CdTe oxide films grown by radio frequency sputtering utilizing argon–nitrous oxide plasma

A. Zapata-Navarro, M. Zapata-Torres, Victor Sosa, P. Bartolo-Perez, and J. L. Peña
Department of Applied Physics, CINVESTAV-IPN, Unidad Mérida, A. P. 73 Cordemex, Mérida Yuc., 97310, México

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Cadmium telluride oxide films (CdTe:O) were grown by a radio frequency sputtering technique using a controlled plasma (Ar–N_2O) on glass slide substrates. The films were studied by Auger electron spectroscopy, x-ray photoelectron spectroscopy, and x-ray diffraction. We demonstrate that with N_2O the oxidation process occurs in a narrow range of partial pressures of nitrous oxide. We find that the films are amorphous and the amount of oxygen incorporated in the films depends on the N_2O partial pressure and saturates at about 55 at. % oxygen. As the amount of oxygen increases the number of Te–O and Cd–O bonds increases. The compounds formed depend on the partial pressure of the N_2O and are of the form $Cd_xTe_yO_z$. When saturation of oxygen is obtained the compound formed is probably $CdTe_2O_5$.

NTRODUCTION

Oxide films have practical applications, e.g., Si and GaAs oxides have been used in metal/insulator/semiconductor and semiconductor/insulator/semiconductor devices.[1–5] The surface passivation of III–V and II–VI semiconductors has been a major problem in the fabrication of devices. Nitrous oxide (N_2O) has been employed as an excellent oxidizing agent; e.g., silicon dioxide films were prepared by photolysis of disilane (Si_2H_6) with N_2O,[6] by plasma-enhanced chemical vapor deposition (PECVD) using a gaseous mixture of silane (SiH_4) and N_2O,[7] and by downstream microwave plasma-enhanced chemical vapor deposition using a gaseous mixture of tetraethoxysilane (TEOS) and N_2O.[8] And recently an oxidation process in hydrogenated amorphous silicon (*a*-Si:H) using nitrous oxide (N_2O) plasma has been developed.[9]

CdTe oxide can have many practical applications, and there have been many studies of oxide formation on CdTe and Hg_xCd_yTe surfaces.[10–17] The growth of CdTe oxide films is possible by rf sputtering deposition with a controlled asma (Ar–O–N).[18] In this work we have grown CdTe oxide films using rf sputtering deposition with a controlled plasma (Ar–N_2O). The concentration of elements was determined by Auger electron spectroscopy (AES) and the chemical bonding was determined by x-ray photoelectron spectroscopy (XPS). We found that films are amorphous by x-ray diffraction (XRD).

II. EXPERIMENTAL DETAILS

The films were deposited on Corning 7059 glass slides by magnetron rf sputtering using a CdTe target with 99.99 at. % purity in an argon–nitrous 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. A series of 10 samples were grown with the total pressure in the chamber at 1×10^{-2} Torr; the N_2O partial pressure was varied in the range from 8×10^{-6} to 9×10^{-4} Torr. The substrate was kept at room temperature and the rf power was 30 W. Before the deposition, the target was sputter-cleaned for 15 min. The growth times were 20 min.

AES and XPS analysis were performed in a Perkin-Elmer PHI 560/ESCA-SAM system, with a base pressure of approximately 2×10^{-9} Torr. AES spectra were obtained with a 2 keV electron beam with typically 0.2 μA current incident at 60° to the surface normal in the E*N(E) mode and numerically differentiated using a 5 point convolution. No further smoothing of the signal was attempted. A scanning step of 0.5 eV/step with an interval of 50 ms was utilized. Under these conditions, the instrumental resolution width, W_r, and the natural width, W_i, for all the elements measured, had a ratio $W_r/W_i<0.3$. For determining atomic concentrations we obtained sensitivity factors for Cd, and Te from a CdTe polycrystal with 99.99 at. % purity from Balzers and for O from CdO mesh with 99 at. % purity from Merck. These results are $S_{Cd}=1$, $S_{Te}=0.68$, and $S_O=0.26$. All Auger measurements were obtained in the scanning mode on three different points of each sample, and from average values, the composition was determinated. XPS and x-ray AES spectra were done in the XPS mode; the x-ray target employed was a Mg anode with a characteristic x-ray energy of 1253.6 eV. XPS and x-ray AES spectra were obtained under two different conditions: (i) a survey spectrum mode in which the spectral resolution was 0.5 eV, and (ii) a multiplex repetitive scan mode in which the resolution was increased to 0.2 eV. Cleaning of the surface prior to both measurements was done with Ar^+ sputtering during 5 minutes with a beam energy of 4 keV and a beam current of 0.36 $\mu A/cm^2$.

