RAPID COMMUNICATION

The role of substrate surface termination in the deposition of (111) CdTe on (0001) sapphire

**S. Neretina · R.A. Hughes · J.F. Britten ·
N.V. Sochinskii · J.S. Preston · P. Mascher**

Abstract The small lattice mismatch and sixfold symmetry offered by the (0001) planes of sapphire make it an ideal substrate candidate for the deposition of (111) CdTe films. There, however, exists a wide disparity in film quality among various researchers with both single crystal and highly twinned, multidomain films being reported. We have developed a pulsed laser deposition process that enables us to deposit nearly single-domain (111) CdTe films exhibiting excellent surface morphology. Such films are deposited on as-received sapphire substrates in vacuum conditions where oxygen is readily available. If, however, film deposition is preceded by the deposition of a submonolayer of aluminum prior to film growth then a secondary CdTe domain emerges with an in-plane orientation having a 180°-in-plane offset from the first domain. These multidomain films show poor crystallographic and morphological properties, similar to what has been reported elsewhere. It is concluded that the singly terminated (0001) sapphire substrates are a prerequisite for the deposition of high-quality (111) CdTe films.

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1 Introduction

From a technological standpoint cadmium telluride is one of the most attractive semiconductor materials with a broad range of applications in such diverse areas as solar cells [1], large area far-infrared focal plane arrays [2], X-ray and γ-ray detectors [3], optical waveguides [4], and optoelectronics [5]. It is also proving itself to be a material of significance on the nanoscale, where nanoparticles [6–8], nanowires [9–11] as well as more intricate structures [12–14] have all been investigated. There exist, however, many material-related issues that inhibit its wider adoption in device applications. In particular, CdTe films show a strong tendency towards multidomain growth that gives rise to high defect densities accompanied by significant surface roughening [15]. While (100)-oriented silicon is an attractive substrate for many applications based on its dominance in the semiconductor industry, it is far from ideal. CdTe, with its zinc blende crystal structure, has a well-established propensity to form films with its (111) plane parallel to the substrate's surface [16]. This tendency gives rise to an interface with a sixfold/fourfold symmetry mismatch: a situation which further exacerbates the multidomain problem through the promotion of geometrically equivalent domains. One approach to mitigate this issue is through the suppression of domains by symmetry breaking on miscut substrates. This approach, combined with the difference in the growth kinetics of the two polarities, has been shown to significantly improve film quality [17].

S. Neretina (✉) · J.S. Preston · P. Mascher
Department of Engineering Physics and Centre for Emerging
Device Technologies, McMaster University, Hamilton,
Ontario, L8S 4L7 Canada
e-mail: neretina@gatech.edu

R.A. Hughes · J.F. Britten · J.S. Preston
Brockhouse Institute for Materials Research,
McMaster University, Hamilton, Ontario, L8S 4M1 Canada

N.V. Sochinskii
Instituto de Microelectronica de Madrid, CNM-CSIC, Madrid,
28760, Spain

Present address:
S. Neretina
Laser Dynamics Laboratory, School of Chemistry
and Biochemistry, Georgia Institute of Technology,
901 Atlantic Drive, Atlanta, GA 30332-0400, USA

Sapphire (α-Al$_2$O$_3$) has long been recognized for having the potential to be a superior substrate for CdTe films [18]. The sixfold symmetry of its (0001) planes offer a heteroepitaxial relationship with (111) CdTe having a lattice mismatch of 3.7%. While a mismatch of this magnitude would be highly detrimental to the epitaxial formation of many materials, CdTe seems to have the ability to accommodate such strains. There exist, however, wide variations in the film quality reported by various research groups with both nearly crystalline and heavily microtwinned, multidomain behavior observed [19–22]. We have routinely deposited nearly single-domain (111) CdTe films on as-received (0001) sapphire substrates [16]. These films show a different domain orientation than the nearly single-domain MOCVD films reported by Zúñiga-Pérez et al. [20]. Such disparities are not unique to CdTe as similar issues exist for both GaN and ZnO films deposited on sapphire substrates [23, 24]. The resulting film quality in these materials is found to be highly dependent on the substrate's surface termination as well as the film polarity it promotes. CdTe likely has similar issues as it has already shown its sensitivity to the surface reconstructions of SrTiO$_3$ [25] as well as homoepitaxial surface preparations [26]. In fact, it is our contention that much of the disparity observed in film quality among various research groups is due to the substrate's surface termination. To verify this hypothesis we undertook a study where we artificially disrupted the surface of the substrate while monitoring the domain structure using two-dimensional X-ray diffraction (2D-XRD) techniques.

