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Influence of the substrate temperature on the structure and surface roughness of $Cd_{0.18}Sb_{0.64}Te_{0.18}$ films

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Using a radiofrequency sputtering deposition technique, ternary $Cd_{0.18}Sb_{0.64}Te_{0.18}$ thin films have been grown on glass substrates at several substrate temperatures (50–250 °C). The samples have an Sb content of about 63 at %, as measured by Auger spectroscopy. The surface roughness, the structural and the electrical properties of the films were studied as a function of substrate temperature. X-ray diffraction (XRD) measurements showed that the structure of the films changes from an amorphous phase, when deposited at lower substrate temperatures, to a mixture of two crystalline phases (CdTe and Sb) for higher substrate temperatures. Atomic force microscopy shows an increase in the surface roughness with an increase in the substrate temperature, clearly showing the formation of crystalline phases with microcrystallite sizes in good agreement with those determined from XRD measurements. The amorphous-to crystalline transition is accompanied by an abrupt increase in the room temperature electrical conductivity of the films. This increase in the conductivity as well as its temperature dependence in the range of room temperature to 150 °C can be understood in terms of an electrical percolation process through the conducting Sb crystallites.

1. Introduction

CdTe is considered to be a highly promising material for optoelectronics applications. Its range of application could be significantly increased if efficient doping could be performed in a controlled manner. The inclusion of a third element into CdTe to effectively dope or to form a ternary compound has been extensively investigated [1–4]. The preparation technique used to produce these ternary materials is important because their physical properties generally depend on their stochiometry. The extent to which these properties vary can be greatly increased if the material can be prepared in the form of thin films containing both amorphous and crystalline phases. Thin films of doped CdTe and alloy materials containing Cd, Te and a third element have been prepared using several techniques such as chemical vapour deposition, thermal evaporation, laser ablation and molecular beam epitaxy. In particular, the radio frequency sputtering (RF sputtering) deposition technique offers the possibility of controlling a wide range of film composition.

In an earlier work (5) we demonstrated that it is possible using the radio frequency sputtering technique to grow CdTe thin films containing various amounts of antimony. In the present work we study the structure, the surface roughness and the electrical properties of $Cd_{0.18}Sb_{0.64}Te_{0.18}$ thin films prepared on Corning glass substrates by RF sputtering at different substrate temperatures (T_s) in the range of 50–250 °C. Samples of this material prepared at T_s values of 100 °C or below show an amorphous structure, smooth surfaces and a thermally activated electrical conductivity, whereas, samples prepared at higher T_s values have an electrical conductivity several orders of magnitude higher with basically no temperature dependence. This latter behaviour can be

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explained by arguments based on the formation of two crystalline phases, Sb and CdTe, one of which (Sb) is more conducting and its volume fraction exceeds the critical fraction for electrical percolation. From the atomic force micrographs it is possible to observe individual crystallites with a size that increases from about 20 to about 50 nm with the increase in T_s.

2. Experimental procedure

The $Cd_{0.18}Sb_{0.64}Te_{0.18}$ films were grown in a diode radio-frequency sputtering system using a water cooled cathode with a CdTe (99.999% pure) target of 4.92 cm^2 in area with a 1.23 cm^2 piece of Sb glued to the target. As substrates, 7059 Corning glass slides were used. The sputtering system was pre-evacuated down to 6.65×10^{-4} Pa and then flushed through with purified argon gas for at least 15 min at the working pressure of 6.65×10^{-1} Pa. Typical growth conditions were as follows: background pressure = 6.65×10^{-4} Pa; argon pressure = 6.65×10^{-1} Pa; RF power = 100 W; target-substrate distance = 7.0 cm; and deposition time = 120 min for a deposition rate of about 2.5 nm per min. Films with a thickness of typically 300 nm were deposited at T_s values of 50, 100, 150, 200 and 250 °C. The substrate was heated using a halogen lamp. The Sb concentration in the films was measured by using the electron spectroscopy for chemical analysis (ESCA) and scanning Auger microscopy facilities of a PHI 560/ESCA-SAM system. The atomic force microscopy (AFM) images were recorded using a Park Instruments Nanoscope operating in the constant force mode. The principle of AFM relies on raster scanning a fine tip across the surface of the samples. Whilst this is performed, the vertical displacement of the tip that is required to maintain a constant force between the tip and the surface is monitored.

