

# MBE GROWTH OF CdTe EPILAYERS ON InSb(111) SUBSTRATES

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## Abstract

We report a study of CdTe layers grown on InSb(111) substrates by molecular beam epitaxy. CdTe/InSb heterostructures prepared under different conditions were characterized *in-situ* by reflection high-energy electron diffraction (RHEED) and Auger electron spectroscopy. As *ex-situ* characterization we used atomic force microscopy (AFM) and Raman spectroscopy. According to the results, an In-Te compound (likely In<sub>2</sub>Te<sub>3</sub>) is formed at the interface. The proportions of the In-Te compound and remaining oxides at the interface depend on the substrate preparation, polarity of the (111) substrate, and annealing temperature before growth. The CdTe growth is smoother on the (111)B surface.

**Keywords:** Molecular beam epitaxy, CdTe/InSb, RHEED, Auger electron spectroscopy, AFM, Raman spectroscopy.

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## 1. Introduction

The development of epitaxial crystal growth of II-VI compound semiconductors by molecular beam epitaxy (MBE) began in the early 80's. However, comparing the advances in II-VI compounds with those reached in III-V compounds, it has not been possible to obtain the same crystalline quality. Consequently, the optical and electrical characteristics necessary to fabricate efficient and durable optoelectronic devices from II-VI compounds are not yet satisfied. CdTe is a semiconductor material with an energy gap of 1.51 eV at room temperature. It is an attractive material due to its numerous and potential applications as infrared and gamma rays detectors, solar cells, etc. On the other hand, InSb has a lattice parameter at room temperature of 6.4798 Å compared to 6.4829 Å for CdTe, giving a lattice mismatch of only 0.05%. Moreover, their thermal expansion coefficients are also very similar; therefore InSb is an ideal substrate for the CdTe epitaxial growth. However, since these compounds belong to a different family of semiconductors, some complications appear during the heteroepitaxy such as: interdiffusion of In and Te atoms [1,2], different valence states producing a space charge at the interface, the formation of a III-VI compound [3], etc.

The purpose of this work is to understand the different processes occurring at the interface of CdTe/InSb(111) during the heteroepitaxial growth by MBE. The substrate preparation, thermal annealing to desorb oxides, substrate polarity, and growth conditions

are the principal parameters considered in order to achieve the objective.

## 2. Experimental

Commercial undoped InSb(111) substrates were used in this work. It was necessary to distinguish between A (In terminated) and B (Sb terminated) faces. The different behavior of the A and B surfaces has been attributed to the electronic configuration of the triply bonded A or B surface atoms, causing a different chemical reactivity. Dislocations present in the substrate are revealed predominately for A surface when a standard oxide etching is used [4]. To distinguish between A and B faces small pieces were cut from an InSb(111) wafer. Then, by using an etching solution of HF:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O at 2:2:16 parts by volume, we were able to distinguish between both faces, observing more etch pits for A surface.

Looking for an appropriate substrate etching for epitaxy, two groups of samples were prepared. For the first group of samples (1-x) the InSb substrate was etched with a 5% bromine-methanol solution. However, as noted in ref. [5], Br-based etching produces oxide residues not easily removed, besides a considerable defect density, and "orange peel like" surfaces are obtained with this solution. Therefore, for the second group (2-x) the InSb substrate was prepared with a CP4 modified etching solution [5], HNO<sub>3</sub>:HF:CH<sub>3</sub>COOH:DI H<sub>2</sub>O at 2:1:1:10. Immediately after etching, the substrates were mounted on molybdenum blocks, and loaded into a Riber 32P MBE system. The base (background) pressure in the MBE chamber was around

$\sim 6 \times 10^{-11}$  Torr. A temperature ramp from 100 to 500°C was used to desorb the oxides. The growths were carried out by using a CdTe cell heated at 450°C, giving a flux pressure of  $1 \times 10^{-6}$  Torr. CdTe layers with different thickness and growth temperatures were prepared. For sample 2-3 an additional Cd flux was used of the same magnitude as the CdTe flux. In table 1 the experimental details of the samples are summarized.

Table 1. Principal data of CdTe/InSb samples. Samples 1-x were etched in a Br-methanol solution, whereas samples 2-x in an acid acetic based solution. The sample 2-3 was grown using an additional Cd overpressure.

