GROWTH AND CHARACTERIZATION OF LEAD-SULFIDE FILMS DEPOSITED ON GLASS SUBSTRATES

SIHAM MAHMOUD and OMAR HAMID

Physics Department, National Research Centre, Cairo, Egypt

Lead-sulfide (PbS) films have been deposited by chemical deposition method on glass substrates. The details of the preparation method are described. The advantage of this method is simple, relatively inexpensive and easily controlled method that is producing large-area films. Some data about the electrical properties, structure, composition of the films and thermal stability of the powder samples are also presented. The structure and crystallite sizes were determined by X-ray diffraction studies. The films are very adherent to the substrates. The films are polycrystalline and average crystallite sizes are 15 nm. The surface morphology of the as-deposited and heated films was studied with a scanning electron microscope. The rate of deposition and terminal thickness have been determined. Hall measurements were performed at room temperature for films deposited on glass substrate to determine the carrier density, Hall mobility and the mean free path of the carriers.

1. Introduction

From the point of view of cost reduction of photovoltaic devices, thin film technology has been identified as a possible solution. The efficiency of the devices depends largely on the properties of the used materials and on the applied deposition technique. Various techniques are available for the deposition of polycrystalline films of semiconducting materials. The growth from the solution is least demanding and with its simplicity makes it very attractive [1–3].
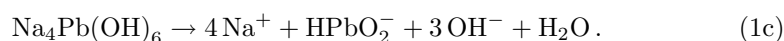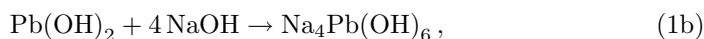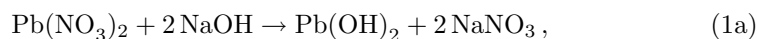
Lead sulfide, an IV – VI semiconductor with a narrow band gap, has been employed usually for the detection of infrared radiation, applications in decorative

coating and in imaging techniques. The samples of lead-sulfide films were prepared by the chemical deposition method. The chemical deposition of PbS has been reported previously by other researchers under different conditions [4–10]. The variations have involved changes in the concentration of the lead acetate or nitrate and thiourea solutions, the temperature of deposition and the use of surface seeding nuclei as a means of improving the properties of the films. Pick [11] discussed the factors which influence film formation in homogeneous precipitation reactions. These include the rate of diffusion of colloidal particles to the glass surface and the influence of crystallization nuclei, which can be formed by the addition of metal ions. The growth and characterization of PbS thin films, deposited on glass, ferro-electric ceramic and single crystals (CdS and Ge) substrates from a water solution of reacting chemicals were investigated [4,6,12]. The experimental results indicate that the properties of the PbS films can vary, depending on the nature of the substrate. The growth rate of PbS films grown by the chemical vapour deposition in the temperature range 698 to 733 K depends on the type of substrate material and increases with increasing temperature. The black films formed that way are polycrystalline PbS with cubic structure [3]. The measurements of Seebeck effect at room temperature show that the conduction is p-type for PbS films deposited on glass. Carrier densities derived from measurements of the Hall effect are equal to those derived from the thermoelectric-power measurements. Therefore, they are interpreted to be equal to the carrier density in the grains of the PbS layer [3].

In the present work, X-ray diffraction pattern (using Philips PW 1390 difractometer), scanning-electron microscope (JOEL-JSM-T20) and the thermal analysis (DCS-50) investigations were carried out with films prepared by the chemical deposition of PbS. The composition of the films was determined by chemical analysis. The carrier density and the mean-free path of the carriers were measured, and the Hall mobility of the films were determined by Hall-effect measurements.