The film structure was studied by using X-ray diffraction, measured with a Siemens D500 (CuK_α) X-ray diffractometer. The room temperature conductivity measurements were performed using the two-electrode method with gold–copper co-planar electrodes. The conductivity behaviour of the films as a function of the temperature was analysed in the range of 25–150 °C.

3. Results and discussion

The grown $Cd_{0.18}Sb_{0.64}Te_{0.18}$ thin films contained different phases depending on the substrate temperature. For T_s values lower than 150 °C an amorphous phase is observed, and for higher T_s values films composed of a mixture of CdTe and Sb both in crystalline form were obtained. The X-ray diffraction patterns of the $Cd_{0.18}Sb_{0.64}Te_{0.18}$ films grown at several substrate temperatures are shown in Fig. 1. An amorphous-like pattern is observed for the films grown at low substrate temperatures between 50–100 °C. The broad diffraction peaks contain signals from both the amorphous $Cd_{0.18}Sb_{0.64}Te_{0.18}$ film and also the amorphous glass substrate, the latter has a broad diffraction band centred at about 26° in 2θ. In addition to the broad amorphous component, the X-ray diffraction pattern for the films grown at 150 °C contains weak but sharp diffraction peaks indicating the onset of crystallization in both the Sb and CdTe phases. The relative increase in the intensity of the crystalline diffraction peaks in the pattern of samples prepared at $T_s = 250$ °C indicates an increase in the volume fraction of these phases. The peaks at diffraction angles of approximately 29 and 39° are identified with the hexagonal Sb structure and correspond to the (102) and (014) crystalline planes, respectively. The peaks at diffraction angles of approximately 24 and 40° are related to the CdTe crystallites. The first of these two peaks corresponds to the diffraction from the c(111) and/or h(002) crystalline planes; and the second one corresponds to the c(220) and/or h(110) crystalline planes. The notation c and h is used to denote the cubic and hexagonal CdTe structures, respectively.

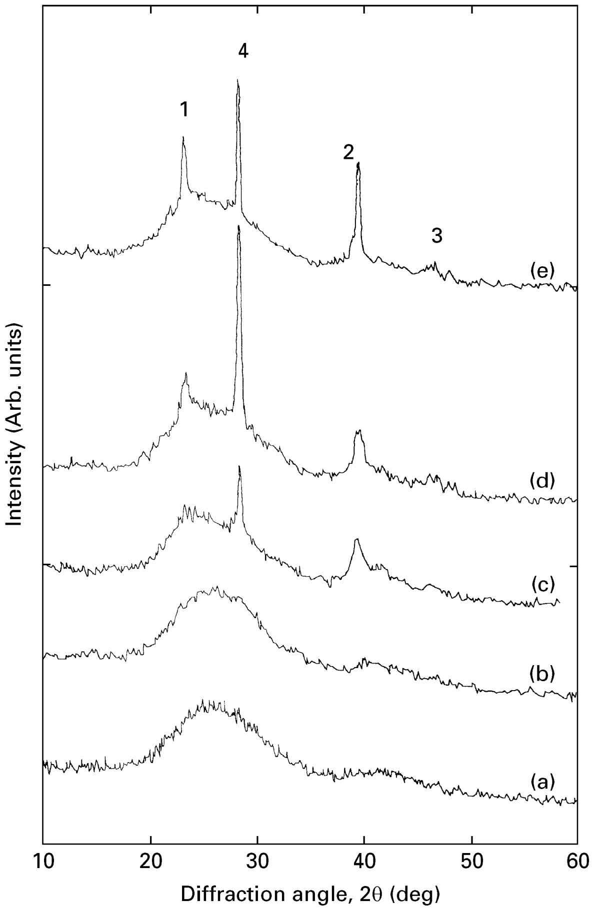

Figure 1 X-ray diffraction patterns of $Cd_{0.18}Sb_{0.64}Te_{0.18}$ films grown at substrate temperatures of (a) 50, (b) 100, (c) 150, (d) 200 and (e) 250 °C. Key to peak indexing (1) CdTe (111) (2) CdTe (220) (3) CdTe (311) and (4) Sb (111).

