# Thermal Annealing in a-CdTe:O Films

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Oxygenated ainorphous cadmium telluride (a-CdTe:O) films were thermal annealed. The behavior of the film properties for different oxygen contents in the *as-grown* sainples and with different annealing temperatures were studied. The oxygen content in the *as-grown* film Setermines the crystalline structure of the annealed material. The structural changes from amorphous to a inixture of crystalline structures can be observed as the electronic transitions in the absorption coefficient, which are due to either both CdTe and $CdTeO_3$ or $CdTeO_3$ and $CdTe_2O_5$. The structure of the annealed samples is studied by X-ray diffraction, and tlie size of the crystallites are calculated from tlie Scherrer formula. The thermal annealing of tlie films in a flow of inert gas can be assumed as an equilibrium process, therefore the Cd-Te-O ternary phase diagram can be used ill the analysis.

## I. Introduction

Oxygenated amorphous cadmium telluride material (a-CdTe:O) lias been the subject of tlie following recent studies[1-6]. The deposition of an insulating oxide thin filin on a semiconductor can often have practical applications, and here we investigate the importance of this new material. For example, thin insulating oxides of Si and GaAs have been used in metal-insulator-semiconductor (MIS) and semiconductor-insulator-semiconductor (SIS) junctions[7-12]. The kinetic of oxidation of c-CdTe and the chemical composition of the oxide have been described in early work, and found to be that of $CdTeO_3$ [13]. Metal-semiconductor (MS) and metal-insulator-semiconductor (MIS) junctions were fabricated usi ig the thermal oxide $CdTeO_3$ [14]. The possibility of ising a similar material grown by some deposition tecinique instead of the thermal oxidation can increase tlie potential of applications. It lias been shown that the energy gap of the a-CdTe:O films can be controlled in the range of 1.5 to about 3.3 eV, and the electrical resistivity from $10^4$ to $10^{12}$ R-em, by increasing the oxygen concentration in the film from 0 to 60 at. % [5].

In order to have a deeper understanding of oxygenated amorphous films of CdTe, we have investigated the optical and the structural changes of samples of this material after therinal annealing.

## II. Experimental details

We have worked with a set of three samples of a-CdTe:O, (M1, M2 and M3), with three different oxygen contents. The samples were prepared on Corning glass 7059 by a reactive RF sputtering deposition technique in a controlled N-O-Ar plasma[1]. The total gas pressure was 1.0 x $10^{-2}$ Torr for each growth. The oxygen partial pressures were 1.0 × $10^{-4}$, 2.0 × $10^{-4}$ and 5.0 x $10^{-4}$ Torr for the M1, M2 and M3 samples, respectively. The contents of Cd, Te and O of each sample are showed in Table I, which were obtained by Auger electron spectroscopy (AES) using the Wang

Table 1: AES measurements obtained froin the set of as-grown a-CdTe:O sarnples studied.

| SAMPLE | at. % of Cd | at. % of Te | at. % of O |
|--------|-------------|-------------|------------|
| M1 | 33 | 34 | 33 |
| M2 | 22 | 21 | 57 |
| M3 | 12 | 22 | 66 |

sensibilities[13,5]. X-ray diffraction patterns showed the as-grown samples to be amorplious.

The films were thermally aiinealed at 150, 300 and 500°C in an inert argon atmosphere. One different piece of each sample was annealed at each temperature. The annealed samples were analyzed by X-ray diffraction and optical transmission. X-ray diffraction patterns were obtained using a D500 SIEMENS diffractometer (Cu-kα line), and for the optical transmission spectra a Perkin-Elmer lambda 9 spectrophotometer was used.

