

Confinement effects on CdTe:O sputtered films prepared at high substrate temperature

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Abstract

Five CdTe:O thin films with a mean thickness of about 200 nm were grown by a reactive radiofrequency sputtering technique in a controlled N-O-Ar plasma. The substrate temperature was held at 500° C during 3 hours of deposition for each sample. The oxygen content in the films was controlled by the gradual amount of nitrogen partial pressure. Structural and optical properties of the grown films were obtained from x-ray diffraction patterns and optical absorption spectra respectively. Samples containing oxygen showed typical diffraction peaks associated with cubic and hexagonal crystalline phases as well as Te oxides. We used the Debye-Scherrer formula to measure the crystallite size and we found a nonlinear shift in the absorption band edge, that arises from strong structural changes in the material, as well as a quantum effect for the material with crystal size smaller than the exciton diameter in CdTe.

INTRODUCTION

Semiconductor technology has advanced to the point where it is now possible to create devices incorporating one-dimensional confinement (quantum wells and 2-D structures). Today, submicron production techniques such as MBE and MOCVD are routinely used to fabricate quantum devices with novel characteristics. As semiconductor technology continues to drive the scaling of electronic device dimensions into the ultrasubmicron and nanodimensional regime, many concepts and phenomena related with ultrasmall and ultrafast devices are being the focus of an intensive research. A principal challenge in the application of quantum-based devices arises from the molecular size considerations: many interesting questions are concerning with the seemingly fragile characteristics of nanodevices. Therefore, there has recently been an increasing interest in the study of the effects of structural and alloy disordering on nanostructures grown under specific conditions. One of the most studied cases corresponds to materials composed of small particles embedded in an insulating matrix. The most important feature associated with those small grains, is a quantum size effect, showed as a shift in the excitonic peak of their optical absorption spectra, as the size of the nanocrystal decreases [1]. Usually, nanocrystalline and composite microcrystalline materials have been prepared, among other techniques, by compressing-sintering methods, colloidal techniques, glow discharge, remote plasma enhanced chemical vapor deposition, laser ablation, vacuum evaporation and radiofrequency sputtering [2].

CdTe has a direct bandgap of 1.5 eV at room temperature, and is a suitable material for electrooptical devices. The structure of CdTe thin films prepared by

cathode sputtering in an argon atmosphere has been mentioned in connection with a photoelectric effect in metal-CdTe-metal structures [3], switching phenomena in amorphous CdTe thin films [4], and high dark conductivity CdTe thin films [5]. Practical application of nanocrystalline materials requires an extensive knowledge of their structural, electrical and optical properties. Additionally, control on the size of the microcrystallite has a great importance in device applications, and it is not yet firmly established if it can be modified by using different deposition conditions [6].

In previous works we reported a method to prepare CdTe nanocrystals with variable sizes from 5 to 35 nm. [7]. We also showed that a transition from cubic to an hexagonal phase appears when incorporation of oxygen atoms into the CdTe lattice occurs [8]. This oxygen incorporation into the CdTe lattice sites has no preferential substitution for Cd or Te atoms. As the radius of an oxygen atom is smaller than a Cd or Te atom, substitutional oxygen atoms may shrink the lattice which finally becomes distorted. We showed that the increase of oxygen content results in the amorphization of the CdTe crystalline structure. We also reported that it is possible to obtain polycrystalline thin films composed by a mixture of CdTe and CdTeO₃ crystallites, by thermal annealing of a-CdTe:O films. [9] In all previous cases, we annealed the samples in the range from 50 to 400° C.

In this work we have studied the effect of the oxygen incorporation into the non-oxygenated cubic CdTe lattice, when the substrate is maintained at 500° C during the RF deposition. Structural and optical characterization of the films were performed by using x-ray diffraction and optical absorption measurements. The energy band gap of each sample was obtained from the optical

absorption spectrum, using a numerical derivative method. We found that, also in this case, oxygen atoms are allowed to incorporate into the CdTe lattice producing structural stresses that result in the amorphization of the material. We observed both cubic and hexagonal phases in all the samples containing oxygen, but we found just a cubic phase in the non-oxygenated one. The average size of the CdTe crystallites was calculated using the Debye-Scherrer formula. We improved the fitting by using two broad gaussian functions in order to distinguish between the halo of the amorphous substrate and the CdTe diffraction peaks. Particle size effects were observed in the optical absorption spectra as a shift of the absorption edge to higher energies.

