Chapter IV. CdTe on Si: A Two Decades Love Story

IV.1. Growth of CdTe on Si(100)

The first epitaxial growth of cadmium telluride on silicon by molecular beam epitaxy (MBE) is reported in 1989 [34]. At this time, the most used substrate for technologic purposes is the silicon oriented in the (100) direction. The growth of CdTe on Si(100) follows a two step procedure, taken from the growth process of CdTe on GaAs [35]: a thin layer (about 100 nm) of CdTe is firstly grown at low temperature (typically 220°C) followed by a thick layer (5 – 10 µm) grown at higher temperature (300°C). The nucleation step is found to be crucial, leading to a 2D growth at the beginning of the growth process. Neglecting this important step results in an initial Volmer – Weber growth (i.e. islands growth), because of the huge 19% lattice mismatch between silicon and cadmium telluride. Even if at the end of the growth, one can expect the islands to coalesce into a film, the resulting quality of the layer is lower than that obtained with an adequate nucleation step. Experimental studies demonstrate that the layer of CdTe grown on Si(100) is oriented in the (111) direction.

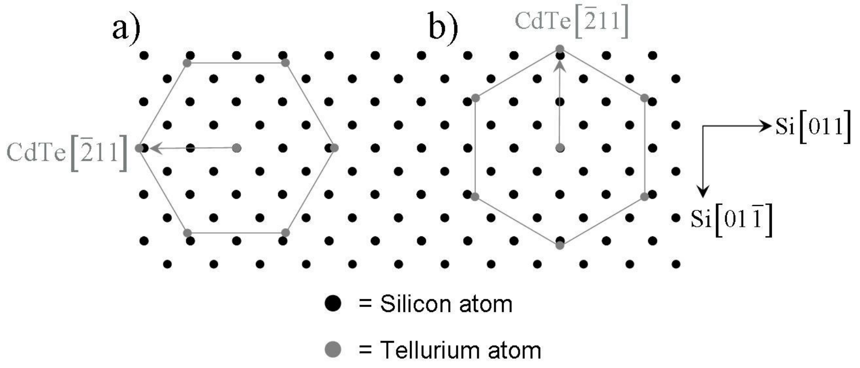

Figure IV-1. Double domains for CdTe($\bar{1}\bar{1}\bar{1}$)B on Si(100) growth.

CdTe grows in the (111) direction on Si(100) to reduce the mismatch between the two semiconductors: the lattice mismatch decreases from 19% when growing CdTe in the (100) direction to 3.4% when the (111) direction is followed. This can be done by aligning the $\left[\bar{2}11\right]$ direction of CdTe with the $\left[0\bar{1}1\right]$ or $\left[0\bar{1}\bar{1}\right]$ directions of Si(100) (Figure IV-1a and b). In the $\left[\bar{2}11\right]$ direction, the distance between two tellurium atoms is $a_{CdTe}\sqrt{3/2}$ where a_{CdTe} is the lattice parameter of CdTe and the distance between two silicon atoms in the $\left[0\bar{1}1\right]$ or $\left[0\bar{1}\bar{1}\right]$ direction is $a_{Si}\sqrt{2}/2$ with a_{Si} being the silicon lattice parameter.

Because of the difference in the orientation of the substrate and the epilayer, the symmetry of the crystalline structure is not the same: 4-fold symmetry for Si(100) and 6-fold symmetry for CdTe(111). The consequence of this difference is the presence of double domains observed during the growth [36, 37]: as presented in Figure IV-1, the $\left[0\bar{1}1\right]$ and $\left[0\bar{1}\bar{1}\right]$ orientations of silicon are rotated by 90° to each other. Hence, the two possible hexagons of CdTe(111) are also rotated by 90°. The double domains can be observed by RHEED during the growth if the size of the domains is larger than the coherence length of the electron beam. Transmission electron microscopy (TEM) performed on CdTe($\bar{1}\bar{1}\bar{1}$)B/Si(100) revealed that the domains have a size of 1 µm, which is far larger than the coherence length. TEM studies also reveal the presence of twins in the layer due to the high symmetry of the crystalline orientations involved [38]. A twin consists of inverting the stacking sequence by removing (intrinsic) or adding (extrinsic) a double layer of CdTe (Figure IV-2).

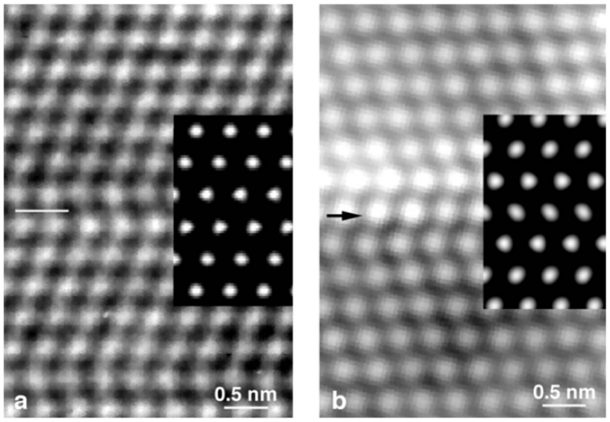

Figure IV-2. a) intrinsic and b) extrinsic lamellar twins [39].

