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Auger relative sensitivity factors for CdTe oxide

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ABSTRACT

The Auger lineshape of Te MNN in measurements of Auger spectra of CdTe oxide films with various degrees of oxidation was analyzed. By using standards from stoichiometric compounds, Auger relative sensitivity factors (RSF's) of Cd, Te and O for CdTe oxide thin films were obtained. The value of the RFS of oxygen is about constant, 0.27-0.28, for the standard compound, CdO, TeO_2 and $CdTeO_3$ (considering the RSF of Cd as 1). However, the obtained RSF of Te changes from 0.69 in CdTe up to 0.87 in $CdTeO_3$. 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 $CdTeO_3$. Considering as if the CdTe oxide films contained Te in a mixture of those two oxidation states, the obtained RSF's of Te could be utilized to determine the presence and relative concentration of CdTe and $CdTeO_3$ in CdTe oxide samples.

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INTRODUCTION

Thin films of CdTe oxide could have several practical applications; such as in the fabrication of high efficiency solar cells [1]. Several studies have been performed about the formation of oxides of CdTe [2-8] and $Hg_{1-x}Cd_xTe$ [9,10] in the last decade. In these studies it has been shown that the chemical composition of the resulting oxide can vary considerably depending on the oxidation conditions.

Because of its speed, easiness and relatively high precision, nowadays it is a common practice to use Auger electron spectroscopy (AES) for the quantitative determination of the relative atomic concentration of the different chemical elements, which constitute the surface of a solid material. In order to perform a quantitative analysis, several operations are required, which typically include instrumental aspects, sample preparation and mounting, as well as data acquisition, handling and analysis. Usually the quantitative analysis develops according to the following steps: (1) Based in the sample morphology and the type of analysis, an algorithm is selected. (2) Most quantitative elemental analyses are performed by utilizing relative sensitivity factors (RSF). (3) The RSF's should be corrected when matrix factors are considered. One of the most important matrix factors is that related with chemical effects because the energy at which an Auger transition appears, as well as its shape, could change noticeably depending on the chemical environment.

Often, in order to perform the quantitative elemental analysis, RSF's from handbooks are utilized [11-13]. However, particularly for materials composed by several elements, considerable errors can occur because most RSF's were determined from pure elements and, in some cases, from compounds of only two elements. Besides, in previous studies of CdTe oxide [2-8], it was noted the need to utilize different RSF's for tellurium, depending on the degree of oxidation. In this work, Auger RSF's of Cd, Te and O in cadmium telluride oxide thin films were determined. Stoichiometric compounds of CdTe, CdO, TeO_2 and $CdTeO_3$ were utilized as standards.

EXPERIMENTAL DETAILS

An ESCA/SAM spectrometer, model 560 from Perkin-Elmer, with a base pressure of 2×10^{-9} Torr was utilized for the AES analyses. A primary electron beam with energy of 2 keV and a current of 0.2 μA was utilized. This low energy of the primary electron

beam was chosen in order to reduce electric charge problems, which typically appear in some cadmium telluride oxide films because of their high resistivity. The Auger electrons were collected by means of a double pass cylindrical mirror analyzer, with an energy resolution of $\Delta E/E = 0.3$ %. The information was digitally saved in the derivative mode, d[E*N(E)]/dE. Auger spectra were measured with an energy increment of 0.5 eV per step with a time interval of 50 ms and the signal to noise ratio was improved by adding over 50 scans. In order to verify the reproducibility of the results, three Auger spectra were performed on each sample. Derivatives, with respect to energy, were obtained numerically by using a 5-point spline routine. No smoothing of the spectra was attempted. Cleaning of the surface, previous to the AES analyses, was performed by means of argon ion bombardment with energy of 4 keV and a current density of 0.36 $\mu A/cm^2$ during 1 min. Care was taken to use low current density in the ion beam and short time during cleaning to reduce induced changes in the stoichiometry of the utilized compounds.

Standard Auger spectra were obtained from the following stoichiometric compounds: polycrystalline CdTe from Balzers with purity of 99.99 %, CdO from Merck with purity of 99 %, TeO_2 from Cerac with purity of 99.999 % and $CdTeO_3$ from Cerac with purity of 99 %.

RESULTS AND DISCUSSION

In Fig. 1 an Auger spectrum in the derivative mode of a CdTe polycrystal is shown. It presents low noise and well-defined peaks, related to the Auger Cd MNN and Te MNN transitions with their minima at about 372.5 and 479 eV, respectively. An Auger spectrum of CdO is presented in Fig. 2, were the peaks related to Cd MNN and O KLL transitions clearly appear at 374 and 513.5 eV, respectively. In Fig. 3, an Auger spectrum of TeO_2 is presented. The Auger Te MNN and O KLL transitions have their minima at 496.5 and 531 eV, respectively. These peaks are shifted in energy probably because of the fact that TeO_2 is a good insulator. This allows charge to accumulate in the analysis area, and a corresponding change in electric potential. In Fig. 4 we present an Auger spectrum of $CdTeO_3$. In this sample, the Auger Cd MNN and Te MNN transitions appear at 377 and 481 eV, respectively, and the Auger O KLL transition, at 515 eV.

