and A-TiO₂ nanoparticles are higher than that of N-TiO₂. According to reported works, oxygen vacancies prefer to bond with the dissociative water [26,27]. More hydroxyl groups thus are produced on the surface of catalyst nanoparticles by oxygen vacancies. The hydroxyl groups are helping to improve the photocatalytic efficiency. The hydroxyl groups act as capture centres for photoinduced electrons leading to effectively separation of the electrons and the holes [28,29].

The photocatalytic stability of the H-TiO₂ (Fig. 3a), A-TiO₂ (Fig. 3b) and N-TiO₂ (Fig. 3c) nanoparticles were confirmed by repetitively degrading methyl orange (MO) in water under the illumination of visible light. The H-TiO₂ and A-TiO₂ nanoparticles were confirmed ten cycles while only five cycles for N-TiO₂ nanoparticles. The H-TiO₂ and A-TiO₂ nanoparticles show more stable and better photocatalytic ability than N-TiO₂ nanoparticles. This implied that more oxygen vacancies leading to higher photocatalytic activity. Compared with the A-TiO₂ nanoparticles, H-TiO₂ powder shows higher photocatalytic efficiency. This implied that the special mixed-phase of H-TiO₂ contribute to its high photocatalytic activity. This heterojunction structure of TiO₂ with anatase, rutile and brookite phase could further reduce the recombination rate of photogenerated carriers [26,30].

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Fig. 1. FESEM images of the (a) H-TiO₂, (b) A-TiO₂ and (c) N-TiO₂ nanoparticles



Fig. 2. Characterizations of H-TiO₂, A-TiO₂ and N-TiO₂ nanoparticles: (a) XRD patterns, (b) FTIR spectra

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Fig. 3. The cycling photodegradations of methyl orange in the presence of the (a) H-TiO₂, (b) A-TiO₂ and (c) N-TiO₂ nanoparticles under visible-light illumination

Under the identical condition, the H-TiO₂ exhibited much higher activity than the A-TiO₂ and N-TiO₂ nanoparticles. The dye molecules were degraded 95% of initial amount with the assistance of H-TiO₂ within 5 hours whilst it took same time for A-TiO₂ to degrade 80% and N-TiO₂ with almost all initial MO molecules, respectively. Compared with efficiencies of N-TiO₂ nanoparticles, the present H-TiO₂ and A-TiO₂ showed superior efficiencies. This is attribute to the abundant surface hydroxyl groups played the capture centers role of photoinduced electrons [30] and the light harvesting increased by the reduced band gap [31,32].

4. CONCLUSIONS

Mix-phase TiO₂ nanoparticles with oxygen vacancies were synthesized through facile acid-assisted hydrothermal synthesis without any post-calcination. By using HCl or CH₃COOH, the synthesized TiO₂ sample H-TiO₂ or A-TiO₂ nanoparticles shows uniform nanoparticles morphology with well dispersion. The oxygen vacancies leading to the abundant surface hydroxyl groups and the mixed-phase TiO₂ leading to the reduced band gap both guaranteed the excellent photocatalytic performance. The H-TiO₂ and A-TiO₂ nanoparticles compared with N-TiO₂ nanoparticles show better photocatalytic performance when employed to assist the degradation of methyl orange in water under the illumination of the visible light. The stable high photocatalytic performance and the facile method of the H-TiO₂ and A-TiO₂ nanoparticles will drive the industrial application.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Assessment of Dielectric Parameters of Hydrogen Bonded Complexes: Tri-n-butyl Phosphate (TBP) with Aliphatic Alcohols Using Huysken–Craco, Palit and Onsager's Methods

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ABSTRACT

This chapter investigates the complex formation of TBP in long chain alcohols viz., 1-hexanol, 1-heptanol, 1-octanol by following Huysken-Craco method, Palit method and Onsager method. Dielectric studies of hydrogen-bonded compounds in non-polar solvents reveal vital details on the development of intermolecular complexes in solution. Hydrogen bonds are a fascinating type of molecular interaction that is essential in a variety of fields, including pharmacology, chemistry, and molecular biology. The mechanism of dipolar complexation involving TBP and three alcohols namely 1-hexanol, 1-heptanol, 1-octanol and in an apolar medium benzene, is investigated by three direct methods viz. Huysken-Craco, Palit and Onsager's Methods using dielectric measurement data at frequency 455kHz and at temperature 303.16 K. The interaction dipole moment, induced polarisation, and apparent complex formation constant for the thermodynamically preferred stoichiometry of 1:1 complex are the parameters assessed in these systems. It is concluded that the complexation is predominantly due to polarization effect involving charge redistribution and the complex formation is most favoured in 1-hexanol system.

Keywords: TBP; long-chain alcohols; interaction dipole moment; induced polarization; h-bonded complex.

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1. INTRODUCTION

Dielectric dispersion investigations of polar liquids such as alcohols, amines, and their equimolar binary mixtures were performed to identify the nature of the connection between molecules owing to hydrogen bonding, dipole moment, and relaxation behaviour phenomena [1]. Commercial solvent extractants have proven useful for recovering different metal ions in the field of separation technology. As a result, research into the molecular behaviour of such extractants may shed light on how extractants and diluents' enhancement properties are affected [2-6]. Tri- n-butyl phosphate (TBP), an effective extractant used for the separation and isolation of plutonium and uranium from fission products and other nuclides in chlorides as well as nitrate media through PUREX process [7-11]. There are many solvents which can effectively extract uranium, plutonium, or thorium from nitric acid solutions but tri-n-butyl phosphate (TBP) is one of the important organic solvents utilized during the acid extraction step in separation process at reprocessing facilities [12]. TBP is a non-ionizing solvent, with high dipole moment ($\mu = 3.0D$) and high dielectric constant ($\varepsilon = 8.03$). Its boiling point is 289°C with decomposition setting in over $143^{\circ}C - 145^{\circ}C$ at 5 mm of mercury. Its viscosity is 2.82×10^{-3} Nsm⁻² and specific gravity is 0.9727 at 25°C [3]. So, it need be blended with suitable polar and apolar diluents for greater dispersal and more apid phase disengagement. Most solvent extraction operations are conducted at ambient conditions without heating TBP and have been performed safely for decades. After the extraction process, raffinate containing fission products and dissolved TBP remains as highly active radwaste which needs to be concentrated in the evaporator for storage and further management [12]. On dilution, the physicochemical properties [4,5] of the mixture containing TBP becomes quite satisfactory for extraction process. Furthermore, formation of a third organo-aqueous phase during extraction complicates the process and reduces the efficiency of extraction. This third-phase, however, can be eliminated by either addition of a polarmodifier to the extractant-diluent mixture or by increasing the temperature of the system [7].