For higher substrate temperatures the relative intensity of the crystalline peaks continues to increase and their full width at half maximum becomes narrower. The latter point is an indication of an increase in the crystallite sizes in both materials. The crystallite size d was calculated from the Scherrer formula [6]:

$$d = 0.94\lambda/(D\cos\theta) \tag{1}$$

where λ is the X-ray wavelength, D is the full width at half maximum, and θ is the Bragg angle. The values obtained for the size of the Sb (CdTe) crystallites for the substrate temperatures of 150, 200 and 250 °C were 18.7 (10.0), 22.5 (10.1) and 28.1 nm (18.6 nm), respectively.

The Sb concentration, as measured by Auger spectroscopy, is about 64 at % for all the samples. In the films prepared at low substrate temperatures the Sb atoms have an amphoteric behaviour, in that, Sb replaces both Cd and Te in the CdTe lattice with equal probability as indicated by the atomic composition in the films. Mainly due to the low surface mobility of the atoms deposited onto the substrates at low temperatures, and also to the large amount of Sb atoms and to the larger atomic radius of Sb compared to that of Cd and Te, the structure of the material acquires a metastable amorphous phase [5]. An increase in the substrate temperature results in the formation of more stable crystalline phases. In our films the two stable crystalline phases are hexagonal Sb and cubic CdTe.

Fig. 2(a–e) shows the three-dimensional surface images of the $Cd_{0.18}Sb_{0.64}Te_{0.18}$ samples for the considered substrate temperatures (50, 100, 150, 200 and 250 °C). Each one of these images was obtained on an area of 1.0 μm^2. As indicated by the vertical scale, samples prepared at T_s values of 50 and 100 °C show surface modulations with an amplitude lower than 2.0 nm. Such atomically smooth surfaces have been previously observed in thin films of other materials that also have an amorphous structure [7]. In general, in amorphous materials prepared at low substrate temperatures, the film growth follows a two dimensional growth pattern which has a tendency to form a more uniform structure, which as previously mentioned is basically associated with the low surface mobility of the species arriving at the substrate. The surface of samples prepared at substrate temperatures of 150, 200 and 250 °C show modulations with amplitudes that increase with T_s, reaching values of approximately 50.0 nm in samples prepared at $T_s = 250$ °C. Note also that the lateral dimensions of these features increase with T_s. A higher T_s results in an increase of the surface mobility of the species on the substrate, favouring phase separation and the formation of stable crystalline structures such as those observed in our XRD measurements.

The electrical properties of a film depend on whether it has an amorphous or crystalline structure. The dependence of the room temperature electrical conductivity of the films grown in this investigation on substrate temperature is shown in Fig. 3. It can be observed that the conductivity abruptly increases from values of the order of $1.0 \times 10^{-4} (\Omega\text{-cm})^{-1}$ for the film grown at the lowest substrate temperature, to conductivities in the range of 1.0×10^{2}–$1.0 \times 10^{3} (\Omega\text{-cm})^{-1}$ for the films grown at higher substrate temperatures. The observed increase for films grown at higher substrate temperatures coincides with the formation of Sb crystallites, as it is shown by the XRD and AFM measurements. From the atomic percentage obtained from the Auger measurements it is calculated that the volume fraction corresponding to the Sb