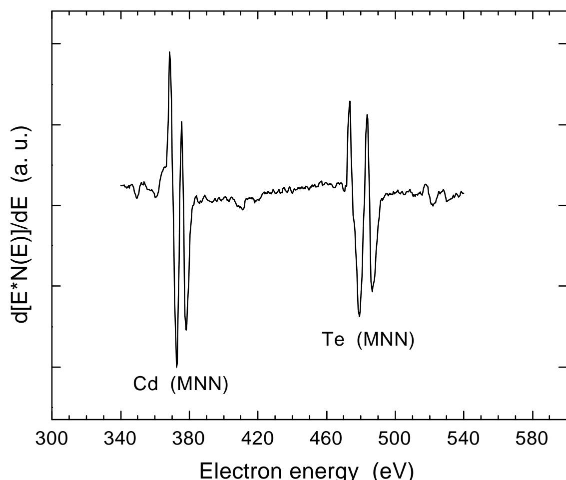

Figure 1. AES espectrum of CdTe

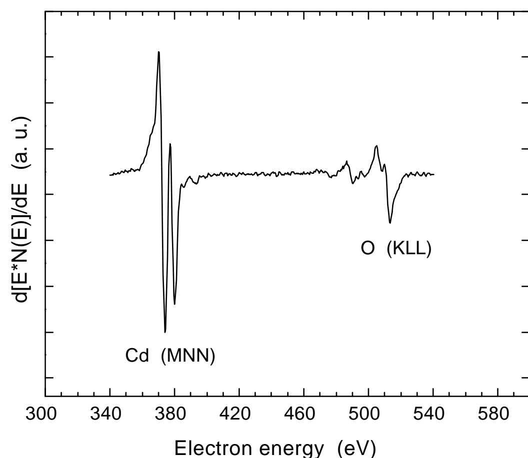

Figure 2. AES spectrum of powder CdO

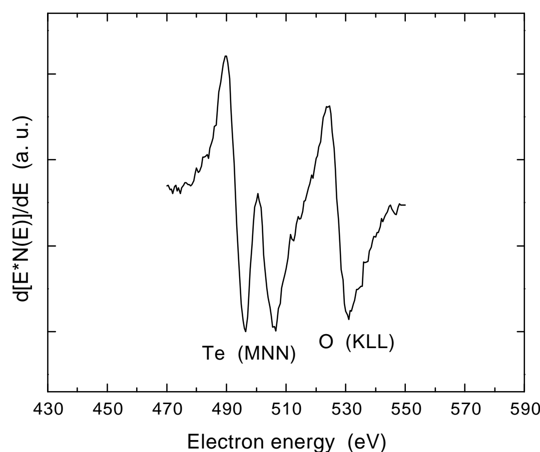

Figure 3. AES spectrum of powder TeO_2

The Auger transitions of Te MNN and O KLL in cadmium telluride oxide present overlapping of peaks, which makes the elemental quantification difficult, for instance when using the area under the corresponding

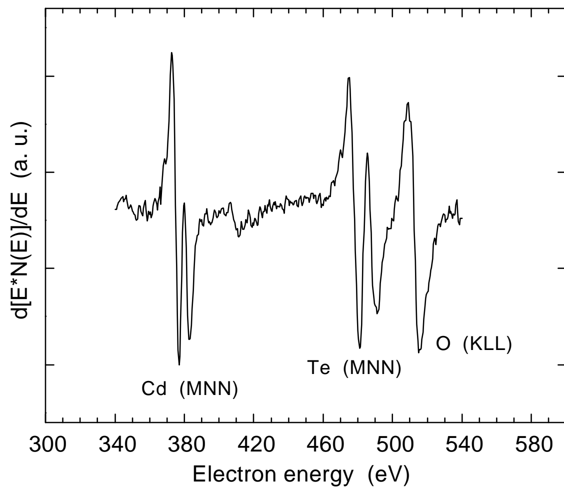

Figure 4. AES spectrum of powder $CdTeO_3$

peaks in the undifferentiated mode, N(E) vs. E. On the other hand, the peak-to-peak intensity method in the derivative Auger spectra for elemental quantification is very common, and in case of a homogeneous surface, the following relationship is utilized:

$$C_x = \frac{(I_x / S_x)}{\sum_i (I_i / S_i)}$$

Where C_x is the atomic concentration of element x, I_x is the peak-to-peak intensity in the Auger spectrum of element x and S_x is the Auger RSF of the transition being considered in element x [11,14].

