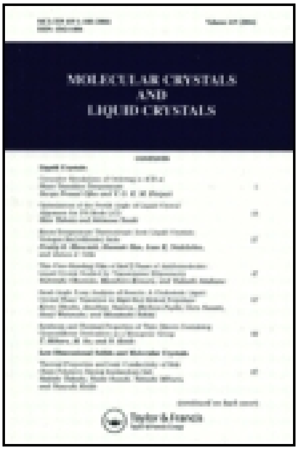

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Defect Distribution and Properties of (211) ISOVPE-MCT Films

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DEFECT DISTRIBUTION AND PROPERTIES OF (211) ISOVPE-MCT FILMS

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Epitaxial films of $Hg_{1-x}Cd_xTe$ (MCT) were grown by Isothermal Vapor Phase Epitaxy (ISOVPE) without Hg overpressure on single crystalline substrates of CdTe and $Cd_{0.96}Zn_{0.04}Te$ with (211)Cd and (211)Te crystallographic orientations. The chemical composition profile was determined using an electronic microprobe on the {110} preferential cleavage surfaces. Experimental values and data from the literature were used to calculate the percentage relative misfit and microhardness profiles. Both were correlated with the misfit dislocations distribution obtained at the interface of the films by chemical etching. The Zn doping in pure CdTe is related with the defect distribution at the film-substrate interface.

Keywords: (211) crystallographic orientation; epitaxial films; $Hg_{1-x}Cd_xTe$; interface; MCT; misfit dislocations

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INTRODUCTION

The $Hg_{1-x}Cd_xTe$ (MCT) with $x = 0.2$ is the most important semiconductor alloy for the infrared detection in the second atmospheric transmission window. Properties like its high optical absorption coefficient, high electronic mobility, low thermal generation rate and a compositionally adjustable bandgap determine this fact [1].

As the growth of bulk MCT single crystals with homogeneous composition is a very difficult process different epitaxial growth techniques (VPE, LPE, MBE, MOCVD) have been successfully developed. It has experimentally been determined that employing CdZnTe substrates, instead of pure CdTe substrates, allows to get a better result. This fact could be explained by considering that the lower dislocation density in the ternary with regard to the binary substrates will determine smaller density of threading dislocations. Moreover, as the lattice parameter of the ternary substrates are closer than the pure CdTe to the MCT with $x = 0.2$, the generation of misfit dislocations decreases (Table 1).

The detectivity of devices, manufactured with this material, depend on dislocation distribution and density. Since these defects are electrically

TABLE 1 Lattice Parameter of the Stress Free Pure and Alloyed Substrates and $Hg_{0.8}Cd_{0.2}Te$ (MCT) Film at 300 K

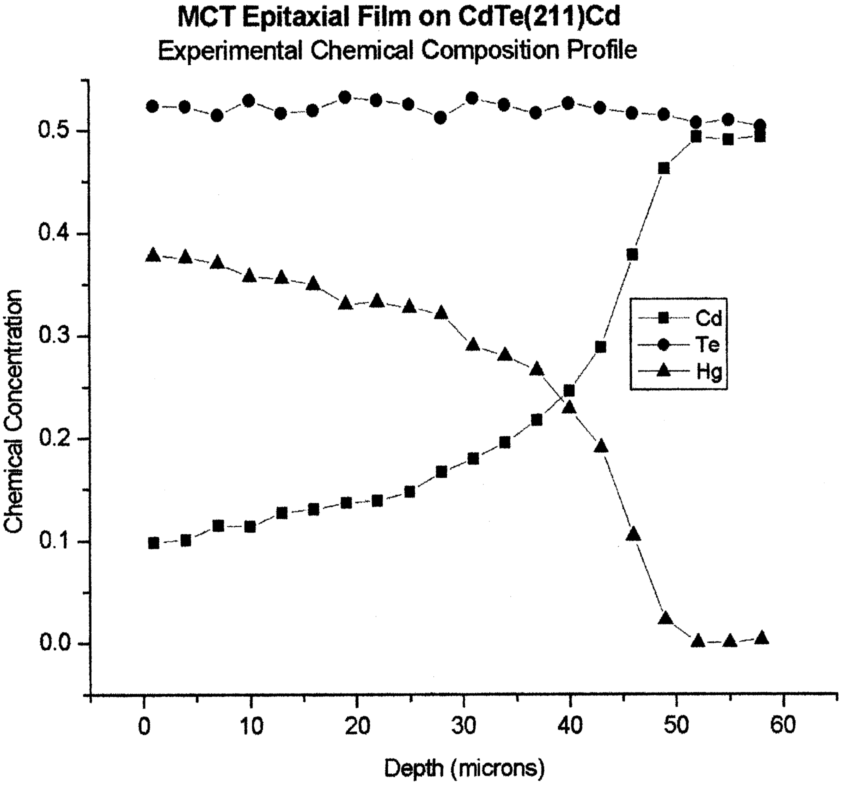
Material	CdTe	$Cd_{0.96}Zn_{0.04}Te$	$Hg_{0.8}Cd_{0.2}Te$
Lattice parameter (Å)	6.4823	6.4656	6.4637

TABLE 2 Average Surface Composition, Thickness, Interdiffusion Coefficients and Electrical Properties of the Epitaxial Films

				Hall effect measurements (77 K)		
Substrate	$\hat{x}$	Thickness (μm)	D* ($cm^2 \cdot s^{-1}$)	p (cm^{-3})	μ ($cm^2 \cdot V^{-1} \cdot s^{-1}$)	ρ (Ω·cm)
Epitaxial films with (211)Cd orientation						
CdTe(211)Cd	0,1705	28,785	$6{,}67.10^{-10}$	$2{,}02.10^{16}$	1923	0,160
CdZnTe(211)Cd	0,1757	21,25	$2{,}71.10^{-10}$	$8{,}88.10^{16}$	1017	0,069
Epitaxial films with (211)Te orientation						
CdTe(211)Te	0,2034	27,72	$9{,}50.10^{-10}$	$7{,}45.10^{16}$	527	0,158
CdZnTe(211)Te	0,1716	18,83	$3{,}05.10^{-10}$	$9{,}66.10^{16}$	954	0,0676

charged, the average lifetime decrease of carriers occur due to recombination processes.

