Semiconductor thin films grown by RF-co-sputtering of CdTe and Al targets

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CdTe is a direct bandgap semiconductor with important applications in radiation detection and photovoltaic devices. However, as any material, it has some limitations. For instance, in the photovoltaic heterostructure CdTe/CdS, among the limiting factors we may mention the difference between the cubic and the hexagonal crystallographic structures of each one of the heterostructure components and the difficulty to obtain p-type CdTe. Some of the limitations found in these systems could be surmounted by producing new materials based on CdTe. In this work we report results on the synthesis and characterization of thin films of the material $Cd_{1-x}Al_xTe$. This alloy is proposed based on the existence of the compounds Al_2Te_3 and $CdAl_2Te_4$. The semiconductors Al_2Te_3 and $CdAl_2Te4$ are part of the family of vacancy ordered semiconductors formed by elements of columns II, III and VI and can be described with the general chemical formulas: $A^{II}B^{III}_2C^{VI}_4$ for ternary compounds and $B^{III}_2C^{VI}_3$for binary compounds.

We have produced thin films of $Cd_{1-x}Al_xTe$ by RF co-sputtering employing CdTe and Al targets under an Ar atmosphere. Al content was controlled by the RF power applied to the Al magnetron. The samples presented hexagonal structure as was determined by x ray diffraction. An increase in the bandgap depending on the Al content was found and values up to 1.64 eV for 3% of Al content were obtained by photoreflectance spectroscopy. The direct bandgap property is established beyond any doubt by the presence of a clear photoreflectance signal. Ellipsometry measurements show changes in CdTe-like critical points energies as result of aluminum incorporation. Electrical characterization results showed that samples present the typical characteristics of semiconductor behavior.

Keywords: Semiconductor alloys; Ordered defect semiconductors; Optical characterization

1. Introduction

There are a good number of compound semiconductors both from the III-V and II-VI groups widely employed in technological devices. Most of the optoelectronic industry is based on III-V compounds while II-VI compounds can be found in diverse application such as IR detection, X-Ray detection, photovoltaic devices, etc. However, the interest to address unsolved technology needs and improve current device performance drives the research to obtain new semiconductor compounds. A strong research effort is being devoted to new ternary and quaternary alloys, for instance CuInGaSe based materials are very promising materials in the area of photovoltaics[1]. A family of semiconductors, scarcely studied, are those materials formed by elements from columns II, III and VI and can be described with the general chemical formulas: $A^{II}B_2^{III}C_4^{VI}$ for ternary compounds and $B_2^{III}C_3^{VI}$ for binary compounds, some of them have been subject of theoretical studies[2- 6]. These compounds have potential application for the development of optoelectronic devices but relatively few experimental research has been carried out with the scarce reports related to bulk materials[7-9]. Also, there are new proposals for their application in electronic devices capable to sustain high radiation doses and in novel electronic devices based on intrinsic heterojunctions[10,11]. A straightforward approach to produce thin films of ordered vacancies materials is to employ a II-VI compound as a precursor and identify the necessary conditions to introduce substitutional group III atoms in the cubic structure of II-VI compounds.

As the number of group III substitutionaly atoms increases we eventually will pass from a doped II-VI

Table 1. Atomic composition for the $Cd_{1-x}Al_xTe$ films studied.

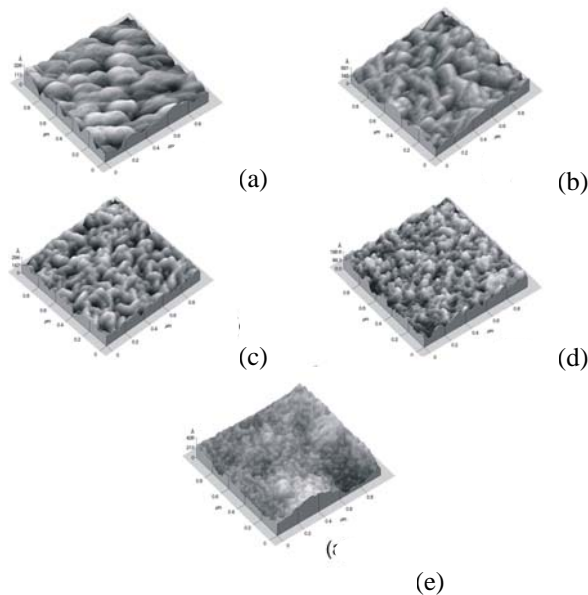| Sample	Cd (at. %)	Te (at. %)	Al (at. %)	T_s (°C)
CMT8	50.0	49.3	0.7	400
CMT9	51.0	47.0	2.0	400
CMT7	48.3	47.0	4.7	400
CMT3	30.0	51.6	18.4	400
CMT5	1.3	36.7	62.0	400
CdTe	49.0	51	0	600
MY1	50.6	48.4	1.0	600
MY5	49.4	48.4	2.2	600
MY9	47.8	48.4	3.8	600
MY6	46.3	50.4	3.3	600

T_s: substrate temperature

Figure 1. Atomic force micrographs for samples deposited at T_s =400 ºC . (a) CMT8, (b)CMT9, (c) CMT7, (d) CMT3 and (e) CMT5.

