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THE INFLUENCE OF HYDRAZINE HYDRATE IN THE PREPARATION OF LEAD SULFIDE THIN FILM *

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Abstract – In this paper a chemical deposition procedure for the preparation of lead sulfide thin film is presented. The details of the preparation method are described. The influence of hydrazine hydrate on the microstructure and deposition rate of lead sulfide thin film has been investigated. The concentration of the lead ions in the deposition bath decreases more slowly when the hydrazine hydrate is added. In the presence of hydrazine hydrate the predominance of (111) as the orientation of film growth is established. Optical absorption spectra, AFM and SEM micrograph have shown that the film was formed from nanometer grains.

Keywords – Lead sulfide, hydrazine hydrate, chemical deposition, thin film

1. INTRODUCTION

Pure PbS is an intrinsic semiconductor at 600 ^{o}C and higher. It is believed that the photoconductivity property of lead sulfide is an intrinsic characteristic of the material and not the result of thermal vibration, impurity or crystal defects. Photoconductivity is, however, greatly enhanced by the introduction of impurity ions or crystal defects into the lattice. It has long been known that polycrystalline lead sulfide films might be used as the basic useful photodetector. The lead sulfide photodetector was brought to the manufacturing stage of development in Germany about 1943. After 5 decades, lead sulfide detectors are still in great demand as sensors for major military systems, as well as industrial, commercial and medical applications [1-2]. In order to prepare the PbS infrared detector, two primary methods: vacuum sublimation and chemical deposition have been used. In both methods, PbS is prepared as a polycrystalline thin film deposited on a glass, quartz, and sapphire or stronsium titanate substrate. The more common fabrication technique for PbS is chemical bath deposition. In the chemical deposition procedure, the substrate is immersed in an aqueous solution of lead salt and thiourea. Sodium hydroxide (NaOH) is added to the solution to complete the deposition of PbS onto the substrate. Although the acidic bath was used by Gadave [3], a basic solution is needed to obtain a good layer of PbS semiconductor having optimum mechanical and electrical properties. It has been shown by several researchers that the photoconductive properties of chemically deposited polycrystalline lead sulfide layers have been affected by different parameters such as deposition condition, impurities and heat treatment processes. As it has been demonstrated with Espevik [4] and Kothiyal [5], the photoconductivity properties of lead sulfide thin film depends on the microstructure

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and morphology of film. They have shown when the grains size of film decrease, the photoconductive properties of film increase. Therefore, in order to control the grains size and make the photosensitive lead sulfide film, different additives and metal ions have been added to the chemical deposition bath. Such additives are used to modify the rate of polycrystalline thin film growth, crystallite size, film thickness and composition. For example, Pentia and his co-workers [6], investigated the effects of reducer and Bi^{3+} ions on the deposition process of lead sulfide thin film. Larramedi et. al, [7], have discussed the influence of KBr concentration on the morphology of the film surfaces. They concluded that the mean grain size of the PbS formed on the substrate increased with the KBr concentration in the bath by a linear dependence. Abarbanel et al. [8], prepared the polycrystalline thin film of lead sulfide by the hot wall technique and studied the influence of the grain growth, Oxygen and Indium on the photoconductivity of PbS thin film. Pop et al. [9], have discussed the effect of reducing additive ($NH_2OH.HCl$) into the photoconductivity properties of lead sulfide thin layers. Basu et al. [10] have reported the chemical deposition of PbS thin film in the presence of thioacetamide, and the dependence of the thickness as a function of the bath parameters has also been studied. In the best of our knowledge, there is no experimental result about the influence of hydrazine hydrate on the microstructure of lead sulfide thin film. In the present work, PbS thin film has been deposited by the chemical method and hydrazine hydrate used as an additive for controlling the rate of deposition and the morphology of the film. The influence of hydrazine hydrate on the photoconductivity properties of PbS thin film will be presented in the next study [11].

An X-ray diffractometer (Philips PW-1729), scanning electron microscope (Philips XL 40), and a Hitachi U-3410 photospectrometer have been used for characterization of lead sulfide thin film, which is prepared using the chemical deposition method.