An important consequence of the growth orientation is that the CdTe surface grown on Si(100) is polar and two stable surfaces can exist: the Cd-terminated CdTe(111)A surface with one dangling bond per atom and the Te-terminated CdTe($\bar{1}\bar{1}\bar{1}$)B surface with one dangling bond per atom also. The polarity of the surface can be observed in-situ by reflection high energy electron diffraction (RHEED) because the reconstruction of the surface is not the same for these two preferential orientations [34, 35, 40]:

- The reconstruction of the CdTe($\bar{1}\bar{1}\bar{1}$)B surface observed by RHEED is a $\left(2\sqrt{3}\times 2\sqrt{3}\right)\mathrm{R}30°$ reconstruction;
- The CdTe(111)A surface leads to a (2x1), c(2x2) or a mix of these reconstructions diffraction pattern.

The polarity observed during the growth is correlated to the preparation of the substrate before the CdTe growth. The Si(100) substrate introduced in the UHV environment is previously cleaned ex-situ according to a modified RCA procedure [41] (see chapter V for more details) leading to the formation of a thin oxide layer with a thickness of about 1 nm. This oxide can be desorbed in the MBE chamber by heating the Si(100) substrate up to 1050°C before cooling it down to the nucleation temperature. If during the cooling step the substrate is exposed to a CdTe flux and that this flux is interrupted when the substrate temperature is between 350 and 400°C, the subsequent growth of CdTe, near 300°C, follows a B polarity. If the CdTe flux is interrupted out of this substrate temperature window, the A polarity is obtained during the subsequent growth of CdTe.

Only CdTe($\bar{1}\bar{1}\bar{1}$)B is suitable for the subsequent HgCdTe growth because CdTe(111)A surfaces remain smooth only at the beginning of the growth by MBE. In contrast, the epilayer of B-polarity grows in a Frank-van der Merwe or layer by layer growth mode even if the thickness exceeds several microns. Moreover, experimental studies reveal that the sticking coefficient of Hg on the CdTe(111)A face is very low [42], leading to reduced growth rates and adding support to the choice of CdTe($\bar{1}\bar{1}\bar{1}$)B as a preferred orientation for MBE growth of HgCdTe.

To avoid the problems related to the high symmetry of the silicon substrate, Sporken *et al.* [34] decide to grow CdTe on vicinal Si(100) wafers, thus Si(100) with reduced symmetry. TEM reveals that by using miscut Si(100) substrates, twins and double domains can be suppressed when a homogeneous thick layer of CdTe($\bar{1}\bar{1}\bar{1}$)B/Si(100) is grown [43]. Indeed, as shown by Xin *et al.* [44], twins appear at the beginning of the growth and are gradually suppressed as the films grow thicker: one orientation overgrows the other one and a twin free surface is obtained if the layer is thick enough. The adequate orientation ensures a twin and double domain free surface and an epitaxial layer of high quality (in terms of homogeneity and full width at half maximum (FWHM) of the diffraction peak by DCRC-XRD) [36, 45-49]. The major disadvantage of this orientation is the cost and the fact that increasing the miscut decreases the crystalline quality of the epilayer (increasing of the FWHM of the diffraction peak by DCRC-XRD [36]).

Finally, it is worth mentioning that it is also possible to grow CdTe(100) on Si(100) using a ZnTe buffer layer. Indeed, the lower lattice mismatch between ZnTe and Si (12%) allows the growth of ZnTe along the [100] direction. The lattice mismatch of only 6% between CdTe and ZnTe leads to CdTe growth in the same orientation [34]. This ZnTe buffer layer technique is also used to grow CdZnTe(100) on Si(100), an alternative substrate for a subsequent growth of MCT [50].

IV.2. Growth of CdTe on Si(111)

In the early 1990s, $(\bar{1}\bar{1}\bar{1})$ is still the preferred orientation for MBE growth of HgCdTe. Therefore, CdTe grown on Si(111) by MBE is intensively investigated in the same period.

If the oxide of the Si(111) cleaned ex-situ by the RCA process is desorbed at 1050°C in the MBE chamber, the growth of CdTe on Si(111) without any buffer layer produces a CdTe(111) film with Cd-terminated surface (i.e. A-polarity) [51]. This polarity is obtained because of the high reactivity between the atoms responsible for the residual pressure of tellurium and Si(111) after oxide removal. Hence, at the end of the cooling step following the desorption of the oxide, the Si(111) is a rough tellurium-rich surface before being exposed to a CdTe flux. As previously stated, the A-polarity is not suitable for the MCT growth. It is then necessary to use a buffer layer to promote the required B-polarity.