It is well established that a reduction in the number of domains gives rise to superior (111) CdTe thin films [17]. The number of allowed domains is strongly influenced by geometrical considerations including lattice mismatch, the polarity of the film, and the film/substrate interface chemistry. From a geometrical standpoint the (0001) surface of sapphire is superior to all other commercially significant substrates. Its crystal structure has a stacking order along its c-axis comprised of two closely spaced aluminum layers followed by an oxygen layer. It, thus, has three possible bulk surface terminations: (1) an oxygen layer followed by two aluminum layers; (2) a double aluminum layer followed by an oxygen layer; or (3) an oxygen layer sandwiched between two aluminum layers. Each of these terminations gives rise to a unique surface chemistry which is further complicated by possible surface reconstructions [27]. From a geometrical perspective, (111) CdTe's fit to the surface is the same regardless of the surface termination (Fig. 1) and yields two possible domains. The only difference between these two domains is a 180° in-plane rotation of the ($\bar{1}11$), ($1\bar{1}1$), and ($11\bar{1}$) planes that emerge from the substrate at an angle of 70.5°.

For each of the allowed domains, it is possible to have either cadmium or tellurium as the initial layer. Moreover, for
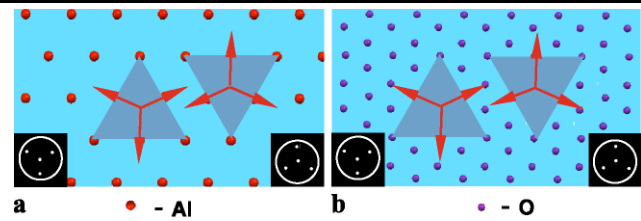

Fig. 1 Schematic showing the epitaxial relationship that the two possible (111)-oriented CdTe domains would have with a (0001) α-Al$_2$O$_3$ substrate terminated with either an (**a**) aluminum or (**b**) oxygen layer. The triangles represent the (111) plane and the arrows symbolize the direction that the ($\bar{1}11$), ($1\bar{1}1$), and ($11\bar{1}$) planes would have as they emerge from the substrate at an angle of 70.5°. Note that the two domains are equivalent except for a 180° rotation. The insets at the corners of the schematics are pictorial representations of the expected (111) CdTe pole figure for the domain nearest to it

each combination of initial layer and domain there are two possible polarities for the film. The concept of polarity refers to the positioning of the tetrahedrally coordinated cadmium atoms relative to the surface. Each cadmium atom bonds to four tellurium atoms and vice versa. For (111) CdTe one of these bonds points vertically while the others extend laterally in the opposite direction at an angle of 19.47°. The polarity of CdTe is determined by whether the single vertical bond extending from every cadmium atom extends upwards or downwards to meet the adjacent tellurium atom. This gives rise to two polarities commonly referred to as (111)A and (111)B. From a structural standpoint the (111)A and (111)B polarities are simply upside-down versions of each other but the polarity can have a profound influence on a film's growth rate [28], surface morphology [15], the ease at which dopants are accepted [16], and on the formation of microtwins [17]. A schematic summary of the possible interfaces is shown in Fig. 2. The interface(s) that form(s) depend(s) upon the surface chemistry established during the initial stages of film deposition and it is this process that determines the polarity of individual domains. In fact, the formation of single polarity films relies upon substrate interactions favoring either an ABCABC... or ACBACB... CdTe stacking order. If no such preference exists multidomain formation is inevitable.

Taking into account both the epitaxial relationship (Fig. 1) and the interface considerations (Fig. 2) it becomes apparent that for (111) CdTe deposited on (0001) α-Al$_2$O$_3$ there exist two possible domains, each of which can have four unique interfaces leading to eight potential film–substrate alignments. Of course, not all of these possibilities are energetically equivalent. It is reasonable to expect that the surface termination of sapphire will play a dominant role in determining whether the film is initiated from a cadmium or tellurium layer. Furthermore, it would not be surprising if the local structure of the sapphire surface influenced both the polarity and the domain structure of the film.
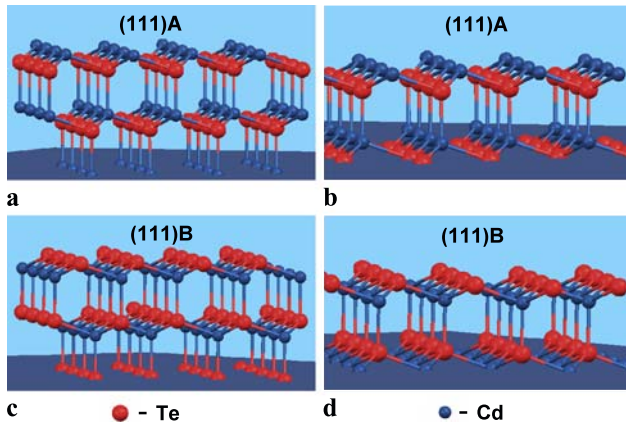
Fig. 2 Schematics of the four possible bulk interfaces that (111) CdTe can form with a substrate. The polarity of the CdTe structures are labeled either (111)A or (111)B