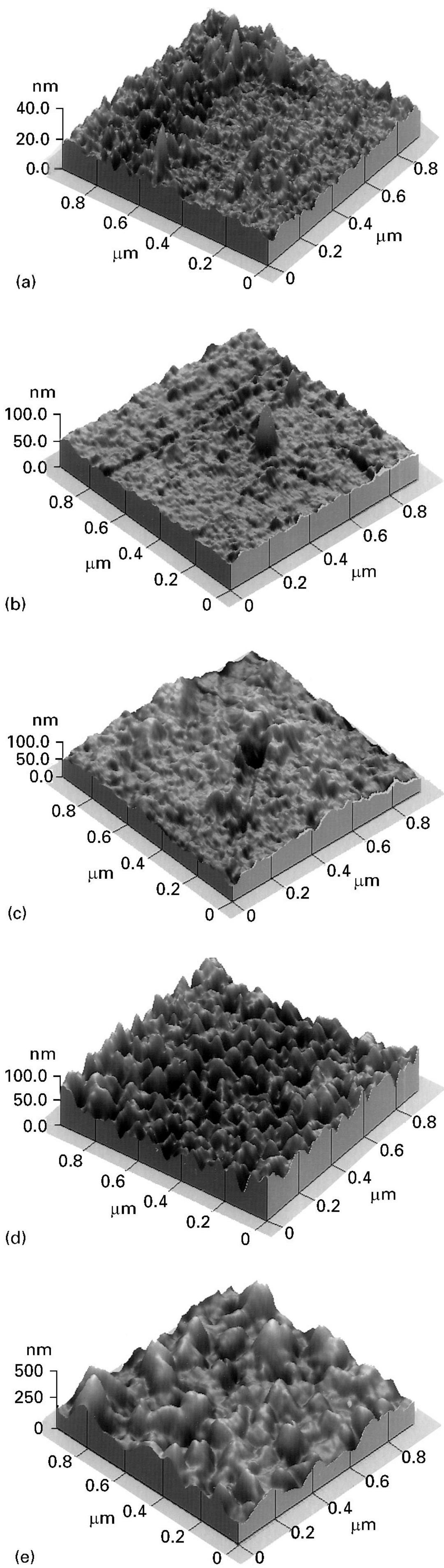

Figure 2 Three-dimensional surface images of $Cd_{0.18}Sb_{0.64}Te_{0.18}$ samples for (a) 50, (b) 100, (c) 150, (d) 200 and (e) 250 °C substrate temperatures, respectively.

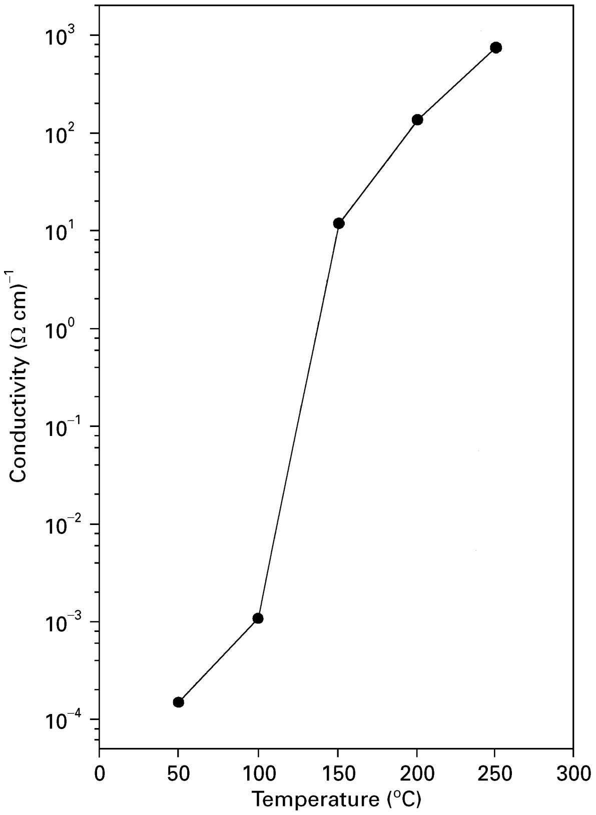

Figure 3 Dependence of the electrical conductivity of $Cd_{0.18}Sb_{0.64}Te_{0.18}$ films on the substrate temperature.