## III. Experimental results

Fig. 1 shows the absorption spectra obtained from sample M1 as-grown, and thermally annealed (300 and 500°C) samples. The low intensity harmonic features are optical interferences. The spectrum of the as-grown sample shows a slight shoulder at about 2.3 eV, growiiig to a maximum near 3.0 eV. The sample annealed at 300°C has lower absorption in the rniddle portion than the as-grown sample. Near 3.0 eV, the curve grows faster than as-grown sample. After annealing at 500°C, the absorption shows a clear change near 1.5 eV, which is magnified in the inset of the Fig. 1, and may be due to the formation of CdTe crystallites in the film

The spectra corresponding to M2 samples, the as-grown and the annealed at 300 and 500°C, are shown in Fig. 2. All curves peak near 4.0 eV The as-grown and 300°C annealed samples have low harmonic absorption due to interference effects, and have the same shoulders observed in Fig. 1. The sample annealed at 500°C shows an absorption shape different than the other samples. At low energy in the 1.5 eV range there is a little
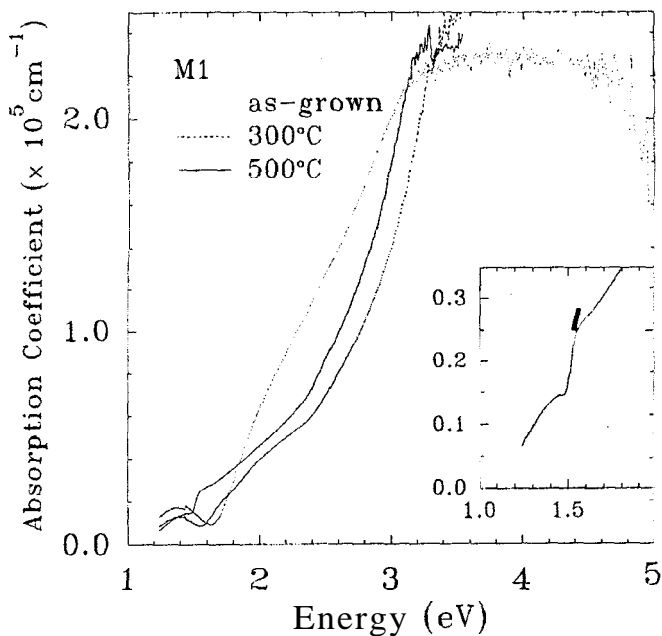
Figure 1. Absorption spectra of a-CdTe:O films, with 33 at. % of oxygen, (M1 samples) *as-grown*, and annealed at 300 and 500°C. The inset of the figure shows the change in the absorption near the energy bandgap of c-CdTe.
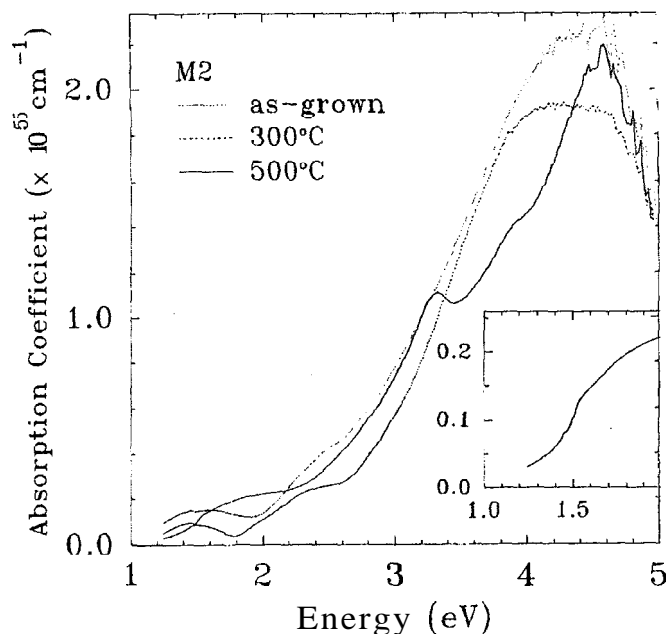
Figure 2. Absoprtion spectra of the a-CdTe:O films, with 57 at. % of oxygen, (M2 samples) *as-grown*, and annealed at 300 and 500°C. The spectrum of the M2 sample annealed at 500°C is similar to c-CdTe at high energies. The inset shows the absorption in the region of the CdTe energy bandgap.
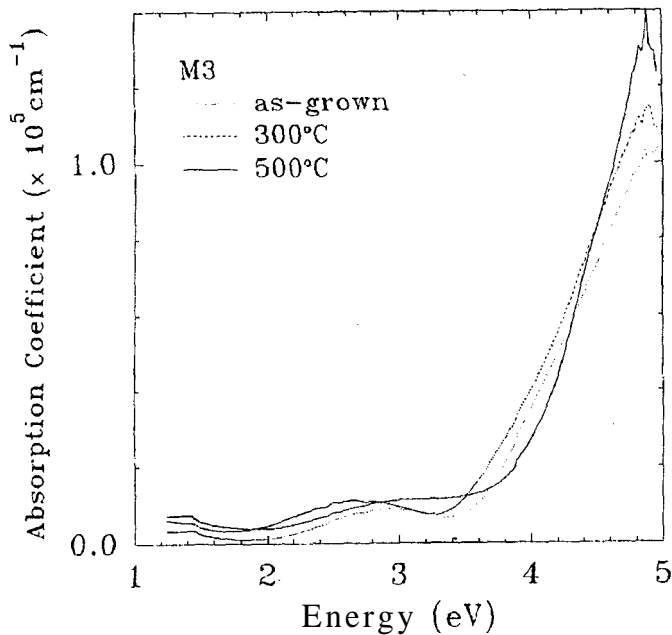
Figure 3. Absorption spectra of a-CdTe:O films, with 66 at. % of oxygen, M3 samples: *as-grown*, and annealed at 300°C and 500°C.



