

Electrodeposition of CdTe Polycrystalline Thin Films: Influence of Electrolyte Anions in Film Composition.

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Received: april 27,1992.

O presente trabalho descreve a eletrodeposição catódica e caracterização de filmes de CdTe obtidos a partir de duas soluções eletrolíticas ácidas diferentes; uma delas contendo TeO₂, CdSO₄ e H₂SO₄, e a outra TeO₂, CdCl₂, e HCl, denominadas banho sulfato e banho cloreto respectivamente. A caracterização dos filmes foi realizada utilizando difração de raios-X e SEM. Foi observada a dependência da composição do filme e da microestrutura com a composição do eletrólito, enquanto as outras condições tais como potencial aplicado, temperatura e carga circulada foram mantidas invariáveis.

This report describes the cathodic electrodeposition and characterization of CdTe films obtained from two different acid electrolyte baths; one of them containing TeO₂, CdSO₄ and H₂SO₄, and the other TeO₂, CdCl₂ and HCl, called sulfate bath and chloride bath respectively. Characterization of films was performed using X-ray diffraction and SEM. It was observed the dependence of film composition and microstructure with electrolyte composition, while the other conditions such as applied potential, temperature and circulated charge were maintained unvariable.

Key words: CdTe; thin films; electrodeposition.

Introduction

Cadmium telluride with its direct bandgap of 1.45 eV and high optical absorption coefficient, is a material of great technological importance for application in photovoltaic and photoelectrochemical solar cells, and optoelectronic devices.

Thin films of this material have been fabricated by a variety of techniques, including: vacuum-evaporation¹, silk screen-printing², electrodeposition, sputtering-RF¹.

Electrodeposition has emerged as a low cost method for the obtention of semiconductor thin films. Furthermore, it is possible to obtain either p- or n-type materials of the desired thickness and with large photoactive areas.

Cathodic electrodeposition was first reported by Panicker *et al.*⁴, using an aqueous acid solution of TeO₂ and CdSO₄. Subsequently, other electrochemical obtention methods appeared, such as: anodic electrodeposition⁵, non aqueous cathodic electrodeposition⁶ and electroless⁷.

In a previous report⁸, we have studied the cathodic electrodeposition of CdTe from an aqueous acid electrolyte bath, containing TeO₂ and cadmium salts. It was shown the Influence of cathodic potential, bath temperature and heat treatment in the composition and microstructure of CdTe thin films.

In this report, we describe the cathodic electrodeposition and characterization of CdTe thin films.

Results obtained with different composition of the

electrolyte are presented, in order to determine the influence of chloride and sulfate anions in the composition and microcrystalline structure of CdTe films.

Experimental

The electrolyte was formulated from deionized water (18 MΩ.m) TeO₂ (Alfa 99.999%), 3CdSO₄·8H₂O, CdCl₂, H₂SO₄ and HCl, all of them analytical grade. A bath called sulfate bath containing 1M CdSO₄, 1x10⁻³M TeO₂ and 0.05M H₂SO₄; and a chloride bath with 1M CdCl₂, 1x10⁻³M TeO₂ and 0.1M HCl were prepared.

CdTe thin films were cathodically deposited under potentiostatic conditions on Ti substrates (0.5 mm thick), with 1 cm² area. Titanium sheets were polished with 600 grit waterproof paper, degreased in acetone, etched in 50% HF aqueous solution for 5 seconds, and then rinsed with distilled water. An usual three-electrode cell geometry was used; saturated calomel electrode (SCE) was employed as the reference electrode, and a Pt sheet of a greater area than that of Ti one was the auxiliary electrode. Cathodic polarization at a constant potential respect to SCE was applied by a LYP-M5 potentiostat, and the circulated charge was controlled by a LYP CD-02 coulombmeter.

The electrolyte bath was thermostatted, maintaining a constant temperature of 60°C during each electrodeposition.