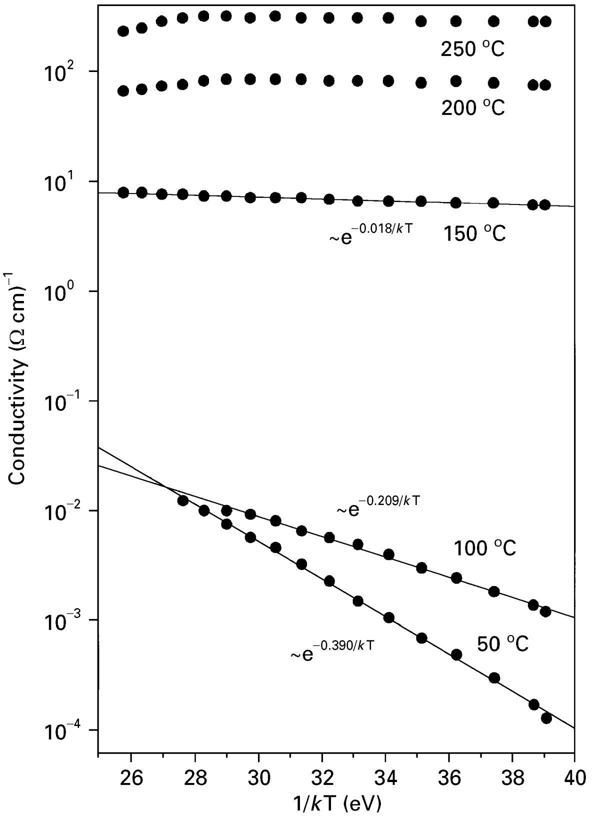

Figure 4 Electrical conductivity of the $Cd_{0.18}Sb_{0.64}Te_{0.18}$ films versus reciprocal of temperature for the samples growth at several substrate temperatures (50, 100, 150, 200 and 250 °C).

crystallites is about 0.43. Considering that for the other crystalline phase, the CdTe, conductivities in the range of 10^2–$10^3(\Omega\text{-cm})^{-1}$ have not been previously reported, not even in the case of highly doped material. Therefore one has to conclude that the conduction in samples deposited at substrate temperatures above 100 °C is due to the Sb crystallites. In a diphasic material, in which one of the phases is more conducting, the critical volume fraction for conductivity percolation of the conducting phase depends on the dimensionality of the system, which is approximately 0.16 and 0.45 for systems having dimensionalities of 3 and 2, respectively [8]. In our films the Sb volume fraction is higher than the threshold for three dimensional percolation and close enough to allow percolation through the Sb conducting phase in the case of having a two dimensional system. A similar behaviour has been observed in the $(CdTe)_{1-X}Te_X$ system [9]. In films prepared at substrate temperatures of 150–250 °C, where the volume of Sb is beyond the percolation limit, the increase in conductivity is probably due to an increase in the Sb grain size or to a reduction in the number of defects in the grains or at the grain boundaries. The conductivity of these samples tends to the semi-metallic conductivity value of bulk Sb of $2.42 \times 10^{-4}(\Omega\text{-cm})^{-1}$[10].

The measurements of the electrical conductivity of the films as a function of temperature support the above conclusions. Fig. 4 shows the temperature dependence of the conductivity for samples prepared at various substrate temperatures. For the samples grown at 50 and 100 °C it is observed that the electrical conduction is thermally activated with an activation energy of 0.39 and 0.20 eV, respectively. The lower activation energy in the samples prepared at a substrate temperature of 100 °C is not clear at this point, but it could be due to a higher degree of structural ordering promoted during growth at higher substrate temperatures. For higher T_s values (150–250 °C) the electrical conductivity is basically independent of temperature, showing a decrease for higher temperatures which is characteristic of semi-metallic materials such as bulk Sb. Semi-metallic behaviour is most evident in the samples grown at 250 °C.

4. Conclusions

In this work we have studied the substrate temperature dependence of the structure, surface roughness and electrical properties of $Cd_{0.18}Sb_{0.64}Te_{0.18}$ thin films. Samples grown at different substrate temperatures have the same Sb atomic content but different structures. Substrate temperatures equal or below 100 °C produce materials with an amorphous structure and smooth surfaces. Higher substrate temperatures result in films whose structure consists of a mixture of CdTe and Sb, both in crystalline form, and a more pronounced surface microstructure due to an increase in particle size. The room temperature electrical conductivity suddenly increases by several orders of magnitude for samples prepared at substrate temperatures above 100 °C. The sudden change in the condutivity and its temperature dependence indicate a percolation process through the conducting Sb particles. The measured Sb content in the films of 64 at%, corresponds to a volume fraction of 0.44 of crystalline Sb, a value that is higher than the threshold for three dimensional percolation and close to that required for a two dimensional percolation.

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