2. EXPERIMENTAL PROCEDURE

In preparation of PbS layers with the chemical deposition technique, different procedures have been used [12, 13]. The main differences in these methods are the kind, concentration of chemical components and additives. The more effective of these chemical additives are considered proprietary, and in the literature these are generally referred to simply as oxidant agent [14, 15], and reducing agent [16]. In our experiment the method of Kicinski [12] has been applied, but the chemical deposition bath involves a different chemical concentration. The chemical reactions that can be considered between lead and sulfur components are as follows [17]:

$$Pb(NO_3)_2 + 4NaOH \rightarrow [Pb(OH)_4]^{2-} + 4Na^{+} + 2NO_3^{-} \quad (1)$$

$$[Pb(OH)_4]^{2-} + SC(NH_2)_2 \rightarrow PbS + 2OH^{-} + CN_2H_2 + 2H_2O \quad (2)$$

Experimental results have shown that the properties of deposited PbS thin film depend on the concentration of lead nitrate (acetate), thiourea, sodium hydroxide, the temperature of the deposition bath and the use of surface seeding nuclei as improving factors of properties of the films. Therefore, several chemical baths have been prepared and the quality of PbS deposited thin films have been checked. The preferred mixture with the following concentrations has been chosen;

A) 30 cc of 2.3 molar sodium hydroxide,
B) 24 cc of 0.6 molar lead acetate,
C) 48 cc of 0.3 molar thiourea,
D) 1 cc of 3.0 molar hydrazine hydrate.

The above solutions are mixed respectively and stirred for 20 seconds. The value of pH must be adjusted near to 12. Then, the mixed solution must be placed in a constant temperature bath at 24°C. The substrate (glass) is placed into the bath and allowed to remain undisturbed for 60 minutes. In the immersion of the substrate, it must be rested at an angle in the deposition solution so that at least one surface receives deposited crystals thereon in a direction unaided by gravity. Following this, the substrate is removed and washed out with water to remove any excess loosely deposited lead sulfide. Strict controls of the deposition parameters such as time, temperature, solution homogeneity, etc. are required to obtain the proper film structure, composition and performance characteristics.

3. RESULTS AND DISCUSSION

In the base of the above procedure, the lead sulfide thin films have been prepared. In Fig. 1, the rates of deposition PbS thin film for two different conditions are illustrated. The thickness of each grown film was calculated from the known mass of the deposit, surface area and its density. For this purpose, a precision balance (Satorious BA110S) with 0.0001 gr standard deviation has been used. It was assumed that the film has a bulk density of PbS (7.569 gr/cm^3). This method has been used for finding the thickness of film [18]. The comparison of two curves shows that hydrazine hydrate decreases the deposition rate. The above results can be explained by the theory of chemical deposition thin films. In order to form a metal sulfide thin film by a controlled ion-by-ion reaction in a chemical bath, it is necessary to eliminate spontaneous precipitation. This can be accomplished by having a fairly stable complex of the metal ions, which provides a controlled number of the free ions according to the equilibrium reaction of the type:

$$M(A)^{2+} \Leftrightarrow M^{2+} + A \tag{3}$$

The concentration of free metal ions at a particular temperature is given by

$$[M^{2+}][A]\frac{1}{[M(A)^{2+}]} = K_i \tag{4}$$

where K_i is known as the instability constant of the complex ion. The smaller this constant, the greater stability of the complex, and hence smaller is the concentration of metal ions in the solution. The concentration and temperature of an appropriate complexion agent control the concentration of the metal ions. As it was presented in the introduction, the system, which is used for the preparation of PbS thin film, contains salt of Pb, thiourea and alkali. The equilibrium of the system depends on the ratio of component concentrations such as $Pb(OH)_2$, $Pb(N_2H_2CS)^{2+}$ and $[Pb(OH)_4]^{2-}$ [19]. Since, the pH of the mixed solution for PbS thin film deposition is high, the $[Pb(OH)_4]^{2-}$ is the relatively stable complexion agent. At a particular temperature PbS will be deposited if the ions product of lead sulfide exceeds the solubility products. The Pb^{2+} released by the $[Pb(OH)_4]^{2-}$ complex and S^{2-} released by thiourea combine at the nucleation center on the substrate to produce PbS thin film. The quantity of ions utilized for film formation depends on the rate of formation of PbS on the substrate surface. This rate depends on not only the ratio of the nucleation center available at the surface of the substrate to those in the volume of the solution, but also on the rate of release of Pb^{2+} and S^{2-} ions. The hydrazine hydrate molecule is a bidentate ligand. It can react with a metal ion to form two different kinds of metal complexes [20, 21]. The shape of these two complexes is shown in Fig. 2. When the hydrazine hydrate is added to chemical deposition bath which has metal ions such as Pb^{2+} the complex II will be formed [21]. Thus, hydrazine hydrate causes a decrease on the releasing rate of Pb^{2+} ions in the bath.