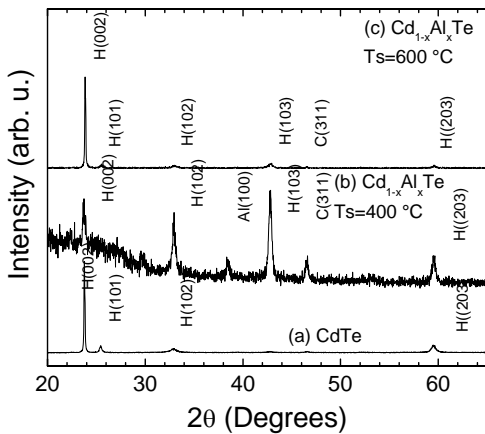**Figure 2.** Representative X-ray diffractograms for (a) CdTe film, (b) $Cd_{1-x}Al_xTe$ films deposited at T_s=400 ºC and (c) $Cd_{1-x}Al_xTe$ films deposited at T_s=400 ºC.

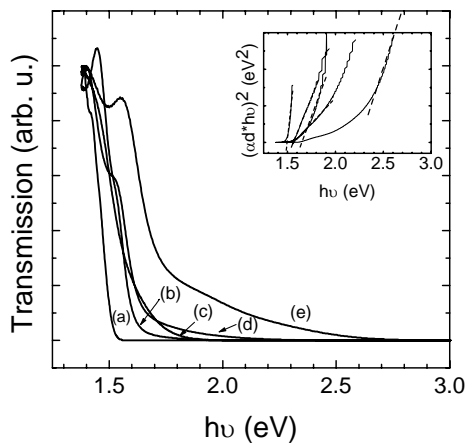**Figure 3.** Room temperature transmission spectroscopy spectra for samples deposited at T_s =400 ºC. (a) sample CMT5, (b) CMT9, (c) CMT3, (d) CMT8 and (e) CMT7. The inset corresponds to the fitting of the transmission spectra to the model of direct transitions between parabolic bands.

compound up to ordered-vacancies semiconductor thin film. We have carried out this approach for the system $(CdTe)_{1-x}(In_2Te_3)_x$ employing the close spaced vapor transport with sources of CdTe, elemental In and the compound In_2Te_3[12-14]. In this work we report for the first time results obtained for the system $Cd_{1-x}Al_xTe$, whose related ordered vacancies compounds are $CdAl_2Te_4$ and Al_2Te_3. We prepared $Cd_{1-x}Al_xTe$ thin films by R.F. co-sputtering employing Al and CdTe targets. Aluminum content was controlled by the RF power applied to Al target. We present in this work results that show that the incorporation of substitutional aluminum in CdTe changes the crystalline structure preserving the semiconductor characteristics of the alloy. The effects on electronic and structural properties are presented.

2. Experimental details

Samples were deposited employing a RF co-sputtering system, base pressure was better than $5x10^{-6}$ Torr. A 5 minute simultaneous pre-sputtering on targets was employed and the work pressure was 15 mTorr for all cases using, 99.999% pure Ar as the process gas. We produced two sets of samples with substrate temperatures of 400 and 600 °C. The power applied to the CdTe target was 30 W and that on the Al target was changed from 45 W up to 70 W in 5 W steps for the set produced at 400 °C. For the other set, 40 W were applied to the CdTe target and 70 W to the aluminum target. The aluminum incorporation was controlled by changing the substrate-target distance. After film growth was completed, the samples were maintained under a pressure $5x10^{-6}$ Torr in the deposition system until room temperature was attained in the substrate holder. The morphological, structural and electronic properties of the samples were obtained by atomic force microscopy, X-ray diffraction, scanning electron microscopy (SEM), optical transmission, photoreflectance and ellipsometry spectroscopies at room temperature. Surface morphology was done employing a Thermomicroscopes Autoprobe-CPR2002 system. Chemical composition was obtained from energy dispersive x ray spectroscopy (EDX). X ray diffraction measurements were carried in a Siemmens D5000 system. SEM and EDX were carried out in a JEOL JMS6300 microscope, absorption and photoreflectance measurements were carried out employing a standard setup controlled by a personal computer and employing a He-Ne laser as modulating source. The electrical properties in dark were measured applying direct current using a 4600 BIO-RAD, DLTS spectrometer.. The studied films were heated at 0.15 K/s from 80 to 450 K with an applied bias voltage of 100 V. The dark current signal was measured with a programmable 617 Keithley electrometer connected to a 465 Gould oscilloscope. Aluminum contacts were deposited on the samples by RF sputtering.
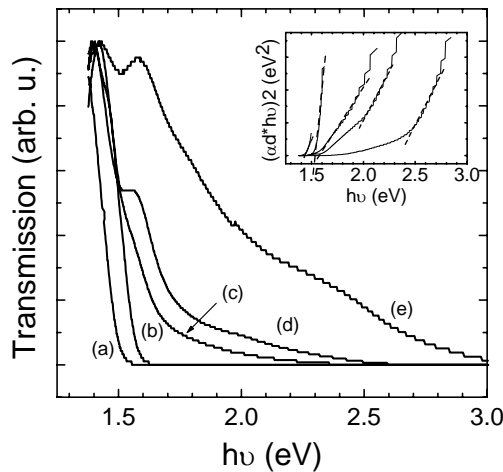
3. Results and discussion