2 Sample preparation

CdTe thin films were deposited using pulsed laser deposition (GSI Lumonics IPEX-848 excimer laser, $\lambda = 248$ nm, laser energy density $= 2$ J/cm^2, laser spot size $= 1.5 \times 3$ mm^2, laser repetition rate 8 Hz). The material was ablated from a stoichiometric CdTe target produced using the modified Bridgman method. Film thicknesses of 300 nm were produced at a growth rate of approximately 1 μm/hour. All films were deposited in high vacuum (6×10^{-7} Torr) on substrates having a miscut of less than 0.5°, heated to 300°C. As previously stated, single-domain (111) CdTe films are routinely deposited on the as-received substrates. In situ oxygen anneals of the substrates immediately prior to deposition produced films that were indistinguishable from those deposited on the as-received substrate strongly suggesting oxygen termination for both scenarios. The application of an aluminum monolayer has proved successful in switching sapphire's surface termination [29, 30]. Here, we deposited a gradient of aluminum over the surface of the substrate immediately prior to film deposition with goals of obtaining aluminum termination, mixed termination, and oxygen termination on different areas of the substrate. Structural and morphological characterization of the CdTe film was then conducted along the gradient.

3 Sample characterization

Structural information was obtained using two-dimensional X-ray diffraction (2D-XRD) techniques. A Bruker SMART6000 CCD detector on a Bruker 3-circle D8 goniometer with a Rigaku RU-200 rotating anode X-ray generator and parallel-focusing mirror optics were used for the data collection. The data was obtained with the detector at −45° using two scans of two-second frames in 1° intervals: (1) a 360°-ϕ-axis scan at $\omega = -185°$ and (2) a 40°-ω-axis scan extending from −185° to −224° at $\phi = 0°$. The surface of the sample was positioned at the optical center of the diffractometer, 5.165 cm from the detector. Data collection was controlled with the SMART (Bruker-AXS) software and data analysis was performed with the GADDS (Bruker-AXS) package. The morphological information was obtained using a Digital Instruments Nanoscope III atomic force microscope (AFM) in a tapping mode.

Figure 3 shows a progression in both the (111) CdTe pole figure and the surface morphology as the substrate termination evolves from oxygen to aluminum. A single (111) CdTe domain is characterized by a (111) pole in the center of the pole figure with the ($\bar{1}11$), ($1\bar{1}1$), and ($11\bar{1}$) poles forming a symmetric, 120° separated ring towards the outer extent of the pole figure. In this 3-dimensional representation the vertical dimension corresponds to the intensity of the pole. The first three pole figures in the series each have six poles in the outer ring (the weak poles in Fig. 3a are not visible as they have an integrated intensity of only 1/1800th of the larger poles) indicating the presence of two domains. It should be noted, however, that the domain with poles near the detection limit in Fig. 3a dominates the response in Fig. 3c. The replacement of well-defined poles with a ring, as seen in Fig. 3d, indicates that the epitaxial relationship has been lost. In this case, the domains grow with their (111) axis perpendicular to the substrates but with an in-plane alignment that is completely random. It is also important to note that these changes in the domain structure are accompanied by a dramatic and progressive deterioration in the surface morphology.