Another study of these authors [8] on mutual correlation factor, g_{ab} , and excess molar polarization, ΔP , in binary mixtures involving TBP indicated the probability of formation of hydrogen bonded complexes between TBP and alcohol. Formation of hydrogen bonded complexes in several liquid mixtures of TBP and water has been reported by a number of authors [8,9]. The significant characteristic of the H-bond is changed in 0 – H separation accompanied by a change in dipole moment, $\Delta \mu$, that indicates the nature of the complex. Polarization effect, charge transfer effect, partial proton transfer effect and complete proton transfer effect were invoked to account for the excess dipole moment in many 0 – H – N and 0 – H – 0 complexes. The present report is an attempt to investigate the complex formation of TBP in long chain alcohols viz., 1-hexanol, 1-heptanol, 1-octanol following Huysken-Craco method, Palit method and Onsager method.

2. THEORETICAL MODELS

2.1 Method I (Huysken and Craco method)

Taking into account reaction field model of the environment, Huysken and Craco developed a relation [10] for mean square dipole moment $\langle \mu^2 \rangle_{exp}$ which reduces to the following form in case of a ternary system of two dipolar liquids and an inert solvent.

$$<\mu^{2}>exp=\frac{9kTV}{4\pi N_{A}}\frac{\left[\frac{\varepsilon-1}{\varepsilon}-3\left\{\frac{3x_{a}V_{a}\,\varepsilon\,a\,\varepsilon\,a-1}{V}+\left(1-\frac{x_{a}V_{a}}{V}\right)\left(\frac{n_{bc}^{2}-1}{n_{bc}^{2}+2\varepsilon}\right)\right\}\right]}{x_{bc}(2\varepsilon+1)\left(\frac{n_{bc}^{2}+2}{n_{bc}+2\varepsilon}\right)^{2}}$$
(1)

where *V* and *V_a* are the molar volume of the mixture and the apolar solvent, respectively, n_{bc} is the refractive index of the polar solute measured at sodium D-line. x_a and x_{bc} are the mole fraction of the solvent and mixture of the polar solute, respectively. ε and ε_a are dielectric constants of the mixture and apolar solvent respectively. *k* is the Boltzmann constant, N_A is the Avogadro number and *T* is temperature in Kelvin.

The term $\langle \mu^2 \rangle_{exp}$ in Eq. 1 corresponds to the value for solute molecules that is alcohol and TBP complex in the apolar solvent. If C_b and C_c are molar concentrations of alcohol and TBP respectively and the concentration range of TBP is less than 1 mole, the contribution to the total dipole moment is mainly due to 1:1 complex. Defining a quantity [11].

$$\mu_m^2 = \frac{\langle \mu^2 \rangle_{\exp}(c_c + c_b) - \mu_c^2(c_c - c_b)}{c_b}$$
(2)

in a domain of concentration where most of the molecules predominantly exist in 1:1 complexed state, it is shown that $\mu_m = \mu_{bc}$ where $C_b >> C_c$.

2.2 Method II (Palits' Method)

This method is based on infinite dilution technique that follows from Debye's model [13]. In this model the excess molar polarization, ΔP , due to hydrogen bonding in the ternary system of TBP and alcohol in an inert apolar solvent for 1:1 complex stoichiometry in terms of molar orientational polarization of alcohol and TBP in the solvent is deduced. From the value of ΔP and effective molar polarization of the mixture in apolar solvent, the dipole moment of the complex, $\mu_{\rm bc}$, is evaluated.

2.3 Method III (Onsager's Method)

Onsager's relation for dipole moment of 1:1 H-bonded system comprising of a ternary liquid mixture in terms of dielectric constant and refractive index that gives the signature of the environment [14] leads to an equation

$$C_{b}\mu_{b}^{2} + C_{c}\mu_{c}^{2} + C_{bc}\mu_{bc}^{2} = \frac{9kT}{4\pi N_{A}} \frac{[(\varepsilon - n^{2})(2\varepsilon + n^{2})]}{(\varepsilon (n^{2} + 2))^{2}} - \frac{(C_{s})}{(\overline{c_{s}})} \frac{(\varepsilon_{s} - n_{s}^{2})(2\varepsilon_{s} - n_{s}^{2})}{(\varepsilon (n_{s}^{2} + 2))^{2}} = \Omega C_{c}$$
(3)

where C_b and C_c are the actual concentration of proton donor and proton acceptor respectively in mol⁻¹ for the complex in the solution, C_{bc} is the actual concentration of 1:1 complex in mol⁻¹, ε is the dielectric constant of the solution, n is the refractive index of the solution, ε_s is the dielectric constant of the solvent, n_s is the refractive index of the solvent, C_s is the concentration of the solvent in moll⁻¹ in the solution, $\overline{C_s}$ is the concentration of pure solvent in mole 1⁻¹ in the solvent itself, Ω is a dipole moment dependent parameter, k is Boltzmann constant, N_A is the Avogadro number and T is the temperature in Kelvin.

If the concentration of proton acceptor is much greater than the concentration of proton donor, $C_{\rm b}$, for the complex in the solution, such that $C_c - C_b \gg K^{-1}$, where *K* is the equilibrium constant of 1:1 complexation and if the non-interacting solvent has zero dipole moment, then Eq. 3 reduces to the form [15].

$$\Omega = \mu_c^2 + \left(\mu_{bc}^2 - \mu_c^2\right) \frac{c_b}{c_c} \tag{4}$$

where μ_c is the dipole moment of the proton acceptor and μ_{bc} is the dipole moment of 1:1 complex which indicates the presence of interactive association between the two species of the molecules that can be obtained from the slope of the curve Ω versus C_b/C_c . However, the curve is no longer a straight line if there is higher order complex in addition to 1:1 complex. This fixes a criterion for choosing the proton concentration C_b and C_c for 1:1 complexation. The μ_{bc} values determined by the three methods are given in Table 3. The mean of the three values is taken as the reliable set of dipole moment of the complexes.