The x-ray spectra were measured by using a Siemens D500 diffractometer. The source was Cu (K_α, $\lambda=0.154\,06$ nm).

III. RESULTS AND DISCUSSION

The 10 films deposited for various partial pressures of N_2O have different colors; the films show a change in color from dark gray to pale yellow as the oxygen content increases up to about 52 at. %. When the sample is saturated

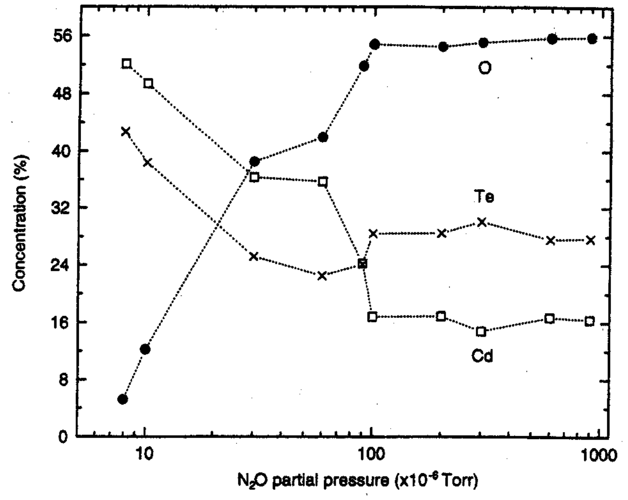

FIG. 1. Atomic concentration in the CdTe:O samples as measured by AES vs N_2O partial pressure.

with oxygen (at about 55 at. %) it is transparent like a glass. In all samples the x-ray diffraction patterns show an amorphous character with the incorporation of oxygen in the CdTe lattice. The films are completely amorphous maybe as a consequence of a homogeneous mixture of the three elements present, indicating the absence of segregated phases. In Fig. 1 we show the results from AES analysis for the atomic concentration of detected elements as a function of the N_2O partial pressure. As the N_2O partial pressure increases from 8×10^{-6} to 6×10^{-5} Torr, the concentration of oxygen increases while Te and Cd decrease, with the amount of Cd greater than Te. At an N_2O partial pressure of 9×10^{-5} Torr, the oxygen continues increasing and the amount of Cd and Te become equal. At an N_2O partial pressure of 1×10^{-4} Torr and up the samples are saturated with oxygen (about 55 at. %). The concentration of Cd and Te remain stable, and the concentration of Te is greater than Cd. We cannot grow a film with more oxygen, as shown in Fig. 1.

Additionally, a film was grown without N_2O. This film is CdTe with 47.8 at. % Cd, 48.5 at. % Te, and 3.6 at. % O. This film is polycrystalline with two different phases, cubic and hexagonal, giving evidence that the presence of oxygen induces structural changes disordering the original lattice.

In order to analyze the nature of the bonding of Cd, Te, and O atoms in the films these were studied by XPS and x-ray AES. We are interested in the qualitative and quantitative nature of bonding of the three elements. Figure 2 shows the multiplex scans for the films grown with different N_2O partial pressures, for the Te $3d_{5/2}$ and $3d_{3/2}$ features. From the literature,[19,20] we associated the peaks with chemical states of Te. In this case, a chemical shift of about 3.2 eV between the Te–Cd in the semiconductor and Te–O in the anodic oxide allows the two states to be measured independently, based on previously reported XPS studies of Te–Cd bonding in CdTe and Te–O bonding in TeO_2, TeO_3, Na_2TeO_4, etc.[19,20] In Fig. 2 we show the spectral changes in the Te $3d_{5/2}$ and Te $3d_{3/2}$ features for the different partial pressures of N_2O and we present the oxygen concentration for the films. In this figure the peaks related to Te–Cd bonds decrease and the peaks related to Te–O bonds increase with the partial pressure of N_2O. At a partial pressure of 1×10^{-4} Torr the Te–Cd bonds disappear and the films only contain Te–O bonds.

