

DETERMINATION OF NANOSTRUCTURES OF THIN LAYERS FROM STUDY OF QUANTAL TRANSITIONS

PËRCAKTIMI I NANOSTRUKTURAVE TË SHITESAVE TË HOLLA BAZUAR NË STUDIMIN E KALIMEVE KUANTIKE

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PERMBLEDHJE

Në kuadër të këtij punimi janë studiuar nanostrukturat e një shtrese filmike të përgatitur në mënyrë eksperimentale. Janë përcaktuar vetitë strukturale dhe elektronike edhe të nanostrukturave të një gjysmëpërçuesi. Tensioni mekanik i nanostrukturave dhe kompozicioni i tyre janë përcaktuar me anë të difraksionit të rrezeve të rëntgenit. Janë matur spektrat difraksionalë të rrezeve të rëntgenit (XRD) për CdTe të elektrodepozituara mbi çelik inoks, mbi nikel dhe për CdTe në formë pluhuri. Me anë të elektroskopit elektronik me rreze depërtuese është bërë përcaktimi i kompozicionit ndërtues. Është përcaktuar koeficienti i absorbimit optik i shtresës së hollë prej CdTe, me trashësi prej 0.95 µm, në funksion të energjisë fotonike. Është përcaktuar kalimi kuantik i drejtpërdrejtë për shtresën e hollë prej CdTe duke fituar vlerën 1.51 eV.

Fjalët çelës: nanostrukturat, gjysmëpërçuesi, absorbimi kuantik, shtresa e hollë.

SUMMARY

Nanostructures on the experimentally prepared thin film layer are studied. Structural and electronic properties of these semiconductor nanostructures are accessed. Strain and composition are evaluated by using high-resolution x-ray diffraction technique. The X Ray Diffraction (XRD) spectra for CdTe electrodeposited on stainless steel, on nickel and for CdTe powder are measured. Transition electron microscopy techniques for composition evaluation are applied. The optical absorption coefficient as a function of photon energy for a 0.95 µm thin CdTe film originally deposited on stainless steel is evaluated. Direct allowed transition in a 0.23 µm thin CdTe film deposited initially on molybdenum at -580 m is determined and the value of 1.51 eV is obtained.

Key words: nanostructures, semiconductors, quantum absorption, thin films.

1. INTRODUCTION

Over the last two decades, preparation of thin film semiconductors for use in photovoltaic devices has become an important subject in technology and in fundamental studies in physics and chemistry. The electrochemical deposition is a low cost deposition method of high quality semiconductor thin films. However,

electrodeposition has become one of the most successful methods of making high-efficiency solar cells. The conversion efficiency of solar cells based on electrodeposited films of cadmium telluride (CdTe) exceeds 11% [1-3]. Thin films of CdTe can be electrodeposited from acidic [1, 2, 3, 4, 5], alkaline [6] and organic [7, 8] electrolytes. The pulsed-electrodeposition technique from

acidic solution has also been reported recently [9, 10]. Films deposited from acidic solution have, so far, produced solar cells with higher efficiencies (16-18%). These films are n-type as deposited and have a high resistivity of $10^4 - 10^6 \Omega \text{ cm}$ [1].

Room temperature electron and hole mobilities of 1100 and $80 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been reported for good-quality crystals. The minority carrier diffusion lengths have been measured by the electron-beam induced current technique to be 2.5 μm and 2.8 μm for n- and p-type crystals, respectively [11].

The optical absorption spectrum of CdTe shows a sharp edge and large absorption coefficients (about 10^5 cm^{-1} for above bandgap radiation). Thus, solar radiation with energy greater than the bandgap energy is absorbed within 1-2 μm from the surface. When the solar cell is designed for photogeneration of EHPs (electron-hole-pairs) to take place in the depletion region, the short minority carrier diffusion length in polycrystalline CdTe thin films has essentially no effect on the carrier collection. CdTe is also noted for its high transparency in the far infrared region

(absorption coefficient: $1.4 \times 10^{-3} \text{ cm}^{-1}$ at 10.8 μm).

Although an extensive work has been done in the past on electrodeposition of CdTe for photovoltaic applications, still some of its fundamental properties need to be explored in further details. Some of them are addressed and studied in this work.

2. EXPERIMENTAL PROCEDURES

Electrodeposition was performed in a 1-liter borosilicate beaker having a Teflon lid with openings for the insertion of various electrodes and thermometer (Fig. 1). The design of the deposition unit proved to be perfect in the sense that deposits were quite uniform and the deposition parameters could be controlled well. Electrodeposition was carried out cathodically on different conducting substrates at a cathode potential in the range of -550 mV to -590 mV with respect to a saturated silver-silver chloride reference electrode (SSC). The electrolyte which was stirred moderately by a Teflon-coated magnetic bar, was a 750 ml purified solution of 1M CdSO_4 (Johnson Matthey, Alfa 20132).