Figure 1 presents AFM micrographs for samples grown at 400 °C. Surface roughness increases with the aluminum content. X-ray representative diffractograms of the studied samples are presented in figure 2. The diffractograms were indexed using the PDF (powder diffraction file) numbers 150770 and 190193, for the cubic and hexagonal phases of CdTe as a guide. Figure 2.(a) presents the X-Ray diffractogram of a CdTe thin film deposited at 600 °C, it is clear the presence of a mixture of cubic and hexagonal phases. Fig 2.(b) shows X-Ray diffractogram from a thin film of $Cd_{1-x}Al_xTe$ with $x = 0.02$ deposited at 400 °C (CMT9): Here, a mixture of cubic and hexagonal phases is clearly indicated by the presence of the peak associated to the plane (311) of CdTe. The presence of an aluminum peak from the planes (100) indicate the presence of aluminum non-incorporated to the $Cd_{1-x}Al_xTe$ lattice. (c) Corresponds to the X-Ray diffractogram from a thin film of $Cd_{1-x}Al_xTe$ with $x = 0.022$ deposited at 600 °C (MY5). There is no presence of aluminum peaks and its crystallographic structure is hexagonal. The lattice parameters obtained for the whole set of samples are slightly lower than the reported for the hexagonal phase of CdTe. Aluminum compositions were obtained from EDX analysis and are presented in Table 1. The produced samples have aluminum contents between 0 and 62 at.%. There is not a clear tendency between Cd, Te and Al contents with the deposition parameters. However we would like to point out that, as expected, MY samples presented a decrease in the Cd content as Al increased while Te content remains constant. Samples with aluminum concentrations higher than 62 at.% presented a metallic aspect and do not present semiconducting characteristics.

Figures 3 and 4 present the results of characterization by optical transmission spectroscopy. Figure 3 presents the results for samples grown at a substrate temperature of 400 °C; (a) corresponds to sample CMT5, (b) to CMT9, (c) to CMT3, (d) to CMT8 and (e) to CMT7. Figure 4 presents the results for samples grown at a substrate temperature of 600 °C; (a) corresponds to a polycrystalline CdTe sample, (b) to MY1, (c) to MY5, (d) to MY9 and (d) to MY6. In both graphs the inset represent the fitting of the transmission spectra, considering Beer´s law as a first approximation, employing the model of direct transition between parabolic bands. From the transmission spectra we clearly observe a shift towards higher energies in the absorption edge and from the fitting an increment in the band gap value. However, the slow increase in the absorption band edge makes hard to obtain reliable values for the band gap with this approach. Because of this we do not report the band gap values obtained from the linear fittings depicted in the insets of figures 3 and 4. All the samples have a surface free of holes so we discard the possibility that the slow decrease of the intensity at high energies in transmission spectra for some samples has its origin in samples with microscopic voids. A possible

Figure 4. Room temperature transmission spectroscopy spectra for samples deposited at $T_s = 600$ °C. (a) polycrystalline CdTe sample, (b) MY1, (c) MY5, (d) MY9 and (d) MY6. The inset corresponds to the fitting of the transmission spectra to the model of direct transitions between parabolic bands.
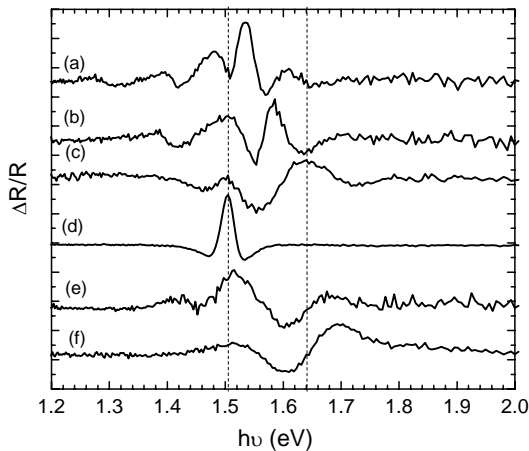

