

COMMUNICATIONS

Experimental evidence of compositional mixture in CdTeO films grown by radio-frequency sputteringA. Iribarren^{a)}*IMRE, Universidad de La Habana, San Lázaro y L, Vedado, Plaza, Ciudad de La Habana 10400, Cuba*

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An analysis of the absorption spectra of amorphous CdTeO films grown by radio-frequency sputtering has been carried out. The behavior and the shape of the spectra suggest the presence of $\text{Cd}_x\text{Te}_y\text{O}_z$ variable-composition compounds ranging between CdTe and CdTeO with 67 at. % oxygen. We present a model based on bond statistics, which describes the absorption profile behavior of this and other materials with similar optical behavior, and models of the composition of such films. © 1999 American Institute of Physics. [S0021-8979(99)00420-X]

Oxide films have had many practical applications in diverse devices. For instance, Si and GaAs oxides have been used for the fabrication of field-effect transistors¹ and for surface passivation. Likewise, due to the wide energy band gap of semiconductor oxides, they can be considered as absorbent layers even in the ultraviolet spectrum region, and as optical windows for optoelectronic applications.

CdTe oxide can be obtained with a controllable energy band gap available for values higher than 1.5 eV for CdTe (Ref. 2) and up to ~3.8 eV according to the oxygen concentration.¹ However, not much work has been done on this material, and those studies gave its chemical composition inaccurately.

As previous papers^{1,3} have shown, from x-ray photoelectron spectroscopy (XPS) measurements in CdTeO samples grown by radio-frequency (rf) sputtering, the number of Te–O bonds increases, whereas the number of Cd–Te bonds diminishes proportionally. The x-ray diffraction measurements show that the samples become amorphous even for low O concentrations (~5 at. %). On the other hand, only two degrees of oxidation of Te seem to be present, namely, Te^{-2} in CdTe and Te^{+4} in oxygenated CdTe. Some authors have thought that the Te–O bonds are associated with CdTeO_3 ,⁴ and others have suggested the co-existence of

CdTe_2O_5 ,^{5,6} but a material with variable composition has also been proposed.^{1,7}

In this communication we report and analyze the behavior of the optical absorption spectra of CdTeO films grown by rf sputtering as a function of the oxygen content. The shape of the profiles suggests the presence of a mixture of $\text{Cd}_x\text{Te}_y\text{O}_z$ compounds. We present a statistical model of the composition and structure of the amorphous CdTeO films. The model is, in principle, applicable to other amorphous compounds.

The CdTeO films, of 1 cm diameter, were deposited on Corning 7059 glass slides by rf reactive sputtering using a 2 in. diam CdTe target with 99.99 at. % purity in an argon-nitrogen oxide atmosphere. The base pressure was 1.5×10^{-6} Torr and the gases used were Ar from Linde with 99.999 at. % purity and N_2O from MG Industries with 99.999 at. % purity. The total pressure in the chamber was 1×10^{-2} Torr. The N_2O partial pressure was varied between 8×10^{-6} and 9×10^{-4} Torr in order to vary the O concentration. The substrates were placed 8 cm from the target, and heated at 50 °C during the process. The rf power was 30 W.

The absorption spectra were obtained by the transmission spectroscopy technique using a system composed of a continuum-spectrum white light source, focusing lenses, a chopper, a Lomo MDR-23 monochromator coupled with a SR 510 lock-in amplifier, and a computer for process controlling and data recording.

Figure 1 shows the behavior of the optical absorption

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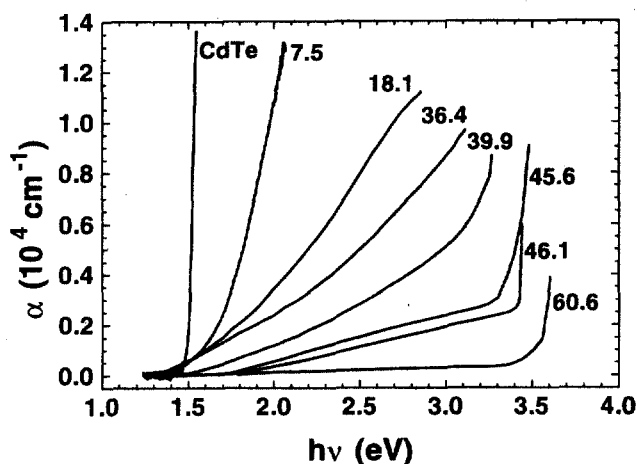


FIG. 1. Behavior of optical absorption profiles as a function of the photon energy for different oxygen concentrations in the sample. The values near each curve correspond to O concentration in at. %.

spectra of CdTeO samples with different O concentrations at 300 K. For the sake of comparison, a spectrum of a CdTe polycrystalline sample is also plotted. The spectra exhibit extended "tails," which increase in the range of 1.4–3.6 eV.