2. Experimental procedure

The lead sulfide films were deposited by the chemical deposition method. Before the deposition, the glass substrates were washed in HNO_3 and distilled water. Then, they were mounted vertically and immersed into the deposition bath containing an equeous solution of the following constituents mixed in the sequence: 0.175M $Pb(NO_3)_2$, 0.57M NaOH, 0.1M $CS(NH_2)_2$ and H_2O. The reaction process is considered as follows:

$$Pb(NO_3)_2 + 2\,NaOH \rightarrow Pb(OH)_2 + 2\,NaNO_3\,, \tag{1a}$$

$$Pb(OH)_2 + 4\,NaOH \rightarrow Na_4Pb(OH)_6\,, \tag{1b}$$

$$Na_4Pb(OH)_6 \rightarrow 4\,Na^+ + HPbO_2^- + 3\,OH^- + H_2O\,. \tag{1c}$$

In the alkaline medium, the thiourea decomposed and released S^{-2} ions which precipitate Pb^{+2} ions from the solution.

$$SC(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + SH^- \, , \qquad (1d)$$

$$HPbO_2^- + SH^- \rightarrow PbS + 2\,OH^- \, . \qquad (1e)$$
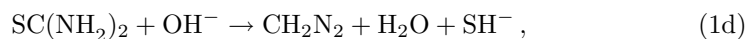
The deposition of the films from a solution involves a nucleation phase in which an initial layer of $Pb(OH)_2$ formed on the glass substrate is chemically converted into PbS by the reaction with S^{-2} ions available in the bath from the hydrolysis of thiourea. The presence of $Pb(OH)_2$ in the as-prepared bath is very vital for the deposition of PbS thin films [9,10]. However, too much of a turbidity would lead to the incorporation of $Pb(OH)_2$ in the films for deposition of longer duration [9,10]. It is speculated that the deposition rate at a constant temperature should be affected mainly by the concentration of thiourea and NaOH. It was found that the increase in the NaOH concentration makes the surface of the deposited film darker and the growth rate decreases slightly. Also, the quantity of thiourea predominantly affects duration of the deposition, while lower concentrations of thiourea give lower growth rates and longer incubation times.

The deposition of the PbS films was done at the room temperature. The advantage of the low temperature used is that during the growth process there is a small possibility for the diffusion of the constituents of the depositing film into the substrate. After the deposition, the slides were removed from the chemical bath after different dipping times, rinsed with distilled water, dried and placed into a desicator. A mirror-like surface was obtained. The thickness of each grown film was calculated from the known mass of the deposit, surface area and density. It was assumed that the film has a density of 7.596 g/cm^3 (of bulk PbS), although these films are expected to have a somewhat lower density than the bulk PbS due to the lower stoichiometry and poorer crystallinity. This method has been in use for finding the thickness of thin films [13,14]. The film thickness is in the 120 to 220 nm range. The bulk ingot material of PbS was prepared by direct fusion of a mixture of the constituent elements (purity 99.999%) in stoichiometric proportions in vacuum sealed silica tube. Hall measurements were made in a standard DC Hall-effect apparatus with a vibrating-read electrometer. Ohmic contacts were made by a simple vacuum evaporation of gold.

3. Results and discussion

Lead sulfide (PbS) is known to crystallize in cubic crystalline lattice with the lattice constant $a = 0.59458$ nm [15]. Atomic coordinates are (0,0,0) and (0,1/2,1/2) for Pb and (1/2,1/2,1/2) and (1,1,1/2) for S. Distances between closest Pb atoms and closest S atoms are 0.42 nm.

Figure 1 shows the XRD patterns of the PbS thin films deposited on a glass slide (a), of the powder collected from the chemical-deposition bath (b) and of the