Sample	$T_{\text{growth}}(^{\circ}\text{C})$	Thickness ( $\text{\AA}$ )	Time (min)	Face
1-1	180	5000	60	A
1-2	200	2500	30	A
1-3	230	1250	15	A
1-4	260	420	5	A
2-1	230	1250	15	A
2-2	230	1250	15	B
2-3	230	1250	15	A

RHEED patterns along the [110] azimuth were observed during the growth, and recorded using a CCD camera connected to a video tape recorder system. Auger electron spectroscopy (AES) measurements were taken before the desorption of substrate oxides, after desorption, and at the end of growth. After the growth, the samples were analyzed in air by atomic force microscopy (AFM), and Raman spectroscopy.

### 3. Results and discussion

First we will discuss the results obtained for samples with different substrate etching. Fig. 1 shows the evolution of RHEED patterns at different stages of growth for the sample 1-3 (Figs. 1a – 1d), and for the sample 2-1 (Figs. 1e – 1h). Figs. 1a and 1e show the RHEED patterns of the substrates as loaded, Figs. 1b and 1f after the annealing process, Figs. 1c and 1g at the first 30 seconds of CdTe growth, and Figs. 1d and 1h at the growth end ( $\sim 1250 \text{ \AA}$ ). From these figures we observe important differences depending on the InSb substrate preparation. From Fig. 1a, the sample 1-3 (Br-methanol etched substrate) has an as-loaded diffuse RHEED pattern without any diffraction spots, typically of an amorphous oxide layer. In contrast, in the RHEED pattern of Fig. 1e from sample 2-1 (acid acetic-based etching) diffraction spots are clearly observed, indicating a thinner oxide layer. After the thermal annealing process diffraction spots from the InSb substrate were observed for both samples (Figs. 1b and 1f). However, the RHEED pattern for sample 2-1 presented

more clear and streakier spots with a  $2 \times 2$  reconstruction typical of an InSb(111)A surface [6]. The better starting substrate surface for the 2-x samples has a strong effect on the CdTe epitaxy. A streakier pattern, indicating a two-dimensional (2D) growth, was observed in the first seconds of growth for the sample 2-1, as compared to sample 1-3 (Figs. 1c and 1g). However, after the first minutes of growth the RHEED pattern became spotty, and a diffuse background appeared. These results suggest a change to a three-dimensional (3D) growth mode. With further growth, crystal defects became evident by the appearance of extra-spots indicating the formation of twinned regions, as observed in the RHEED patterns of Figs. 1d and 1h.

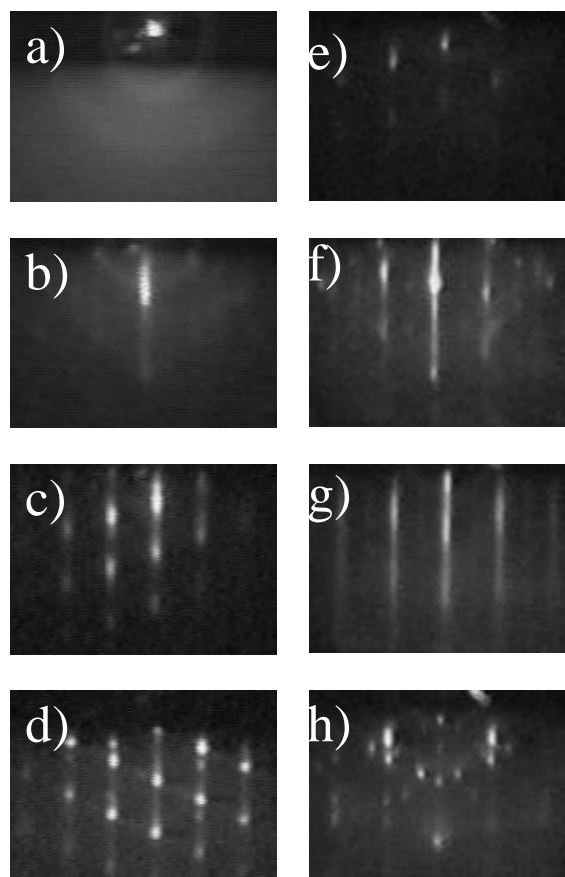


Fig. 1 RHEED patterns at different stages of growth for the sample 1-3 (a-d), and for the sample 2-1 (e-h). Figs a) and e) show the RHEED patterns of the substrates as loaded, b) and f) after the annealing process, c) and g) at the first 30 sec of CdTe growth, and Figs. d) and h) at the growth end ( $\sim 1250 \text{ \AA}$ ).