In polycrystalline CdTe the profile is relatively sharp, however, the CdTeO profiles vary more gradually and soften the sharpness of the absorption edge region as the O content increases. For higher O content the profiles maintain the tail, but with low absorption values, and a pronounced increase appears again at higher energies. For samples of about 60 at. % O, the tail values are very low and the profile increases sharply at $h\nu \approx 3.6$ eV.

Such behavior has also been observed, not only in this material,⁸ but also in CdPbO (Ref. 9) and in CdSTe,¹⁰ unlike the typical tails of amorphous or disordered compounds such as chalcogenide glasses and hydrogenated silicon, which extend no farther than 500 meV below the absorption edge.¹¹ This indicates that we are not in the presence of band tails due to disorder, but, in fact, of a mixture of $Cd_xTe_yO_z$ -type compounds that was previously suggested in this material^{1,12} and in CdSTe.¹⁰ At low O concentrations the dominant material is CdTe, and the mixture arises as the O content increases up to high values at which only one material seems to dominate again.

We propose that the CdTeO material is composed of $Cd_xTe_yO_z$ clusters or molecular subunits with different degrees of polymerization ($PD=y$). The polymerization defines the amount of structural TeO_4 present in each molecular subunit.¹³

In the formation of oxygenated CdTe, the presence of basic subunits of TeO_4^{-4} is expected. Te–O bonds structurally form a polyhedron, which shows a tendency to be distorted in tellurite compounds. These primary structural fragments are classified into a TeO_4 trigonal bipyramid (tbp) and a TeO_3 trigonal pyramid (tp).¹⁴ In TeO_2 glasses, most of the tellurium atoms form TeO_4 tbps which are connected by Te– O_{eq} and Te– O_{ax} –Te linkages,¹⁴ in which one tellurium atom is surrounded by two oxygen atoms at axial positions (O_{ax}) and by two oxygen atoms at equatorial positions

TABLE I. CdTeO compounds with the smallest atom amounts.

x	y	z	$k=x+y+z$	r_j
1	1	3	5	0.60
2	1	4	7	0.571
1	2	5	8	0.625
3	1	5	9	0.555
4	1	6	11	0.545
1	3	7	11	0.636

(O_{eq}). A lone pair of electrons occupies a third equatorial position.¹⁵

In our compositional mixture model the number of O atoms belonging to $PD \geq 1$ TeO_4 clusters is given by $z=3y+1$, and the cluster valence is $v=4y-2(3y+1)=-2y-2$. We have not allowed TeO_3 subunits in our model since most of the tellurium atoms form TeO_4 tbps,¹⁴ which can be linked to Cd cations or to other TeO_4 tbps through O bridges. In this way the $Cd_x^{+2}Te_y^{+4}O_z^{-2}$ molecular subunits are formed. On the other hand, the valence balance imposes the condition $2x+4y-2z=0$. Thus we have an indeterminate equation in integers (Diophantine equation) for x , y , and z .

The O concentration of each compound is given by $r_j = z/(x+y+z)$. Thus

$$y = \frac{2r_j - 1}{2 - 3r_j} x \equiv f(r_j)x, \quad (1)$$

where j identifies each compound, and $0 \leq f(r_j) < \infty$, from where $0.5 \leq r_j < 0.67$. The numbers of Cd (X) and Te (Y) atoms in the plasma are equal, since the cathode is of stoichiometric CdTe, while the number of oxygen (Z) atoms varies according to the partial pressure of the gas containing it. Hence, the atom source with N atoms that participates in the process fulfills $Z=rN$, and $X=Y=(1-r)N/2$.

In order to obtain the possible compounds, the z values were modified, and x was allowed to range between 1 and $(z-1)$. The first x , y , and z values obtained under such conditions are shown in Table I. The oxygen concentration is also shown.

