Ion channelling Rutherford backscattering spectrometry structural characterization of CdS/CdTe heterostructures

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Abstract

We report on the structural characterization by ion channelling Rutherford backscattering spectrometry (RBS) of thin (less than 3 μm) CdS epitaxial layers grown on {111}A-oriented CdTe substrates by chemical vapour deposition. The overall crystalline quality of the present epilayers has been studied as a function of their thickness. Also, the occurrence of single crystal growth *vs.* highly textured polycrystalline growth has been checked by studying channelling angular dips at different ^{4}He$^+$ beam energies. The CdS epilayers turned out to be essentially single crystalline, although the present RBS measurements show that extended defects are contained in the layers and at the CdS/CdTe interfaces. The dechannelling beam energy dependence allows us to identify these defects as stacking faults, whose concentration profile in the epilayers is reported.

1. Introduction

The growth and characterization of CdS/CdTe-based heterostructures continue to be the subject of much research effort, because these heterostructures have potential applications in the field of photovoltaic solar cells. Their main advantages are related to the physical characteristics of the constituent materials: in fact, the energy gap value of CdS (*i.e.* 2.42 eV at 300 K) makes it suitable as a semiconducting material for the realization of highly conductive window layers, whereas the corresponding value for CdTe (*i.e.* 1.44 eV) is near optimum for photovoltaic solar energy conversion. Research in this field has initially focused on the study of low-cost, polycrystalline, thin film devices, resulting in photoconversion efficiencies typically below 10%. However, since the early works of Yamaguchi and co-workers [1, 2], the use of solar cells based on the epitaxial CdS/CdTe heterostructure has gained increasing attention in the attempt to improve cell efficiencies. Although the maximum theoretical efficiency of the n-CdS/p-CdTe heterojunction is 19.7% under AM0 (air mass zero) sunlight spectral conditions [2], actual cell performances are limited by problems concerning the conductivity control of, and the realization of low resistance ohmic contacts on, p-type CdTe [3, 4]. Meyers [5] proposed a novel p–i–n solar cells structure of the type p-ZnTe/i-CdTe/n-CdS in which CdTe is used as an intrinsic absorber layer, thereby avoiding the above-mentioned problems. Recently, monocrystalline p-ZnTe/i-CdTe/n-CdS solar cell structures have been realized by sequential metallo-organic vapour phase epitaxy (MOVPE) of ZnTe and CdTe layers on CdS substrates, resulting in device efficiencies of up to 13% under AM1 (air mass one) illumination [6].

Despite their attractive features, the CdS/CdTe-based heterostructures raise the problem of matching the hexagonal (wurtzite) CdS lattice with the cubic (zincblende) lattice of CdTe. As a consequence, several substrate orientations have been investigated to assess the growth of both CdTe/CdS and CdS/CdTe heterostructures. The best epitaxy has been reported recently [7] for CdTe layers deposited by MOVPE on non-metal surfaces of {0001}- and {0116}-oriented CdS

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substrates, their epitaxial relationships being {111}CdTe∥{0001}B-CdS and {37$\bar{5}$}CdTe∥{01$\bar{1}$6}B-CdS respectively. However, thin lamellar twins were shown to affect CdTe layers deposited on {0001}-oriented CdS substrates, whereas no twinning has been reported for the {01$\bar{1}$6} orientation. Similarly, the growth of CdS epitaxial layers on oriented CdTe substrates has been extensively studied by several authors. Until now, only three CdTe substrate orientations have proved successful in growing CdS epitaxial layers, namely {110} [8], {221} [9] and {111}A [1]. For the first two orientations, no precise epitaxial relationships seem to hold, although for {221}-oriented CdTe substrate a relationship close to {01$\bar{1}$6}CdS∥{221}CdTe has been suggested. However, growth on {111}A-oriented CdTe gives rise to the well-known epitaxial relationship {0001}CdS∥{111}A-CdTe, resulting in a 9.74% mismatch for the in-plane lattice parameters.

Despite such a high value of the lattice mismatch, 10.5% efficiency has been reported for n-CdS/p-CdTe solar cells grown by H_2 transport on {111}-oriented CdTe [1]. To our knowledge, very few structural studies have been reported in the literature about {0001}CdS∥{111}A-CdTe heterostructures. In a previous paper [10], the high crystalline quality of thick (3–30 μm) hexagonal CdS epilayers grown by chemical vapour deposition (CVD) on {111}A-CdTe has been demonstrated by channelling Rutherford backscattering spectrometry (RBS). In this work, we investigate the structural properties of relatively thin (less than 3 μm) CdS epilayers. Their overall crystalline quality has been studied as a function of the epilayer thickness. The occurrence of single crystal growth vs. highly textured polycrystalline growth has been checked by studying channelling angular dips at different $^4He^+$ beam energies. Moreover, the presence of extended defects in the layers has been detected and their nature determined by analysing RBS channelling spectra as a function of the ion beam energy. This allowed us to identify these defects as stacking faults and to calculate their concentration profile in the CdS epilayers.

