ELSEVIER

Journal of Molecular Structure 349 (1995) 85–88

Journal of MOLECULAR STRUCTURE

OPTICAL PROPERTIES OF THIN SOLID FILMS OF LEAD SULFIDE

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The technique of electroless chemical deposition was used for preparation of thin solid films of lead sulfide (PbS). The thin solid PbS films were deposited on a glass substrate previously coated with a very thin layer of Cu_2S. The optimal temperature of deposition was between 343 and 363 K. The thickness of these films was controlled by changing the concentration of the reaction solutions and the deposition time.

The optical properties of these thin solid films of different thickness were determined by means of near infrared spectroscopy, Raman spectroscopy and visible spectroscopy.

1. INTRODUCTION

Thin solid films of PbS have been a subject of interest for many years, mainly because of their photocondutive properties. However, many of their physical properties were found to be dependent on the methods and conditions of preparation. They were usually prepared by the methods of chemical deposition on glass substrates [1-3] using different solutions in alkaline media. For preparation of thin solid films of PbS we used a technique of electroless chemical deposition on glass substrate, on which a very thin transparent film of Cu_2S was coated. The thickness of the PbS films prepared in this way was no more then 60 nm. This is the opposite way of preparing PbS-CuS film reported by Garcia *et al.* [4]. They used chemically deposited PbS films on glass for chemical deposition of Cu_xS.

As a part of a thorough study on optical and electrical properties of these films, in this paper we present some of the optical characteristics of thin solid PbS films. For this purpose, we prepared transparent thin solid films of PbS by the method of electroless chemical deposition technique in acidic media and we recorded the near infared, visible and Raman spectra of these films.

0022-2860/95/$09.50
SSDI 0022-2860(95)08715-X

2. EXPERIMENTAL DETAILS

2.1. Deposition of the films

Good quality PbS thin solid films were obtained by an electroless chemical deposition technique. This technique has been recently used in our laboratories to deposit copper sulfide films of variable composition [5,6], as well as for deposition of thin solid films of different materials such as Sb_2S_3 and Bi_2S_3.

Glass substrates were previously coated with a thin film of Cu_2S (< 30 nm in thickness). The substrates used were standard microscope glass slides. The glass substrates were previously treated as reported earlier [6]. The substrates were then immersed in a hot bath (323-333 K) for chemical deposition. After that, the temperature was raised between 343-363 K, during the time interval 5-25 min and a deposition of thin PbS films was observed. The thickness of the films was varied by varying the deposition time. The adhesion of the films to the Cu_2S substrate is very satisfactory. The PbS films are glassy grey and mirror like.

For total volume of 100 cm^3 solution for chemical deposition, the following constituents, mixed in a given sequence were needed:

-40 cm^3 of 0.1 mol /dm^3 of $Pb(CH_3COO)_2$
-20 cm^3 of 1 mol/dm^3 of $Na_2S_2O_3$ (sodium thiosulfate)
-0.3 cm^3 of glacial CH_3COOH (acetic acid)
-The rest up to 100 cm^3 is H_2O.

The above method is very similar to the one reported recently [7] except that the concentration has been slightly altered and that the PbS thin films were deposited on a glass substrate coated with a very thin film of Cu_2S.

2.2. Postdeposition annealing

After the deposition, the films were washed with water and dried in air. The optical and X-ray measurements on these films were performed before and after air bake for 1 h at 423 K.

2.3 Characterization of the films

The thickness of the films was determined by the gravimetric method. The estimated film thickness of the PbS varied between 20 and 60 nm.

X-ray patterns of the deposited films were recorded on a diffractometer, model JDX. They showed that the deposited material was crystalline. The presence of the characteristic diffraction peaks confirmed that the chemical composition of the films corresponds to stoichiometric PbS (galena type). Near infrared and visible transmission spectra of thin films were taken on AVIV UV-VIS-NIR spectrophotometer model 17DS.

Raman spectra of films were recorded using DILOR XY multichannel spectrophotometer with Ar^+ ion laser excitation in an Olympus microscope, which, when used with a X400 objective allows signals to be collected from a volume of ~ 1μm^3. The Raman spectra of PbS thin films showed only one line in the low frequency region, at around 140 cm^{-1} which is most probably due to the vibration of the PbS lattice.

3. RESULTS AND DISCUSSION

The optical transmission and absorbance spectra of PbS films were recorded in the spectral region from 300 to 2000 nm. The optical spectra of PbS films are shown in Fig. 1. while in Fig. 2 are shown the transmission and absorbance spectra of the thickest PbS film.