Figure 5. Room temperature photoreflectance spectroscopy for samples grown at $T_s=400$ ºC: (a) CMT9, (b) CMT8 and (c) CMT7; and grown at $T_s=600$ ºC: (d) CdTe thin film, (e) MY9 and (f) MY6. The fitting to the theoretical model is shown with circles. Broken lines are just a guide to the eye.
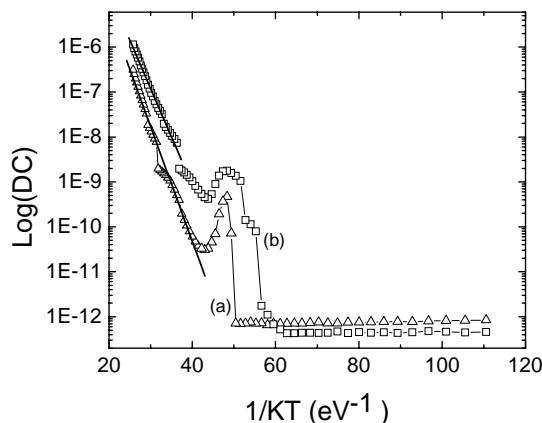

Figure 6. Representative curves for dark conductivity. (a) sample MY6 and (b) sample CMT9.

explanation for the slow decrease in the transmission spectrum of samples grown at 400 ºC is the presence of a mixture of $Cd_{1-x}Al_xTe$ alloys with different aluminum contents and different band gap values. This explanation is supported by the evidence obtained from the X-ray results about the presence of metallic aluminum which will imply that only part of the aluminum has been incorporated in the CdTe lattice shifting the band gap.

In the case of the transmission spectra for samples grown at 600 ºC we also found hard to obtain reliable band gap values from the analysis of the transmission spectra. For samples deposited at 400 ºC there is not any correlation between the aluminum content and the absorption band edge shift while for samples deposited at 600 ºC an apparent relationship is observed between the band edge shift and the aluminum content, see Table 1. However it is necessary to determine quantitative band gap values. From the transmission spectroscopy results there is not a clear difference in the electronic properties of samples grown at different substrate temperatures. In order to evaluate the characteristics of the band gap we employed photoreflectance spectroscopy.

Photoreflectance spectroscopy is a well established modulation technique useful in the characterization of direct band gap semiconductors and it is very sensitive to crystal quality and surface states because of its effect on the conduction and valence bands of a semiconductor[15]. Figure 5 present the room temperature photoreflectance spectra for samples grown at a substrate temperature of 400 ºC: (a) sample CMT9, (b) sample CMT8 and (c) sample CMT7; and grown at substrate temperature of 600 ºC: (d) a CdTe thin film, (e) sample MY9 and (f) sample MY6. A very important conclusion can be drawn from the fact that a photoreflectance signal may be obtained from the $Cd_{1-x}Al_xTe$ thin films: it is that the alloying process preserves the direct characteristic of the CdTe band gap. For samples grown at lower temperature it is apparent the presence of two signals. This could be interpreted as evidence of the presence of a mixture of two phases. The change in electronic properties of the $Cd_{1-x}Al_xTe$ thin films with aluminum content is also observed from ellipsometric measurements as a red shift of the CdTe critical points $E1(3.3 eV)$ and $E1+\Delta1(3.87 eV)$. A deeper discussion will be presented elsewhere16. Figure 6 presents the representative curves for dark conductivity. (a) corresponds to sample MY6 and (b) to sample CMT9. Both curves present characteristics of semiconductor transport with activation energies of 0.26 eV (MY6) and 0.22 eV (CMT9). The peak around 50 eV^{-1} has been associated to Te vacancies in CdTe[17, 18]. Preliminary Hall effect measurements indicated that samples have p-type conductivity. A complete understanding of the alloying process is still necessary but it is clear that we have obtained a CdTe-based new material whose band gap can be varied by controlling the amount of Al.

Conclusions

RF co-sputtering has been successfully employed to obtain films of a new semiconducting $Cd_{1-x}Al_xTe$ alloy using Al and CdTe targets. The aluminum incorporation has been controlled with applied RF power, substrate temperature is essential to obtain substitutional incorporation of aluminum.

The bandgap of the semiconducting $Cd_{1-x}Al_xTe$ alloy is direct, its value can be controlled with the amount of substitutional aluminum and its crystallographic structure is hexagonal with lattice parameters very close to those of hexagonal CdTe. At low temperatures there is a mixture of alloys with different aluminum content. The higher aluminum concentration obtained in this study was 3.8 At.% but the higher band gap value of 1.64 eV corresponds to an aluminum concentration of 3 At.%, because of differences in the incorporation of aluminum in substitutional sites.

Acknowledgements

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