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Determination of optical constants of CdS_xSe_y electrodeposits

I. RODRÍGUEZ, J. GONZÁLEZ-VELASCO
Universidad Autónoma de Madrid, Facultad de Ciencias, Cantoblanco, 28049 Madrid, Spain

The optical constants $n(\lambda)$ and $\alpha(\lambda)$ have been determined for CdS_xSe_y films electrodeposited on to glass doped with SnO_2. From a $(\alpha h\nu)^2$ versus photon energy plot, a value for the direct band gap of the electrodeposited polycrystalline semiconductor of $E_g = 1.83$ eV was obtained, which indicates a low proportion of S^{2-} in the thin films formed.

1. Introduction

The importance of sunlight absorption capacity of semiconductor materials has led to different studies on optical constants of semiconductor thin films in the visible and infrared wavelength ranges [1–4].

CdS_xSe_y semiconductor films could be a potential material for use in photoelectrolysis of water, an interesting method for the production of hydrogen. According to Gerischer [5], an ideal band gap of around 2.2 eV would be necessary for the photodissociation of water (1.23 eV would be the free energy predicted by thermodynamic calculations, plus an excess energy corresponding to the overvoltages for hydrogen evolution and, especially, for oxygen evolution). Also, the band edges should be located in such a way that minority carriers (holes in the cases of *n*-semiconductors) would be able to oxidize water to oxygen, which would require from 0.5–0.9 eV, according to the electrocatalytic features of the semiconductor surface, and that electrons could reduce protons to hydrogen. As known, n-CdS is an ideal material in relation with its band gap and band edge location, which are adequate for water photodissociation. Unfortunately, n-CdS electrodes, photocorrode with high velocity, due to the large value of the surface rate between photogenerated holes and its own polycrystalline material, giving rise to reactions of the type

$$n\text{-SCd} + 2h \rightarrow S + Cd^{2+} \quad (1)$$

in which Cd^{2+} ions go to the solvent and the semiconductor becomes covered with a layer of sulphur which impedes the access of photons to the semiconductor material, as well as produces an isolation between semiconductor and electrolyte, and consequently hindering the formation of the space charge region.

Thus, a good strategy for obtaining an adequate material for water photodissociation could be to obtain a new class of semiconductor which should accomplish the requirements for band gap and band edges location, by electrodepositing S_xSe_yCd electrodes. Such a semiconductor should show a band gap of between 2.4 and 1.7 eV, the wider, the higher is the proportion of S^{2-} ions in the compound. Electrodeposits of this kind of semiconductor from solutions containing SeO_3^{2-}, Cd^{2+} and sulphur coming from $S_2O_3^{2-}$, are formed with a low S^{2-} content. Therefore, they present band gaps closer to 1.7 eV (band gap corresponding to CdSe) than to 2.4 eV (band gap corresponding to CdS) [5]. On the other hand, the not too good quality of the electrodeposits make them easily photocorrosible and sulphur deposits on the surface lower the light absorption capacity of the material. These properties and others can influence the performance of polycrystalline thin film semiconductor photoelectrochemical cells. Therefore, a good characterization of the electrodeposited films from the photoelectrochemical point of view [6] or with respect to their optical properties constitutes an important contribution to their study. The values obtained for this compound can be compared with previously calculated and measured values of the optical constants for monocrystalline thin films of cadmium chalcogenides [7], or of some polycrystalline materials of the same compounds, which were found to vary with the method utilized for obtaining the semiconductor material [8, 9].

2. Experimental procedure

2.1. Film preparation

The CdS_xSe_y electrodeposits were made by immersing a plate of glass doped with SnO_2 in a plating bath whose composition was 3M H_2SO_4, 4×10^{-3} M Na_2SeO_3, 5×10^{-3} M $CdSO_4$ and 5×10^{-2} M $Na_2S_2O_3$, galvanostatically at $I = 5$ mA for 5 min and at 25 °C. Films of around 0.3 μm thickness were obtained, which were rinsed and used for photoelectrochemical or optical measurements without previous annealing.