Material properties, such as hardness, lattice parameter and thermal expansion coefficient, are affected by the Cd-Hg interdiffusion as it takes place at the interface of the epitaxial film/substrate. The aim of this work is to determine how those changes affect the dislocation distribution and to get a deeper insight of the mechanisms that control the interaction epitaxial film-substrate.



(a)

FIGURE 1 MCT Epitaxial Film on CdTe(211)Cd. 1a) Experimental Chemical Composition Profile on a cleaved cross section {110} plane. 1b) Percentage Relative Misfit and Concentration Profile. 1c) Vickers Microhardness and Concentration Profile. 1d) Micrograph of the chemically etched surface of the cleaved {110} plane.

EXPERIMENTAL PROCEDURE

Single crystalline CdTe and $Cd_{0.96}Zn_{0.04}Te$ were used with crystallographic orientation (211)Cd and (211)Te. The crystalline orientation was checked by x-rays diffraction (Laue technique). The substrates were commercially acquired from the company II-VI Inc. (USA).

The substrates were mechanically and mecanochemically polished with 1 micron alumina slurry and Br_2 (1%) in ethylenglycol solution respectively, to get mirror like surfaces previously to the growing process.

The growth was carried out by ISOVPE without Hg overpressure, with the source and substrate temperature at $(610 \pm 1)°C$. Meanwhile the growth time was 3,25 hours.

The characterization of the substrates and epitaxial films were made by employing the following techniques:

- Structural characterization: optical and scanning electron microscopy, preferential chemical etching, x-ray diffraction (Laue technique).

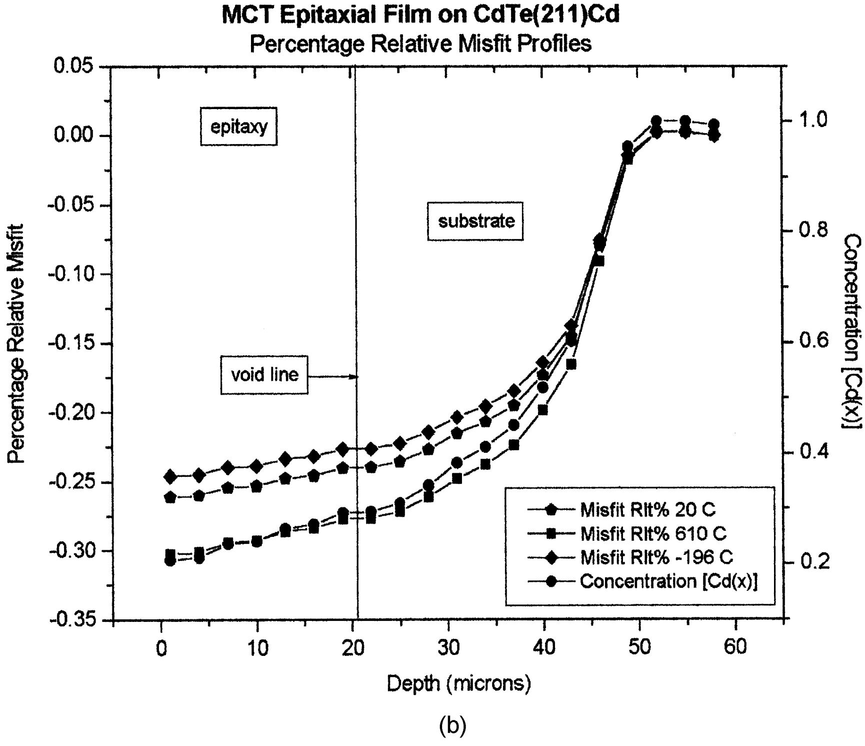
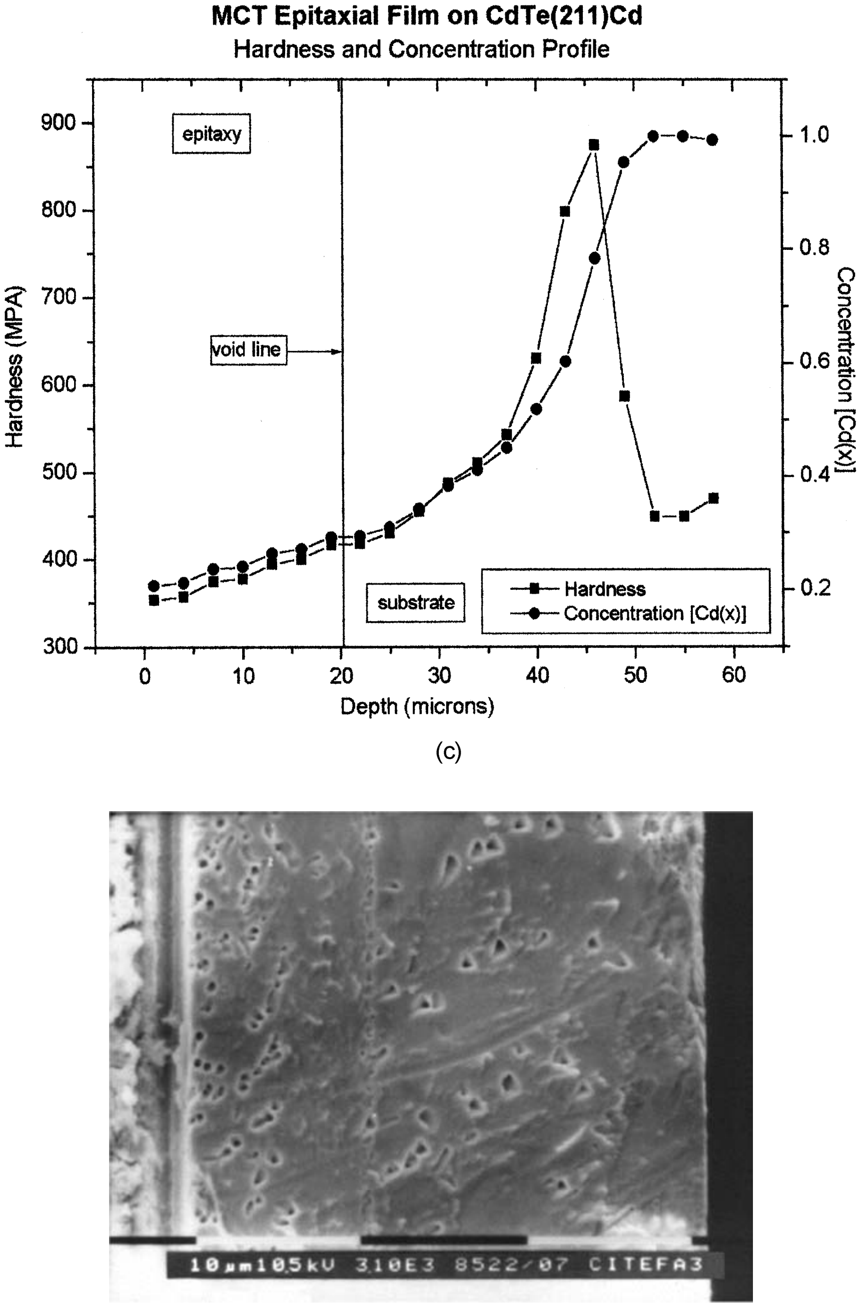


