

XPS analysis of oxidation states of Te in CdTe oxide films grown by rf sputtering with an Ar-NH₃ plasma

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Using rf-sputtering, CdTe oxide films were grown on glass substrates in a controlled plasma of Ar-NH₃. The elemental concentration and oxidation state of Te were determined by x-ray photoelectron spectroscopy. When the NH₃ partial pressure increases from 3×10⁻⁶ to 1×10⁻⁴ Torr, the relative atomic concentration of oxygen incorporated in the films increases, whereas those of Cd and Te decrease. For the NH₃ partial pressures of 6×10⁻⁶ Torr and smaller than 7×10⁻⁵ Torr, in films of CdTe oxide coexist different oxidation states of Te, Te⁻² as in CdTe and Te⁺⁴ as in CdTeO₃. While that for NH₃ partial pressure of 1×10⁻⁴ Torr and up, the films only contain the oxidation state Te⁺⁴. With x-ray diffraction it is observed that when the NH₃ pressure increases the oxide films of CdTe become amorphous.

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1. Introduction

Recently proposed practical applications, such as the fabrication of high efficiency solar cells [1], have motivated several studies about the formation of oxides of CdTe [2-7]. It has been shown that the relative atomic concentration of the resulting oxide thin films can vary considerably depending on the oxidation conditions. Reactive radio frequency (rf) sputtering has been widely used for CdTe oxide (CdTe:O) films deposition using Ar-O₂-N₂ [4-5] and Ar-N₂O plasmas [6,7]. Oxidation of CdTe is more efficient with Ar-N₂O than with Ar-N₂-O₂ plasma. Although nitrogen is one of the components of the plasma, incorporation of nitrogen in the prepared CdTe films has never been reported. The role of nitrogen is to catalyze the oxidation of CdTe incorporating oxygen from the plasma. In this work, we prepared a set of CdTe:O thin films by means of rf sputtering varying the pressure of an Ar-NH₃ plasma. The saturation of oxygen is reached when the amount of nitrogen (or NH₃) introduced is sufficient to react with all the residual oxygen in the vacuum chamber. The chemical composition and chemical bonding were determined by x-ray photoelectron spectroscopy (XPS), while the crystallographic structure of the samples was studied by x-ray diffraction (XRD).

2. Experimental Details

A set of CdTe:O films were prepared in a sputtering system equipped with a magnetron and an rf source from

Advanced Energy Products, with a maximum output power of 600 W. We used a 2" CdTe pressed target 99.999 at. % purity (Cerac). As working gases we used Ar 99.999 at. % (Linde) and NH₃ 99.9 at. % (Air Products). Films were deposited on corning glass slides 13×13 mm, degreased and ultrasonically cleaned. Deposition time was 90 minutes and substrate temperature was kept constant at 50 °C. Film deposition was performed after a system base pressure of ~ 3×10⁻⁶ Torr was reached. The total working gas pressure in the vacuum chamber was 2×10⁻² Torr; introducing initially a partial pressure of NH₃, from 3×10⁻⁶ Torr up to 1×10⁻⁴ Torr, and filling up the rest with Ar. Before deposition the target was sputtered in the reactive atmosphere for 10 min. XPS analyses were performed in a Perkin-Elmer PHI 560/ESCA-SAM system, equipped with a double-pass cylindrical mirror analyzer, with a base pressure of 1×10⁻⁹ Torr. Argon ion sputtering was performed with 4 keV energy ions and 0.36 μA/cm² current beam, yielding to 3 nm/min sputtering rate. XPS spectra were obtained after 5 min of Ar⁺ sputtering. For the XPS analyses, samples were excited with 1486.6 eV energy AlK_α x-rays. XPS spectra were obtained under two different conditions: (i) a survey spectrum mode of 0-1150 eV, and (ii) a multiplex repetitive scan mode. The spectrometer was calibrated using the Cu 2p_{3/2} (932.4 eV) and Cu 3p_{3/2} (74.9 eV) lines. Binding energy calibration was based on C 1s at 284.6 eV.

The crystallographic structure of the samples was studied by XRD by means of a Siemens D5000 system operating at 40 kV and 35 mA, using the grazing incidence technique.