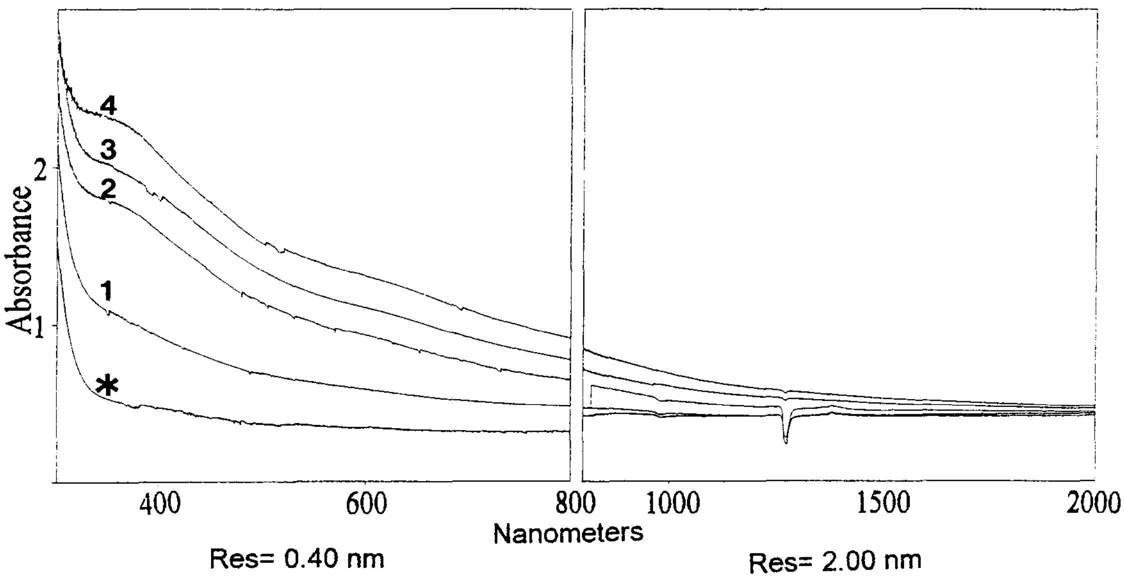

Fig.1. Optical absorbance spectra of thin solid films of PbS of different thickness. Estimated film thickness for the film marked with 1 is ≈ 20 nm, compared with ≈ 60 nm for the film marked with **4**. The star represents the optical spectrum of the substrate.

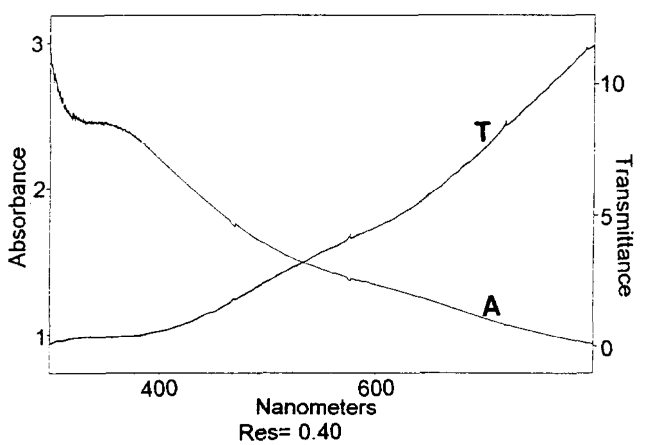

Fig 2. Optical transmission and absorbance spectra of PbS film. Estimated thickness: 60 nm.

It is seen from the spectra (Fig. 1) that for films of thickness of about 20 nm the absorbance is considerably lower then for the films thicker than 20 nm.A greater film thickness producing a glassy appearance of the film surface, which increases the absorbance of the films.The absorbance of the Cu_2S substrate, on the other hand, is in agreement with the previously reported data [5].

Annealing of the films did not bring about any significant changes in the optical characteristics of the films. It is obvious that the annealing time and/or the annealing temperature has to be varied in order to determine any possible changes in the optical spectra of the annealed PbS thin films.

4. CONCLUSION

The PbS thin films show gradual increase in absorption with the increase of the thickness of the films. The maximum absorption is at about 350 nm. The optical spectra revealed that in the near infrared region the films are partly transmitive.

Annealing of the films for one hour at 423 K did not bring about any significant changes in the optical characteristics of the films. This is in contrast to the results obtained from the conductivity measurements [2].

Unfortunately, the energy gap of the PbS thin films could not be detected in these optical measurements, since it exceeds considerably the range of the near infrered and visible region. The mid-infrared spectra of these thin films have not yet been obtained. However, judging from the present visible and near infrared spectra, this will most probably fall in the infrared region between, 2500 and 5000 cm^{-1}.

The present optical measurements should be regarded only as a preliminary result on this type of PbS films. Some more optical measurements are needed, in particular in mid-infrared region, as well as optical reflectance spectra of PbS films of different thickness and different annealing conditions.

ACKNOWLEDGMENT

This work has been carried out as a part of a joint research program under the ALIS link program sponsored by the British Council and the Ministry of Science of the Republic of Macedonia.

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