The probability of formation of compounds with $PD \geq 1$ can be calculated by a combinatorial analysis, and is given by

$$P_{xyz} = \frac{C_{2x}^X C_y^Y C_{3y+1}^Z}{C_{2x+4y+1}^N}. \quad (2a)$$

Hence,

$$P_{xyz} = \frac{(2x+4y+1)!}{(2x)!y!(3y+1)!} r^{3y+1} \left(\frac{1-r}{2}\right)^{2x+y}, \quad (2b)$$

where C_u^v is the number of combinations of v objects taken u at a time.

Figure 2 shows the probability of formation of the most probable $Cd_xTe_yO_z$ compounds normalized to Cd_2TeO_4 . The probability distribution diminishes as the unit size increases. The other most probable compounds are $CdTeO_3$ and $CdTe_2O_5$. The latter compound is precisely the one formerly proposed to exist in CdTeO, as mentioned above. However,

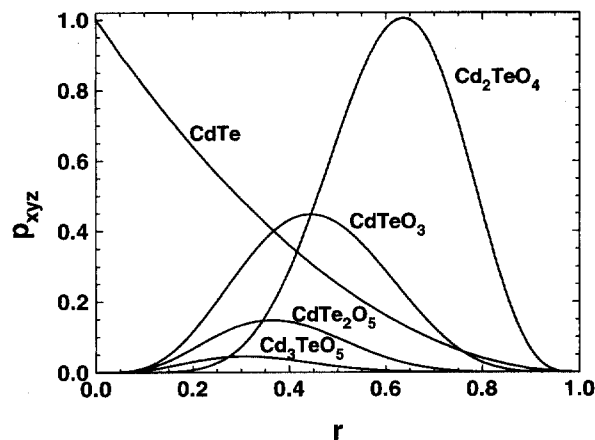


FIG. 2. Comparison of the most probable CdTeO compounds normalized to Cd_2TeO_4 .

no work has unequivocally demonstrated which compound really dominates or exists. Taking into account the fact that the probability of formation for Cd_2TeO_4 is larger than that for CdTeO_3 and CdTe_2O_5 we propose that it is a significant compound in highly oxygenated CdTeO samples. The compound Cd_2TeO_4 , whose molecular subunit is $\text{Cd}_4\text{TeO}_4^{+4}$, is a TeO_4 compound with the four O atoms bound to Cd atoms. This compound has never been considered in CdTeO thin films. Moreover, the probability of forming CdTe is found to be higher than for any compound of CdTeO. However, in a previous report¹⁶ it was proved that a major reactivity in the reaction of Te and O forms Te–O bonds with the highest bond enthalpy,¹⁷ and consequently the most stable. Hence, TeO_4 structures are favored and they dominate over CdTe and CdO. That primary structure rules the formation of the films in competition with CdTe formation according to the plasma composition.

$\text{Cd}_x\text{Te}_y\text{O}_z$ clusters can share some O atoms with either neighboring structures or Cd atoms. Moreover, binding of a CdTeO subunit with CdTe molecular subunits is also possible through Cd bridges. Thus, multiple combinations of bonds among different subunits form $\text{Cd}_{x+n}\text{Te}_{y+n}\text{O}_z$ -type microclusters with $r_j = z/(x+y+z+2n)$, where n is the number of CdTe subunits. The units formed are repeated randomly in the material and have different characteristics. Therefore, the energy band gap has local values and fluctuates spatially.

The fact that TeO_4^{-4} rules the formation of the film explains the amorphization even for low O concentrations, although variation of the local atom coordination also contributes. Compositional variation must be expected in compounds with three or more elements, in which there exist several forms of binding. This trend will be moderated by growth conditions.

The absorption coefficient can be proved to be the sum of the contributions of each $\text{Cd}_{x+n}\text{Te}_{y+n}\text{O}_z$ unit, i.e.,

$$\alpha = \sum_j \delta V_j \alpha_j, \quad (3)$$

where α_j is the absorption coefficient of each compound j , and δV_j is the volume fraction of the compound j in the sample and is given by $R p_{xyzn}$. R is a factor related to the reactivity of the species, and p_{xyzn} is the probability of formation of a j unit.

In conclusion, from the behavior and shape of the absorption spectra of CdTeO samples we infer that the films are formed of $\text{Cd}_x\text{Te}_y\text{O}_z - (\text{CdTe})_n$ molecular units. We presented a statistical model that justifies it, explains previous results, and gives the Cd_2TeO_4 compound as very probable in highly oxygenated samples. We proposed the composition dependence of the absorption coefficient in such materials.

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