

Crystallite size effect in PbS thin films grown on glass substrates by chemical bath deposition

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Nanocrystalline PbS thin films were grown on glass substrates using Chemical Bath Deposition (CBD) method. The presence of nanocrystals was revealed by optical absorption and photocurrent measurements. We have compared the absorption threshold between large size and nanocrystalline PbS. Our study was performed in order to demonstrate that the size of the PbS thin films crystallites affects the photoelectric properties of the material. Using the Scanning Electron Microscopy (SEM) we have determined that the grains inside large size PbS crystallites are 300 nm. From the optical absorption measurements we have determined that the size of PbS nanocrystals is between 5-50 nm. The photoconduction measurements show that large size PbS has a maximum in infrared situated at 2.4 μm , and in PbS nanocrystalline thin film this maximum is shifted toward smaller wavelengths towards visible and near infrared.

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1. Introduction

Nanocrystalline thin films are of significant interest for a large variety of electronic and optoelectronic devices. The quantum effects that come up when the crystal size drops below 30 nm change in a fundamental way the material properties, which can be used to design a new generation of devices. The growth techniques used to obtain nanocrystalline materials and the investigation of their properties are thus of considerable interest [1]. In this paper photocurrent and absorption measurements are used to examine the interaction between the nanocrystalline material and electromagnetic radiation. The understanding of these processes is essential for the applications concerning radiation detection and emission in visible and infrared. The method used in this work to prepare the PbS nanocrystals is the Chemical Bath Deposition (CBD). This method is inexpensive and does not require sophisticated vacuum equipment. The substrate used for deposition is glass and electrical ohmic contacts are obtained by evaporating gold in a coplanar configuration.

2. Experimental

Two sets of PbS samples were prepared: „standard” and „nanocrystalline” thin films. The glass substrates were very carefully cleaned using an oxidant mixture ($\text{K}_2\text{Cr}_2\text{O}_7 : \text{H}_2\text{SO}_4 = 1:10$), HNO_3 , 1% EDTA) and were thoroughly rinsed with distilled water before deposition. The cleaning of the substrate surface is of crucial importance for the quality of the film that will be obtained afterwards. The substrates were introduced vertically in a

chemical bath containing an aqueous solution consisting of: $\text{Pb}(\text{NO}_3)_2$ 0.06M, thiourea $\text{SC}(\text{NH}_2)_2$ 0.24M, NaOH 0.6 M and a reducing agent (hydroxylamine, hydrochloride, $\text{NH}_2\text{OH}\cdot\text{HC}$ 0.1 M) [2]. The deposition temperatures for the two films were 22 °C and 24 °C and the deposition time was 17 minutes in both cases.

For photoelectrical measurements gold electrodes in a coplanar configuration were evaporated in vacuum on the surface of the PbS for both types of films. The final active area is $5 \times 5 \text{ mm}^2$. For optical absorption measurements, the absorption area is given by the dimensions of the exit slit of the monochromator set to $2 \times 2 \text{ mm}^2$. The photoconductive measurements were performed with modulated light using the standard setup consisting of an ORIEL monochromator, a lock-in amplifier (model SR830SDP), a Keithley Electrometer (model 6517A), a dc voltage source (model Grunding 3000), an incandescent lamp and a mechanical chopper (model Ithaco 383A).

3. Results and discussions

The presence of nanocrystals in PbS films was demonstrated by optical absorption and photocurrent measurements. As a result of inhomogeneities in the grown layer the spectral characteristics are different for different probed sites on the sample's surface. However, the presence of nanocrystalline material is evidenced in all cases by a maximum in the absorption spectrum in the visible – near infrared region of the spectrum, in the range 400 – 1250 nm, as shown in Fig. 1 (a), (b). In this spectral range macroscopic PbS has minimal absorption, as evident from Fig. 1b.

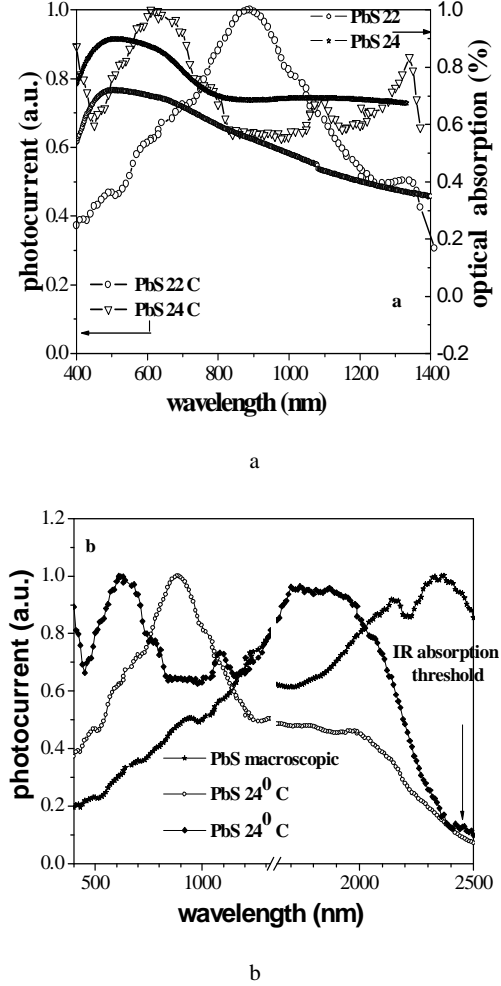


Fig. 1. Optical absorption and photocurrent spectra: a) Photocurrent spectra response (left) and corresponding optical absorption spectra (right) for nanocrystalline PbS; b) photocurrent spectra for nanocrystalline PbS and macroscopic PbS.