Auger spectra of the second group of samples after the thermal annealing to desorb the substrate oxide layer are shown in Fig. 2. Even though that the acetic acid-based etching produced RHEED patterns with good characteristics, we can still observe oxide residues in Fig. 2

after the annealing. This shows the difficulties to completely remove the oxides from the InSb substrate. These oxides may affect the growth in different ways. For example, the dangling bond distribution is modified, thus affecting the incorporation of Cd and Te atoms. Furthermore, interstitial oxygen, induced vacancies, and stacking faults may perturb the growth. All these factors can modify the lattice constant and, in general the coherence of growth. Therefore, methods to efficiently remove the substrate oxides are necessary. An increase in the annealing temperature or annealing time is not recommended since this could cause a severe loss of the surface stoichiometry. The use of a flux of atomic hydrogen could be a solution since this method has been proved to be useful for the cleaning of GaAs substrates.

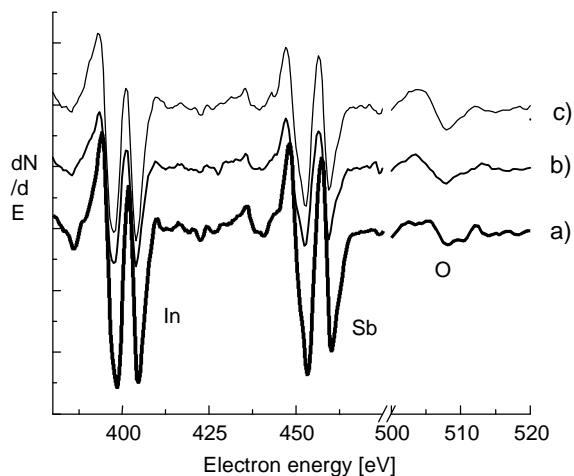


Fig 2. Auger spectra after the thermal annealing to desorb oxides for samples: (a) 2-1, (b) 2-2, and (c) 2-3.

Now we will compare the results obtained for the (111)A face with those for (111)B, with the same substrate preparation (acid acetic-based etching). Fig. 3 shows the evolution of RHEED patterns at different stages of growth for the sample 2-2 with an InSb(111)B substrate (Figs. 3a – 3d), and for the sample 2-3 grown with an additional Cd overpressure on an InSb(111)A substrate (Figs. 3e – 3h). Figs. 3a and 3e show the RHEED patterns of the substrates as loaded, Figs. 3b and 3f after the annealing process, Figs. 3c and 3g at the first 30 seconds of CdTe growth, and Figs. 3d and 3h at the growth end ( $\sim 1250 \text{ \AA}$ ). The initial stages of CdTe growth on (111)A and (111)B faces are very similar, as observed in Figs. 3c and 3g. However, as growth proceeds the RHEED patterns for the (111)A face became spotty (Fig. 3h), as previously explained. In sharp contrast, the RHEED patterns for the growth on the (111)B face remained streaky during all the growth (Fig. 3d). This shows that the CdTe growth is smoother on InSb(111)B substrates.

A Cd overpressure was used for the sample 2-3 in order to prevent the formation of an In-Te compound at the

interface, as was noted by D.R. Zahn and co-workers [7]. Another advantage is to decrease the density of Cd vacancies in the CdTe film. However, the use of an additional Cd overpressure did not produce significant changes in the evolution of RHEED patterns during growth, as can be observed by comparing Figs. 1e-1h with Figs. 3e-3h. But, as we will show by AFM and