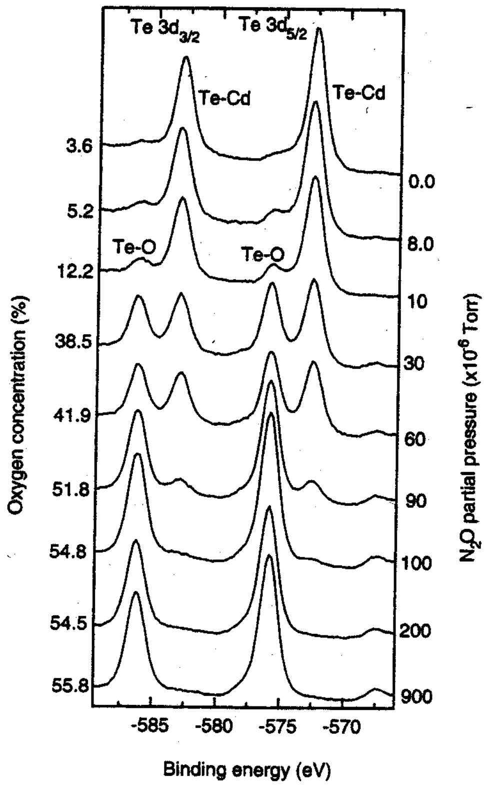

FIG. 2. Te 3*d* XPS spectra vs oxygen concentration and N_2O partial pressure for CdTe:O.

In order to analyze the quantitative nature of bonding of Te, we fitted a gaussian curve to the Te $3d_{5/2}$ peaks and estimated the amount of Te–Cd and Te–O bonds from the percent of the area of each peak (Te–Cd and Te–O) in the Te $3d_{5/2}$ peaks. The variation of content of Te–Cd and Te–O bonds with the oxygen concentration is shown in Fig. 3. This figure shows that when the oxygen increases from about 5 to about 42 at. %, the Te–Cd bonds decrease from ~84 to ~48 at. % and Te–O bonds increase from ~12 to ~52 at. %. For an oxygen concentration ~52 at. %, Te–Cd bonds are ~9 at. %, and Te–O bonds are 81 at. %. At an oxygen concentration ~55 at. % there exist only Te–O bonds.

Figure 4 shows the Cd $M_4N_{45}N_{45}$ and $M_5N_{45}N_{45}$ x-ray AES features (i.e., x-ray induced Auger transitions involving the *M* and *N* levels of Cd). We studied these features instead of XPS features because the splitting between Cd–Te and Cd–O core levels, as revealed in the XPS spectra, is considerably smaller than the splitting between the Te–Cd and Te–O satellite components of the core levels.[19,20] We do not find any oxide-induced doublet structures, possibly because we do not have sufficient resolution in the PHI 560 instrument to resolve them, and as such we have used x-ray AES features to discriminate between Cd–Te and Cd–O bonding.[15–17] The Cd *MNN* x-ray AES features are at different energies for Cd–Te and Cd–O bonding in CdTe and CdO

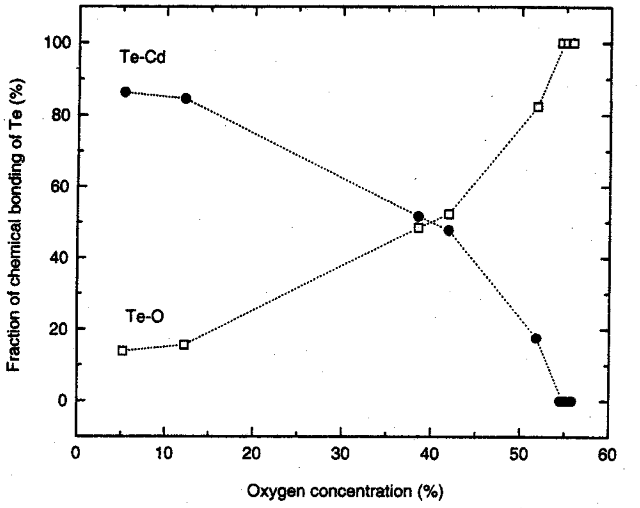

FIG. 3. Fraction of Te–Cd and Te–O bonds in CdTe:O samples vs oxygen concentration.

or $CdTeO_3$, respectively.[15–17,19,20] The Cd *MNN* x-ray AES features do not display a distinct doublet for Cd–Te and Cd–O bonding as do the Te XPS features for Te–Cd and Te–O bonding. Instead, these features shift in energy and change in shape as a transition occurs between Cd–Te and Cd–O bonding. The Cd *MNN* x-ray AES features in the Fig. 4 show a shift in energy of about 1 eV, and change in shape with the partial pressure of N_2O. This change occurs for a N_2O partial pressure from 8×10^{-6} to 9×10^{-5} Torr and the shape is similar to the spectrum of tellurite in the monotellurite reported by Davis *et al.*[16] At N_2O partial pressures from 1×10^{-4} to 9×10^{-4} Torr the energy and shape of the Cd *MNN* x-ray AES features are constant. The total shift of this Cd *MNN* x-ray peak is about 1 eV and this change is related to the change in Cd bond from Cd–Te to Cd–O.[17,19,20]