It can be seen in Fig. (3) that in the presence of hydrazine hydrate the concentration of lead ions in the solution decrease slower than without it. Puiso [22] has shown that the growth crystallographic orientation and microstructure of the film depend on the Pb^{2+} concentration ions in the solution of the deposition process. Therefore, the presence of hydrazine hydrate would change the growth rate and microstructure of film. When the rate of deposition and the nucleation center on the substrate are high, the size of the grain would decrease and film will be formed from very small grains. This subject can be confirmed by the optical absorption spectrum of film. In the absence of hydrazine hydrate, the optical absorption spectrum has several peaks between a 600 to 800 nm wavelength, and hydrazine hydrate homogenize the size of grain and the peak of absorption will be shifted into a shorter wavelength. The image of AFM shows that the film, which is prepared in the absence of hydrazine hydrate, has a one-dimensional needlelike structure with a different size (Fig. 4). Therefore, it is reasonable to observe several peaks in the absorption spectra of the film. The optical absorption of two different films has been taken by a Hitachi U-3410 photospectrometer and is shown in Fig. (5 a, b). The size of PbS nanoneedles formed within the deposited film can be estimated from the position of the absorption band [23, 24]:

$$E(r) = (hc)/\lambda \tag{5}$$

$$E(r) = \left[E_g{}^2 + \frac{2\hbar^2 E_g \left(\frac{\pi}{r}\right)^2}{0.085 m_e} \right]^{1/2} \tag{6}$$

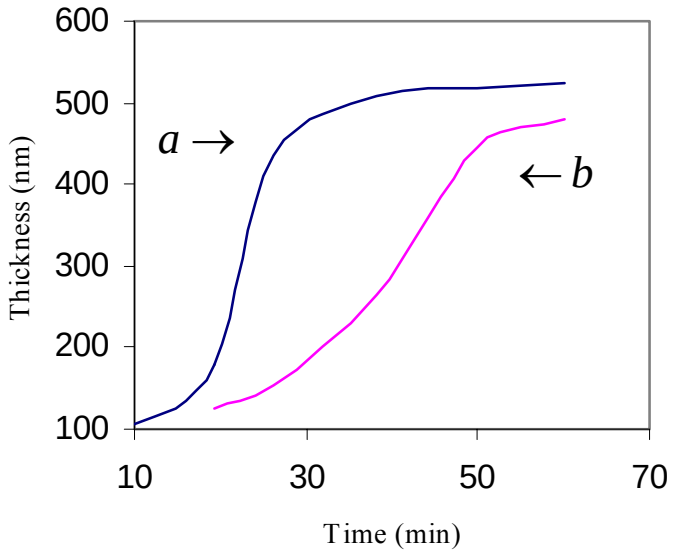

Fig. 1. Variation of PbS film thickness with deposition time for different baths
(a) without hydrazine hydrate, (b) with hydrazine hydrate