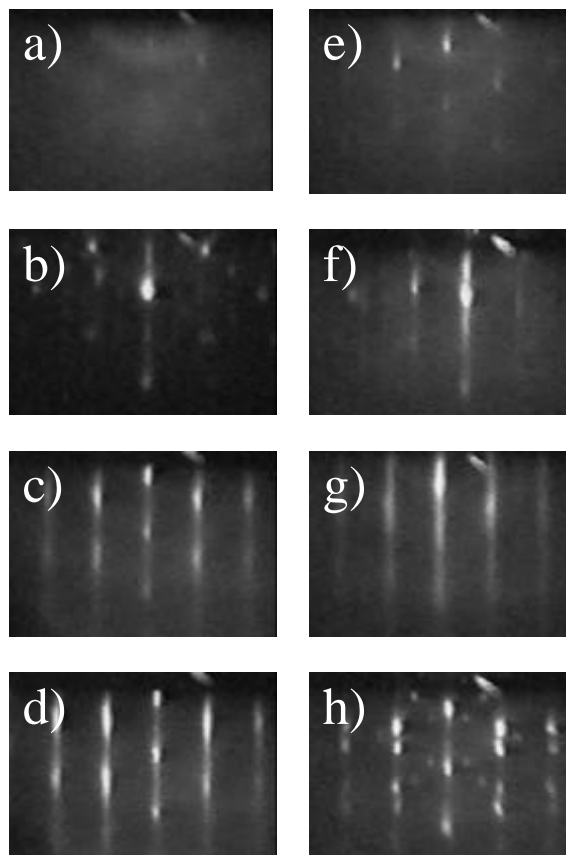


Fig. 3 RHEED patterns at different stages of growth for the sample 2-2 (a-d), and for the sample 2-3 (e-h). Figs a) and e) show the RHEED patterns of the substrates as loaded, b) and f) after the annealing process, c) and g) at the first 30 sec of CdTe growth, and Figs. d) and h) at the growth end ( $\sim 1250 \text{ \AA}$ ).

Raman spectroscopy the sample grown with a Cd overpressure presents better properties. Fig. 4 shows the Auger spectra taken after the growth for samples 2-x. Only the signals from Cd and Te were observed. Thus, within the detection limit of AES, the presence of diffused In and residual O should be restricted to the interface. The Cd/Te peak ratio for sample 2-1 is 1.73, and for sample 2-3 is 2.02, thus confirming a larger Cd incorporation for the last sample. AFM measurements of samples 2-x are shown in Fig. 5. The RMS roughness values are 60.8, 20.3 and 45.4  $\text{\AA}$ , for samples 2-1, 2-2 and 2-3, respectively. The smoother surface was obtained for the growth on the InSb(111)B substrate, confirming the RHEED results.

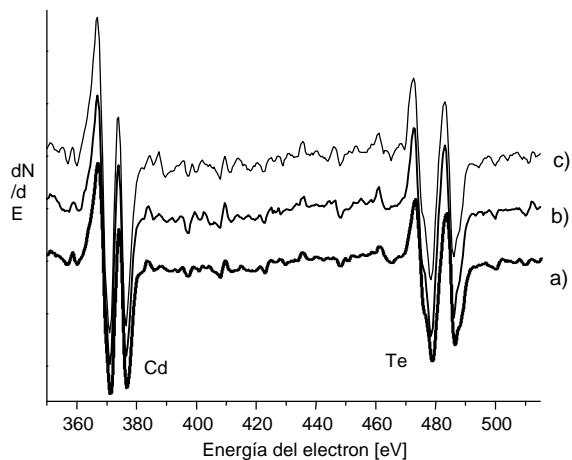


Fig. 4 Auger spectra after the CdTe growth for samples: (a) 2-1, (b) 2-2, and (c) 2-3.