EXPERIMENTAL DETAILS

Polycrystalline CdTe thin films were grown by a reactive RF sputtering technique, using a CdTe target (99.999 % purity) in an argon-oxygen-nitrogen atmosphere. The samples named T0, T1C, T1D, T1B and T1A were grown on 7059 Corning glass substrates heated at 500°C during 3 hours of deposition. The nitrogen partial pressure was varied from 4×10^{-7} to 1.3×10^{-4} Torr. XRD patterns were obtained with a D500 SIEMENS diffractometer (CuK α line). Absorption spectra were obtained with a Perkin Elmer Lambda 9 spectrophotometer. Oxygen concentrations are calculated from Auger measurements [10].

RESULTS AND DISCUSSION

In Fig. 1 are shown the XRD patterns for the samples. The oxygen content gradually increases from the T1C sample to the top of the graphic. The capital C or H after the plane indices corresponds to the cubic and the hexagonal phases of a crystalline structure, respectively. It can be observed a diffraction peak at 23.6° that belongs to the (111)C CdTe. At the bottom curve (T0 sample), this is the only visible peak, and corresponds to the preferred orientation of the as-grown non-oxygenated sputtered CdTe films. As the oxygen content increases, three more peaks become clear at 39.2° , 42.4° and 46.1° . These peaks are related with the (110)H, (103)H and (311)C diffraction planes of CdTe. As it can be seen, two major features are shown in the XRD pattern for the T1D sample: a large amount in the relative intensity of the (111)C peak, as compared with the other samples and an additional diffraction peak at 26.65° , which, according to standards of powder diffraction corresponds to TeO₂ in the (110) direction. In addition, the peaks (110)H and (103)H have almost disappeared. The top pattern corresponding to the T1A sample, with the highest oxygen content, has the lower relative intensity and broader diffraction peaks, as a consequence of its very small grains.

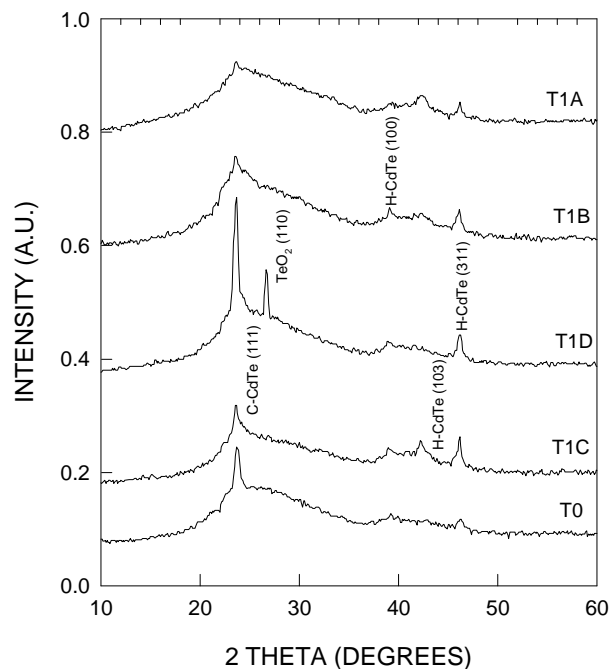


Fig. 1. X-ray spectra . Oxygen content increases from bottom curve to the top

The pattern evolution in Fig. 1, suggests that the increasing of oxygen content leads to the formation of oxides, and finally, to the amorphization of the material.

We show in Fig. 2 the optical absorption of the films. The base line of each plot has been shifted upward in order to appreciate the changes in the optical transitions. As it can be seen, the first optical transition occurs near 1.5 eV, which typically corresponds to the bulk CdTe band gap.