2.4 Interaction Dipole Moment

When a proton donor of dipole moment μ_b forms a hydrogen bond with proton acceptor of dipole moment, μ_c , the direction of μ_b and μ_c with respect to b - H - c axis can be defined by angles θ_b and θ_c respectively (Fig. 1). If θ_b and θ_c differ from zero, one can define an azimuthal angle φ which describes the rotational position of θ_c around the hydrogen bond with respect to the plane formed by this bond and θ_b . The formation of the H-bonding is accompanied by the interaction dipole moment of the molecules involved and the displacement of electron. As a

consequence, the dipole vector of the 0 - H - 0 bridge which is different from the vector sum is given by

$$\mu *= \mu_{OH} + \mu_c + \Delta \mu \tag{5}$$

where $\Delta \mu$ is the interaction dipole moment of the complex. Keeping in mind the co-linearity of hydrogen bond for the most favourable structure of 1:1 complex one can have

$$\mu_{bc}^{2} = \mu_{b}^{2} + \mu_{c}^{2} + (\Delta \mu)^{2} + 2\mu_{b}\mu_{c}\cos\theta_{b}\cos\theta_{c} + 2\mu_{b}\mu_{c}\sin\theta_{b}\sin\theta_{c}$$
(6)

for more stable configuration [15] in which potential energy is minimum, $\phi = \frac{\pi}{2}$ and the interaction dipole moment of complex reduces to

$$\Delta \mu = \left(\mu_{bc}^2 - \mu_b^2 \sin^2 \theta_b - \mu_c^2 \sin^2 \theta_c\right)^{1/2} - \mu_b \cos \theta_b - \mu_c \cos \theta_c.$$
(7)

3. EXPERIMENTAL DETAILS

All the chemicals used were of AR grade and were obtained from E Merck Ltd. They are purified by standard procedures [16,17] before use. The details of experimental technique used for measurement of dielectric constant, refractive index and density were the same [18] as reported earlier [19,20]. The apparent molecular polarizations at zero concentration in a solvent containing varying amount of TBP were determined for all alcohols studied. The variation of dielectric constant, refractive index and density with weight fraction of proton donor and limiting value of molar polarization in TBP-benzene and TBP-alcohol systems were evaluated.

4. RESULTS AND DISCUSSION

The relevant data have been presented in Tables 1, 2, and 3 and displayed in Fig. 1.



Fig. 1. The geometry of 1:1 complex of TBP + aliphatic alcohol

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In the concentration range less than 1 mole, TBP exists in monomer-dimer equilibrium and 0H proton in alcohol form a hydrogen bonded complex with TBP. We have calculated the bond angles θ_b and θ_c with the help of R – 0 bond moment value 1.14 and 0 – H bond moment value as:

 $\begin{array}{l} (\theta_{\rm b})_{1-\rm hexanol} = 43^{\circ}43.4'; \\ (\theta_{\rm b})_{1-\rm heptanol} = 43^{\circ}53'; \\ (\theta_{\rm b})_{1-\rm octanol} = 41^{\circ}27' \\ (\theta_{\rm c})_{\rm TBP} = 0^{\circ}; \end{array}$

in specifying the distribution of μ_b and μ_c with respect to b-H-c axis [13] using R-OH angle (θ)110°,101° and 102°42′ for 1-hexanol, 1-heptanol and 1-octanol, respectively.

It is generally observed [21] that the hydrogen bonds formed by P = 0 group should be along the SP^3 lone pair direction. Thus, the angle between 0 - H bond and the axis of P = 0 bond is taken as $43^{\circ}43.4', 40^{\circ}53'$ and $41^{\circ}27'$ for 1hexanol, 1-heptanol and 1-octanol, respectively. Though such an assumption is not strictly valid, the calculation of Shuster [22] shows that the potential energy is minimum when hydrogen bond is directed along the lone pair direction. Also, it has been found that in structures with the same orientation of the functional groups forming the hydrogen bond, the arrangement with the smallest dipole moment has the lower energy [23]. Hence the possible structure for the systems studied can be represented as in Fig. 1.

The values of dielectric constant (\mathcal{E}), refractive index (*n*) and and density (ρ) were measured for varying concentrations of proton donor and are recorded in Table 1. In the concentration range $C_b \gg C_c$, the values of Ω are computed through Eq. 4 and are plotted against C_b/C_c . From the nature of the curve for Ω versus C_b/C_c , it is observed that the plots are straight for $C_b = 2 \text{ mol}^{-1}$ in 1-heptanol and 1-hexanol systems while at 3.5 mol^{-1} in 1 -octanol system. This suggests that there is 1:1 complexation in all the three systems. In the present study, the complex formation takes place due to linkage between H^{δ +} of OH group of alcohol and 0^{δ -} of P = 0 group of TBP represented as



Because of the presence of oxygen atom of TBP and hydrogen atom of alcohol in the linear chain, the charge distribution between them is likely to be favoured. Further oxygen atom is SP^3 hybridised and the shape of TBP is almost pyramidal, there is lot of space available for the OH to penetrate and enter into complexation. An analysis of Table 3 shows that the dipole moments of all the systems studied are not equal to the scalar sum of the individual components. This indicates interactive association between two species of molecules.