FIGURE 1 Continued.



(c)

(d)

FIGURE 1 Continued.

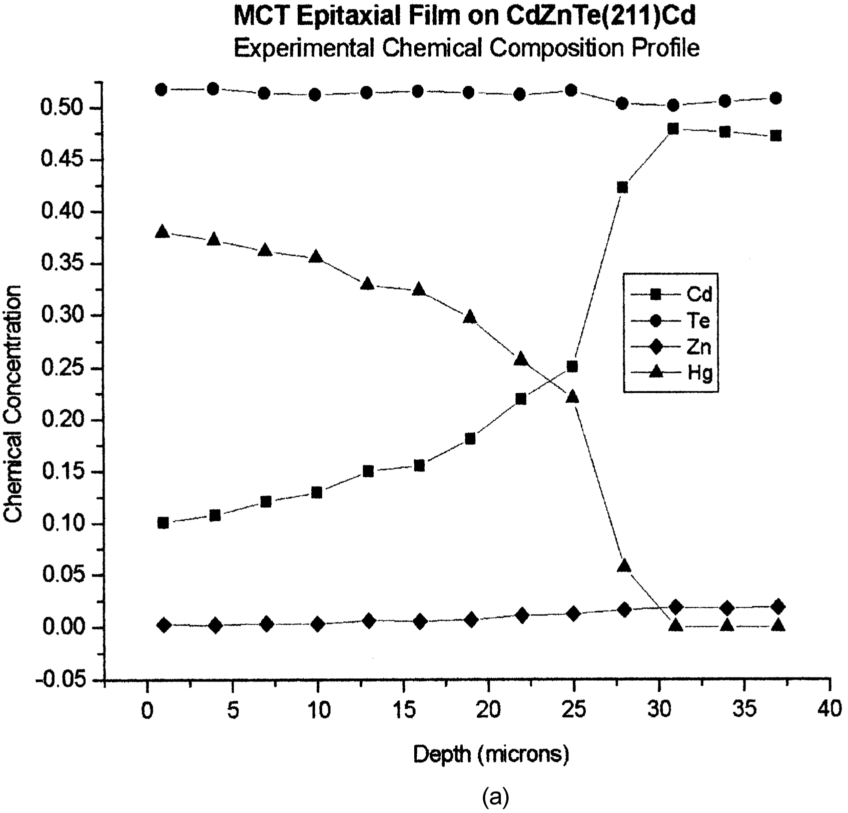


FIGURE 2 MCT Epitaxial Film on CdZnTe(211)Cd. 2a) Experimental Chemical Composition Profile on a cleaved cross section {110} plane. 2b) Percentage Relative Misfit and Concentration Profile. 2c) Vickers Microhardness and Concentration Profile. 2d) Micrograph of the chemically etched surface of the cleaved {110} plane.

- Chemical composition: electron microprobe in the wavelength dispersive mode (CAMECA), using pure Cd, Zn and Te as standards. The Hg was evaluated by difference. The measurements have been obtained on the preferential cleavage planes of {110} perpendicular to the grown film surfaces.
- Electrical properties: resistivity and Hall effect measurements at 77 K.

RESULTS AND DISCUSSION

The properties of the epitaxial films grown on the different substrates are shown on Table 2: surface average chemical composition, interdiffusion coefficient and electric properties.