From this graph, we obtained the first derivative in order to accurately evaluate the inflection point. It is shown as a maximum for each pattern in Fig. 3. This point corresponds to the absorption band edge.[11] As compared with T0 (the non-oxygenated sample), the obtained band edge values are shifted to higher energy values.

The average grain sizes for the samples were calculated from the width at half peak intensity of the (111)C diffraction peak, using the Debye-Scherrer broadening formula. The results are shown in Fig. 4. All the calculated values, are smaller than 14 nm, the exciton diameter in CdTe [11,12]. Thus we have nanocrystalline grain sizes and therefore the observed shift of the bandgap to higher energy values is a quantum confinement effect already reported by the authors for nonstoichiometric CdTe thin films in a previous work [7].

In Table 1 we listed our principal results for each sample. We have added an extra column, where we have

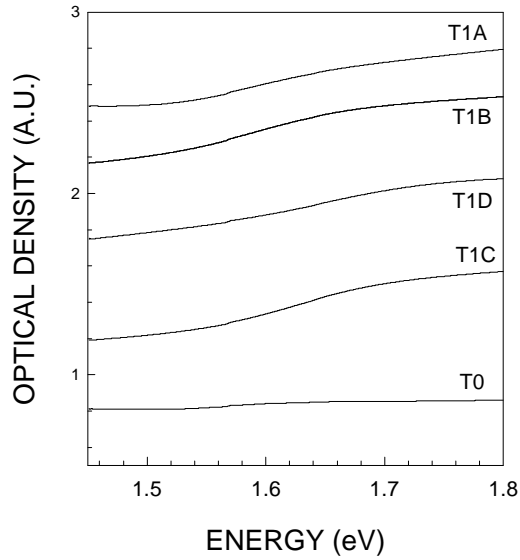


Fig.2. Optical absorption. Each inflection curve appoints for the first optical transition.

calculated the grain size for each sample, using an expression proposed from a reduced mass model by Efros *et al* [13], in order to contrast these values with our calculations. Although it is an approach calculated for the energy band gap of the cubic CdTe, it would serve us as a reference for comparative purposes.

The mentioned formula is as follows: $E_g = E_{gb} + \frac{1}{4} h^2 \mu^{-1} R^{-2}$, where $E_{gb} = 1.5$ eV is the bulk band gap value, $\mu = 0.08 m_0$, the reduced mass of the exciton in bulk CdTe, R is the particle radius, m_0 is the electron rest mass ($m_e = 0.11 m_0$, $m_h = 0.35 m_0$) and E_g is the absorption peak position (Fig. 3).

As we can see in Table 1, there is a fairly well agreement between both crystal size values for the T1A sample. It is poor for the TO and T1B samples, and it

| Sample | Energy (eV) | Grain size (nm) | Grain Efros <i>et al</i> (nm) | Interplanar distance Å |
|--------|-------------|-----------------|-------------------------------|------------------------|
| TO | 1.57 | 7.52 | 6.6 | 3.76 |
| T1C | 1.63 | 7.39 | 4.97 | 3.73 |
| T1D | 1.65 | 11.2 | 4.6 | 3.77 |
| T1B | 1.6 | 6.46 | 5.78 | 3.73 |
| T1A | 1.61 | 5.85 | 5.56 | 3.76 |

Table 1.-Grain size comparison between data points and calculated values from the work by Efros *et al*.

becomes worse for the T1D sample. The discrepancies should be, among other factors, due to the slightly larger exciton reduced mass for the hexagonal CdTe crystalline phase. Furthermore, the above theoretical approximation is based on the assumption of pure crystalline material, thus, this comparison could help us to shed light on the theoretical models. From this Table we can observe a slight expansion of the interplanar distance (less than