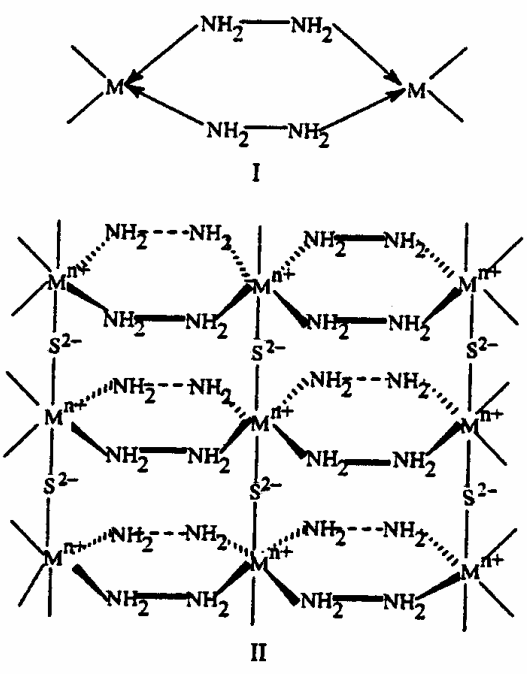

Fig. 2. The shape of two different kinds of metal ion-hydrazine complexes

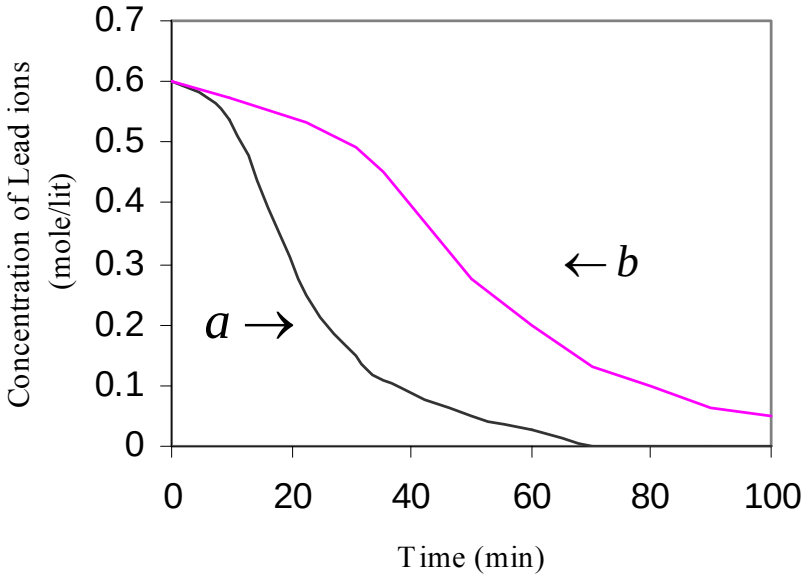

Fig. 3. Variation of Pb^{2+} ion concentration in chemical deposited bath with time; (a) without hydrazine hydrate, (b) with hydrazine hydrate

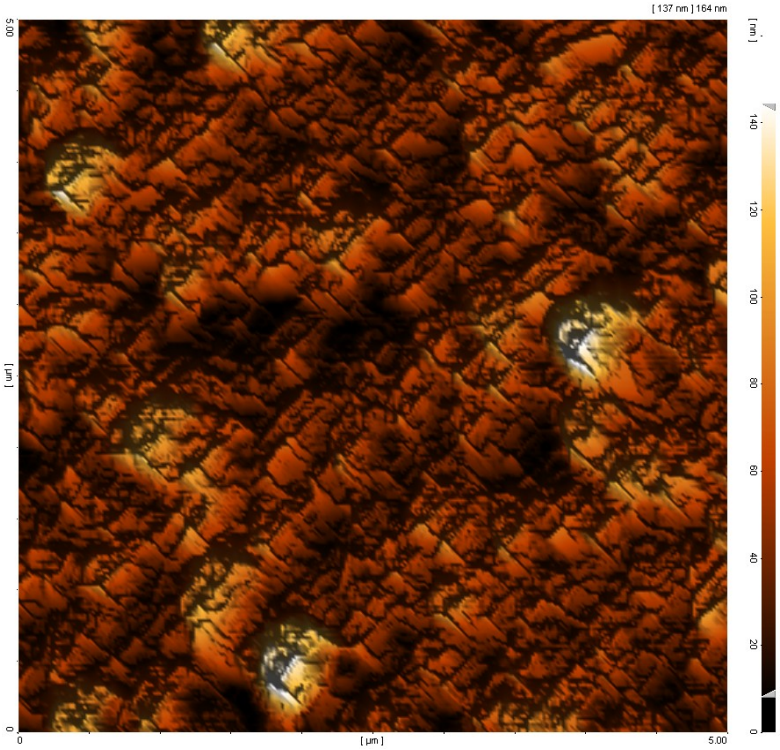
[137 nm] 164 nm
[nm]
140
120
100
80
60
40
20
0
5.00
[µm]
0
[µm]
5.00

Fig. 4. (a)