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3. Results and Discussion

With increasing ammonia partial pressure, there is a gradual change in color from dark gray to pale yellow to transparent, as the oxygen content increase. The film obtained presents thicknesses between 0.8 and 1.5 μm ; it decreases when the partial pressure of NH_3 increases. In Figure 1 (left), XPS survey spectra for the samples A1, A4, A5 and A9 as a function of NH_3 partial pressure are presented. In this figure, the Te $3d_{3/2}$ (586 eV), Te $3d_{5/2}$ (576 eV), O 1s (533 eV), Cd $3d_{3/2}$ (415 eV) and Cd $3d_{5/2}$ (409 eV) core level principal peaks can be observed. Also, the Cd_{Auger} (1113 eV), Te_{Auger} (1009 eV), O_{Auger} (978 eV), Te $3p_{1/2}$ (873 eV), Te $3p_{3/2}$ (823 eV), Cd $3p_{1/2}$ (656 eV), Cd $3p_{3/2}$ (621 eV), Te $4d_{5/2}$ (44 eV) and Cd $4d_{5/2}$ (15 eV) peaks notice an increase in the O 1s peak as a function of the NH_3 partial pressure.

Relative atomic surface concentrations were determined using the integrated area under Cd ($3d_{5/2}$), Te ($3d_{5/2}$) and O (1s) principal peaks and a formula for quantification [8]. The Te ($3d_{5/2}$) transition presents an additional peak at higher binding energy related to oxygen in the sample. Different relative sensitivity factors (RSF) were obtained for each contribution of the Te ($3d_{5/2}$) peaks. For Te ($3d_{5/2}$) bonded to Cd, Te-Cd, we used a RSF of $S_{\text{Te}} = 1.55$, as obtained from polycrystalline CdTe, while for Te ($3d_{5/2}$) bonded to oxygen, Te-O, we utilized a RSF of $S_{\text{Te}} = 1.31$, as obtained from a CdTeO_3 standard [9]. The variation of the RSF of Te is attributed to the difference in oxidation

state of this element, which goes from Te^{-2} in CdTe up to Te^{+4} in CdTe_3 . We also used a RSF of Cd ($3d_{5/2}$) of $S_{\text{Cd}} = 1$ and a RSF for O (1s) of $S_{\text{O}} = 0.15$, obtained also from a CdTeO_3 standard. Both contributions of Te (Te-Cd and Te-O) were added together to obtain a total relative atomic concentration of Te. Results of these calculations of quantification are presented in Table I (columns 3, 4 and 5). As the NH_3 partial pressure increases from 3×10^{-6} to 3×10^{-5} Torr, the relative atomic concentration of O increases smoothly while those of Cd and Te decrease, with the Cd concentration slightly higher than that for Te. At NH_3 partial pressure of 5×10^{-5} Torr, the concentration of O starts to level off at about 62 at. %, indicating saturation of O. In previous works [4,6], CdTe:O films were grown by rf sputtering technique using a controlled plasma of Ar- O_2 - N_2 [4] and Ar- N_2O [6] and the calculated Cd, Te and O relative atomic concentrations were obtained utilizing AES measurements.

Unfortunately, quantification by AES is inconvenient for Te since it is not correct to use a single S_{Te} when it is in different oxidation states, as has been recently demonstrated using standard compounds [7,9]. The Auger S_{Te} changes by about 30 % when the oxidation state of Te varies from Te^{-2} in CdTe to Te^{+4} in CdTeO_3 [9]. However, in our case, as presented in Table I for all NH_3 partial pressures, the relative atomic concentration of Te presents a value close to the corresponding Cd concentration, since the utilized target is a high purity CdTe pressed powder.