A potentiostat-galvanostat Fabelle Mod. MA 110 and a PAR Mo. 175 Universal Programmer were used for controlling the electrochemical deposition. A platinum counter electrode was used in the electrodeposition cell.

2.2. Optical measurements

Reflectance and transmittance measurements were carried out in a Cary 17-D double-beam spectrophotometer. The thicknesses of the samples were obtained

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by means of a "Talystep" from Taylor Hobson Instruments.

3. Results and discussion

Fig. 1 shows spectral transmittance and reflectance curves for a CdS_xSe_y/SnO_2/glass system.

The values of $n(\lambda)$ and $\alpha(\lambda)$ as derived from the experimental reflectance and transmittance data for the system are illustrated in Figs 2 and 3. For the case of $n(\lambda)$, three different refractive index maxima can be seen, localized at wavelengths of around 650, 900 and 1100 nm, respectively. The first maximum at around 1.8 eV coincides with the direct transition showed by the semiconductor material electrodeposited as can be seen in the following figures. This behaviour contrasts with that reported for CdSe polycrystalline electrodes [10] in which only a maximum in the refractive index, localized at about 680 nm, was found. The two new maxima found for S_xSe_yCd samples may be due to the presence of irregularities in the electrodeposits obtained, in which the formation of some amounts of elemental sulphur electrodeposited on the semiconductor surface cannot be excluded.

The curves of the absorption coefficient of CdS_xSe_y electrodes versus wavelength show a rapid increase in absorption coefficient at $\lambda < 800$ nm, probably due to a direct optical transition in the CdS_xSe_y crystals formed. The values obtained for α are higher than those found in the literature [11] for CdSe monocrystalline thin films, although the direct transition for both materials seems to be very close.

In order to derive the gap corresponding to this transition, i.e. the direct band gap for the CdS_xSe_y electrodeposited compound, $(\alpha h\nu)^2$ was plotted versus $h\nu$, as in Fig. 4. Using a least-squares fitting, a value for $E_g \simeq 1.8$ eV and a slope of 3.52×10^9 eV^{-1} cm^{-2} were found. The value of the band gap coincides with that obtained in a photoelectrochemical determination of the action spectrum for S_xSe_yCd samples [6]. The value of the slope is very close to that cited for the direct transition of CdSe electrodes obtained from electrodeposition [10]. A band gap of 1.8 eV indicates that only a small amount of S^{2-} ions were able to electrodeposit in place of Se^{2-} ions, which electrocrystallize much easier.

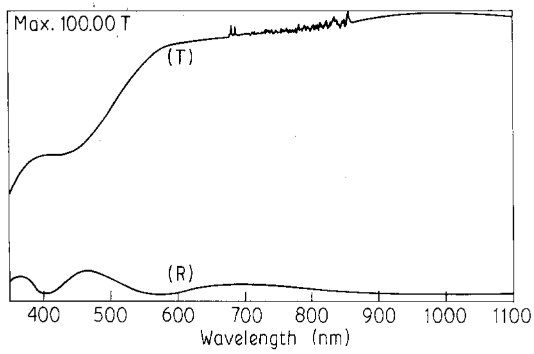

Figure 1 Plot of reflectance, R, and transmittance, T, data taken at different wavelengths for a sample of CdS_xSe_y grown on glass covered with SnO_2.

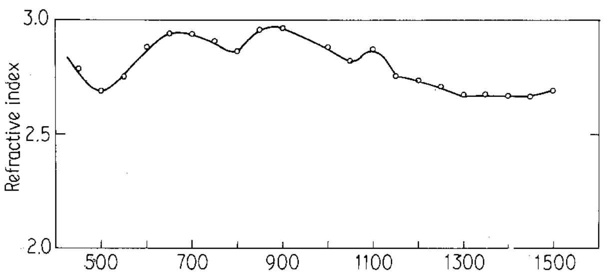

Figure 2 Plot of refractive index versus wavelength for the same sample as in Fig. 1.