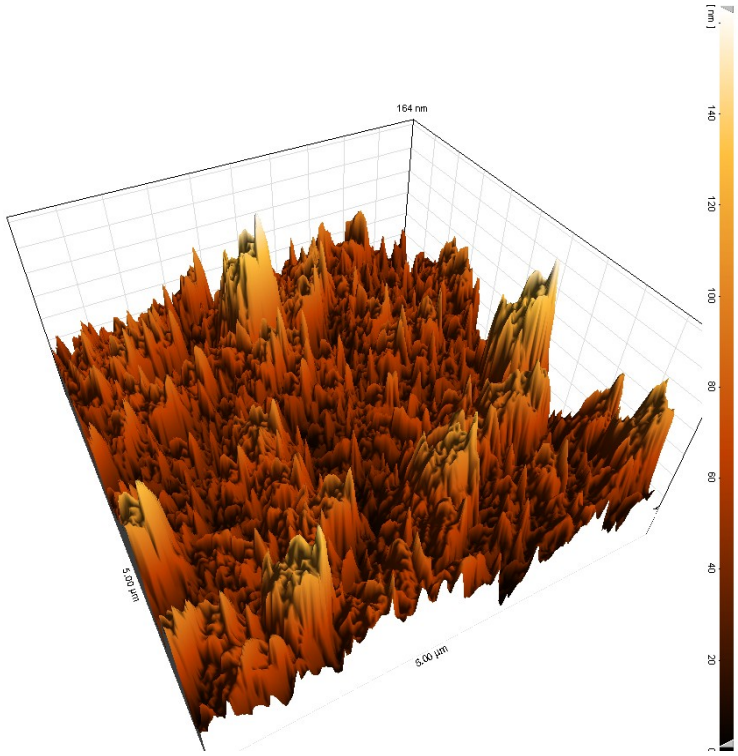
164 nm
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Fig. 4. (b)

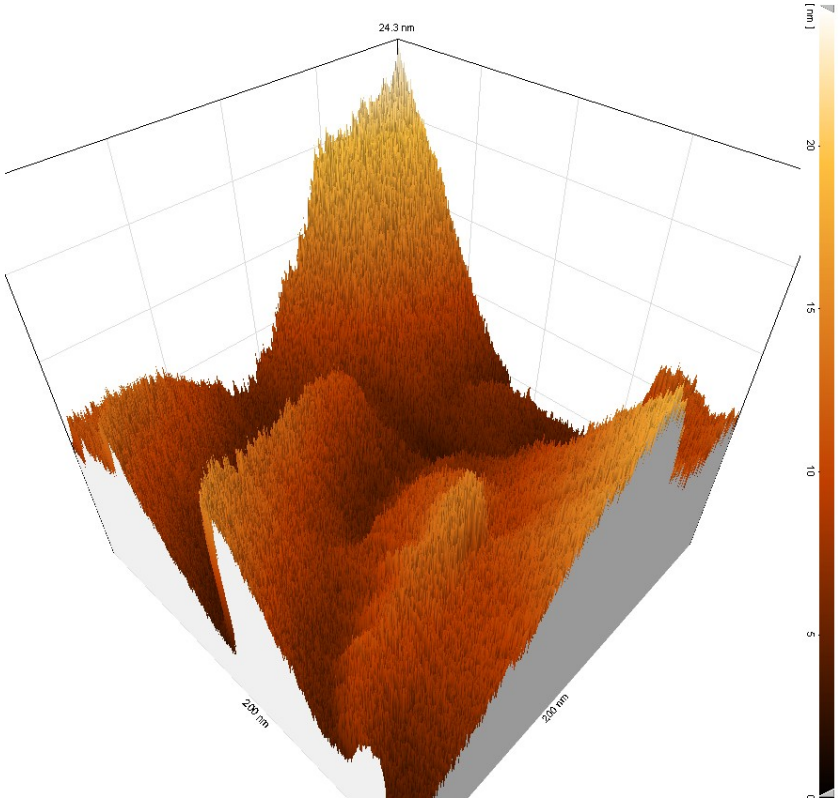

Fig. 4. (c)