2. Experimental details

{0001}-oriented hexagonal CdS layers have been grown on {111}A-CdTe by CVD using H_2 as the transport agent from the source to the deposition region [11]. Nominally stoichiometric CdS of 99.999% purity from Cerac, Inc. was used as the starting material. The {111}-oriented CdTe substrates, supplied by Cominco, Inc., were lapped and polished with diamond paste to a mirror finish. The {111}A face of the CdTe substrates was identified by selective etching [12] in 1HF:1HNO$_3$:1CH$_3$COOH. A light etch of the sub-

strates using a 1%Br-methanol solution for 1 min immediately before the introduction into the growth chamber was followed by an in situ thermal etch at 600°C for 15 min in an H_2–N_2 (2:1) gas flow. The present CdS epitaxial layers were grown in a 300 SCCM total H_2 flow at a deposition temperature of about 600°C, the source temperature being 100°C higher. These conditions resulted in a CdS growth rate of about 0.1 μm min^{-1}. Total CdS epilayer thicknesses ranging from 0.5 to 3.0 μm were considered in the present work.

A high precision goniometer with both repeatability and an overall precision of 0.01° [13] was used for the structural characterization by ion channelling. To minimize the accumulation of damage induced by the analysing beam, care was taken when moving the beam spot on the sample surface, after a given value of the total beam charge was integrated. $^4He^+$ beam energies of 1, 2 and 4 MeV were used for the present measurements.

3. Results and discussion

Figure 1 shows the 2.0 MeV $^4He^+$ RBS spectra in aligned conditions along the CdS c axis for three samples with different epilayer thicknesses, i.e. 0.5 μm (T60), 0.9 μm (T62) and 3 μm (T61). The random spectrum for sample T60 is also reported in Fig. 1 for comparison. The energy-to-depth conversion for our geometry has been obtained by using the stopping power in ref. 14. The interface width is much larger than the experimental depth resolution. This fact could be due to interface mixing between CdS and CdTe
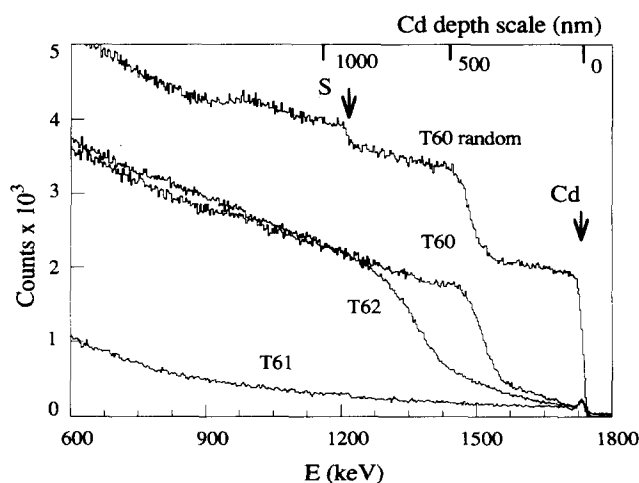

Fig. 1. 2.0 MeV $^4He^+$ RBS spectra in channelling condition along the c axis of growth for the three samples investigated with different epilayer thicknesses: (T60) 0.5 μm, (T62) 0.9 μm, (T61) 3 μm. The random spectrum for the sample T60 is reported for comparison.

and/or to thickness inhomogeneities in the epilayers. The spectra show clear Cd surface peaks and relatively low channelling yields. The surface minimum yield χ_{min}, i.e. the aligned yield just behind the surface peak normalized to the random yield, is reported in Fig. 2 as a function of the epilayer thickness for the three samples in Fig. 1. The minimum yields for thicker samples are also shown [10]. It appears that the χ_{min} value rapidly decreases with increasing CdS layer thickness up to a few micrometres, and then it reaches a minimum which is slightly higher than the theoretical estimate given by Barrett [14], i.e. $\chi_{min}^{B} = 0.0398$.