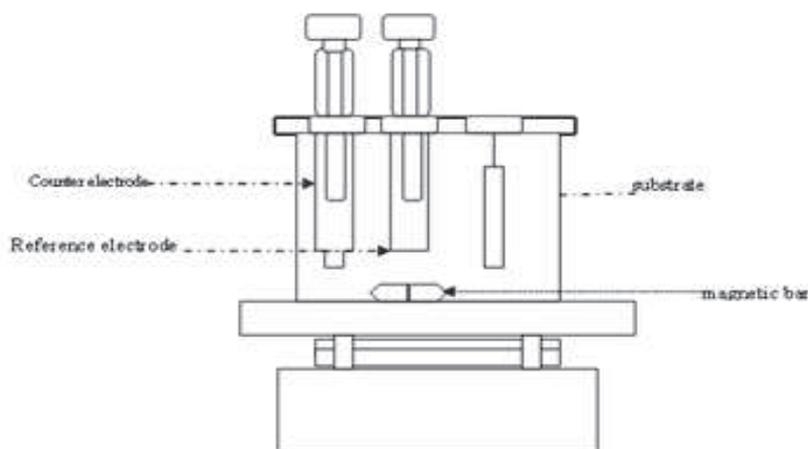


Fig 1. Schematic diagram for the electrodeposition apparatus

The composition of films and the preferential orientation of grains were determined by X-rays diffraction (XRD) using a Siemens diffractometer model D500 ($\text{CdK}\alpha$; 0.15406 nm). Scanning electron microscopy (SEM) and energy dispersive

electron microprobe analysis (EMA) were performed using a Joel (JSM-6300) microscope. The specular reflectance measurements were performed in the wavelength range of 0.2-3.3 μm

using a Varian (Carry-5E) double-beam spectrophotometer.

3. CONVENTIONAL CHARACTERIZATION OF THE STRUCTURE AND COMPOSITION

The XRD spectra for CdTe films deposited on SS and Ni, and for CdTe powder are shown in Fig. 2. The preferential orientation of films on SS is the (111) planes parallel to the substrate surface; same is true for films on nickel but with a less degree in preferential orientation. The preferential orientation of (111) is not due to the characteristics of metallic substrates or the potentiostatic mode of deposition which were used; the same preferential orientation has been observed for films deposited on SnO₂ [4, 12], CdS/SnO₂ [13] and CdS/ITO – coated glass [5]. This preferential orientation has also been shown in films deposited in pulsed and in galvanostatic modes of electrodeposition [13]. The orientation along (111) increases as the deposition potential becomes more negative [14]. This may be the reason for the difference in the XRD patterns a and b in Fig. 2.

The effect of annealing on the recrystallization of films is presented in Table 1. Annealing in either air or nitrogen at 300° C, for 1 h, increases the intensity of (220) and (311) peaks indicating that the orientation of grains changes towards random. This effect is more pronounced in films deposited from solutions having a higher concentration of cadmium and is in accordance with other reports [13] which indicate orientation changes toward random up to a certain time of annealing before it starts to move back towards the textured state as a result of grain growth.

In Table 1 it can be seen that the effect of annealing for 1 hour in air and in nitrogen on the relative XRD peak intensities for CdTe film deposited on stainless steel (SS) and on nickel (Ni); these are the same samples whose as-deposited XRD patterns are shown in Fig. 2.

The composition of the CdTe films was determined by EMA with an intrinsic CdTe single crystal (99.99%, Johnson Matthey 20117) as a reference sample. The sample chosen for this study was a 1.1 μm CdTe film deposited on SS at

$V = -580$ mV (vs. SSC). The film did not go under any treatment before measurements. The reference single crystal was etched in 1% bromine in methanol for 2 min, followed by etching in 1 M KOH in methanol for 3 min, rinsing in water and drying in nitrogen; this procedure produces stoichiometric surface for CdTe [15]. The reference sample was used to determine the ratio of the Cd detection efficiency factor for Te as 1.2309.

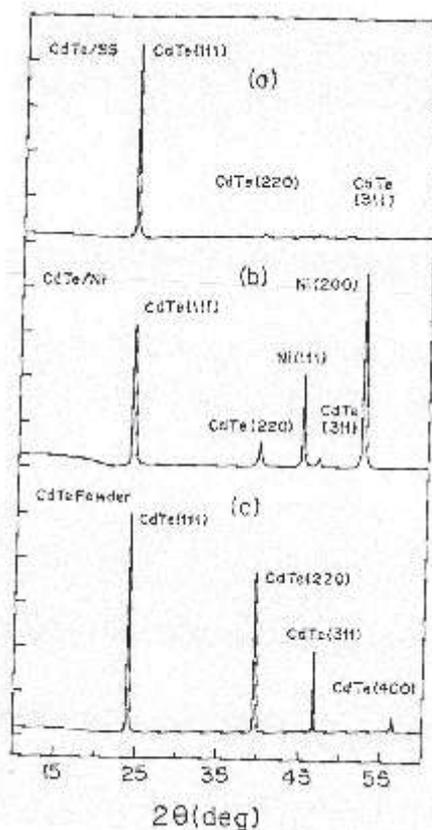


Fig 2. The XRD spectra from CdTe electrodeposited on stainless steel (a), on nickel (b) for CdTe powder (c). The film on stainless steel is 1.1 μm thick and was deposited at $V = -550$ mV (vs. SSC).