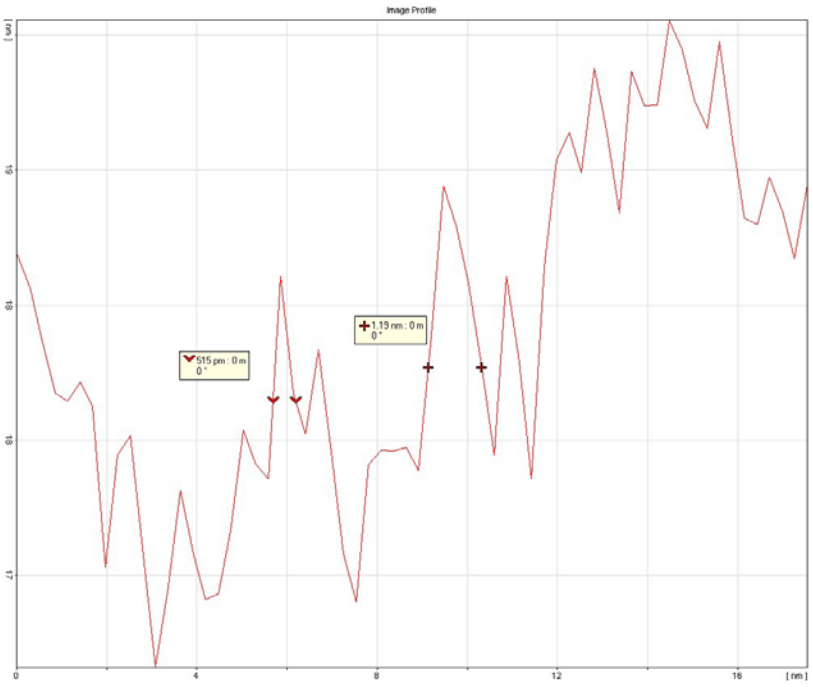

Fig. 4. (d)

Fig. 4. AFM images of lead sulfide thin film which was prepared in the absence of hydrazine hydrate and taken in an area μm^2; (a) 25, (b) 25, (c) 0.04, (d) profile of sample (c)

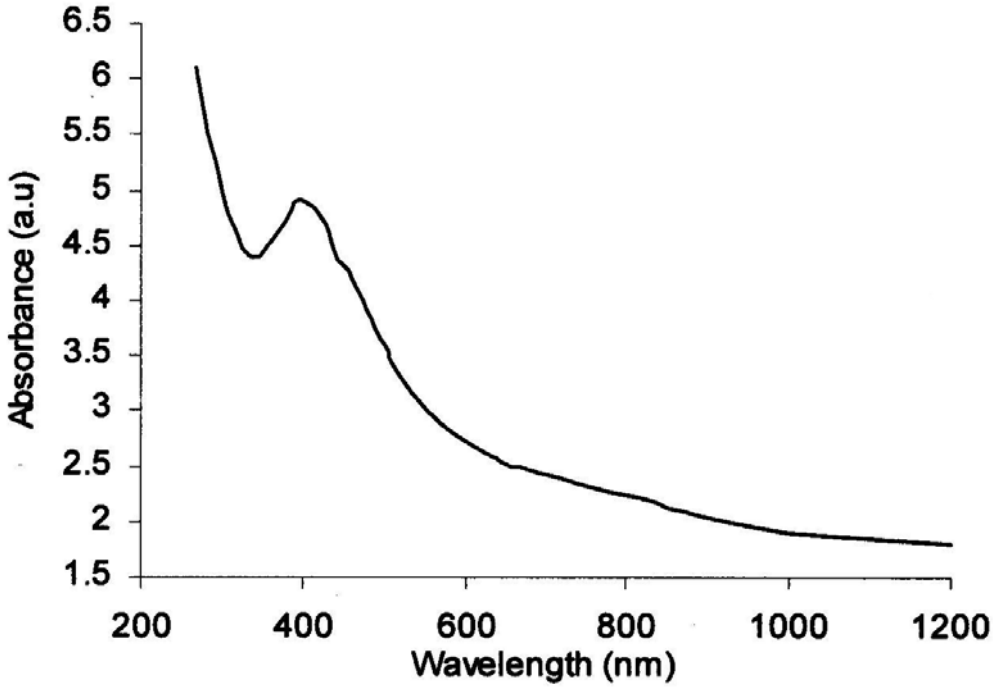

Fig. 5. (a)