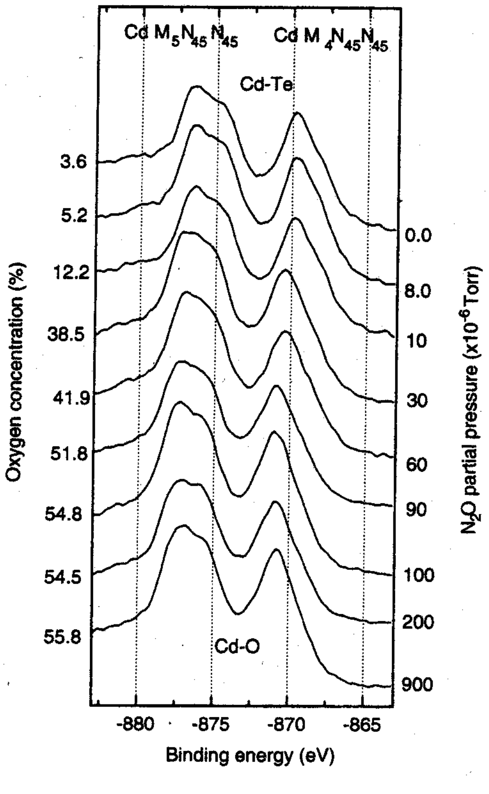

FIG. 4. Cd *MNN* x-ray AES spectra vs oxygen concentration and N_2O partial pressure for CdTe:O.

The N_2O partial pressure modifies the concentration of the elements in the films, resulting in three regions. At a partial pressure of N_2O of 8×10^{-6} Torr, the film has about 5 at. % oxygen; this oxygen is sufficient for the film to become amorphous. The amount of Cd is about 52 at. % and Te is about 43 at. %, so we conclude that the oxygen was incorporated in the film substituting for Te. At N_2O partial pressures from 8×10^{-6} to 6×10^{-5} Torr, the amount of O increases while Te and Cd decrease with the N_2O partial pressure, as shown in Fig. 1. Figure 2 shows that Te–O bonds increase considerably with partial pressure of N_2O, and at 6×10^{-5} Torr the peaks related to Te–O bonds are bigger than those for Te–Cd. In this region, as we pointed out earlier, the content of Te–Cd bonds decreases from ~84 to ~48 at. % and Te–O bonds increase from ~12 to ~52 at. %. Figure 4 shows that the Cd *MNN* x-ray AES feature shifts gradually to higher binding energies and changes in shape; we attribute the change to the transition between Cd–Te and Cd–O bonding.[17] This leads us to propose formation of a ternary material with the chemical formula $Cd_xTe_yO_z$, and not $(CdTe)_{1-x}O_x$, as suggested by Espinoza-Beltrán *et al.*[21] When the partial pressure of N_2O increases the oxygen incorporation into the CdTe lattice involves substitution of both Cd and Te, with a preference to substitute for Te in the lattice.

At an N_2O partial pressure of 9×10^{-5} Torr the concentrations of the elements are about 24 at. % for Cd and Te, and about 52 at. % for the oxygen; in this film the Te–O bonds are more common than the Te–Cd bonds (about 80 at. % of the Te bonds are Te–O). This behavior suggests that there exists a transition region. The phase diagram of the Cd–Te–O system by Helms[22] indicates that at these concentrations the oxide would consist of a mixture of CdTe and $CdTeO_3$ at equilibrium, and not a mixture of TeO_2 and CdO. Accordingly we propose that this film is basically $CdTeO_3$ with residual CdTe, having the short-range order of the amorphous state. The films are pale yellow in color, in accord with a crystal of $CdTeO_3$ reported by Robertson *et al.*[23]