As reported in a previous work [10], the surface morphology suggests a highly textured grain structure for the present CdS epilayers. Nevertheless, it has been demonstrated that their structure in the near-surface region is single crystalline at least for the higher thickness values. However, a possible textured columnar growth could explain the higher χ_{min} values obtained for the present thin layers. To investigate this point, channelling dips for the conditions aligned with the c axis were recorded at different beam energies. In fact, it has been shown [15] that ion channelling is able to qualify the texture of a polycrystalline material by measuring the experimental critical angle $\Psi_{1/2}$ as a function of the beam energy E, using the expression

$$\Psi_{1/2}^{2} = \sigma^2 \ln 2 + \Psi_1^2 = \sigma^2 \ln 2 + \frac{const}{E}$$

where σ is the standard deviation of the crystallite orientation distribution and Ψ_1 is the channelling critical angle for a perfect single crystal.

Figure 3 reports the square of the experimental critical angle $\Psi_{1/2}$ vs. the reciprocal of the beam energy for the same samples as in Fig. 1. The theoretical values [14] are also reported for comparison. It can be
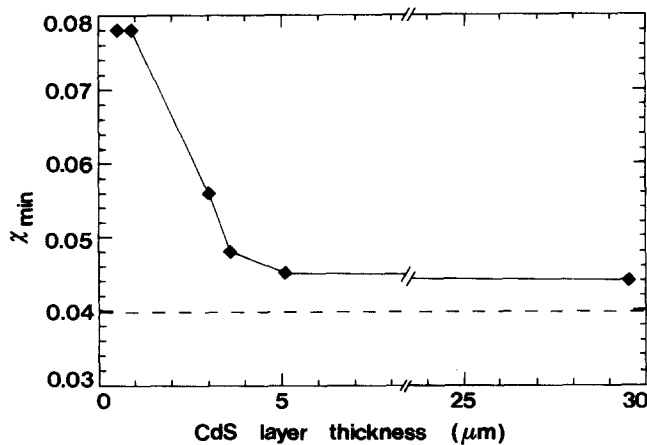
seen that our experimental values are systematically slightly lower than the predicted values; moreover, they can be fitted by a straight line whose zero energy intercept coincides with the origin within the experimental uncertainties, thus excluding misalignments higher than a few hundredths of a degree from point to point in the layers. These results lead to the conclusion that even relatively thin CdS epilayers are essentially single crystalline.

From Fig. 1 it appears that the channelling yield for sample T61 is very low, indicating a reduced amount of defects in the layer. It appears that the corresponding yields for the thinner samples smoothly increase up to depth values which roughly correspond to the interfaces, at which point sudden jumps take place. Below the interfaces, the yields of the two samples are equal and the dechannelling rates are nearly the same as that of sample T61. We can thus divide the dechannelling yield profiles into two regions, i.e. (i) the surface and (ii) the interface region, where different types of defects seem to be present.

The nature of these defects and their depth distribution can be deduced by comparing the normalized channelling yield as a function of depth with the corresponding yield for the perfect crystal. In fact, the total disorder $N_D(t)$ integrated from the surface to a depth t can be obtained by the equation [16]

$$\ln \frac{1 - \chi_V(t)}{1 - \chi_D(t)} = N_D(t) \sigma_D = \int_0^t n_D(t') \sigma_D \, dt'$$

where $\chi_V(t)$ and $\chi_D(t)$ are the normalized yields for the reference and the defected crystal, respectively, and σ_D is the dechannelling factor typical of the particular type of defect actually present in the crystal; finally, $n_D(t')$ is the local defect volume density.

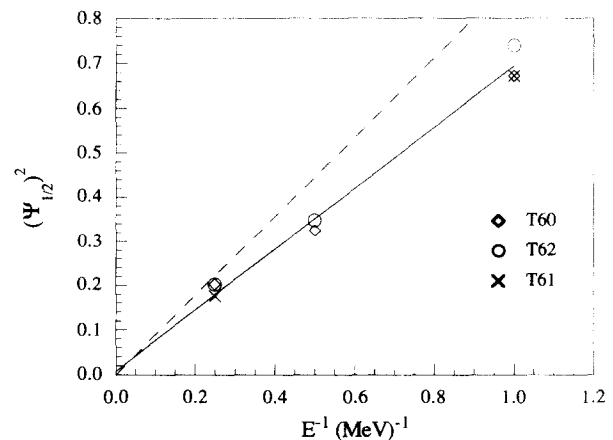Fig. 2. The surface minimum yield χ_{min} as a function of the CdS epilayer thickness.

Fig. 3. The square of the experimental critical angle $\Psi_{1/2}^2$ as a function of the reciprocal of the ion beam energies. The solid line represents the linear best fit of the data, whereas the dashed line represents the theoretical estimate.