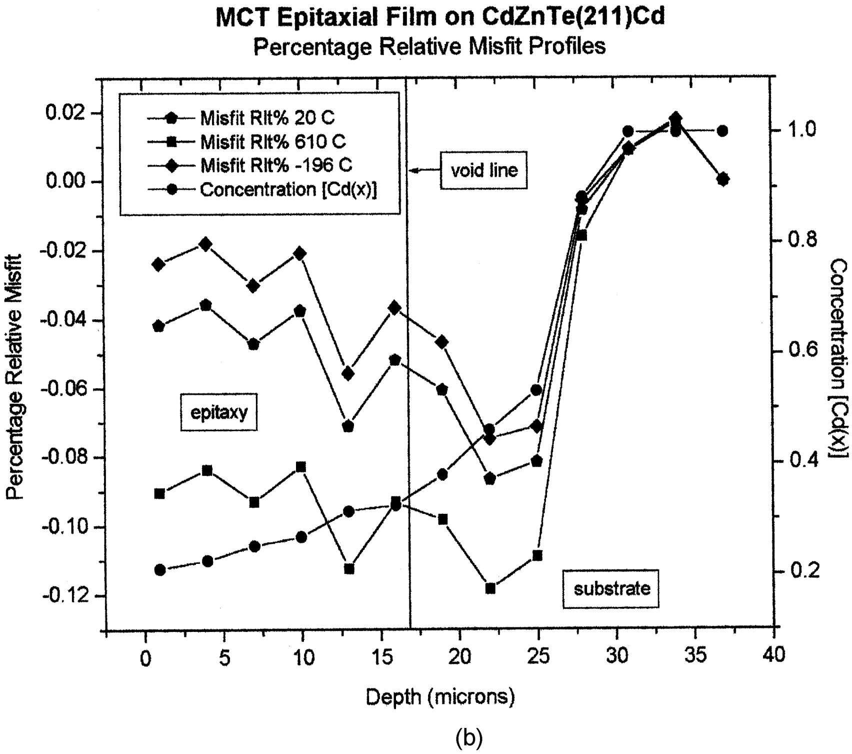


FIGURE 2 Continued.

P type films with concentration and mobility values comparable to those obtained by the authors of this work in films with other crystalline orientations and to other literature references [1,2–5] were obtained.

Figures 1a–4a show the plot of the experimental chemical composition profiles obtained with the electronic microprobe measurements.

The composition values (x) and (v) were calculated with the experimental chemical concentration (%at) keeping in mind that the chemical formulas of the epitaxial films are the following ones:

$$[Cd_xHg_{1-x}]_{1-y}Te_y \qquad \left\{[Cd_xHg_{1-x}]_{1-v}Zn_v\right\}_{1-y}Te_y$$

Figures 1b–1c, 2b–2c, 3b–3c and 4b–4c show the plots of the chemical concentration (x) vs. depth (h) for the different epitaxial films.

The Hg-Cd interdiffusion coefficients were calculated by means of Fleming-Stevenson's method, using the following Equation [6].

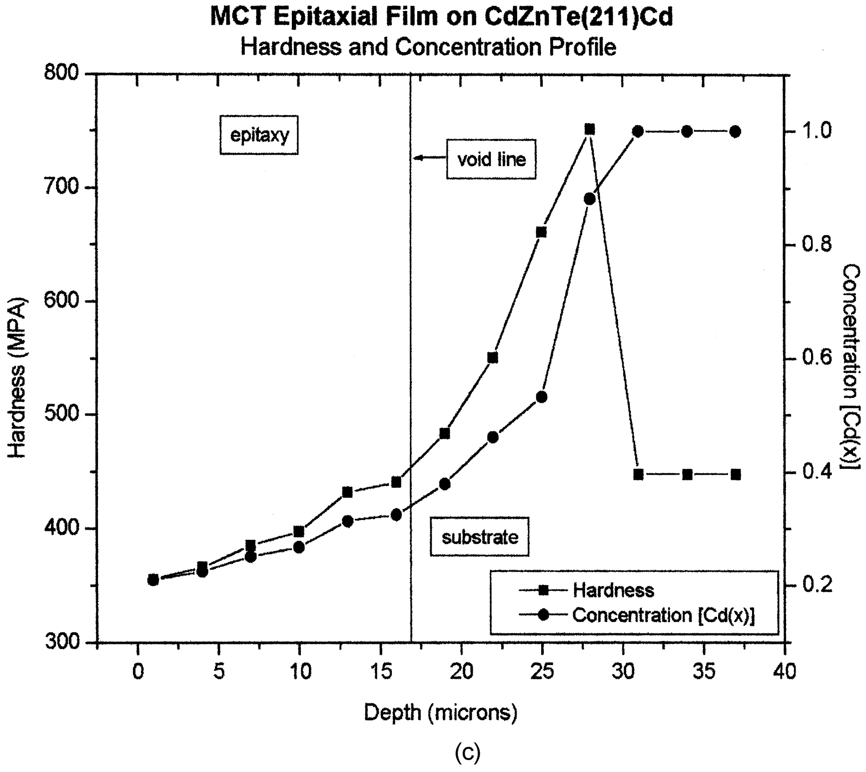


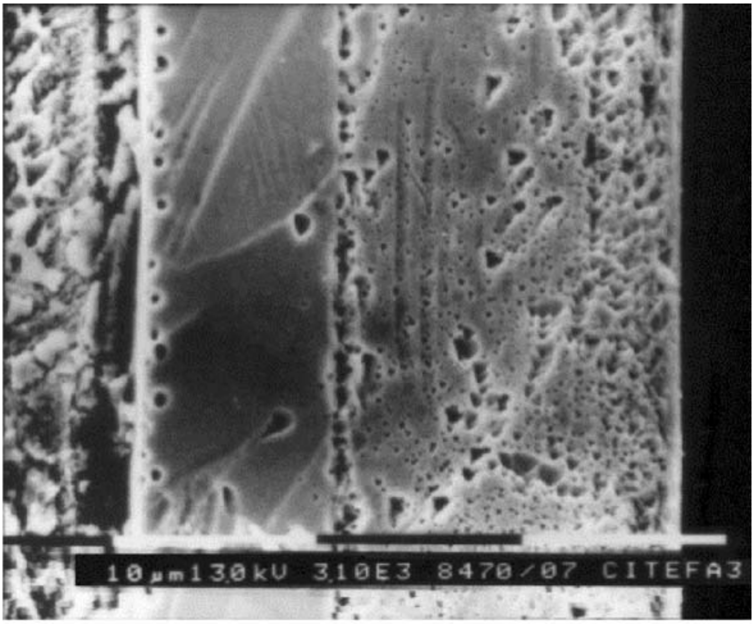
FIGURE 2 Continued.