4 Discussion

The result shown in Fig. 3a, by itself, demonstrates that the (0001) α-Al$_2$O$_3$ surface is amenable to single-domain (111) CdTe film deposition. This likely originates from an oxygen surface termination that gives rise to a single energetically preferred interface. The remainder of the figure demonstrates that this situation is compromised for the case of mixed termination where multidomain growth gives rise to a poor surface morphology with a possibility of mixed polarities. It is also of note that the progression of pole figures tends towards a 180°-domain reversal as aluminum is added. The fact that Zúñiga-Pérez et al. [20] show a nearly single-domain CdTe film, corresponding to this reversed domain, strongly suggests that their sapphire substrate is aluminum terminated, possibly through the reducing effects of the hydrogen carrier gas used in their MOCVD reactor [31]. If this is indeed the case then it would allow one to conclude that high-quality single-domain films require singly
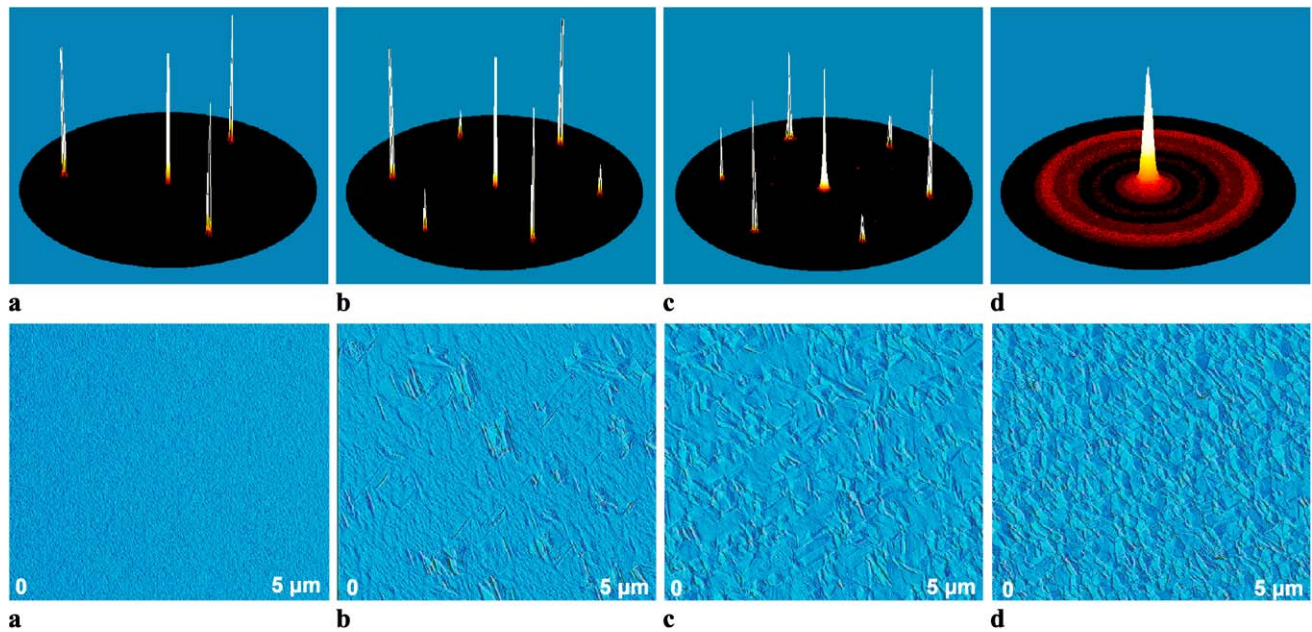
Fig. 3 (111) CdTe pole figure data and the corresponding AFM images showing the evolution of the domain structure and the surface morphology as the substrate termination evolves from oxygen to aluminum (*left* to *right*). (**a**–**c**) Note that the poles in the (111) CdTe pole figure switch from one domain to the other as aluminum is added. (**d**) At high aluminum concentrations the in-plane alignment of grains is random

terminated surfaces but the type of the termination is of less significance. Atomic valences would further suggest that our films form a cadmium/oxygen layer interface while theirs form a tellurium/aluminum layer interface. Such a tellurium/aluminum interface could have mixed termination in the sense that parts of the surface could exhibit a single layer of aluminum while others a double layer. With these facts in mind, it may appear somewhat contradictory that the progression shown in Fig. 3 does not achieve complete domain reversal, but this, in fact, is not unexpected. Aluminum oxidizes quickly as the base pressure of the growth chamber is only 9×10^{-7} torr. The formation of metallic aluminum islands on the surface prior to aluminum monolayer formation [32, 33] would also adversely affect the progression. The complete deterioration in the domain structure shown in Fig. 3d demonstrates the impact on epitaxy once aluminum metal begins to accumulate on the surface of sapphire.

The deterioration in film quality due to a mixed surface termination is not unique to CdTe. The surface termination of (0001) α-Al$_2$O$_3$ is a well-studied problem, but not completely understood [27, 34–37]. This body of work, however, demonstrates that there exist wide variations in the surface that depend on such factors as thermal treatments and exposure to water vapor. To circumvent these surface termination issues sapphire substrates are routinely nitrated prior to the deposition of GaN [23], a process that has also proved successful for ZnO films [38]. The fact that this issue has not been similarly addressed for CdTe likely accounts for much

of the reported variations in film quality. With sapphire substrates undergoing various levels of thermal cleaning in a wide range of ambients prior to CdTe film deposition it is not surprising that such variations in film quality exist.

5 Conclusions

In summary, the surface termination of (0001) α-Al$_2$O$_3$ has a strong effect on the domain structure and surface morphology of (111) CdTe thin films. By maintaining a single termination over the surface of the substrate it is possible to obtain nearly single-domain films with excellent surface morphologies.

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