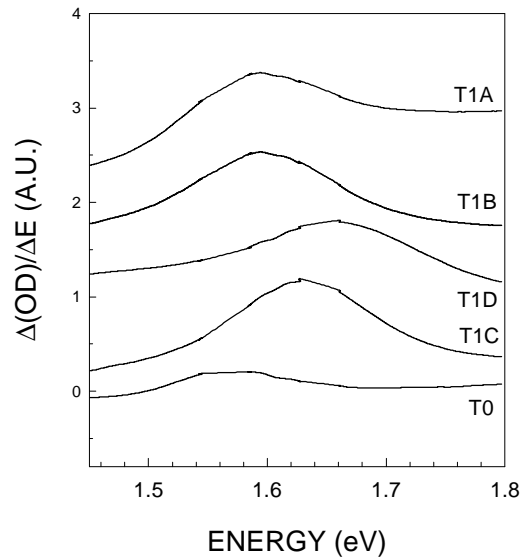


Fig. 3. Derivative of Optical absorption. Each maximum corresponds with the absorption band edge.

0.015 Å) from the non-oxygenated sample to the rest of them.

The observed behavior of the energy band gap and particle size, can be explained as follows: oxygen atoms are capable to incorporate interstitially into the CdTe lattice. This causes an structural disorder and a slight expansion of the interplanar distances. According to the diffraction spectra (Fig.1), this interstitial oxygen enhances the formation of hexagonal CdTe phase. Thus, our films are composed by a mixture of both cubic and hexagonal CdTe phases. The high reactivity of oxygen to Te atoms leads to the formation of TeO_2 (T1D sample). This bonding produces internal stresses that finally results in the amorphization of the material.

In a previous work [14], it was showed that oxygen contents exceeding 7 % amorphizes the material. Below this limit, in the range of 3-4 % of oxygen contents, hexagonal and cubic crystalline phases are present in the films. In another work [15], it was showed that the structure of the deposited films was also dependent on the substrate temperature during deposition, and films deposited within a range between 200-400 °C had a mixed cubic and hexagonal structure.

We have now a high temperature of the substrate during deposition, so, we have even lower oxygen concentrations when hexagonal phases and amorphization of the material occur.

The initial upward shift in energy from TO to T1D (Fig. 3) is due to this structural disorder and phase transformation. Similar E_g shifts have been observed in CdS. [16,17] Additionally, T1D sample is a mixture of CdTe and TeO_2 crystallites. Although this oxide is clearly visible in the XRD for the T1D sample, it probably begins its formation at lower oxygen contents.

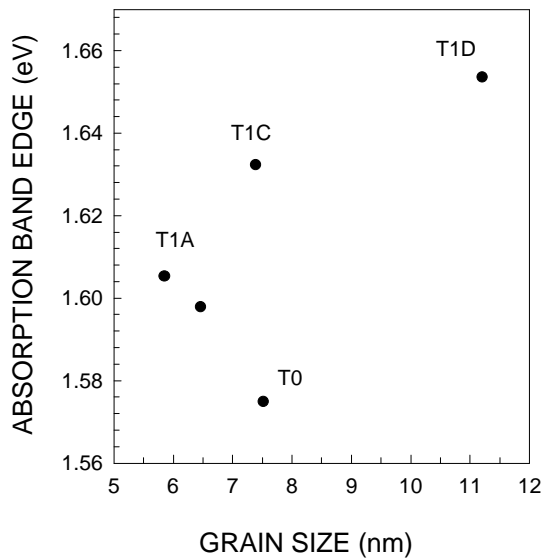


Fig. 4. Crystallite diameter against absorption energy

We think that even the T1C sample is a composed mixture of CdTe and small amounts of oxide insulating crystallites. Similar effect was found and discussed in the work of Potter *et al* [11], and that could explain the large observed crystallite sizes for T1C and T1D in Fig. 4. Similar large CdTe crystallite sizes at larger energy values than expected, have been reported for CdTe oxidizing as TeO_2 [18]. Furthermore, the energy shift from an hexagonal phase is larger than the energy shift for a cubic phase. Thus, another possible explanation for the larger than expected values of the energy shift from T0 to T1C and T1D samples, could be due to this hexagonal phase as the predominant one in the T1C and T1D films.