powder from the thermal ingot (c). The *d*-values of the lines obtained from XRD patterns were calculated and compared with the corresponding values for PbS in
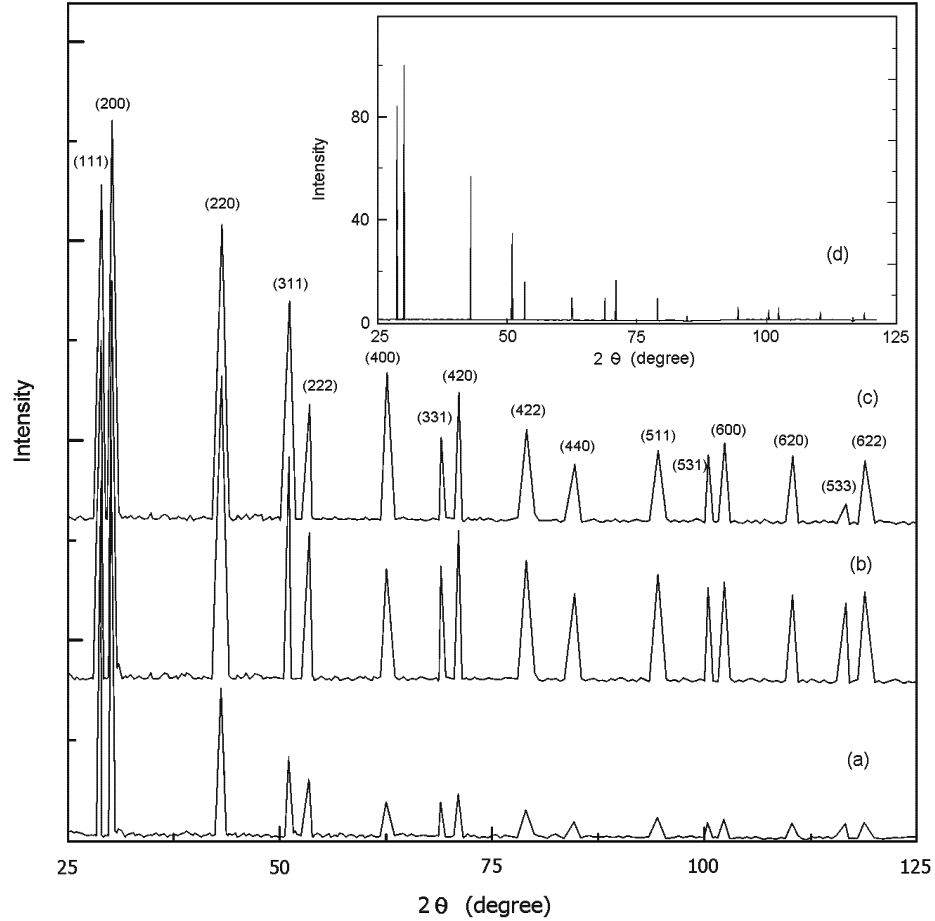

Fig. 1. X-ray results for chemically deposited PbS: a) thin film, b) powder, c) powder from the thermal ingot and d) JCPDS card.

the JCPDS card in Table 1. The derived *d*-values are in good agreement with the standard values, which conform that the film constitutes of PbS. Well-defined (111), (200), (220), (311) and (222) peaks are observed in the XRD pattern. The film is polycrystalline. The average crystallite sizes of 15 nm were determined by measuring the full width at half maximum of the (111), (200) and (220) peaks and using the Scherrer formula [16]

$$T = \frac{k\lambda}{D} \cos\theta \,. \tag{2}$$

For PbS films deposited on glass, the nucleation rate is considered to be larger than the growth rate due to the great number of nucleation centres that exist on the surface of the substrate [4]. This could explain that PbS films deposited on glass are compact and with crystallites of small size.

TABLE 1. *Comparison of the observed d-values (in units of 10^{-10} m) for PbS (derived from Fig. 1) with the JCPDS card.*

hkl	JPCDS (d)		Film-chem. (a)		Powder-chem. (b)		Ingot (c)	
	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0
111	3.429	84	3.43	90	3.426	85	3.428	83.9
200	2.969	100	2.986	100	2.969	100	2.969	100
220	2.099	57	2.096	38	2.095	76	2.098	74
311	1.79	35	1.789	21	1.788	56	1.79	55
222	1.714	16	1.713	15.6	1.715	37	1.715	29
400	1.484	10	1.482	9.9	1.483	28	1.482	37
331	1.362	10	1.36	9.9	1.361	28.2	1.362	21
420	1.327	17	1.326	11.9	1.325	37.7	1.325	32.2
422	1.212	10	1.211	8	1.212	30.3	1.211.	23
511	1.1424	3	1.142	6.3	1.142	27	1.142	18
440	1.0489	6	1.049	5.1	1.049	22	1.049	14.5
531	1.0034	5	1.003	5.1	1.0029	23.7	1.0031	17
600	0.9893	6	0.988	5.9	0.989	25.1	0.988	20
620	0.9386	4	0.937	5.1	0.939	22.5	0.938	17
533	0.905	2	0.903	4.7	0.904	20	0.904	5
622	0.8952	4	0.893	5.1	0.894	22.9	0.894	16