$D^* = [x^0\ (1 - x^0)\ H]/[2t\ (1 + x^0)\ (dx/dh)_{surf}]$
x^0: average surface chemical composition.
h: depth measurements from the epitaxial surface
H: h value when x = 1 (that means no Hg)
t: growth time
$(dx/dh)_{surf}$: concentration gradient in the epitaxial surface (h = 0).

The concentration gradient $(dx/dh)_{surf}$ at the surface was obtained by linear regression using for each epitaxial film the nearest points to the surface in the plot (x vs. h).

The interdiffusion coefficients differ at most by an order of magnitude and they were comparable with values obtained by the authors of this work and by other researchers that employed different growth conditions [6,7].

The lattice parameter continuously varies due to the Hg-Cd interdiffusion process at the growth temperature. The mismatch causes stress and deformation at the interface. For a layer with a thickness lower to the



(d)

FIGURE 2 Continued.

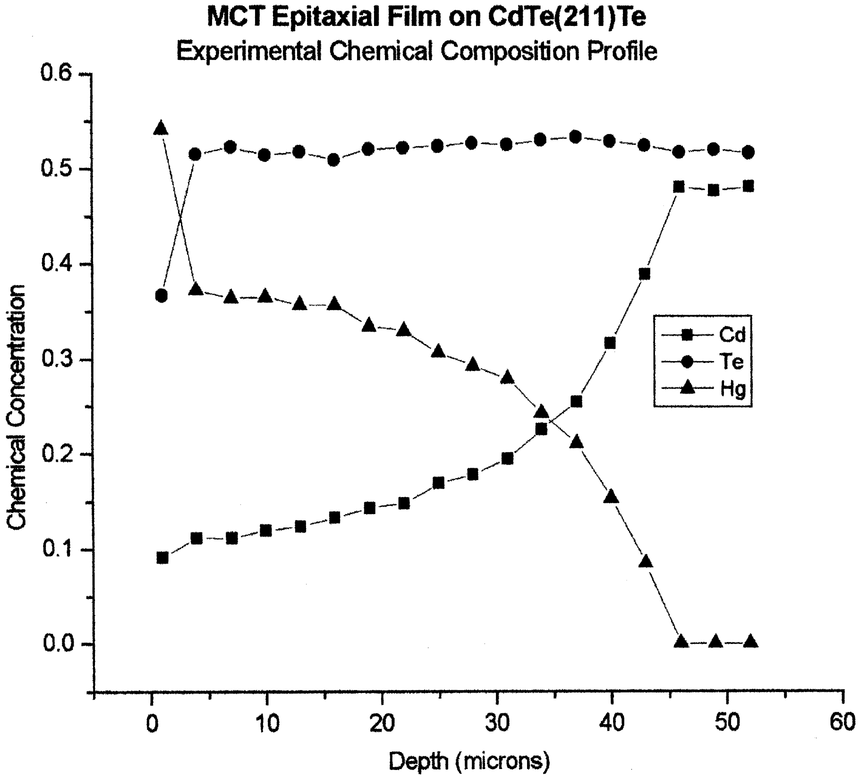
critical thickness (of the order of 1 µm for these systems), a homogeneous strain takes place. When the thickness is larger than the critical value, misfit dislocations are generated, since the process is energetically favorable [8,9]. The generation and motion of the misfit dislocations not only take place at the growth temperature but also when the growth finishes and the system is cooled down to room temperature or to 77 K, operation temperature of IR MCT detectors. The different thermal expansion coefficients of the substrate and the film determine additional lattice misfit and stress which determine the generation and motion of dislocations.

This result is considered by means of the calculation of the "percentage relative misfit" [f(h)] defined by the following equation:

$$f(h) = \{[a_e(h) - a_s]/a_s\} \cdot 100 \tag{1}$$

$a_e(h)$: epitaxial film lattice parameter at an h depth from the film surface.
$a_s(h)$: stress free lattice parameter of the substrate.

The epitaxial film lattice parameter a_e were calculated using empirical relationships [10,11] and the substrate experimental values [$a_s(h)$] (Table 1):



(a)

FIGURE 3 MCT Epitaxial Film on CdTe(211)Te. 3a) Experimental Chemical Composition Profile on a cleaved cross section {110} plane. 3b) Percentage Relative Misfit and Concentration Profile. 3c) Vickers Microhardness and Concentration Profile. 3d) Micrograph of the chemically etched surface of the cleaved {110} plane.