$C_b(\text{mol}^{-1})$	$C_c(\text{mol}^{-1})$	ε	n	$\rho(\text{gcm}^{-3})$	Ω (debye $^{-2}$)	μ_m (debye)		
1-hexanol + TBP in benzene								
2	0.4	4.663	1.4599	0.869	8.8793	4.094		
	0.6	5.100	1.4592	0.872	10.2894	4.180		
	0.8	5.665	1.4584	0.876	12.0878	4.312		
	1.0	6.908	1.4561	0.885	15.9990	4.693		
2.5	0.4	5.569	1.4556	0.868	9.4804	4.220		
	0.6	5.950	1.4546	0.871	10.4622	4.310		
	0.8	6.445	1.4529	0.875	11.7316	4.438		
	1.0	7.528	1.4495	0.884	14.4904	4.800		
3	0.4	6.221	1.4538	0.864	9.2972	4.226		
	0.6	6.680	1.4524	0.867	10.0964	4.320		
	0.8	7.256	1.4506	0.871	11.4951	4.450		
	1.0	8.539	1.4466	0.881	14.2103	4.805		
3.5	0.4	6.893	1.4456	0.861	9.2992	4.203		
	0.6	7.330	1.4444	0.863	10.0964	4.374		
	0.8	7.907	1.4428	0.867	11.1483	4.444		
	1.0	9.212	1.4393	0.876	13.5211	4.803		
1-heptanol + TBP in benzene								
2	0.4	4.822	1.4674	0.871	9.2283	4.120		
	0.6	5.490	1.4648	0.876	11.3854	4.263		
	0.8	6.610	1.4624	0.882	13.5215	4.453		
	1.0	6.820	1.4600	0.887	15.6148	4.601		
2.5	0.4	5.287	1.4560	0.868	8.7394	4.085		
	0.6	5.930	1.4565	0.873	10.3726	4.265		
	0.8	6.590	1.4532	0.879	12.0842	4.430		
	1.0	7.240	1.4509	0.884	13.7439	4.588		
3	0.4	6.109	1.4515	0.864	9.1063	4.155		
	0.6	6.798	1.4483	0.869	10.5969	4.330		
	0.8	7.427	1.4466	0.874	11.9322	4.491		
	1.0	7.976	1.4437	0.879	13.1256	4.643		
3.5	0.4	7.044	1.4467	0.860	9.5473	4.255		
	0.6	7.600	1.4425	0.864	10.6099	4.398		
	0.8	8.244	1.4396	0.869	10.8070	4.561		
	1.0	8.652	1.4365	0.875	12.5956	4.715		
1-octanol +	TBP in benze	ene						
2	0.4	4.650	1.4786	0.869	8.4493	4.050		
	0.6	5.143	1.4782	0.874	9.9982	4.149		
	0.8	5.668	1.4778	0.878	11.6219	4.254		
	1.0	6.158	1.4773	0.884	13.1245	4.439		
2.5	0.4	5.006	1.4687	0.864	7.8259	3.991		
	0.6	5.665	1.4686	0.868	9.4706	4.122		
	0.8	6.179	1.4683	0.874	10.7412	4.203		
	1.0	6.894	1.4682	0.879	12.3727	4.327		

Table 1. Value of dielectric constant ε , refractive index n, density ρ , dipolar function Ω and mean dipole moment μ_m of the solute species alcohol + TBP in benzene

$C_b($ mol ⁻¹ $)$	$C_c($ mol ⁻¹ $)$	8	n	$\rho(\text{gcm}^{-3})$	Ω (debye $^{-2}$)	μ_m (debye)
3	0.4	5.629	1.4627	0.859	7.9152	4.022
	0.6	6.301	1.4620	0.864	9.3131	4.132
	0.8	6.867	1.4614	0.869	10.4806	4.210
	1.0	7.659	1.4611	8.750	12.0901	4.342
3.5	0.4	6.372	1.4579	0.855	8.1731	4.159
	0.6	7.093	1.4565	0.860	9.4616	4.161
	0.8	7.807	1.4550	0.865	10.7353	4.244
	1.0	8.509	1.4538	0.871	11.9779	4.298

Table 2. Data for estimation	of molar	polarization	of alcohol	and TE	3P in
	benze	ene			

W ₂	$\rho(\text{gmcm}^{-3})$	ε	n
Solute 1-hexanol	• •		
0.005	0.8742	2.67	1.4943
0.009	0.9740	2.69	1.4937
0.017	0.8736	2.72	1.4928
0.035	0.8726	2.79	1.4907
0.049	0.8718	2.84	1.4892
0.065	0.8710	2.90	1.4872
0.077	0.8704	2.95	1.4857
0.093	0.8696	3.20	1.4838
Solute 1-heptanol			
0.010	0.8784	2.72	1.4972
0.020	0.8781	2.76	1.4964
0.040	0.8775	2.80	1.4944
0.050	0.8771	2.85	1.4934
0.060	0.8768	2.88	1.4924
0.070	0.8765	2.92	1.4914
0.086	0.8750	2.98	1.4902
Solute 1-octanol			
0.010	0.8720	2.60	1.4924
0.020	0.8718	2.64	1.4916
0.035	0.8716	2.70	1.4906
0.053	0.8712	2.77	1.4888
0.065	0.8708	2.82	1.4878
0.080	0.8705	2.88	1.4866
0.090	0.8702	2.94	1.4850
Solute TBP			
0.010	0.8732	2.68	1.4874
0.020	0.8740	2.75	1.4868
0.032	0.8752	2.83	1.4862
0.046	0.8764	2.93	1.4854
0.065	0.8782	3.06	1.4842
0.075	0.8792	3.13	1.4832
0.085	0.8802	3.19	1.4830

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By using the mean value obtained from all the methods, it is observed that the mean dipole moment of the complex, μ_{bc} , decreases in the order.

1-hexanol > 1-heptanol > 1-octanol.

The trend of variation of induced polarization P_{bc} , and the dipole moment of the hydrogen bonded bridge, μ^* , are observed to be of the same order as that of μ_{bc} . This may be compared with the results of our earlier corroborative work [24] involving ultrasonic and dielectric measurements in these systems. It is observed that the values of parameters such as available volume, V_a , acoustic impedance, Z, molar compressibility, ω , and molar sound velocity, R, increases in the sequence

1 - hexanol < 1 - heptanol < 1 - octanol,

while the values of intermolecular free length, L_f , isentropic compressibility, β_s , and internal pressure, π_i and Gibb's free energy of mixing, ΔG^E deccreases in the order

1-hexanol > 1-heptanol > 1-octanol.

On the other hand, excess viscosity, η^E , excess Gibb's free energy of mixing, ΔG^E are found to be negative in the entire compositional range in all these systems. According to Tiwari et al. [25] and Kalgud [26], this is an indication of formation of complex between component liquids in the mixture and is influenced by the strength of interactions [27]. Furthermore, it is observed that the mutual correlation factor, g_{ab} , and excess molar free energy, ΔF_{ab} , obtained from dielectric studies decreases in the order 1-hexanol > 1-heptanol > 1-octanol. The point of inflexion in the curve for these parameters is relatively sharp in 1hexanol system. Further, the extent of departure of g_{ab} from unity [28] is maximum for 1-hexanol indicating greater interaction. The mutual correlation factor, g_{ab} , in 1-hexanol, 1-heptanol, and 1-octanol systems remains less than unity over the entire concentration range of TBP indicating the predominance of β -clusters with antiparallel orientation between them. In the presence of greater steric hindrance in higher chain alcohols in a highly viscous TBP medium, relatively stable structure with antiparallel orientation and linear linkage is a greater possibility in all these systems. The results of all these studies indicated strength of interaction to be maximum in 1-hexanol system which also finds corroboration in the highest value of μ_{bc} , μ^* and $\Delta \mu$. It also shows that the tendency of complex formation in 1-hexanol is relatively more. Because of steric factor it is likely that relatively longer chain alcohols will have less probability of complex formation due to the wood-pile linkage in TBP [29] whereas for relatively smaller alcohols the tendency is stronger due to switching mechanism prevalent in alcohol systems. Furthermore, the positive value of $\Delta \mu$ also decreases in the order

1-hexanol (0.931D) > 1-heptanol (0.579D) > 1 - octanol(0.510D).