Apart from this absorption maximum, an absorption band is observed in the infrared range 1250- 2400 nm of the spectrum. In this range, macroscopic PbS exhibits an important absorption also. Two absorption thresholds are apparent from Fig. 2, one in the near infrared and the other in infrared. The absorption threshold of macroscopic PbS ($E_g = 0.41$ eV) is 3 μm at room temperature. The absorption threshold of nanocrystalline PbS in infrared is 0.49-0.51 eV, corresponding to nanocrystals of larger size, close to that corresponding to the macroscopic material. The absorption threshold in the near infrared region of the spectrum is 1.23-1.28 eV from absorption measurements and 0.93 – 1 eV from photocurrent measurements, respectively, as shown in Fig. 2. Apart from these absorption thresholds, as mentioned before, we notice in Fig. 1 and Fig. 2 two pronounced maximums in the near-infrared – visible range of the spectrum. They correspond to an energy of the incident radiation of $E = 2.7$ -2.8 eV in

absorption measurements and to $E = 1.4$ eV (PbS 22 °C) and $E = 2$ eV (Pb 24 °C) in photocurrent spectra respectively. We attribute these maxima to excitonic effects in small size PbS nanocrystals [3].

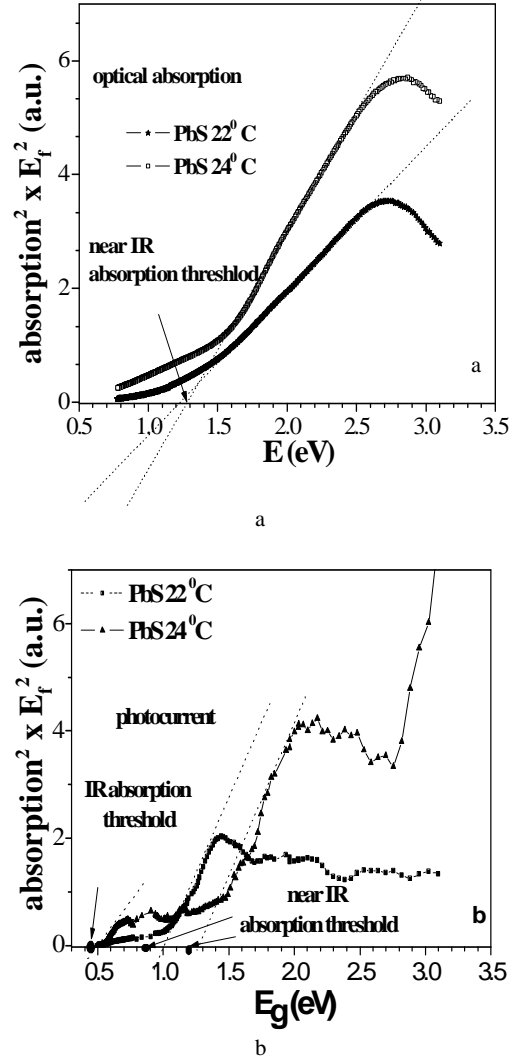


Fig. 2. $\alpha^2(\hbar\omega)^2 = f(\hbar\omega)$ Spectra for absorption threshold determination: a) optical absorption measurements; b) photocurrent measurements.

In a semiconductor material, assuming in a first approximation parabolic bands (the effective mass approximation) and for a nanocrystalline radius R , the increase of the band gap due to quantization effects in the conduction and valence bands is given by:

$$\Delta E_g = \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.786e^2}{\epsilon R} \quad (1)$$

where m_e , m_h are the effective masses of the electron in the conduction band and of the hole in the valence band, respectively and $\epsilon = 17.3$ is the dielectric constant of PbS.

ΔE_g is the increase in bandgap of the nanocrystalline material compared to macroscopic PbS. The first term in (1), depending as $\approx \frac{1}{R^2}$, is due to the presence of quantized electronic and hole levels while the second term represents the Coulomb energy depending as $\approx \frac{1}{R}$, inversely proportional with the nanocrystal radius R.

Eq. (1) includes the basic physical principles underlying the increase in bandgap when the nanocrystalline size decreases but is not quantitatively correct for dimensions smaller than 10 nm. Taking into consideration that the bands are not parabolic a quantitative fitting can be obtained with a very good agreement between theory and experiment [4]. Using these already published data we estimate a nanocrystalline size of 4-5 nm corresponding to $E = 1-1.25$ eV, 3.8 nm for $E = 1.4$ eV, 2.7 nm for $E = 2$ eV and 2 nm for $E = 2.7-2.8$ eV, respectively.

4. Conclusions

Because no excitonic effects were observed in large size nanocrystalline PbS, we attribute the absorption

threshold at 1- 1.25 eV to the presence of nanocrystals of 4-5 nm in size and the maxima in the range 2.7-2.8 eV to excitonic absorption that becomes important when the nanocrystalline size drops below 2 nm. The possibility to vary the bandgap of PbS in the range 0.41 – 2.7 eV is an important material property, which opens the way to a new class of applications.

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