Figure 4. X-ray diffraction spectra of M1 **as-grown** and for 150°C, 300°C and 500°C annealed samples, with **33** at. % of oxygen.

change while in the 3.3 eV range there is a clear shoulder. This shape may be due to the presence of CdTe crystallites, similar to M1. The inset in Fig. 2 shows the mentioned change of the absorption spectrum.

The absorption spectra of the M3 sainples are shown in Fig. 3. The curves corresponding to *as-yrown* and 300°C annealed samples are similar. These absorption spectra have low intensity interferences, and absorption peaks near 4.8 eV. In this figure, the absorption spectrum for the sample annealed at 500°C is different than that of c-CdTe. This behavior can be due to the absence of CdTe crystallites after thermal annealing. The weak absorption at energies lower than 4.0 eV is due to the presence of some crystalline structure with high bandgap enelgy.

X-ray diffraction spectra froin the a-CdTe:O films (M1 samples) are shown in Fig. 4 which shows the structural evolution of the samples with the annealing temperature. The spectrum of tlie glass substrate overlaps tlie diffraction spectra for the *as-grown* and the 150°C arnealed samples. The spectrum for the 300°C annealed sarnple shows the beginning of crystalline CdTe character. The material crystallizes like
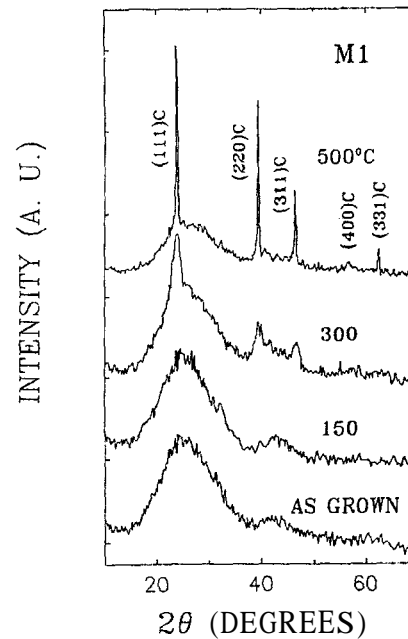
CdTe(15-770: Joint Committee on Powder Diffraction Standards, JCPDS - 1972), showing all the main reflection planes, for the 500°C thermal annealing. From these spectra is possible to obtain an estimation for the CdTe crystallite size, by using the Scherrer formula[15], which gives an error of about ± 10%. The grain size obtained after 300°C annealing is 71Å, and 367Å after the 500°C thermal annealing.

Fig. 5 shows the X-ray spectra of the *as-grown* M2 sample and the M2 samples annealed at 150, 300 and 500°C. Note that only the highest temperature annealing shows crystalline structure. The identified crystalline structure is $CdTeO_3$ (22-129: JCPDS - 1972). Froin Scherrer formula the $CdTeO_3$ estimated grain size estimated is: 37Å. The CdTe signal is not observed over the noise.