For the T0, T1B and T1A samples, the larger E_g values can be explained as a quantum size effect and the confinement of electron-hole pair occurred in the microcrystallites. [19,20]

We finally present, in Fig. 5, the absorption band edge versus the grain size of the samples. For comparative purposes, we have added extra points taken from a previous work where the studied samples (S1, S2), were thermally annealed during 3 hours in an Ar flux.[7] As it can be seen, the observed particle sizes of T1A, T1B, and T0 are almost in agreement with a fitting based on a theoretical inverse square radius versus energy curve given in the figure, and proposed in the mentioned work by Efros *et al*.

The chosen sample S1(60°C) was a mixture of CdTe and CdTeO₃. Thus, the oxygenated surroundings for this Fig. 5. Grain sizes versus energy of samples T, as compared with samples S from a previous work. The solid line is based on a theoretical approximation described in the inset.

sample are similar to T1C and T1D. That would explain the higher than expected energy for these samples. The grain size for the sample S1(80°C) is beyond the exciton Bohr radius. That would explain its mismatch with the theoretical curve

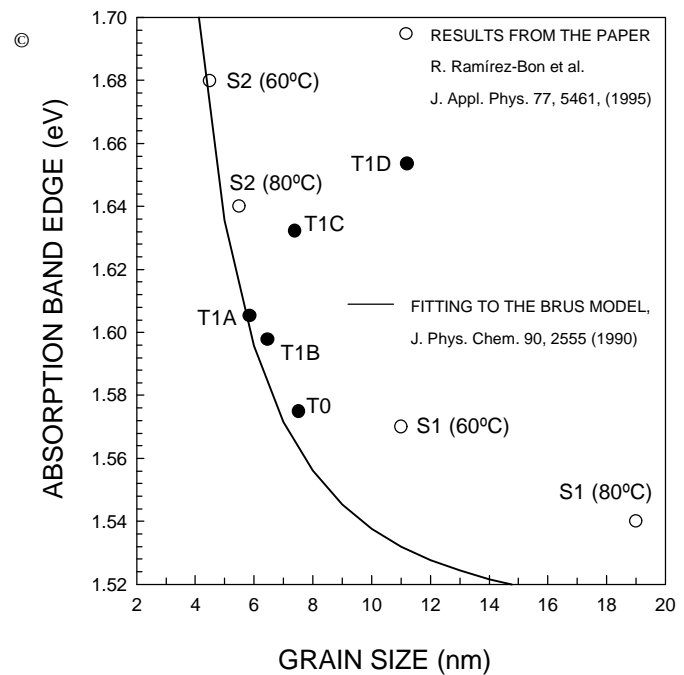


Fig. 5. Grain sizes versus energy of samples T, as compared with samples S from a previous work. The solid line is based on a theoretical approximation described in the inset.

The picture arising from this plot is that while T0, T1A and T1B samples are mostly composed of CdTe crystalline grains, T1C and T1D samples correspond to materials composed of CdTe grains mixed with oxygen atoms and oxide crystallite grains in a strongly stressed environment.

CONCLUSIONS

We have studied the structural data obtained from X-ray and optical absorption pattern of five sputtered CdTe thin films grown in a controlled N-O-Ar, when the substrate is held at 500°C.

Incorporation of oxygen atoms into the CdTe cubic lattice, takes place even when the substrate is maintained at high temperature.

Small amounts of this controlled oxygen incorporation promotes the formation of hexagonal CdTe phase, producing a slight lattice expansion. Also, low oxygen concentrations lead to the formation of Te oxides and the observed energy shift is probably related with this initial structural distortion and phase transformation. Furthermore, the large grain size at large absorption energy could be caused by substitutional incorporation of these Te oxides into lattice sites, as well as the phase transformation.

At larger oxygen concentrations, Te oxides disappear, the CdTe diffraction peaks become broader suggesting that the films are becoming amorphous, and the gap energy shifts to higher energy, revealing a quantum confinement effect due to the smaller particle size.

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