The first growth of CdTe$(\bar{1}\bar{1}\bar{1})$B on Si(111) is performed using a CaF_2 or BaF_2 buffer layer [52]. Even if the polarity is the one needed for technological applications, the difference in the thermal expansion coefficients between CdTe and CaF_2 and BaF_2 are respectively of 638% and 623%. The consequence of this huge difference is that these buffer layers are not useful for long life applications: the yield of a device based on this structure should rapidly decrease because of the numerous thermal cycles creating cracks and the peeling of the epilayer.

CdTe$(\bar{1}\bar{1}\bar{1})$B growth on Si(111) can also be achieved thanks to the passivation of the oxide-free silicon surface with arsenic (As_4) [53]. The silicon substrate is exposed to the arsenic flux prior to oxide desorption and during the subsequent cooling procedure. The flux is interrupted when the substrate temperature reaches 350°C. For the growth of a thick CdTe epilayer, two methods can be used:

- Direct growth on As/Si(111) [54, 55];
- Growth on a buffer layer of ZnTe on As/Si(111) [56].

In both cases, the quality of the thick CdTe layer is very good: a FWHM of 87 arcsec for the diffraction peak by DCRC-XRD for a 5 µm thick CdTe($\bar{1}\bar{1}\bar{1}$)B/As/Si(111) layer and a FWHM of 60 arcsec for a 10 µm thick CdTe($\bar{1}\bar{1}\bar{1}$)B/ZnTe($\bar{1}\bar{1}\bar{1}$)B/As/Si(111) with a ZnTe buffer layer of 20 nm. Because of the difference in the thickness of the CdTe top layer, it is very difficult to judge the advantage of using a ZnTe buffer layer. Another point to stress is that the defect density of these layers is very low: a measured etched pit density as low as $2x10^5$ defects per cm² has been reported in the best studies. This measurement is performed using a process developed by Everson *et al.* [57]: the idea is that defects can be revealed by chemical etching to the point where etch pits can be observed under a Nomarski microscope.

Characterization of B-polar CdTe layers grown on As passivated Si(111) is achieved mainly via microscopy techniques: transmission electron microscopy (TEM) and scanning tunneling microscopy (STM) [54, 56, 58, 59]. It is shown that, after the desorption and the cooling of the substrate under arsenic, one monolayer of As is formed by replacing the top layer of silicon atoms having one dangling bond in the Si(111) 1x1 surface (Figure IV-3) by arsenic atoms presenting one free doubly occupied orbital. The saturated electronic structure explains the passivation of the surface. When CdTe (or ZnTe) is deposited afterwards, Cd (or Zn) atom makes a single bond with arsenic, leaving 3 dangling bonds. The Cd – Cd (or Zn – Zn) bond is weak compared to the Cd – Te (or Zn – Te) bond so that Te atoms will fill the 3 dangling bonds of Cd (or Zn), leading to a Te atom with a single dangling bond. This mechanism explains the B-polarity observed after arsenic passivation. These experimental observations have been confirmed by theoretical studies [60].

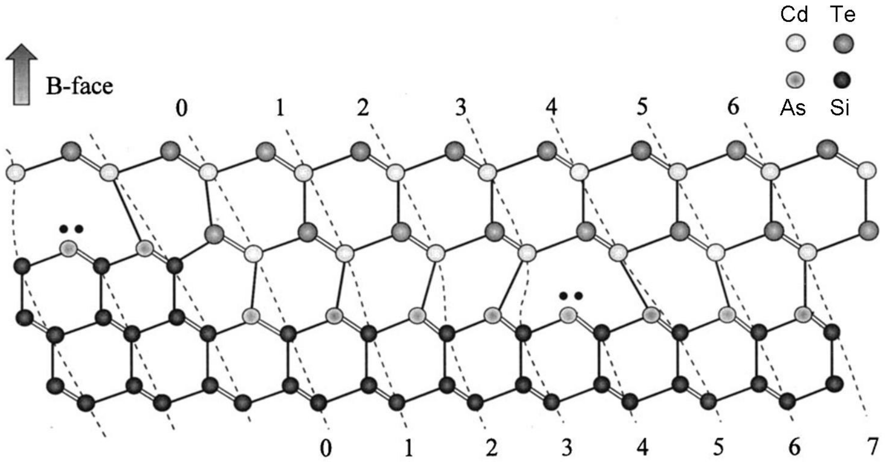

Figure IV-3. Growth mode of CdTe($\bar{1}\bar{1}\bar{1}$)B/As/Si(111) [56].