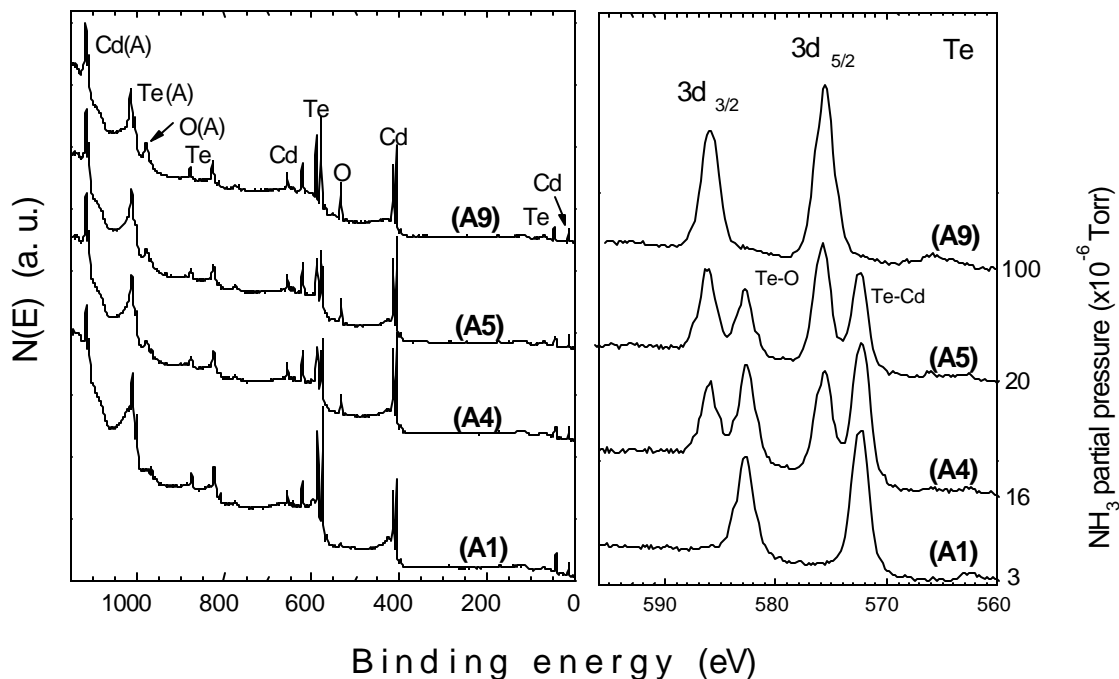


Figure 1. XPS survey (left) and Te 3d (right) of CdTe oxide grown with different NH_3 partial pressures.

Table 1. Relative atomic concentration and percentage bonds in CdTe oxide grown with different NH₃ partial pressures.

Sample	NH ₃ Pressure ($\times 10^{-6}$ Torr)	Relative atomic concentration (%)			Percentage of bonds	
		Cd	Te	O	Te-Cd (Te ⁺⁴)	Te-O (Te ⁻²)
A1	3	42.6	43	14.6	96	4
A2	6	35.7	33.5	30.8	85.6	14.4
A3	8	31.7	30	38.4	78	22
A4	16	28.3	23.7	48	51.9	48.1
A5	20	26.6	21.3	52.1	39	61
A6	30	23.2	19.5	57.3	17.4	82.6
A7	50	22	16.5	61.5	7.9	92.1
A8	70	21.1	16.7	62.2	6.6	93.4
A9	100	19.2	18.6	62.2	0	100

These calculations offer smooth tendencies, different from those previously reported for CdTe oxide films grown under different N₂O partial pressures [6], were for low N₂O partial pressures, Cd concentration appears to be larger than Te, while for high N₂O partial pressures, Cd concentration seems to change and become smaller than Te.

In Figure 1 (right) we show characteristic XPS region spectra (Te 3d_{5/2} and Te 3d_{3/2} peaks) for samples A1, A4, A5 and A9 grown under different NH₃ partial pressures. In these XPS region spectra we can observe the appearance of additional Te 3d_{5/2} and Te 3d_{3/2} peaks, which start showing up at a NH₃ partial pressure of 3×10^{-6} Torr and continue growing until they become dominant at higher NH₃ partial pressures. In previous studies [6,7], we associated the extra peaks to a different chemical state of Te. The Te 3d_{5/2} peak at a binding energy of 572.4 eV correspond to Te-Cd bonds, and the Te 3d_{5/2} peak at a binding energy of 575.6 eV correspond to Te-O bonds.

We can estimate the relative percentage of Te-Cd and Te-O bonds considering the area under each Te 3d_{5/2} peak, and the results are presented in Table I (columns 6 and 7). In this table we show that when the NH₃ partial pressure increase from 3×10^{-6} to 7×10^{-5} Torr, the Te-Cd bonds decrease from 96 to 7 % and Te-O bonds increase from 4 to 93 %. For higher NH₃ partial pressures (1×10^{-4} Torr and above), the Te-Cd bonds almost disappear and the films mainly contain Te-O bonds. Within this results and the atomic concentration results we can say that for NH₃ partial pressures up to about 7×10^{-5} Torr, Te⁻² and Te⁺⁴ oxidation states coexist in the films; for NH₃ pressures of 1×10^{-4} Torr and above, the films practically consist of CdTeO₃. The behavior of the present prepared CdTe oxide films is practically equal to those we prepared at similar conditions in Ar-N₂O plasma [7], where coexistence of Te⁻² and Te⁺⁴ followed by saturation with oxygen at about 60 at.% and formation of CdTeO₃ was observed.