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The 0 – H bond induces a moment in a highly polarizable lone pair charge-cloud in the P = 0 group of TBP and this induced polarization moment would account for $\Delta\mu$. The excess dipole moment values ($\Delta\mu$) were found to be positive for TEA + aromatic alcohols, *n*-butanol + acetophenone, *n*-butyl amine +*n*-butanol systems studied by Misra et al. [30,31], Shanmugasundaram et al. [32] and Tripathy et al. [11] respectively assuming a planar conformer for binary system.

Huysken et al. [33] have shown that if $\Delta\mu$ is the total increment in dipole moment, then $\Delta\mu = 0.5D$. This is found to be so whether the H-bond is purely electrostatic or purely ionic, the other 50% should arise from electronic displacement. However, the $\Delta\mu$ values in the present investigation are greater than 0.5D. Meyyappan et al. [34] have shown that by employing the minimized distances of 1.03 Å and 1.04Å for the free and hydrogen bonded OH, and the maximum order of displacement of O....O distance as 0.025Å, the magnitude of $\Delta\mu$ should be around 0.3D to 0.4D. Furthermore, calculation based on Frank's method [35] shows that contribution of induced polarization effect is of the order of 0.1D to 0.15 D. However, the value of $\Delta\mu$ listed in Table 3 are also higher than both. As it can not arise solely out of interaction moment induced by the charge-cloud, this may lead to the following possibilities.

(i) the formation of complex of higher order like



(ii) partial proton transfer in which the electron delocalization is more predominant than the proton transfer. Delocalization and dispersion interactions accompanying the partial proton transfer complex between TBP and alcohol molecules may be the physical model of H – bonded complexes. In such a physical model $\Delta\mu$ may have two components-one coming from induced dipole moment and another due to the presence of charge transfer in the ground state. Thus, it is reasonable to expect a charge transfer arising out of the inter molecular charge redistribution to the polarization effect. Apparent complex formation constant in these systems is found to decrease in the order:

1-hexanol(0.064) > 1-heptanol(0.02) > 1-octanol(0.01).

Liquids	μ _b (debye)	μ_{bc} (debye)		Meanµ _{bc} (debye)	μ* (debye)	P _{bc} (g cm ³ mol ⁻¹)	$\frac{\Delta P}{(\text{gmcm}^3 \text{ mol}^{-1})}$	<i>K</i> (cm ⁻¹ mol ⁻¹)	Δμ (debye)	
		Method I	Method II	Method III						
1-hexanol	1.55	4.803	5.019	5.671	5.164	5.441	536.046	77.82	0.064	0.931
1-heptanol	1.71	4.264	5.146	5.586	4.999	5.089	502.338	108.58	0.02	0.579
1-octanol	1.68	4.141	5.063	5.504	4.903	5.025	483.230	65.574	0.01	0.510

Table 3. Variation of μ_{bc} , μ^* , P_{bc} , ΔP , K and $\Delta \mu$ of three long chain alcohols with TBP in benzene, $\mu_c = 3$ (debye)

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It further supports our findings that complexation is more favoured in relatively smaller alcohol like 1-hexanol. It may be of interest here to note that in our earlier study on mutual correlation of actor, g_{ab} , in these systems we had indicated that the geometry of the complex, may perhaps need modification due to steric factors. The presumption that $\theta_c = 0^\circ$ should be revised to the extent that TBP dipole moment may be inclined to the 0 - H axis instead of lying along it. However, this change will not necessitate any significant alteration in the nature of value of $\Delta \mu$. Hence, we may not be wrong to conclude that the complex formation is due to charge redistribution and 1-hexanol may be used as a more efficient modifer, in comparison to 1heptanol and 1-octanol, in the extraction process.

5. CONCLUSIONS

Two conclusions resulted from the study. Firstly, the higher order of complexation between TBP and long chain aliphatic alcohols like 1-hexanol, 1-heptanol, 1-octanol is predominantly due to polarization effect involving charge redistribution and secondly, the complex formation is maximum in 1-hexanol system. Hence, 1-hexanol may be used as more efficient modifier in comparison to 1-heptanol and 1-octanol in the extraction process involving TBP as an extractant.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Bohr's Model of Hydrogen Atom: A Review

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ABSTRACT

This chapter has provided an alternate method of solving simple problems in atomic physics under Bohr's model to aid good mental picture of hydrogen atom to scientists. Two values of fundamental physical properties of an electron in the hydrogen atom has been identified. By limiting the orbiting electrons to a series of circular orbits having discrete radii, Bohr could account for the series of discrete wavelengths in the emission spectrum of hydrogen. Light, he proposed, radiated from hydrogen atoms only when an electron made a transition from an outer orbit to one closer to the nucleus. These physical properties ($v_e = 174090.938 m s^{-1} \& p_e = 1.585860888 \times 10^{-25} k g m s^{-1}$) are constant in nature. The aim for the review was to contribute to the solution of disagreement between the Bohr's wavelength ($\lambda_o = 91.12nm$) and the Balmer's experimental observation ($\lambda_a = 91.18nm$) for the emission spectrum of hydrogen two other constants $\delta = 7.199822 \times 10^{-10} eVm$ and atom. There are $\xi = 1503796277 m^{-1}$ that were identified in the Bohr's equation of the hydrogen

atom. The four fundamental physical constants can be applied to multi-electron systems because they are inherent characteristics of an electron. They can also be derived from the steady state hydrogen atom Schrodinger's equation. For a

be derived from the steady state hydrogen atom Schrodinger's equation. For a deeper understanding, these constants may be scrutinised for their determination. The study recommends that current quantum atomic models and equations governing quantum physics should be revisited for better applications and understanding of the physical world.

Keywords: Bohr's model; hydrogen atom; constant velocity.