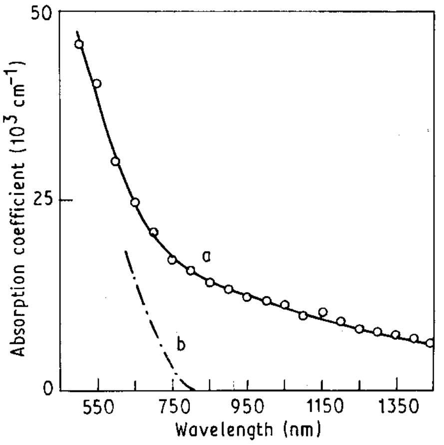

Figure 3 Plots of the absorption coefficient versus λ (nm) for (a) CdS_xSe_y polycrystalline electrodeposits and (b) a CdSe single crystal.

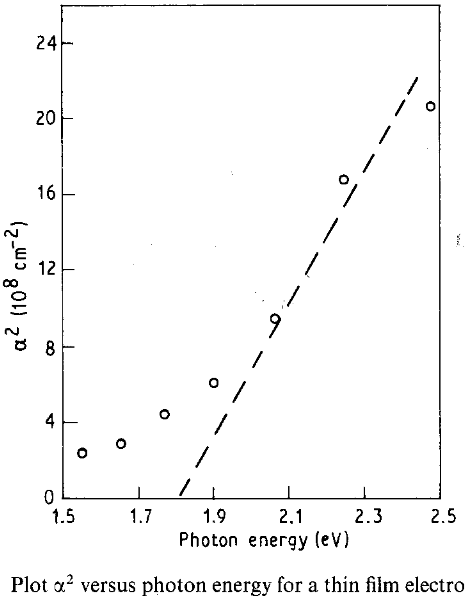

Figure 4 Plot α^2 versus photon energy for a thin film electrodeposit of S_xSe_yCd.

Fig. 5 shows a plot of $\alpha^{1/2}$ versus photon energy, from which an indirect band gap of 1.5 eV can be deduced for the electrodeposits obtained. The 830 nm corresponding to this transition are in agreement with the presence of a maximum at 900 nm in the plots of the refraction coefficient versus wavelength.

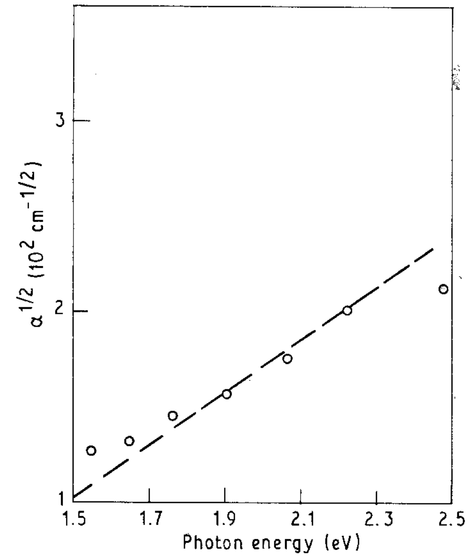

Figure 5 Plot of $\alpha^{1/2}$ versus photon energy for a thin film electrodeposit of S_xSe_yCd indicating an indirect transition at 1.5 eV.

4. Conclusions

The results presented, together with those given for the photoelectrochemical characterization of S_xSe_yCd electrodeposits [5], indicate that the electrodeposition of this chalcogenide is difficult under the experimental conditions used. Only a small amount of the negative ions forming part of the crystalline lattice are found to be S^{2-} ions. Also the transmittance curve shown in Fig. 1 indicates that the crystalline thin film obtained is not very good. This plot, as well as the maxima of the refraction index at 900 and 1.100 nm, suggest the presence of sulphur or selenium deposits which could explain the $\alpha^{1/2}$ versus $h\nu$ plot given in Fig. 5, indicating an indirect transition at around 1.5 eV.

An improvement of the electrodeposited semiconductor material is obtained by a post-deposition annealing, which increases the crystallinity of the films and homogenizes the S_xSe_y ratio in the compound studied.

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