It is possible to calculate the RSF's of Cd, Te and O by using the above equation and measuring the corresponding intensities in Auger spectra of standard compounds with known stoichiometry. Since the Auger Cd MNN transition is known that does not show appreciable changes [2], for several cadmium containing compounds and since the sensitivity factors that we are going to obtain are relative, we could as well take the Cd MNN transition as being equal to one, and the others (of Te and O), relative to this. By doing this ($S_{Cd} = 1$) and considering Fig. 1, of CdTe, and Fig. 2, of CdO, we obtain the following RSF's for tellurium and oxygen: $S_{Te} = 0.69$ and $S_O = 0.28$. The RSF here obtained for the Auger Te MNN transition, from CdTe, is smaller about 16 % as compared to that previously obtained ($S_{Te} = 0.80$) by Fang Wang *et al.* [2]. They used an energy resolution in their electron energy analyzer of $\Delta E/E = 0.6$ %, and ours was of 0.3 %. Using low resolution induces considerable deformation and rounding in the differentiated Auger peaks, which blurs details and produces a more pronounced reduction of intensity in sharp peaks than in wider ones, as it can be noticed comparing the Cd Auger peaks presented here and those of Fang Wang *et al.* [2]. Consequently, this effect that induces errors in the determination of RSF's was much reduced in our spectra.

We could use the obtained RSF of oxygen (from CdO) in order to calculate the RSF of Te in TeO_2, which results $S_{Te} = 0.72$. Finally, taking again $S_{Cd} = 1$, the calculated RSF's of Te and O for $CdTeO_3$ are $S_{Te} = 0.87$ and $S_O = 0.27$, respectively. In Table 1 we list the obtained RSF's for the studied compounds. We can notice that the RSF of Te changes from 0.69 for CdTe up to 0.87 for $CdTeO_3$. It has been already suggested by Fang Wang *et al.* [2] and by Zapata-Navarro *et al.* [15] to use different RSF's for Te in CdTe and in $CdTeO_3$. The need for different RSF's for Te in different compounds could be explained in terms of changes in the shape of the involved Auger transitions originated by the various chemical environ-ments in each Te compound. Considering this situ-ation, we should take into account that Te has an oxidation state of -2 in CdTe and +4 in TeO_2 and in $CdTeO_3$. Furthermore, the RSF of oxygen remains about the same, $S_O = 0.28$ for CdO and TeO_2 and $S_O = 0.27$ for $CdTeO_3$ (see Table 1), which could be due to the fact that oxygen keeps its oxidation state in these compo-unds. The obtained relative sensitivity factor of oxygen, $S_O = 0.27$-0.28, is very close to those obtained experimentally [2,16] and theoretically [17] by other groups, whose values are between 0.26 and 0.28.

Table 1. Auger relative sensitivity factors for the studied compounds.

Compound	S_{Cd}	S_{Te}	S_O
CdTe	1	0.69	—
CdO	1	—	0.28
TeO_2	—	0.72	0.28
$CdTeO_3$	1	0.87	0.27

In order to determine the atomic concentration of Cd, Te and O in CdTe oxide samples, we could consider the possibility of the coexistence of the two most common Te oxidation states, Te^{-2} and Te^{+4}. This means that we could present the stoichiometry of the films in the following form: $Cd_1^{+2}\ Te_x^{-2}\ Te_y^{+4}\ O_z^{-2}$. Using different values for the subscripts, we obtain the representation of several common compounds with these elements, such as: CdTe ($x = 1$, $y = z = 0$), CdO ($x = y = 0$ and $z = 1$), $CdTeO_3$ ($x = 0$, $y = 1$ and $z = 3$) and TeO_2 ($x = 0$, $y = 1$, $z = 2$ and eliminate Cd). Charge neutrality is preserved if we satisfy the equation $x - 2y + z = 1$. In several previous works about CdTe oxide [3-8], it has been observed that CdTe and $CdTeO_3$ are the main formed compounds, which means that there

Table 2. Relative atomic concentration in oxigen satured CdTe oxide thin films of Ref. [6] and this work.