1. INTRODUCTION

The Bohr's theory on the hydrogen atom is incompatible with the atom model of QM, since his model is corpuscular, and the atom considered in quantum mechanics is undulatory. The first incompatibility arises from the fact that,

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whereas the electron in the Bohr's hydrogen atom is susceptible to be submitted to a centripetal acceleration, unlike the electron in the atom of quantum mechanics cannot be submitted to any centripetal acceleration, which cannot actuate on a wave [1]. Despite its limitations, Neil Bohr's theorem of the hydrogen atom can still be applied to the study of atomic structure in quantum physics because it gives students an easy mental representation [2-4]. His theory on hydrogen atom worth examining because it provides concrete transition from real classical world to the abstract world of quantum theories [5,2,6,7]. The hybridization between space science and quantum physics is attracting a growing attention for the many possibilities it has to offer, from quantumenhanced satellite-based communication and Earth observation, to the leverage of quantum sensing and interferometry, to the exploration of elusive physical phenomena, including dark matter and quantum gravity [8,9]. The theory based on basic newtonian physics principles was able to predict scientific formula for the approximate calculation of discrete spectrum of the hydrogen atom [3,6,10,4].

Bohr's prediction was close but not exact to the Balmer's experimental observation because it was assumed that the proton in the nucleus remains at rest while the electron orbits around it [5,6,10]; though in reality both particles rotate about their common centre of mass [5,10,4]. The centre of mass is shifted close to the massive proton [5,4]. However, proton is not entirely motionless [10,4]. Advanced studies and analysis account for the motion of the massive proton which slightly changes the energies of the electron at stationary states to one part in two thousand which is necessary to revise the error [10,4].

However, upon arithmetical arrangements of the physical parameters in Bohr's equation for the hydrogen atom at stationary states, it is obviously seen that the electron in the hydrogen atom exhibits another motion besides orbiting [11]. This motion actually has effect on the total energy of the electron and has caused significant error in the subsequent quantum models [12,13]. Based on the equations presented in this paper, the motion is an intrinsic property and its magnitude is constant at all levels of quantised energy states. As a result, it provides the electron a constant momentum at each energy level.

The effect of this motion on the energy states of an electron bound to the nucleus has not been considered on various quantum atomic models. Therefore, it is very important to further probe into studies and analyses of the energy states of an electron in the hydrogen atom. Also, this constant motion of an electron may influence the fundamental properties and other quantum parameters that describe the energy state of an electron in the hydrogen atom.

2. THEORIES

Bohr's equation for the hydrogen atom at the steady state is given by:

$$E_n = -\frac{me^4}{8\varepsilon_o^2 h^2 n^2} \tag{1}$$

Equation for the postulate on angular momentum:

$$mv_n r_n = \frac{nh}{2\pi} \tag{2}$$

Equation for Bohr's radius is given by:

$$r_n = \frac{\varepsilon_o n^2 h^2}{\pi m e^2} \tag{3}$$

$$n^2 h^2 = \frac{\pi m e^2 r_n}{\varepsilon_o} \tag{4}$$

$$E_n = -\frac{me^4}{8\varepsilon_o^2} \times \frac{\varepsilon_o}{\pi me^2 r_n} = -\frac{e^2}{8\pi\varepsilon_o r_n} = -\frac{\delta}{r_n}$$
(5)

From (5), the energy of an electron bound to the nucleus in the hydrogen atom at the steady state is inversely proportional to its corresponding Bohr's radius.

$$\delta = 1.153538564 \times 10^{-28} Jm \tag{6}$$

$$\delta = 7.199822 \times 10^{-10} \, eVm \tag{7}$$

$$E_n = -\frac{\delta}{r_n} = -\frac{h}{h} \times \frac{\delta}{r_n} = -\frac{\delta}{h} \times \frac{h}{r_n} = -v_e \times \frac{h}{r_n}$$
(8)

$$v_e = \frac{\delta}{h} = \frac{1.153538564 \times 10^{-28} Jm}{6.62606896 \times 10^{-34} Js}$$
(9)

$$v_e = 174090.938 m s^{-1} \tag{10}$$

$$\Delta E = hf = v_e h \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \tag{11}$$

$$f = v_e \left(\frac{1}{r_1} - \frac{1}{r_2}\right) \tag{12}$$

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$$E_n = -\frac{v_e h}{r_n} \tag{13}$$

$$r_n = \frac{nh}{2\pi m v_n} \tag{14}$$

$$E_n = -v_e h \times \frac{2\pi m v_n}{nh} = -2\pi m v_e \left(\frac{v_n}{n}\right)$$
(15)

$$\Delta E = 2\pi m v_e \left(\frac{v_1}{n_1} - \frac{v_2}{n_2}\right) \tag{16}$$

$$f = \frac{mv_e}{\hbar} \left(\frac{v_1}{n_1} - \frac{v_2}{n_2} \right) \tag{17}$$

$$f = \xi \left(\frac{v_1}{n_1} - \frac{v_2}{n_2} \right) \tag{18}$$

$$\xi = 1503796277 m^{-1} \tag{19}$$

$$p_e = mv_e = 9.10938215 \times 10^{-31} kg \times 174090.9385 ms^{-1}$$
⁽²⁰⁾

$$p_e = 1.585860888 \times 10^{-25} \, kgms^{-1} \tag{21}$$

$$2\pi mv_e = 9.964257829 \times 10^{-25} \, kgms^{-1} \tag{22}$$

Some velocities of an electron in various Bohr's orbits:

$$v_1 = 2187691.253 m s^{-1} \tag{23}$$

$$v_2 = 1093845.627 m s^{-1} \tag{24}$$

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$$v_3 = 729230.419 m s^{-1} \tag{25}$$

$$v_{\rm A} = 546922.8135 m s^{-1} \tag{26}$$

Schrodinger's Steady State Equation for Hydrogen Atom:

$$E_n = -\frac{me^4}{32\pi^2 \varepsilon_o^2 \hbar^2} \left(\frac{1}{n^2}\right) = \frac{E_1}{n^2} = \frac{v_e h}{r_n} = 2\pi m v_e \left(\frac{v_n}{n}\right)$$
(27)

$$E_{1} = -\frac{me^{4}}{32\pi^{2}\varepsilon_{o}^{2}\hbar^{2}} = -\frac{\hbar^{2}}{2ma_{o}^{2}}$$
(28)

Where:

m is the mass of an electron; *e* is the fundamental charge of an electron; *h* is the Planck's constant; *n* is the principal quantum number; \mathcal{E}_o is the permittivity of vacuum; a is the Bohr's radius; v_n is the orbital velocity corresponding to the principal quantum number concerned; v_e is the proposed classical spin velocity for the electron from Bohr's hydrogen model; *f* is the emitted/absorbed frequency due to electron quantum transition; ΔE is the energy emitted/absorbed due to electron quantum transition; E_n is the energy of an electron corresponding to the principal quantum number concerned; r_e is the proposed classical constant momentum due to electron spin; and δ , ξ are physical constants deduced from the classical hydrogen atom of the Bohr's model.