For T = 300 K:

$$a[Hg_{1-x}Cd_xTe] = 6.4628 + 0.0084x + 0.0168x^2 - 0.0057x^3 \qquad (2)$$

$$a[(Hg_{1-x}Cd_x)_{1-v}Zn_vTe] = a[Hg_{1-x}Cd_xTe] - [0.4175 - 0.02(1 - x)]v \qquad (3)$$

For T ≠ 300 K, the dependence of the lattice parameter with the temperature is calculated by means of the product of the equations (2) and (3) with the factor:

$$[1 + 4\{4.9 - 0.9(1 - x) + 3.4v\}10^{-6}\Delta T] \qquad (4)$$

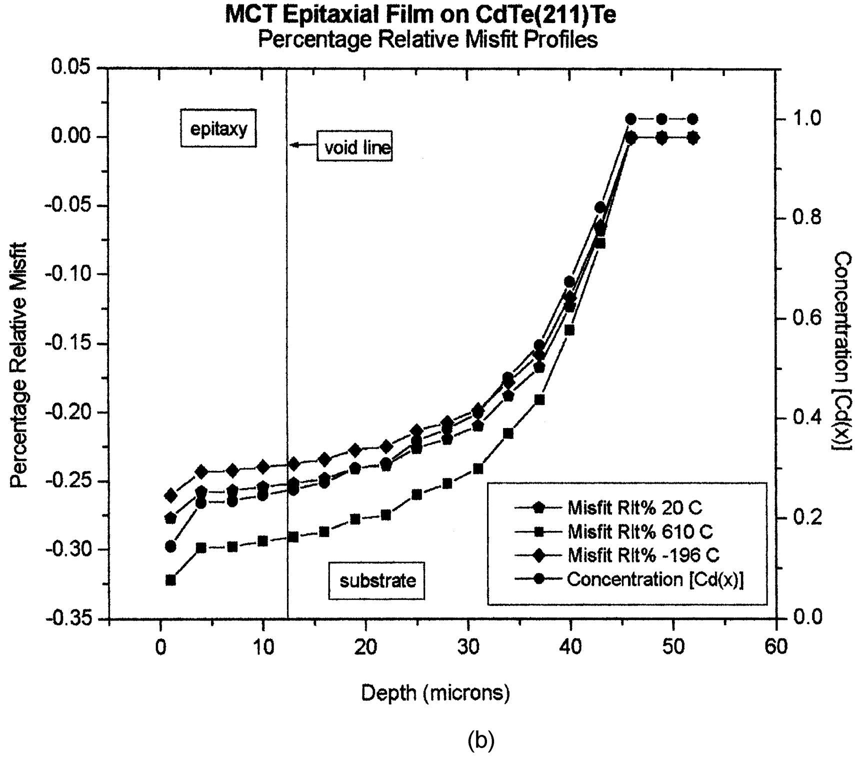


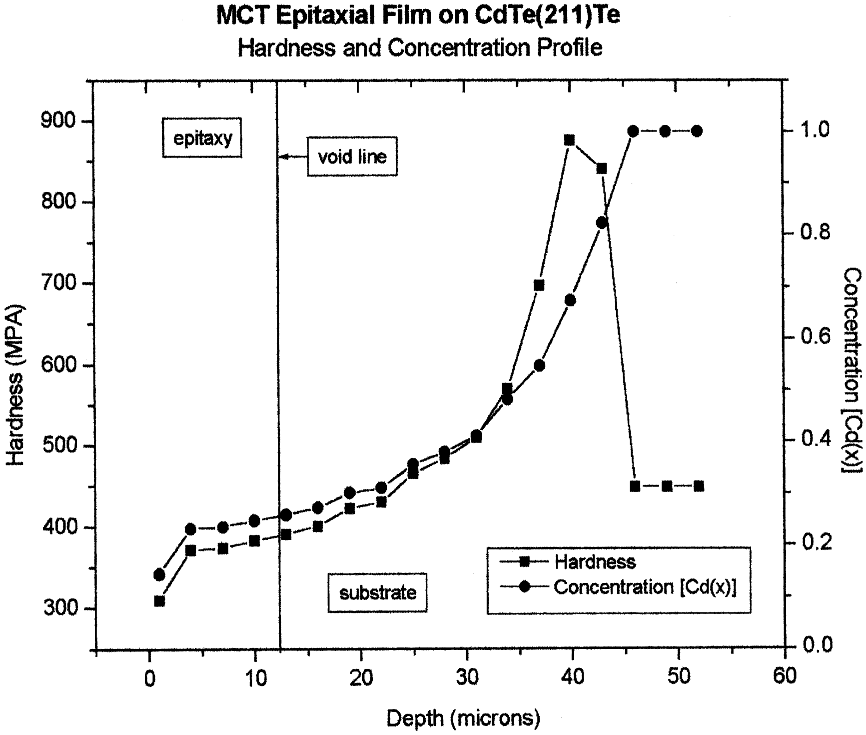
FIGURE 3 Continued.

The percentage relative misfit, for the three mentioned temperatures, were calculated as a function of the depth using Table 1 and Eqs. (1–4) and all of them were plotted and superimposed over the chemical composition profile (x vs. h). (Figs. 1b–4b).

As misfit dislocations move toward the interface softest areas, where the shear modulus decreases, it is necessary to know the relationship between the hardness profile and the misfit dislocations position (Gutkin *et al.* [11], Utke *et al.* [12]).

The dependence between the microhardness Vickers and the concentration Cd(x) is obtained by means of the experimental data from Schenk *et al.* [13]. The profiles of both functions were plotted superposed. (Figs. 1c–4c).

The distribution of misfit dislocations was obtained, by chemical etching with the Hähnert *et al.* [14] reagent (Figs. 1d–4d), on the preferential cleavage surfaces of the {110}.



(c)

FIGURE 3 Continued.

When the epitaxial growths were obtained on pure CdTe substrates, as can be observed in the corresponding micrographies (Figs. 1d–3d), the misfit dislocations can mainly be observed on the films towards the epilayer surfaces. To the left of the "void line" (original substrate surface) and in adjacent form, these defects disappear and they reappear, with a larger density, near the "overetched area". This effect is due to the fact that the reagent does a fast and no preferential chemical etching when the alloy composition is larger to $x = 0.45$, preventing the resolution of the etch pits in the area.