The differential-scanning calorimeter (DSC) spectra for the powder samples (chemical deposition and thermal ingot) are shown in Fig. 2. Figure 2a shows two exothermic peaks, the first at 260.59 °C, which can be attributed to the growth of grain size. The second peak (at 432.04 °C) indicates that at higher annealing temperatures a transformation to another crystalline state may occur. The thermal-ingot powder (Fig. 2b) shows a high-intensity exothermic band at 278.72 °C and an endothermic band (398.59 °C) at higher temperatures.

Lead sulfide is formed when the ionic product (IP) of Pb^{+2} and S^{-2} exceeds the solubility (SP) of PbS. The ratio $IP/SP = S$ defines the super-saturation of the ions over the PbS and can be varied by choosing the appropriate initial concentration of the reactants. When $S > 1$, the ions combine on the substrate and in the solution to form PbS nuclei which grow with time to give film and precipitate, respectively. Once PbS is formed, it acts as a catalyst for preferential further deposition of fresh portions of PbS. As the catalytic PbS surface develops both on the surface and in the volume of the solution, the proportion of PbS formed on the substrate is determined by the ratio of nuclei formed on the substrate and in the solution.
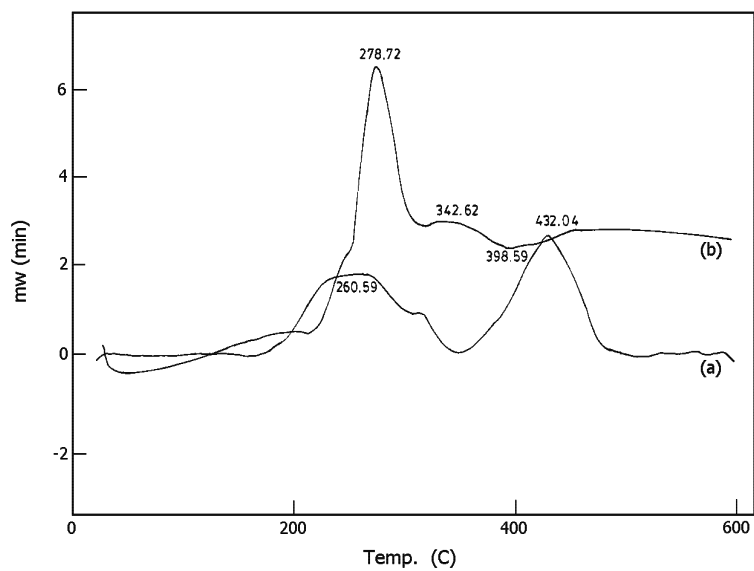
Fig. 2. Differential scanning calorimeter spectra of PbS *powder samples, a) chemical deposition, b) thermal ingot.*
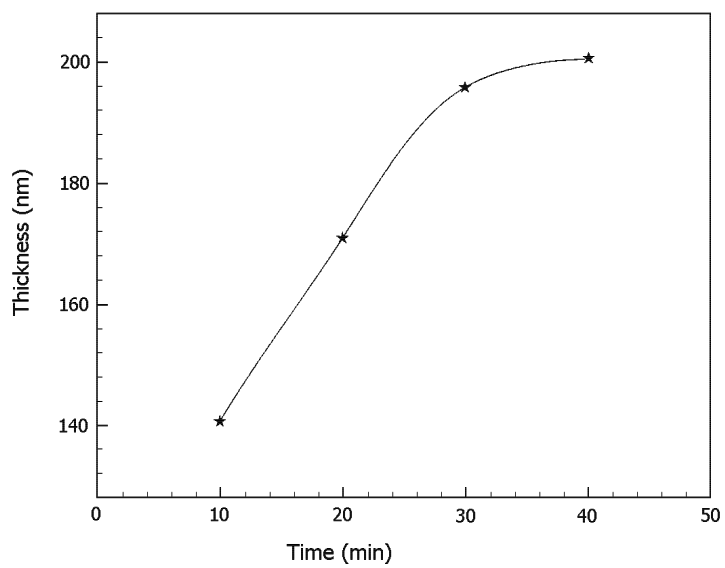