X-ray spectra of the M3 samples, *as-yrown* and annealed, are shown in Fig. 6. The sample annealed at 300°C does not show a crystalline signal. The sample annealed at 500°C shows a strong diffraction signal identified as $CdTeO_3$(20-1301: JCPDS-1972) and $CdTe_2O_5$(20-169: JCPDS-1972). The grain size of both materials are similar in the range of 100Å.
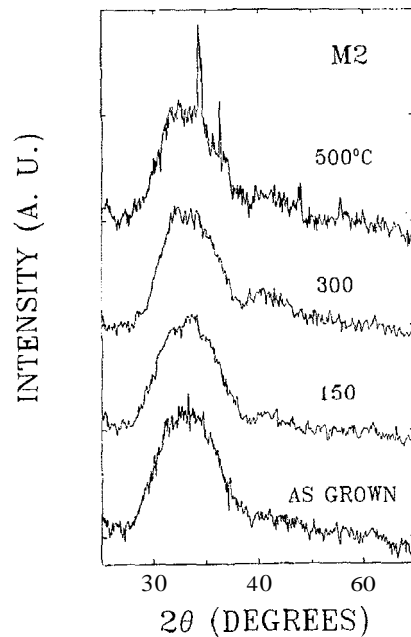
## IV. Discussion and conclusions

We have presented measurements on annealed a-CdTe:O samples with three different oxygen concentrations. From X-ray diffraction we have found that the material crystallizes as CdTe and $CdTeO_3$ for the M1 and M2 samples, and a.s $CdTeO_3$ and $CdTe_2O_5$ for the M3 samples. These results are in agreement with the Cd-Te-O ternary phase equilibrium diagrams[13].

The absorption spectra of the M1 and M2 annealed samples are dominated by the CdTe material. The as-grown M1 and M2 samples are amorphous and have absorption spectra similar to annealed samples. After annealing at 500°C, the M1 and M2 samples have spectra quite similar to c-CdTe[16,17]. One may assume that the absorption of the amorphous material is dominated by low proportions of amorphous CdTe bonding. The $CdTeO_3$ does not affect the spectra because it has an energy bandgap of 4.0 eV[14].

For the M3 samples, the absorption border is shifted to higher energies, unlike M1 and M2 samples. The absorption edge is near the energy bandgap of $CdTeO_3$. After annealing, the absorption spectra have changed little. From the X-ray spectra, it appears that annealed samples at 500°C are a mixture of $CdTeO_3$ and $CdTe_2O_5$ crystallites. The crystallized sample has an absorption spectrum similar to the amorphous structure. We can suppose that the amorphous structure of a-CdTe:O, for high oxygen concentrations, is dominated by bonding like $CdTeO_3$ and possibly by $CdTe_2O_5$ bonding, as well.

## Acknowledgements

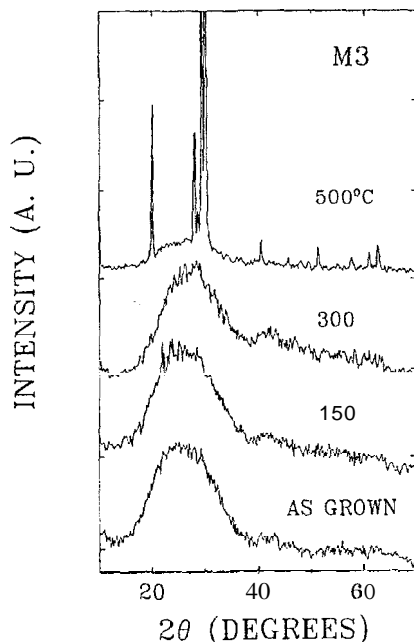Figure 5. X-ray diffraction spectra of sample M2 *as-grown* and for 150°C, 300 and 500°C annealed samples, with 57 at. % of oxygen.



Figure 6. X-ray diffraction spectra of sample M3 *as-grown* and for 150°C 300 and 500°C annealed samples, with 66 at. % of oxygen.

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