Films characterization was performed by X-ray diffraction studies, employing a Philips 1051 diffractometer, Cu

K_{α} radiation. ASTM cards were used as standards. The superficial microstructure of some of the films was determined using scanning electron microscopy (SEM).

Results

X-ray diffraction patterns of CdTe films electrodeposited at -0.45 V and 60°C are shown in Fig 1. Diffraction patterns a) and b), correspond to films electrodeposited from sulfate and chloride bath respectively. Pattern a) show the presence of CdTe peaks corresponding to (111), (220) and (311) crystallographic directions. These films, with a cubic structure, have a lattice constant of 6.6 \AA (ASTM value $a_0=6.481 \text{ \AA}$), being the preferential orientation in the (111) plane. Peaks corresponding to metallic tellurium are not observed in these films electrodeposited from sulfate bath.

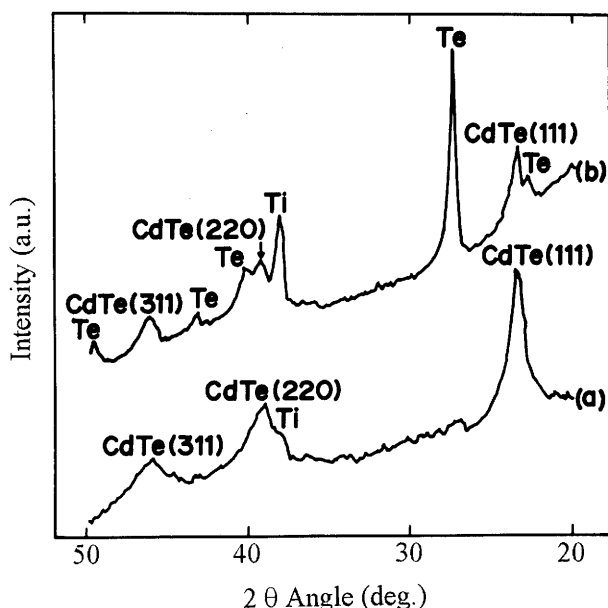


Figure 1. X-ray diffraction patterns of films electrodeposited from -0.45 V Vs SCE and 60°C , from a) sulfate bath, and b) chloride bath.

Films obtained from chloride bath at same conditions show the presence of metallic tellurium, in addition to the CdTe peaks. It is possible to observe a darkening of the films surface during the electrodeposition, under these conditions.

The influence of bath composition in crystallite size, determined from values of full width at half maximum of X-ray diffraction peaks by means of Scherrer formula, is not revealed; results also confirmed by SEM.

To study the influence of chloride in the bath, increasing quantities of chloride are added to sulfate bath. Electrodepositions from sulfate bath with 0.5, 1.0, 1.5 and 2.0 M in NaCl are performed. The dependence of X-ray peaks intensity (corresponding to tellurium and (111), (220) and (311) CdTe texture) on chloride concentrations, is represented in the graphic of Fig 2. For the design of the graphic, tellurium peak corresponding to $2\theta=27.7^{\circ}$ was chosen, because of its high intensity that carry a minor error. A variation in intensity of (111) CdTe X-ray peak with the addition of chloride in the bath is observed. A

decreasing in this peak intensity, in addition with an increasing in tellurium one is revealed, while chloride concentration becomes higher. Appreciable changes in intensities are not observed in the X-ray diffraction peaks corresponding to (220) and (311) CdTe crystallographic directions. Neither changes in crystallite size are appreciated, comparing full width at half maximum values of the CdTe X-ray diffraction peaks, for different chloride concentrations.