3. DISCUSSION

Upon valid arithmetical arrangements of the equations (8), (12), (17) and (27); it is seen that electron in the hydrogen atom naturally exhibits another motion and momentum besides the orbital motion described in the theory. Actually, this motion may be spinning in nature [14,11,13] as suggested by Goudsmit and Uhlenbeck in a classical view. The motion is also observed in Schrodinger's equations for hydrogen atom at the steady state.

From the equations (11) & (16), change in energy state from an allowed orbit to another is not affected by the velocity, V_{ρ} of the motion. Also,

equations (12) & (17) suggest that frequency of radiation emitted upon quantum transition is unaffected by the motion, v_e , of the electron. Likewise, the momentum is also observed to be constant in (15), (16) & (27). However, the orbital angular velocity, v_n changes in magnitude whenever principal quantum number, n is altered.

4. CONCLUSIONS

From Bohr's and Schrodinger's equation for an electron bound to the nucleus of the hydrogen atom at steady state, electron in the hydrogen atom describes a constant motion at $v_a = 174090.938 m s^{-1}$. Also, besides the angular momentum propounded by the Bohr's model, there exist another momentum exhibited by the electron at $p_e = 1.585860888 \times 10^{-25} kgms^{-1}$. This momentum may confirm the statement of both Dirac and Darwin who suggested that the momentum-energy of an electron is the sum of mechanical momentum-energy and the electromagnetic momentum-energy. However, unlike orbital motion and angular momentum that changes in magnitude at each energy level, these two properties remain constant irrespective of the energy level. Hence, they are intrinsic properties exhibited by the electron in the hydrogen atom. Although the motion was derived through classical approach, it may contribute to the reason why Sommerfield's formulae for energy level could not predict the Lamb effect or hyperfine structure. Also, the effect of this suggested rotational motion may basically account for the origin of magnetic moment exhibited by electrons that was suggested by Pauli.

In conclusion, the source of error to the inconsistency between Bohr's and Balmer's wavelength is not only due to the effect of the motion of proton on the energy state of the electron but the considerations for the motions of electron also. Moreover, this paper has provided an alternate classical approach and ideas in solving trivial problems under Bohr's model of hydrogen atom for better understanding.

5. RECOMMENDATIONS

There exist many advanced scientific models in quantum physics describing atomic nature and energy states of electrons but each has its own assumptions, complications and limitations. However, these atomic models basically left out considerations for such important physical constants identified in this study. Particularly, Schrodinger's quantum atomic model on the hydrogen atom at steady state failed to consider such physical properties that existed in Bohr's theory. The study recommends that current quantum atomic models and equations governing quantum physics should be revisited for better applications and understanding of the physical world.

AUTHOR'S CONTRIBUTION

The sole author designed, analysed, interpreted and prepared the manuscript.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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Fundamental Research and Application of Physical Science Vol. 6 Bohr's Model of Hydrogen Atom: A Review

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Ideal Flow Solution Comparison over a 90-Degree Angle Point Using CVBEM and FEM

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ABSTRACT

Complex Variable Boundary Element Method (CVBEM) is an emerging numerical approach for simulating flow problems, including groundwater flows. Benchmarking the solution from CVBEM with other established approaches, like the Finite Volume Methodologies (FVM), will showcase its reliability. In this work, the flow fields from the CVBEM and FVM are compared for an ideal flow over a 90-degree angle point. The comparison focuses on the flow vector's magnitude and direction. This test problem was chosen to showcase the reliability of CVBEM for groundwater flow applications. The close agreement between the two results underscores the accuracy of the CVBEM solution.

Keywords: Complex variable boundary element method; finite volume method; ideal fluid flow; 90-degree angle point; computational fluid dynamics.

1. INTRODUCTION

In the field of computational fluid dynamics, the finite volume method is dominant over other numerical techniques like the finite difference and finite element methods because the underlying physical quantities are conserved at the discrete level [1]. Through the use of computational fluid dynamic (CFD) software programmes like Fluent and OpenFOAM, finite volume methodologies have historically been used to analyse fluid flow issues, including groundwater models. The groundwater resources of the earth have for a long time been subjected to degradation as a result of man's increasing utilization of natural resources and worldwide industrialization. Since then, mathematical models of groundwater flow have been widely used for a variety of purposes ranging from water supply studies to designing contaminant cleanup [1]. A number of other domain

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modelling strategies, like the finite element and finite difference numerical approaches, are also frequently used in fluid flow analysis, they are all constrained by the requirement of a volume mesh, the properties of which can have a significant impact on both the accuracy and solution time of the computations [2]. Such difficulties can be overcome in groundwater flow models when the groundwater equipotentials are coupled with streamlines [3], an approach that is embedded in the complex variable boundary element method (CVBEM).

While the advantages of the CVBEM over domain modeling methods, such as FVM, are specifically described by Johnson et al. [4], and the CVBEM has been applied successfully to ideal fluid flow problems [5], this is the first such work in which the flow vectors are calculated directly from the CVBEM and compared to the results of a domain method. Specifically, a CFD computer program utilizing a finite volume methodology, known as EasyCFD, is used to develop a flow field vector outcome at a 90-degree angle point which is then compared with a similar vector flow field outcome that is developed by the CVBEM.

Such a CVBEM vector flow field is a direct result of the CVBEM approximation function for the conjugate component. In addition, the vector flow field can be developed using vector gradients of the CVBEM potential function outcome, which has application to three-dimensional flow problems. What is particularly new, as presented in this chapter, is the development of a procedure to develop stream function flow trajectory vectors based upon vector calculus gradients of the CVBEM potential function (that is, the real part of the CVBEM complex variable function outcome), as opposed to being based upon the CVBEM stream function (the imaginary part). Because the CVBEM solution solves the boundary value problem (BVP), the CVBEM flow trajectory vectors should properly represent the ideal fluid flow direction and magnitude of the flow regime. In other words, for the considered important ideal fluid flow application problem, the CVBEM solution should be the exact solution to the BVP, and the produced fluid flow trajectory vectors should be correctly determined. The flow field vector outcomes from EasyCFD are used to verify and validate the development of flow trajectory vectors by the CVBEM for ideal flow problems.