Fig. 3. Thickness of PbS *films as a function of deposition time.*

Figure 3 shows a typical curve for film thickness as a function of the dipping time. In the initial stage of the growth, the thickness increases at a fast rate. Subsequently, the rate decreases, resulting in a terminal thickness. The rate of deposition is high in the initial stages of growth because the concentration of Pb^{+2} and S^{-2} ions is high. As more and more PbS is formed, the solution becomes depleted of ions, resulting in a lower rate of deposition. The rate of deposition becomes zero, resulting in a terminal thickness, when the concentration of Pb^{+2} and S^{-2} ions decreases to a values such that $S < 1$.

The growth mechanism of formation of PbS films, deposited on glass substrate for different dipping times and for different annealing, is supported by the investigations with the scanning electron microscope, as seen in a series of electron micrographs in Fig. 4. The photographs were taken under the same conditions of the electron energy (20 keV) and magnification (6000×) to compare the size of the crystallites. The figures show a cross-like needle-shaped crystalline structure with a fair amount of inter-crystallite space. As the film thickness increases, these needle-like crystallites grow in size and more inter-spaces appear. The sample shown in Fig. 4d was annealed at 473 K for one hour; the formation of large, irregular clumps of PbS could be observed. The electron micrograph indicates the presence of randomly oriented inter-grown aggregate crystals in a heterogeneous size distribution (Fig. 4e).

In single-crystal semiconductors, there is a simple relationship between the Hall coefficient R_H and the free-carrier density N

$$N = \frac{r}{eR_H} \,, \tag{3}$$

where the scattering factor r is close to unity. Combined with the measurement of conductivity σ, this yields the well-known equation for the Hall mobility

$$\mu_H = R_H \sigma \,. \tag{4}$$

The mean free path ℓ of the carriers can be estimated from the following relation

$$\ell = \frac{h}{2e} \left(\frac{3n}{\pi} \right)^{1/3} \mu_H \,, \tag{5}$$

where h is the Planck constant and e the electron charge.

In the case of polycrystalline films, difficulties arise due to the fact that the electrical properties of such films are usually dominated by charge trapped at grain boundaries, resulting in carrier depletion over part or all of the grains. In other words, the carrier density is spatially inhomogeneous, and the interpretation of Hall-effect measurements is no longer straightforward. Volger [17] proposed a geometric model for an inhomogeneous material consisting of conducting grains separated by more-resistive inter-granular material. He showed how the measured Hall effect could deviate appreciably from the Hall effect appropriate to the grains