The main disadvantage of the high symmetry of the (111) face is the high density of twins during the CdTe growth, which is not suitable for the MCT overgrowth. Hence it is desirable to use an alternative substrate with lower symmetry, yet allowing the growth of thick epitaxial layers with a degree of perfection (for FWHM and etched pit density) comparable to the results obtained on Si(111).

IV.3. Growth of CdTe on Si(211)

The growth of CdTe(211)B was achieved for the first time on a GaAs(211) substrate [61]. The advantage of the (211) orientation is that there is no axis of symmetry for the surface. The loss of symmetry axis makes the formation of double domains and twins difficult [62]. However, in order to avoid contamination by diffusion of gallium in the CdTe epilayer and to ensure easy processing and reduced cost of fabrication, a suitable alternative to GaAs(211) is Si(211). Another advantage of Si(211) is that this face is composed of Si(111) and Si(100) planes, well-known surfaces for the growth of CdTe.

In the 1990s, the first growth of CdTe(211)B/Si(211) was achieved by molecular beam epitaxy. At that time, the growth process was adapted from the one reported by de Lyon *et al.* [63] to optimize the quality of the surface in terms of FWHW of the diffraction peak by DCRC-XRD and etched pit density.

The Si(111) and Si(100) planes forming the (211) surface make respectively an angle of 19.47° and 35.26° with this Si(211) surface. These silicon faces are highly reactive, especially the Si(111) face which easily adsorbs tellurium when the oxide obtained after the RCA process is desorbed at 1050°C. Following the same growth scheme as the one for CdTe(111) on Si(111), the Si(211) substrate is first exposed to an arsenic flux before the desorption of the oxide and during the cooling following the desorption. This procedure again leads to a passivation of the clean surface. If CdTe is grown on As/Si(211) substrate without any additional buffer layer, two crystalline orientations are observed by RHEED and XRD: CdTe(211) and CdTe(331). A ZnTe buffer layer must be previously grown to suppress the undesired (331) orientation: at the beginning of the CdTe growth on ZnTe(211)B/As/Si(211), the two orientations coexist but the (211) face quickly takes the advantage on the (331) face, leading at the end to a monocrystalline CdTe(211)B/ZnTe(211)B/As/Si(211) structure [64-66]. TEM analysis of this structure reveal that the surface is double-domains free and, if the layer is more that 100 nm thick, the surface is twin free. In the first 100 nm, twins can be observed.

The ZnTe(211)B buffer layer can be grown by three different ways:

- Growing the ZnTe layer at low temperature (typically 220°C) using a ZnTe effusion cell. This layer is then annealed at higher temperature (380°C) under CdTe and/or Te_2 flux. A second growth at a temperature of 320°C can eventually be realized. This buffer layer growth technique is used to realize high quality CdTe layers with an etch pit density between $2\ 10^5$ and $5\ 10^5$ defects per cm² [65];
- The ZnTe buffer layer can be grown by migration enhanced epitaxy (MEE). This technique requires two effusion cells: one with Zn and one with Te_2. The substrate is alternatively exposed to Zn and Te_2 fluxes to create a layer by layer growth of ZnTe [66];
- A thin ZnTe layer can be deposited at very low substrate temperature (about 40°C). This layer is then annealed at higher temperature before a thicker second growth is carried out by MEE [67].

The CdTe/Si(211) structure is still not well known. However, knowing that the (211) face is mostly composed of Si(111) terraces, one can expect to find similar characteristics for the growth on Si(211) and Si(111). Experimental work using X-ray photoelectron spectroscopy (XPS) [68] and theoretical simulations [69] studied the Si(211) surface exposed to As_4 and Te_2 (to simulate the first layer of the ZnTe buffer layer). It is proposed that arsenic atoms replace Si atoms of the Si(111) terrace and Te atoms bind to the remaining Si atoms (at the edge of the Si(100) terrace). Figure IV-4 represents a schematic for the position of As and Te atoms on the Si(211) surface.

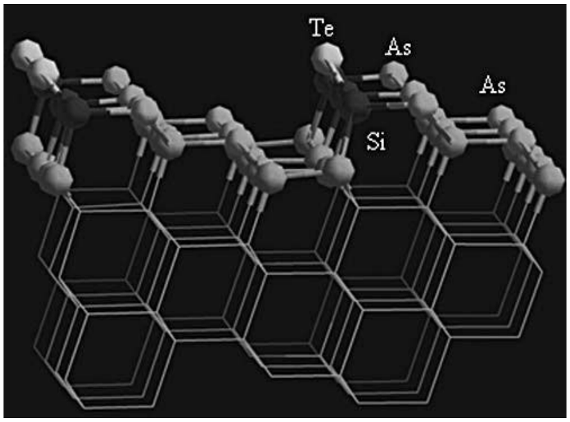

Figure IV-4. Te/As/Si(211) structure [68].