In the epilayers grown on CdZnTe the misfit dislocations were mainly observed in substrate areas adjacent to the "void line" and towards the film surface (Figs. 2d–4d).

In agreement with Takigawa *et al.* [15], that worked with MCT grown by LPE on CdTe and CdZnTe substrates, and with our own previous works

(d)

FIGURE 3 Continued.

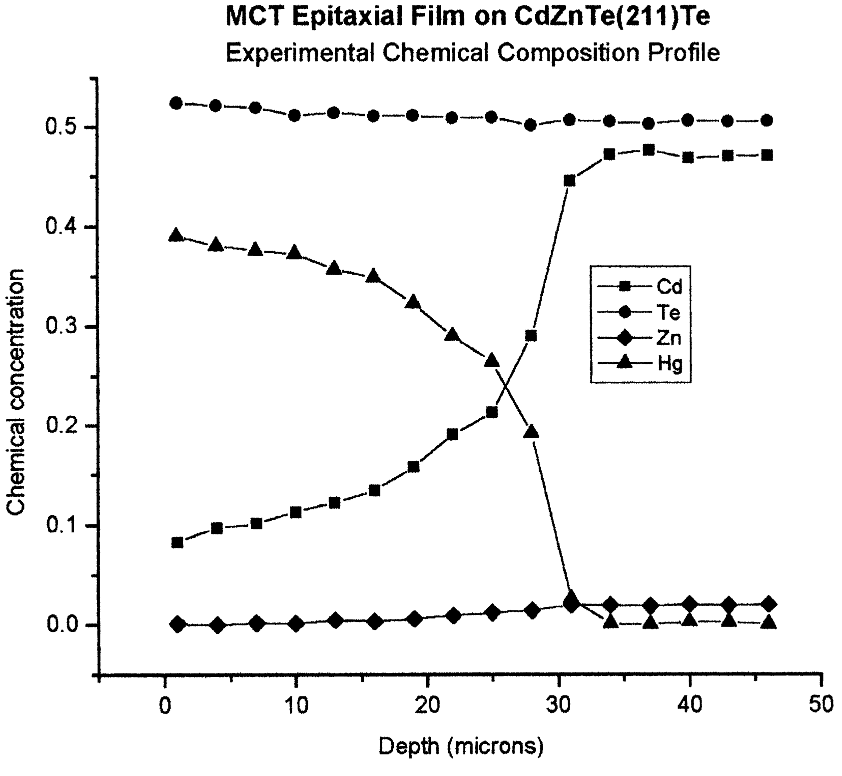
[16], with MCT films obtained on pure and alloyed CdTe substrates, in different crystalline orientations, the conclusions were:

- In the initial stage of growth the misfit dislocations were generated on the substrate adjacent to the "void line".
- If the substrate is pure CdTe, the defects move toward the epilayer surface because the hardness decreases in that direction (Figs. 1d–3d).
- If the substrate is CdZnTe, the misfit dislocations are fixed due to its interaction with the hardening entities (ZnTe4) [17] (Figs. 3d–4d).

The Hg-Cd interdiffusion determines the displacement of the maximum, greatest slope of the percentage relative misfit towards the "substrate bulk" meanwhile the growth goes on.

This generates new misfit dislocations. The dislocation distribution on the micrographies corresponding to pure CdTe (Figs. 1d–3d) and to CdZnTe (Figs. 2d–4d) allow us to guess:

- In the films grown on pure CdTe the dislocations were generated in the region of maximum slope of the percentage relative misfit (this region moves toward the bulk of the substrate during the growth).



(a)

FIGURE 4 MCT Epitaxial Film on CdZnTe(211)Te. 4a) Experimental Chemical Composition Profile on a cleaved cross section {110} plane. 4b) Percentage Relative Misfit and Concentration Profile. 4c) Vickers Microhardness and Concentration Profile. 4d) Micrograph of the chemically etched surface of the cleaved {110} plane.

- In the films grown on CdZnTe the generation of dislocations ocurrs only in this region if the Zn concentration remains below certain threshold which inhibit the process.

This last interpretation is based on the increment of the area in which the dislocations are present when the growth times are larger [7]. The increase of the growth time allows a deeper Zn diffusion which determines a more extensive area with Zn concentrations below the mentioned threshold.

In the epilayers grown on pure CdTe it is observed that the maximum slope in the percentage relative misfit does not considerably change with temperature and that the profiles, which correspond to the growth