in such a configuration. Measurements of the carrier density by Hall effect or by thermoelectric power give the density of free holes in the grains [18].
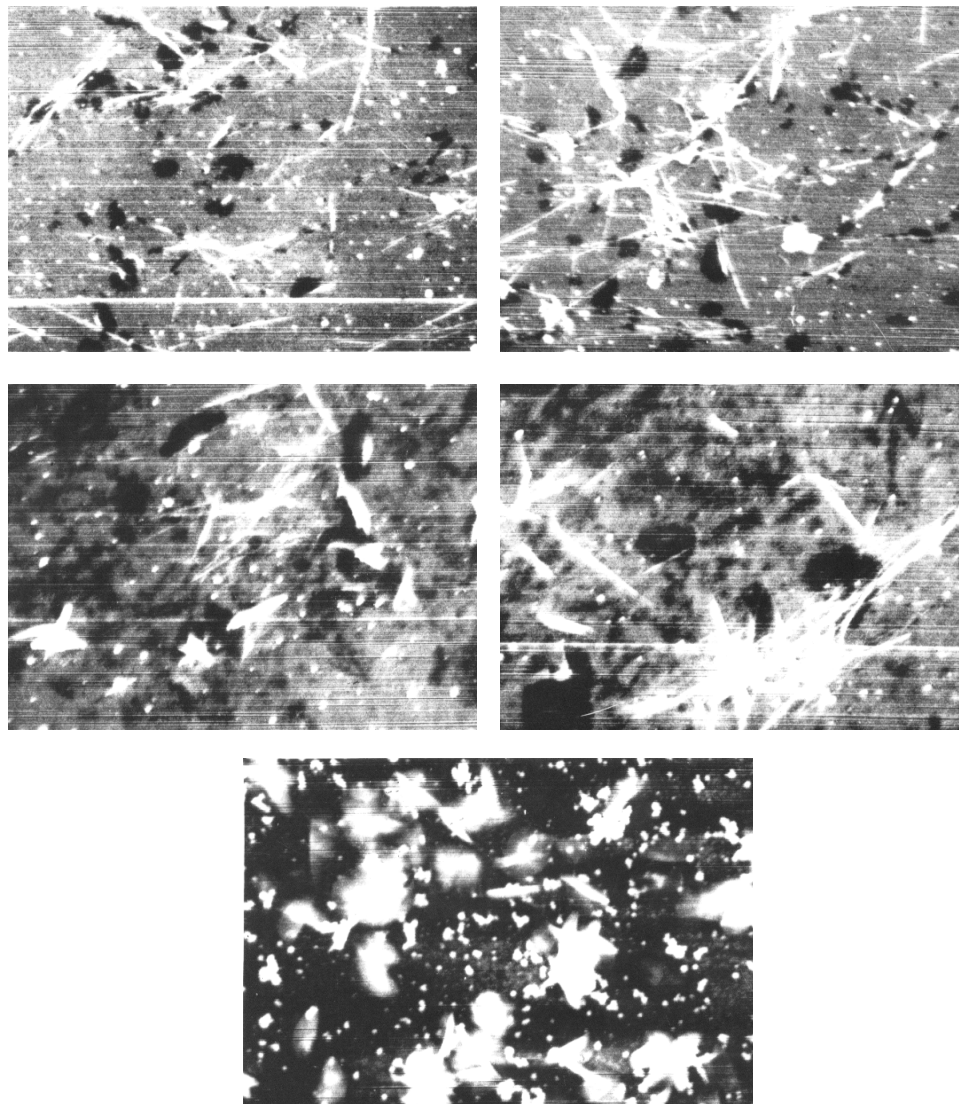

Fig. 4. Scanning electron micrographs of PbS films prepared in different ways, enlargement 6000×. Dipping times and the thickness of the films were: a) 10 min, d = 141 nm, b) 20 min, d = 171 nm, c) 30 min, d = 196 nm, d) 40 min, d = 201 nm, e) 40 min, d = 201 nm, but also annealed at 473 K for 1 hour.

Equations (3) to (5) were applied for the calculation of the carrier density, Hall carrier mobility and the mean free path of the as-deposited PbS thin films prepared

in this work. The thickness and the resistivity of the films were approximately 0.2 μm and 5 Ωcm, respectively. The measurements of the Hall effect confirmed the p-type conduction for PbS films deposited on glass substrate. The carrier concentration was estimated at about 2.5×10^{17} cm^{-3} and the mobility is about 5 cm^2/Vs. These values give the mean free path of the carriers, ℓ, of 0.642 μm. These results are in a good aggreement with the results in the literature [4,19]. The measured Hall mobility is very small compared to the value of 500 cm^2/Vs, expected at room temperature for a single crystal of PbS [20].