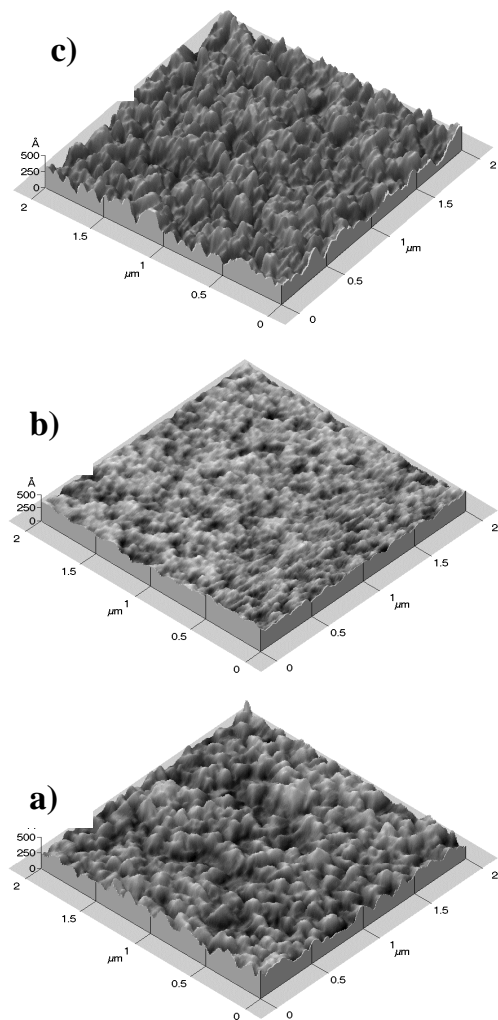


Fig. 5 AFM images of samples: (a) 2-1, (b) 2-2, and (c) 2-3.

We also observed an improvement on the surface morphology for the sample grown with a Cd overpressure. Note that a III-VI compound is thermodynamically favored to be formed at the CdTe/InSb interface, as explained in ref. [3]. According to ref. [7] an  $\text{In}_2\text{Te}_3$  compound can be present at the interface. Strong strain effects can be expected in case this compound is formed, since its lattice constant is  $6.16 \text{ \AA}$ , which is about 5% smaller than the CdTe and InSb lattice constants. This difference may produce a much smaller critical thickness to relax the strain, changing the growth from a 2D to a 3D mode.

Raman spectroscopy is a sensitive technique, which could give us more information of the processes occurring at the interface. Fig. 6 shows Raman spectra of samples 2-x and sample 1-3. A Raman spectrum of the InSb substrate is also included in this figure for comparison. CdTe optical modes are observed around 140 and 167  $\text{cm}^{-1}$  for epitaxial samples, but in different quantity and proportion. In all the samples small peaks around 100 and 130  $\text{cm}^{-1}$  are observed, suggesting the presence of the  $\text{In}_2\text{Te}_3$  compound. For the sample 1-3, prepared with Br-methanol, a peak around 153  $\text{cm}^{-1}$  associated to Sb is clearly observed. This peak is not observed for the acetic acid-based etched substrates. This may indicate that the amount of Sb segregated during the annealing process to desorb the oxides is larger for the substrates prepared with Br-methanol. On the other hand, a peak around 126  $\text{cm}^{-1}$ , associated to Te [8], is found in all samples. It is not clear at the moment why this peak is larger for the samples 2-x, as compared to sample 1-3. For the (111)B face (sample 2-2) the intensity of this peak is smaller compared with that of the (111)A face. For the sample 2-3 grown with a Cd overpressure, the intensity of this peak decreased. This is consistent with a higher incorporation of Cd atoms in the epilayer.

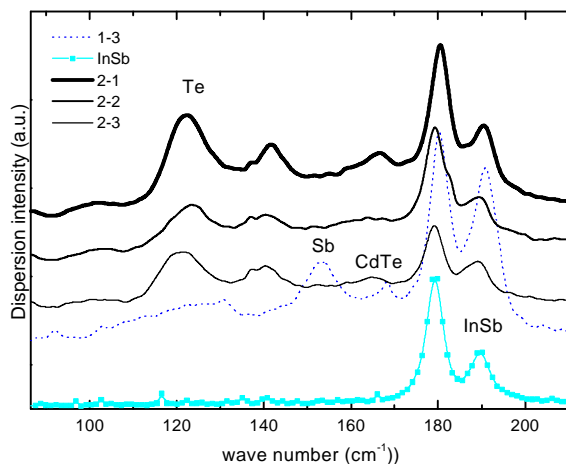


Fig. 6 Raman spectra from samples 2-1, 2-2, 2-3, and 1-3. A spectrum from an InSb substrate is included for comparison.

#### 4. Conclusions

We have shown the importance of InSb(111) substrate surface preparation for the growth of CdTe. Etching based in acetic acid gives in general better surfaces with thinner oxides and streakier RHEED patterns during growth. For the (111)B face, the epitaxy is improved as shown by smoother CdTe surface and streaky RHEED patterns. A Cd overpressure gives smoother surfaces and decreased the formation of segregated Te. These results have motivated more ex-situ studies of the substrate before and after the etching process. Also, we are attempting to improve the desoxidation process to eliminate the oxide residues without degrading the surface stoichiometry.

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