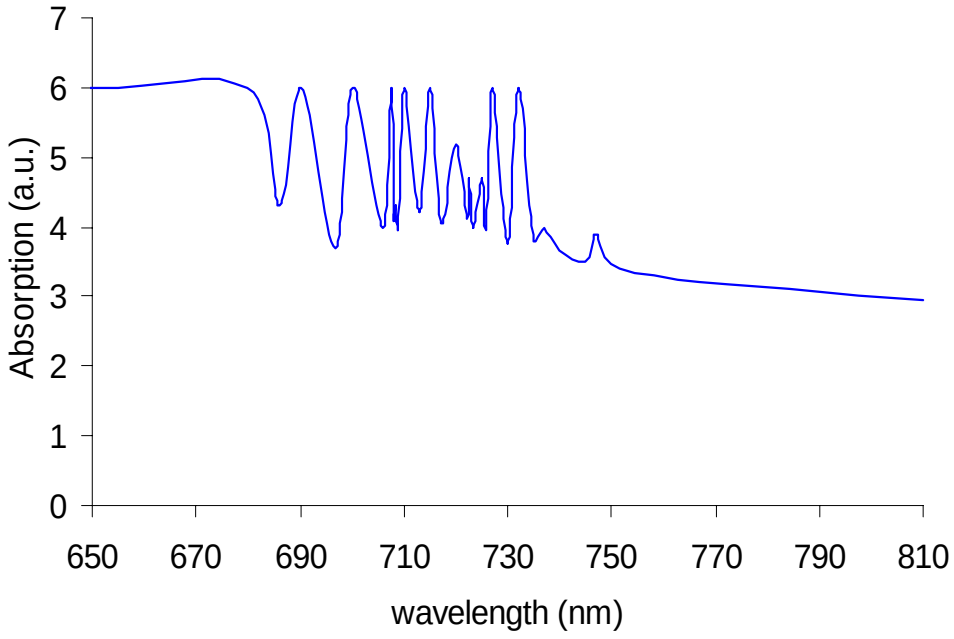

Fig. 5. (b)

Fig. 5. The optical absorption spectrum of chemically deposited lead sulfide thin film (a) with hydrazine hydrate, (b) without hydrazine hydrate

In the above equations, r is the radius of the nanoneedle, E_g is the band gap energy of PbS (0.41ev), c is the velocity of light, h is the Planck constant, λ is the wavelength of the absorption spectrum peak, and m_e is the free electron mass. According to the above equations, the size of the cluster in the lead sulfide thin film that is prepared in the presence of the hydrazine hydrate is estimated about 2 nm. Optical absorption spectrum emphasizes that the size of nanoneedles would be decreased if hydrazine hydrate is used.

Figure 6 shows the XRD pattern of the PbS thin films deposited on the substrate with hydrazine hydrate (a) and without hydrazine hydrate (b). The Cu K_α was used as X-Ray source. The d-values of the lines obtained from the XRD pattern have been compared with the corresponding values for PbS in the JSCDA card. The derived d-values are in good agreement with the standard values, which confirms that the film constitutes PbS. It is evident from Fig. 6 that the (111) direction for film growth is dominant when the hydrazine hydrate is added to the chemical deposition bath. In order to prove the nanometer size of grain, the Scherrer method has been used. The average crystallite size of 120 nm was determined by measuring the full width at half maximum of the (111), (200) peaks and using the Scherrer formula [25];

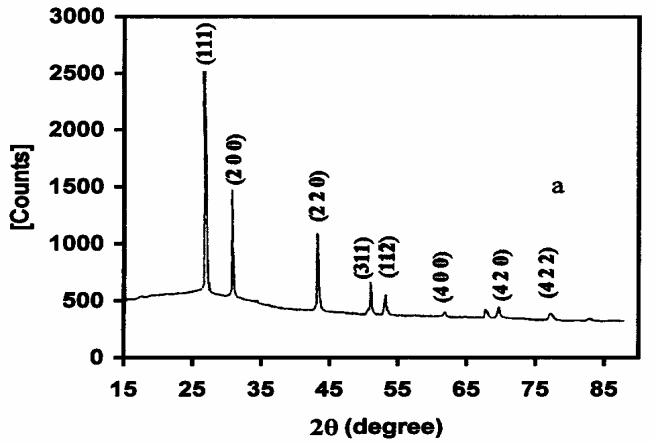

Fig. 6. (a)

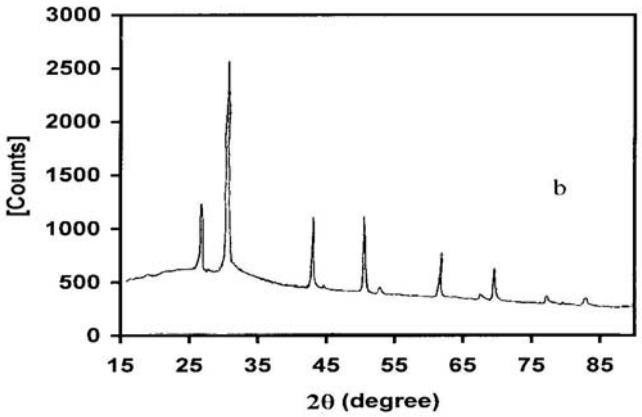

Fig. 6. (b)

Fig. 6. X-Ray diffractograph of chemically deposited lead sulfide film on a glass
(a) with hydrazine hydrate, (b) without hydrazine hydrate

$$B = \frac{\lambda K}{DCos\,\theta} \tag{7}$$

In this equation, B is full width at half maximum peak, D is the diameter of the grain and K is a constant. Figure 7 shows the chemical analysis and SEM morphology of deposited PbS thin film in the presence of hydrazine hydrate. The first peak, which belongs to the carbon element and oxygen peaks, are due to gaseous carbon components that were absorbed to the surface during sample storage. Optical absorption spectra and SEM micrograph have shown that the film was formed from nanometer grains.