At an N_2O partial pressure 1×10^{-4} Torr, the oxygen concentration reaches saturation. The concentration of Te in these films is twice the concentration of Cd and the concentration of O is about four times the concentrations of Cd. We pointed out earlier that the concentration of elements was obtained utilizing Auger sensitivity factors from CdTe and CdO and not from a ternary compound like $CdTeO_3$ or $CdTe_2O_5$. Such saturation can be understood because the film forms a material with maximum oxygen content like $CdTe_2O_5$. The Te–Cd bonds disappear and the Cd *MNN* x-ray AES feature shifts about 1 eV and changes shape from the Cd *MNN* x-ray AES feature of the film grown without N_2O. This shape is similar to that reported for $CdTeO_3$ by Davis *et al.*[16] The phase diagram of the $CdO–TeO_2$ system by Robertson *et al.*[23] indicates that at these concentrations of Cd, Te, and O, the oxide would consist of a mixture of $CdTeO_3$ and $CdTe_2O_5$ in equilibrium. Accordingly, we propose that the material grown in these films is basically $CdTe_2O_5$ in an amorphous state. This oxide was reported by Davis *et al.*[16] in anodic oxide on $Hg_{0.8}Cd_{0.2}Te$.

IV. CONCLUSIONS

In this article we have shown that *a*-CdTe:O films can be grown by rf sputtering with a controlled plasma ($Ar-N_2O$). The film growth depends on the partial pressure of N_2O. There are three regions. (i) At a partial pressure of N_2O from 8×10^{-6} to 6×10^{-5} Torr the oxygen content increases, and the Cd and Te content decreases, showing that there is a substitution of Cd and Te by O in the original CdTe lattice. The effect of introducing oxygen is the generation of strong structural deformation in the lattice due to the small oxygen atomic size and high reactivity with cadmium and tellurium [illegible]sulting in shorter bonds in the amorphous state as those in [illegible]e crystalline lattice. The resulting material is an amorphous homogeneous mixture that can be represented by chemical formula $Cd_xTe_yO_z$. (ii) At a partial pressure of N_2O of 9×10^{-5} Torr the oxygen concentration continues increasing and Cd and Te concentrations are equal, and it is concluded that the material formed is basically *a*-$CdTeO_3$. (iii) At 1×10^{-4} Torr the oxygen concentration reaches saturation and the material obtained is basically *a*-$CdTe_2O_5$.

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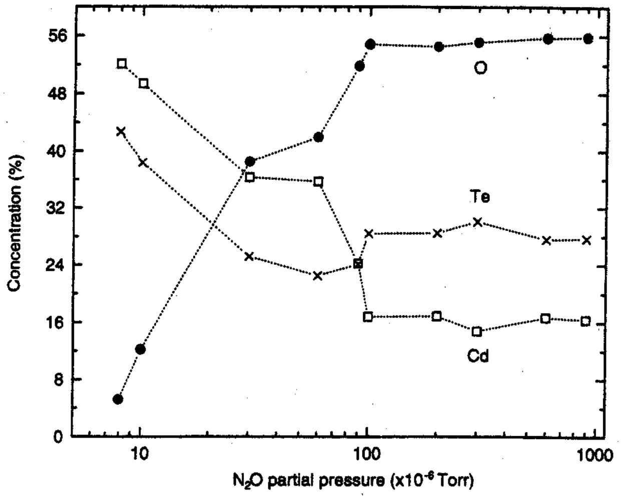

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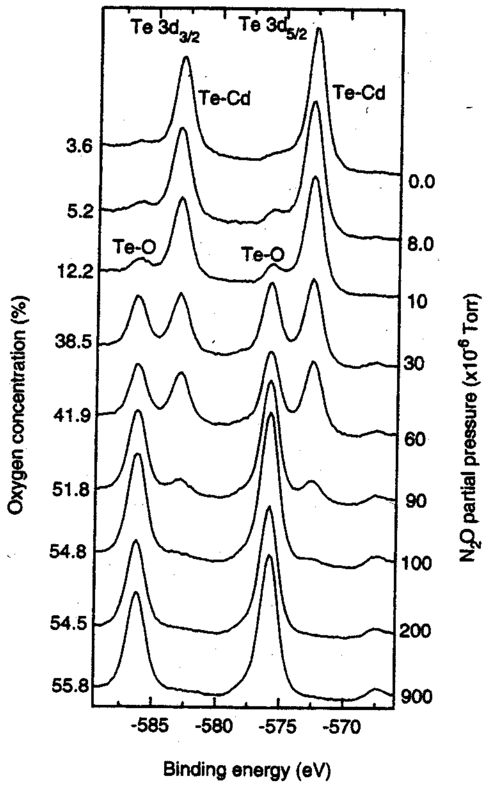

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