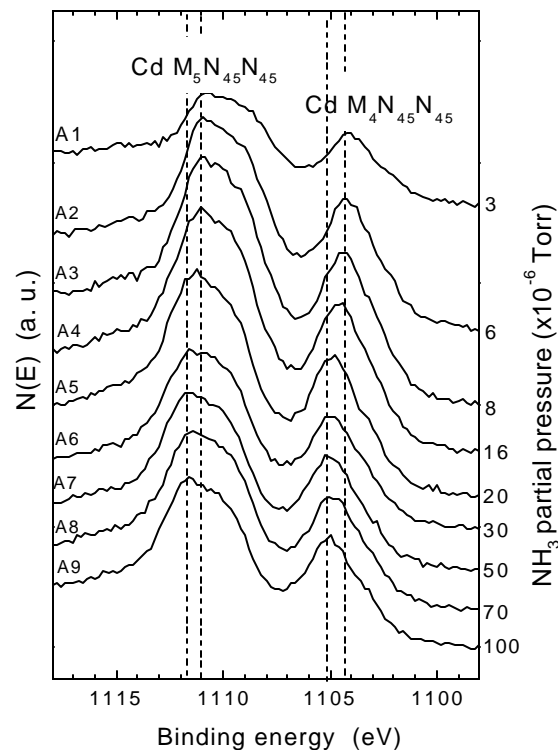
In Cd 3d we do not find any oxide induced doublet structure, and as such we have used x-ray Auger feature to discriminate between Cd-Te and Cd-O bonds [3,10].

In Figure 2 we show the Cd M₅N₄₅N₄₅ and Cd M₄N₄₅N₄₅ x-ray Auger features. As we can notice, these features do not display a distinct doublet for Cd-Te and Cd-O bonds as

do the Te 3d XPS features for Te-Cd and Te-O bonds. Instead, they shift smoothly in energy and change in shape as a transition occurs between Cd-Te and Cd-O bonds.

The total shift of this Cd MNN x-ray Auger peak is about 0.8 eV and it appears to be related to the change in Cd bonding from Cd-Te to Cd-O. In XPS spectra the shift in energy is caused by the charge transfer effect [2]. When CdTe is oxidized to form CdTeO₃ there is no change in the chemical state of the Cd and consequently no noticeable energy shift in this element.

In Figure 3 we present XRD patterns obtained from the samples grown under different NH₃ partial pressures. All samples, except that prepared under an NH₃ partial pressure of 3×10^{-6} Torr, present featureless patterns, indicative of an amorphous structure.

**Figure 2.** Cd MNN X-ray Auger spectra of CdTe oxide grown with NH₃ partial pressure.

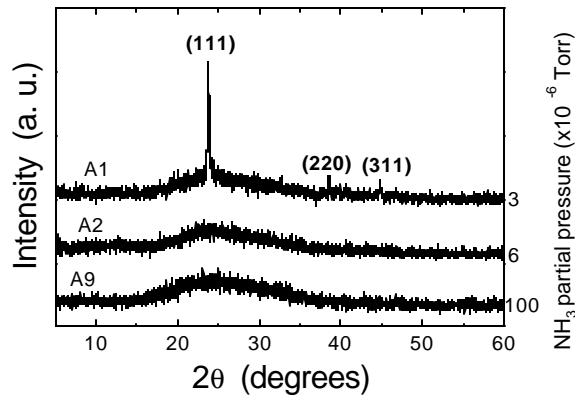


Figure 3. X-ray diffraction patterns of CdTe oxide grown with NH_3 partial pressure.

Sample prepared at the lowest NH_3 partial pressure shows a diffraction pattern presenting some crystalline features with a [111] cubic, [220] cubic and [311] hexagonal CdTe preferential orientation. By comparison, films grown with $\text{Ar-N}_2\text{-O}_2$ [4] or $\text{Ar-N}_2\text{O}$ [6,7] plasmas, become amorphous for an O concentration ~ 7 at. %. This tendency to become amorphous after incorporation of some O into the CdTe lattice seems to be common for CdTe oxide films prepared under different plasmas, and has been explained in terms of the aleatory formation of Te-O and Cd-O bonds during films growth [11]. The fast disappearance of the XRD peaks of the films may be attributed to a reduction in the surface mobility of the sputtered species as a result of gradually increasing the partial pressure of NH_3 .

Conclusions

In this work we have shown that the changes in chemical composition as a function of NH_3 partial pressure during deposition, indicate that O incorporates in the films up to about 62 at. %, while the Cd and Te decrease to 19 at. %. At NH_3 partial pressure of 1×10^{-4} Torr, the Te-Cd bonds are strongly reduced and the Te is mainly bonded to O. The Cd MNN xray Auger feature shows a shift in energy of about 0.8 eV as a function of NH_3 partial pressure. This shift appears to be related to the change in Cd bonding from Cd-Te to Cd-O. Films prepared at NH_3 partial pressure of 3×10^{-6} Torr present crystallinity with a [111] cubic CdTe orientation, while those prepared at higher NH_3 partial pressure are amorphous. The amorphous material formed at the higher NH_3 partial pressure appears to be mainly amorphous CdTeO_3 .

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