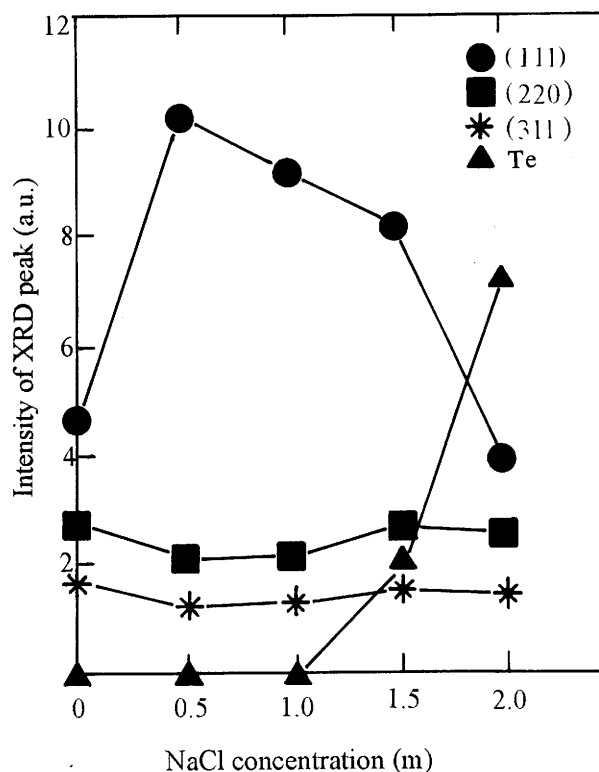


Figure 2. Intensity of the diffractions peaks corresponding to (111), (220) and (311) CdTe crystallographic directions, and metallic tellurium, as a function of chloride concentration in sulfate bath.

Discussion

The difference between the diffraction patterns of films electrodeposited from sulfate and chloride bath is really remarkable, making evident that films composition is influenced by the anions used in the electrolyte bath. Furthermore, the darkening of the surface in films obtained from chloride bath is a consequence of a variation of their composition, that revealed metallic tellurium presence.

It is possible that the use of a strongly adsorbed anion, like chloride instead of sulfate, affect the electrodeposition mechanism.

An important dependence between the direction of crystallite growth and chloride concentration in the sulfate bath, is revealed. In films deposited from sulfate bath, a (111) direction of preferential growth is observed, as well as in ones obtained from the same bath with 0.5, 1.0 and 1.5M in chloride anion. When 2.0M is attained, a preferential growth orientation is not appreciated. The growth in (220) and (311) directions is not appreciably influenced by the

addition of chloride anions. This anion would not be involved in the growth corresponding to (220) and (311) directions.

Conclusions

The film composition, but not the crystallite size, is influenced by the bath composition. Furthermore, the addition in the sulfate bath of increasing quantities of chloride show a variation in the intensity of (111) CdTe peak. The presence and increase in intensity of tellurium peak is influenced by chloride anion. When 2.0 M concentration of the anion is attained in the sulfate bath, a preferential crystallite growth direction is not appreciated, in contrast with the definite direction of preferential growth showed in films from electrolyte bath without chloride or with lower concentrations.

The occupation of active sites in the electrode surface by chloride is a possibility that is being studied and is now in progress.

References

1. G.S.Sanyal, A. Mondal, K. C. Mandal, B. Chosh, H. Saha and M.K.Mukherjee, *Solar Energy Materials* **20**, 395 (1990).
2. H. Matsumoto, K.Kuribayashi, H. Uda, Y.Komatsu, A. Nakano and S. Ikegami, *Solar Cells* **11**,367 (1984).
3. M. Takahashi, K. Uosaki and H.Kita, *J. Appl. Phys.* **55**, 3879 (1984).
4. M.P.R. Panicker, M.Knaster and F.A.Kroger, *J. Electrochem. Soc* **125**,566 (1978).
5. D.Ham, K.K.Mishra, A.Weiss and K.Rajeshwar, *Chem. Mat.* **1**, 619 (1989).
6. R.B.Gore, R.K.Pandey and S.K.Kulkarni, *J. Appl. Phys.* **65**, 2693 (1989).
7. R.N.Bhattacharya, K.Rajeshwar and R.N.Noufi, *J. Electrochem. Soc.* **131**, 939 (1984).
8. S.Bonilla and E.A.Dalchiele, *Thin Solid Films* **204**, 397 (1991).