Sample	Using: RSF's of Ref. [6]			Using: $S_{Cd} = 1$, $S_{Te} = 0.87$, $S_O = 0.27$		
Pressure, 10^{-4} Torr	Cd (%)	Te (%)	O (%)	Cd (%)	Te (%)	O (%)
1	17	28	55	18	24	59
2	17	29	55	18	24	58
3	15	30	55	16	25	59
6	17	28	56	18	23	59
9	16	28	56	18	23	59
Average	16	29	55	18	24	59

is a stoichiometric ratio of one-to-one between Cd and Te. On the other hand, in other previous works on CdTe oxide, there are speculations about the possible formation of other compounds such as $CdTe_2O_5$ [6,9,18]. However, those assessments were deduced from AES quantitative analyses performed using wrong RSF's because the chemical environment was not considered, which means, a single Te RSF was utilized.

In view of the results given above, it is reasonable to consider the possibility that, in the differentiated Auger spectrum, the Te MNN peak in the CdTe oxide samples be the result of the addition of two contributions: $dN(E)/dE = A + B$, were A is the peak-to-peak amplitude of Te with oxidation state -2 (like in CdTe) and B is the peak-to-peak amplitude of Te with oxidation state +4 (like in $CdTeO_3$). In a previous work [14], our group reported the way the possible relative concentrations of the oxidation states Te^{-2} and Te^{+4} vary in CdTe oxide samples. The calculation for the relative concentration of CdTe and $CdTeO_3$ in CdTe oxide samples could be performed as follows: using the fact that for the standard compound $CdTeO_3$ the ratio I_O/I_{Cd} is 0.8, and since in this compound all Te is in oxidation state Te^{+4}; then, applying this in CdTe oxide samples, we should divide the ratio of intensities I_O/I_{Cd} by 0.8 and assign the result to the relative concentration of $CdTeO_3$. As expected, an increase of I_O, going from zero up to saturation, corresponds to a decrease of the relative concentration of CdTe with an increase of that of $CdTeO_3$. This result is also consistent with previous XPS results [6], were it is observed that, monitoring the Te $3d_{5/2}$ XPS peak, the fraction of Te-Cd bonds decrease while that corresponding to Te-O gets increased when the oxygen concentration increases.

In Table 2, columns 2-4, we reproduce atomic concentrations of Cd, Te and O as reported by Zapata-Navarro *et al*. [6]. In that work, thin films of cadmium telluride oxide were grown by r.f. sputtering in an Ar-N_2O atmosphere and are reported atomic concentrations of the film constituents as a function of N_2O partial pressure (see Fig. 1 of Ref. [6]). In that report, a single RSF of Te was utilized to determine atomic concentrations. It was obtained from a CdTe polycrystal, which means, from a material containing Te in an oxidation state of +2. It can be observed that for N_2O partial pressures larger than 9×10^{-5} Torr there is saturation of oxygen in their films. From this saturation, it is expected that these films be of a chemical composition with a stoichiometry close to $CdTeO_3$. Considering this situation, the RSF of Te (S_{Te}) utilized in the calculation of the atomic concen-trations of the oxygen saturated samples conveys a large uncertainty. The average atomic concentrations for these oxygen saturated films, using RSF's of Ref. [6], are: $C_{Cd} = 16$ at. %, $C_{Te} = 29$ at. % and $C_O = 55$ at. %. The obtained stoichiometry is far from the expec-ted $CdTeO_3$, particularly for Te having the largest difference.

Using the RSF's obtained with the above mentioned procedure for Cd, Te and O from $CdTeO_3$, allows to obtain the atomic concentrations presented in columns 5-7 of Table 2. In this case, average atomic concentrations for the oxygen saturated films are: $C_{Cd} = 18$ at. %, $C_{Te} = 24$ at. % and $C_O = 59$ at. %. It can be noticed that these atomic concentrations are reasonably close to the expected stoichiometry of $CdTeO_3$ (18, 24, 59 vs. 20, 20, 60). Probably, the used standard could cause some difference in the calculated stoichiometry due to the fact that the RSF's were obtained from $CdTeO_3$ powder, which has a different electrical resistivity than the CdTe oxide films that could modify slightly the intensity of the Auger peaks.

CONCLUSIONS

In this work, by analyzing the Auger lineshape of Te MNN in the acquired Auger spectra of CdTe oxide films with various degrees of oxidation and using standards from stoichiometric compounds, Auger relative sensitivity factors (RSF's) of Cd, Te and O for CdTe oxide thin films were obtained. The value of the RSF of oxygen is about constant, 0.27-0.28, for the studied compounds, CdO, TeO_2 and $CdTeO_3$

(considering the RSF of Cd as 1). On the other hand, the obtained RSF of Te changes from 0.69 in CdTe up to 0.87 in $CdTeO_3$. 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 $CdTeO_3$. Considering as if the CdTe oxide films contained Te in a mixture of those two oxidation states, the obtained RSF's of Te could be utilized to determine the presence and relative concentration of CdTe and $CdTeO_3$ in CdTe oxide samples.

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