The $N_D(t)\sigma_D$ values measured at the end of the first (surface) region for different ^{4}He$^+$ beam energies are reported in Table 1 for the two thinnest samples in Fig. 1. In our calculations we assumed the $\chi_V(t)$ values to be coincident with the normalized yield of sample T61. It appears that the defects in the epilayers have a dechannelling probability independent of the beam energy, indicating that these defects are stacking faults. Moreover, as the same holds true for any intermediate depth between the surface and the interface, it also can be concluded that stacking faults are the main defects in the present CdS epilayers.

From the derivative of $N_D(t)\sigma_D$ the defect concentration profile $n_D(t)$ can be obtained. The result is shown in Fig. 4 where the interface has been chosen as the origin of the profile. It appears that the two profiles mimic each other and show a slow decrease in $n_D(t)$ with increasing distance from the CdS/CdTe interface. These data are in agreement with those of Fig. 2, showing that an epilayer thickness of at least 3 μm is necessary to obtain a good surface quality.

As far as the second (interface) region is concerned, the fact that the channelled fraction after the interface yield jump is the same for the spectra of the two thinnest samples of Fig. 1 indicates that the density of these defects is nearly independent of the epilayer thickness. The ion channelling analysis of the interface defects is complicated by the double-layered structure

of the overall defect distribution. However, the normalized yield after the interface roughly correlates with the square root of the ion beam energy, suggesting that the interface defects are misfit dislocations formed to accommodate the high lattice mismatch involved with the CdS/CdTe heterostructure.

The presence of stacking faults in CdS epilayers grown on {111}A-CdTe substrates never has been observed before, although similar results have been recently reported by Brown et al. [17] for CdS epilayers deposited on {111}B GaAs by MOVPE, for which dense arrays of irregularly spaced stacking faults on close-packed planes parallel to the CdS–GaAs interface have been observed by conventional transmission electron microscopy and attributed to the dimorphism of CdS at the low growth temperatures involved with MOVPE. However, the hexagonal (wurtzite) phase is the stable phase of CdS at the relatively higher growth temperatures (550–750 °C) required for the CVD process. In this respect, it should be noted that the characteristic stacking fault concentration profile reported in Fig. 4 strongly indicates that the formation of these defects in the CdS layers is somewhat related to the CdS–CdTe interface. In fact, stacking faults are generally associated with partial dislocations and, therefore, they can contribute to the removal of the high lattice mismatch in the CdS/CdTe heterostructure along with misfit dislocations.

TABLE 1. The integrated disorder $N_D\sigma_D$ values as measured at different ^{4}He$^+$ beam energies for the two thinnest samples

Energy (keV)	$N_D\sigma_D$(T60)	$N_D\sigma_D$(T62)
1000	0.15 ± 0.02	0.19 ± 0.02
2000	0.16 ± 0.02	0.22 ± 0.02
4000	–	0.18 ± 0.02

4. Conclusions

The epitaxy of CVD-grown CdS epilayers on CdTe substrate has been studied by means of RBS channelling for different epilayer thicknesses, extending a previous work to thinner layers. The main results of the present work can be summarized as follows.

(1) {0001}-oriented hexagonal CdS epilayers on {111}A-CdTe substrates are single crystals independent of their thickness.

(2) In the interface region, a high density of defects is present, which can be reasonably identified with misfit dislocations, as required to accommodate the large lattice misfit between the two structures.

(3) An additional defect distribution spanning from the interface to the surface has been observed, these defects being identified as stacking faults. Their depth concentration profile decreases slowly with increasing CdS–CdTe interface distance, and a good surface crystalline quality can be obtained for CdS epilayer thicknesses above about 3 μm.

Finally, it has been suggested that the higher stacking fault density in regions of the epilayer close to the CdS–CdTe interface is symptomatic of their role in
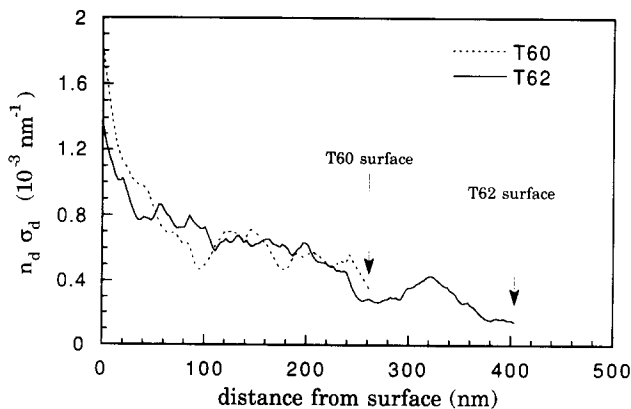

Fig. 4. The stacking fault concentration profile in arbitrary units as a function of the distance from the interface for samples T60 and T62.

removing the heterostructure lattice mismatch along with misfit dislocations, although further studies are clearly required on this subject.

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