4. OPTICAL OR QUANTUM MECHANICAL TRANSITIONS

To study the optical or quantum transitions in the electrodeposited films of CdTe, a 0.23 μm thick pin-hole-free film was deposited on

molybdenum. The thickness was selected low to be able to extend the transmittance measurements to high photon energies. The absorption coefficient spectrum of the film was determined from the transmittance spectrum using the same technique described in our papers

[16, 17, 18, 19,] The analysis of these data revealed that in the energy range of $E = 1.49 - 1.77$ eV, $(\alpha E)^2$ against E consists of two very close straight segments, as theoretically is explained elsewhere [18, 19] which is observable only in an extended scale.

Sample	As-deposited			300°C (air)			300°C (N ₂)		
	(111)	(220)	(311)	(111)	(220)	(311)	(111)	(220)	(311)
CdTe/SS	100	1	0.8	100	2	1	-	-	-
CdTe/Ni	100	18	5.5	100	27	9.6	100	34.3	12.5
CdTe powder	100	73.5	36.2	-	-	-	-	-	-

Table 1.

In Figure 3 the experimental results of the absorption coefficient as a function of photon energy for the single-crystal CdTe are shown. On the other hand, the experimental results for the direct allowed transition at 1.51 eV are shown in Fig. 4. This is in agreement with corresponding intercepts of E axis that are the measure of two direct allowed transition 1.49 eV and 1.53 eV [19]. The corresponding intercepts with the E axis provide two direct allowed transitions at 1.49 and 1.53 eV.

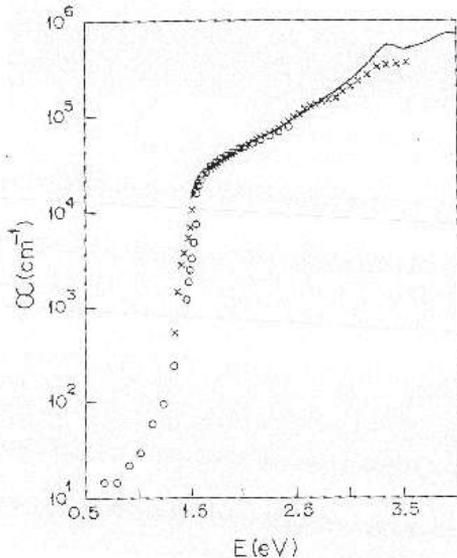


Fig. 3. Optical absorption coefficient as a function of photon energy for a 0.95 μm thick CdTe film

originally deposited on stainless steel at a deposition potential of -580 mV (o), for a 0.23 μm thin film deposited initially on molybdenum at -580 mV(x), and for single-crystal CdTe (solid line).

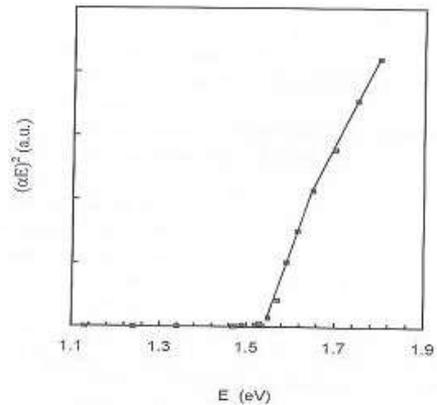


Fig. 4. Direct allowed transition in a 0.23 μm thin CdTe film deposited initially on molybdenum at -580 mV.

This is in excellent agreement with the most recent value (1.514 eV) reported for single crystal CdTe at room temperature [20].

5. SUMMARY AND CONCLUSIONS

Electrodeposition of CdTe can be quantitatively explained by a 6-electron-transfer reaction based

on the diffusion process of HTeO_2^+ cations. Deposited films are nearly stoichiometric with a relatively large grain size (a fraction of 1 μm) which increases with the film thickness. The preferential orientation of the grains is (111), regardless of the substrate material, and this preferentiality increases as the deposition potential becomes more negative, whereas it decreases under the effect of annealing in either air or nitrogen at 300°C.

The measured interference patterns, not included here, are much more pronounced in the reflectance (due to the intensity ratio for incident and reflected light) than in the transmittance spectra and as a result, dispersion measurements can be extended to much lower wavelengths. The dispersion results show an excellent agreement between the films and the single-crystal data down to a wavelength of 0.355 μm . However, in the approximate range of 0.8 to 1.3 μm the films dispersion falls slightly below that for the single crystal. The films optical dispersion can be described by the classical bound electrons dispersion model. The optical measurements reveal a direct allowed transition at 1.51 eV which is in excellent agreement with 1.514 eV reported for CdTe single crystal at room temperature.

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