4. Conclusion

Microstructure characterization was carried out by X-ray diffraction and scanning electron microscopy in order to determine the crystallite size and to study the surface morphologies of the as-deposited and of heat-treated films of PbS. The grain size of the films, as observed by SEM, is found to increase with increasing thickness, and a clear change in the films was observed due to annealing. It was established by X-ray analysis that PbS films prepared on glass substrates are polycrystalline and the primary direction was (111). The as-deposited PbS films have p-type conductivity and a low resistivity (5 Ωcm). The carrier density, Hall mobility and the mean free path of the carriers of PbS films are in the range 2.5×10^{17} cm^{-3}, 5 cm^2/Vs and 0.642 μm, respectively.

References

[1] S. Yamage, A. Yoshikawa and H. Kasa, Japan J. Appl. Phys. **26** (1987) 1002.

[2] J. L. Boone, S. A. Howard and D. D. Martin, Thin Solid Films **176** (1989) 143.

[3] N. I. Fainer, M. Kosinova, Yu. M. Rumyantsev, E. G. Salman and F. A. Kuznetsov, Thin Solid Films **280** (1996) 16.

[4] I. Pintilie, E. Pentia, L. Pintilie, D. Petre, C. Constantin and T. Botila, J. Appl. Phys. **78**, 3 (1995) 1713.

[5] K. M. Gadava, S. A. Jodgudri and C. D. Lokhande, Thin Solid Films **245** (1994) 7.

[6] L. Davis and M. K. Norr, J. Appl. Phys. **37**, 4 (1966) 1670.

[7] C. Nascu, V. Vomir, V. Ionescu and I. Pop, Rev. Roumaine Chem. **40**, 2 (1995) 127.

[8] I. Pop, C. Nascu, V. Vomir and V. Ionescu, Rev. Roumaine Chem. **39**, 1 (1994) 31.

[9] P. K. Nair and M. T. S. Nair, J. Phys. D **23** (1990) 150.

[10] P. K. Nair and M. T. S. Nair, Semicond. Sci. Technol. **4** (1989) 807.

[11] H. Pick, Z. Phys. **126** (1949) 12.

[12] S. Watanabe and Y. Mita, J. Electrochem. Soc. **116**, 7 (1969) 989.

[13] A. E. Rakshani and J. Varghese, Solar Energy Mater. **15** (1987) 238.

[14] D. L. Douglass, Solar Energy Mater. **10** (1984) 1.

[15] Landolt-Börnstein Handbook, New Series 111/1402, Springer-Verlag, Berlin/Heidelberg (1986), p. 301.

[16] B. D. Cullity, *Elements of X-Ray Diffraction*, Adison-Wesley, Amsterdam (1978) p.102.

[17] J. Volger, Phys. Rev. **79** (1950) 1023.

[18] E. Espevic and R. H. Bube, J. Appl. Phys. **42** (1971) 3513.

[19] G. H. Blount, P. J. Schreiber and D. Smith, J. Appl. Phys. **44** (1973) 978.

[20] R. S. Allgaler and W. W. Scanlon, Phys. Rev. **111** (1959) 1029.

RAST I PROUČAVANJE TANKIH SLOJEVA OLOVNOG SULFIDA
TALOŽENOG NA STAKLENU PODLOGU

Tanke slojeve olovnog sulfida (PbS) taložili smo kemijskom metodom na staklene podloge. Podrobno se opisuje način pripreme. Prednost te metode jest jednostavnost, relativno malen trošak i postupak koji se lako nadzire a postižu se slojevi velike ploštine. Opisujemo električna svojstva, strukturu i sastav, te toplinsku stabilnost praškastih pripremaka. Strukturu i veličinu kristalića odredili smo difrakcijom rendgenskog zračenja. Slojevi odlično prijanjaju na podloge. Slojevi su polikristalinični a prosječna veličina zrna je 15 nm. Izgled površine svježe pripremljenih i opuštenih slojeva smo istraživali skenirajućim elektronskim mikroskopom. Odredili smo brzinu taloženja sloja i krajnju debljinu. Mjerenjem Hallovog efekta na sobnoj temperaturi slojeva taloženih na staklenoj podlozi odredili smo gustoću nositelja, Hallovu pokretljivost i duljinu srednjeg slobodnog puta nositelja.