2. METHODOLOGY AND SOFTWARE

2.1 Complex Variable Boundary Element Method (CVBEM)

The CVBEM originates from the real variable Boundary Element Method (BEM) that was developed by Carlos Brebbia [6,7]. In short, the CVBEM set of basis functions spans a vector space that is an element of the BVP solution being examined. This means that the CVBEM outcome is the solution to the BVP and not only satisfies the problem boundary conditions, but it also satisfies the partial differential equation (PDE) of the governing Laplace equation. Because the CVBEM develops a well-defined function that applies throughout the problem domain (and also in the exterior of the problem domain), the flow field vector trajectories are calculated directly from the CVBEM approximation function rather than by the usual estimation of point values throughout the problem domain.

Consequently, not only does the CVBEM develop an approximation function that solves the governing partial differential equations throughout the problem domain and in the exterior of the problem domain, but the streamline vector trajectories are derived directly from the CVBEM approximation function by either direct use of the conjugate function outcome or by use of vector gradient operation upon the CVBEM resulting potential function outcome. Further descriptions of CVBEM modeling and the mathematical underpinnings of the method can be found in several publications [8-13]. Consequently, a rigorous examination of the CVBEM will not be repeated here.

2.2 Finite Volume Method

To develop the finite volume solution, the CFD software EasyCFD was used to set up and solve the 90-degree angle point fluid flow model. EasyCFD is a CFD software tool for the numerical simulation of fluid flow in a boundary-fitted mesh. The Navier-Stokes equations: mass, momentum, and energy, are solved via a finite volume methodology. Specific details and validation regarding the EasyCFD program can be found in several publications [14-16].

2.3 Test Problem Description

The selected test problem is of two-dimensional ideal fluid flow at a 90-degree angle point. This test problem has been the subject of several computational modeling assessments and is considered in the current work due to the availability of the analytic solution, and the challenge of developing the flow field vector trajectories for a highly spatially variable flow field problem. The CFD model is used to simulate flow at a 90-degree angle point, as shown in Fig. 1.

The modeling domain in which the results are compared is a square defined within the total modeling space, as shown in Fig. 1 (area of comparison), with vertices at (0,0) (0,2) (2,2) (2,0). The square domain is the focus of all three outcomes for the vector field developments and comparisons. The area of comparison does not include the entire FVM model domain, as a portion of the domain was constructed to isolate the inlet and outlet, and the flow effects thereof, from the 90-degree angle point, and thus cannot be assumed to replicate ideal flow in the 90-degree angle point.

In order to directly compare the FVM results to the CVBEM application and the available analytic solution, it was necessary to approximate the ideal flow in the FVM model. This was accomplished in EasyCFD by defining the fluid as water ($\rho = 1000 \text{ kg/m}^3$, $\mu = 0.001 \text{ N*s/m}^2$), the flow type as laminar (to ignore turbulent effects), and the boundary walls as symmetry boundary conditions (*i.e.* slipwalls). The FVM solution was considered converged when all residuals (u, w, mass) were less than 5e–6.

For the analytic solution, the mathematical description of the streamline function is directly available from the conjugate function of the complex variable monomial $w(z) = z^2$ [9]. The CVBEM model results in the analytic solution function as well when the CVBEM basis function specification includes complex variable monomials as well as the usual sums of products of complex polynomial and

complex logarithm basis functions. Thus, three outcomes are available for comparison; namely, the FVM computational outcome of a set of highly discretized point estimates; the CVBEM approximation function outcomes; and the analytic solution.



Fig. 1. CFD model domain and area of comparison to CVBEM results



Fig. 2. CVBEM problem domain with potential isocontours and velocity vector field

2.4 Flow Field Vector Trajectory Development

For the CFD application, the flow field is developed by a finite volume computation that is made in addition to the usual post-processing interpolation of point estimates of fluid flow properties for the subject problem. For the analytic solution and the CVBEM outcome approximation function, flow field vectors are determined by direct use of the function of the conjugate or by application of the vector gradient operator upon the modeling outcome of the CVBEM approximation potential function. The CVBEM test problem solution can be seen in Fig. 2.

3. RESULTS

Comparisons of the vector trajectories between modeling approaches are displayed in Fig. 3 and Fig. 4. The FVM velocity vectors and streamlines are displayed in red, overlaid on the CVBEM potential isocontours and vector field. From Fig. 3 and Fig. 4, the flow field vector trajectories are seen to be in good qualitative agreement as to vector direction for the considered FVM and CVBEM applications.

A quantitative comparison of the error between the 2 methods with respect to vector magnitude and direction can be found in Fig. 5 and Fig. 6. Each grid point represents a node in the model domain as determined by its coordinates. The color of the box is an indication of the magnitude of the error, as determined by the difference between the vector magnitude (Fig. 5) or vector direction (Fig. 6) between the CVBEM and FVM models. In Fig. 5, a positive error indicates that the FVM model velocity vector was larger in magnitude than the CVBEM velocity vector, while the opposite is true for a negative error. In Fig. 6, a positive error indicates that the CVBEM velocity vector, while the opposite is true for a negative error. For reference, a 0-degree angle was defined as a velocity vector pointing in the positive x direction with the angle increasing counter-clockwise.



Fig. 3. Overlay of CVBEM velocity vectors on FVM model velocity vectors (size of vectors is not correlated between the two models)

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Fig. 4. Overlay of CVBEM velocity vectors on FVM model streamlines



Fig. 5. Error measurement of velocity magnitude of FVM model results as compared to CVBEM solution

The comparison of vector magnitudes shows that the maximum absolute error is less than 0.1 m/s, with an average absolute error of 0.03 m/s, or average relative error of 1.1%. Similar agreement is found when comparing vector direction, which shows that the maximum absolute error is 10.1 degrees, with an average absolute error of 0.4 degrees. Even better agreement is found when comparing points not located along the x- or y-axis (0.7 degrees maximum absolute error, 0.15% average relative error).





Fig. 6. Error measurement of velocity vector angle of FVM model results as compared to CVBEM solution

4. CONCLUSION

Comparison of the CVBEM and FVM flow field trajectory vectors for the target problem of flow in a 90-degree angle point shows good agreement between the considered methodologies, achieving an average relative error of 1.1% in velocity magnitude and 0.15% in velocity direction. This is the first such work in which velocity vectors developed by the CVBEM are compared to the results from an FVM model, and the results indicate that the flow trajectory vectors developed from the complex variable boundary element method are correctly determined and properly represent the ideal fluid flow velocity and direction.

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