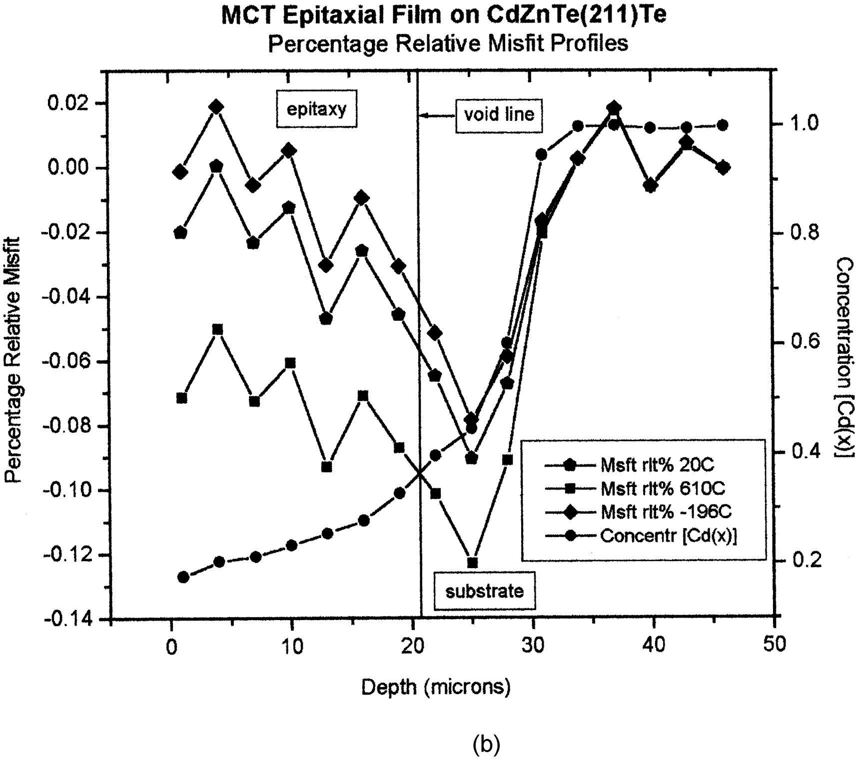


FIGURE 4 Continued.

temperature at 610°C, present the largest variations in the lattice parameter in the interdiffusion area (Figs. 1b,3b). In consequence the generation of misfit dislocations could happen at this temperature. Once the system accommodates the "misfit" it does not generate new dislocations anymore. It should be pointed out that the distribution of misfit dislocations cannot be detected for chemical compositions $x \geq 0.45$, since the solution of Hähnert *et al.* [14] overetch the material at those concentrations. Several attempts have been made, with negative results, with different dilutions of the reagent, according to the suggestions of the authors, with the purpose of revealing the dislocations in the region of the cleavage with $x \geq 0.45$. The surface was intensely etched by the different solutions.

This work allowed us to determine that the presence of dislocations in ISOVPE grown MCT epitaxial films interface are mainly influenced by the substrate material (in this case pure or alloyed CdTe) and no by the crystalline orientation [16].

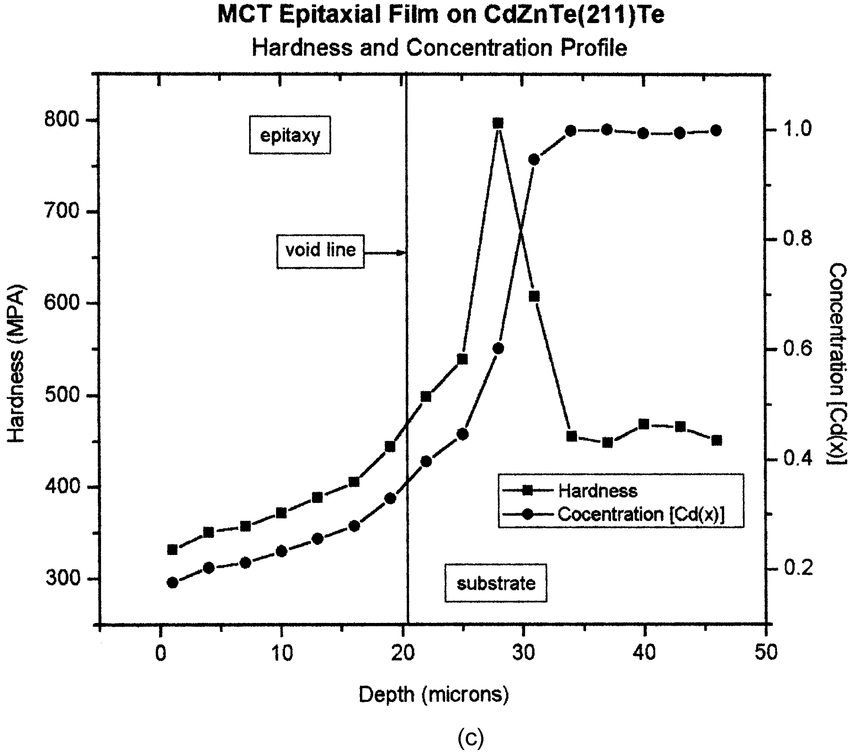


FIGURE 4 Continued.

CONCLUSIONS

The concentration gradient (x), the microhardness Vickers and the percentage relative misfit were related in MCT epitaxial films grown by Isothermal Vapor Phase Epitaxy (ISOVPE) without Hg overpressure, on CdTe and $Cd_{0.96}Zn_{0.04}Te$, in the crystallographic orientations (211)Cd and (211)Te. It was determined that many of the misfit dislocations are generated in the substrate area adjacent to the "voids line" in the initial growth stage. If the substrate is pure CdTe the dislocations slip towards the epilayer surface because the hardness decreases in that direction. If the substrate is CdZnTe the dislocations are pinned due to their interaction with $ZnTe_4$ (hardening entities).

The Hg-Cd interdiffusion determines the displacement of the maximum slope of the percentage relative misfit towards the bulk of the substrate, as the growth takes place. The area in which the dislocations appear is more narrow in the epilayers grown on CdZnTe that in the ones grown on CdTe.

(d)

FIGURE 4 Continued.

This effect is due to the fact that if the Zn concentration is larger than certain threshold then inhibits the process. The generation of dislocations in the films could mainly happen at the growth temperature of 610°C. The maximum slope of the percentage relative misfit does not have a substantial change with the temperature. This was observed at all temperatures (196°C, 20°C and 610°C). The greatest variations in the lattice parameter occurred in the interdiffusion area, corresponding to the growth temperature. From this observation it is deduced that once the system accommodates the "misfit" it does not generate new dislocations. This result is coincident with those found in (111)Cd, (111)Te, (100) and (110) crystalline orientations.

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