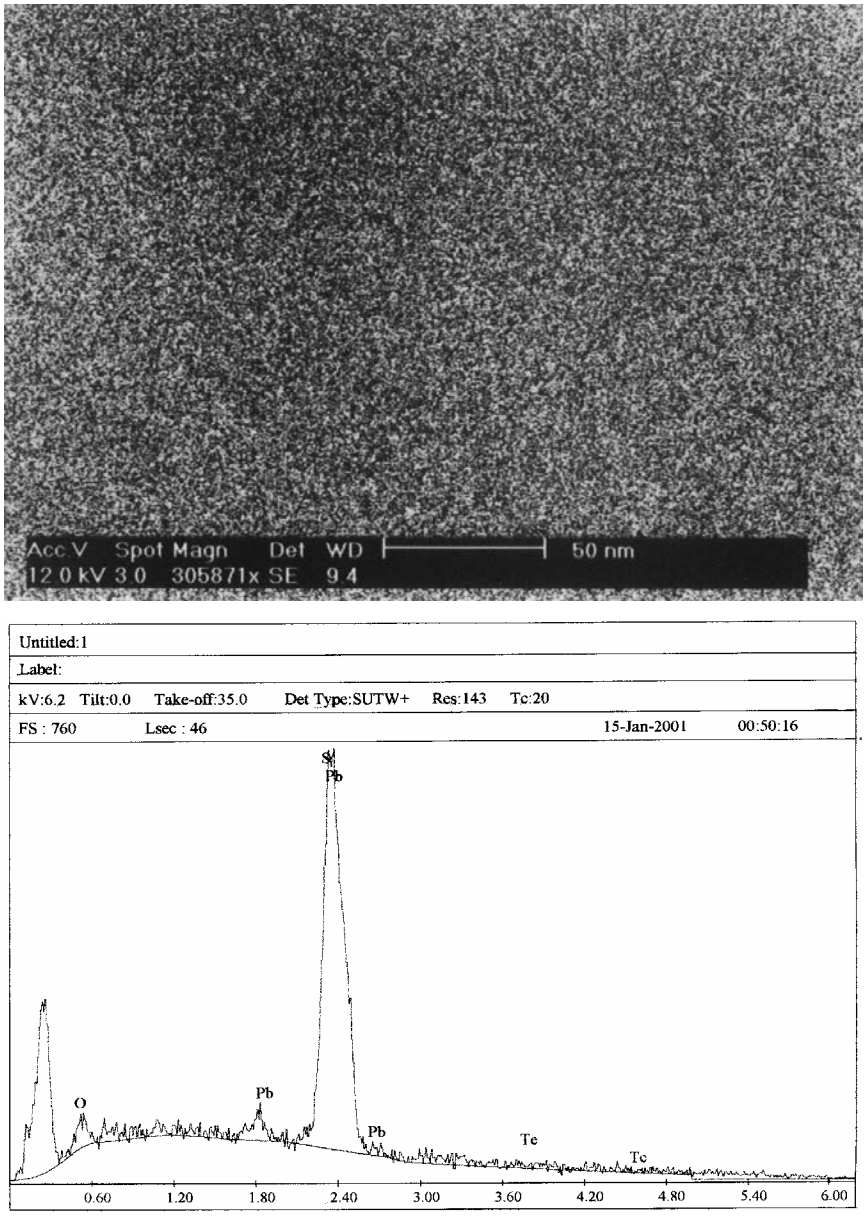

Fig. 7. Chemical analysis and surface morphology of a deposited lead sulfide thin film in the presence of hydrazine hydrate

4. CONCLUSIONS

Crystallographic structure, chemical analysis and surface morphology of chemically deposited lead sulfide films have been investigated by X-ray diffraction and scanning electron microscopy. It was concluded by X-ray analysis that PbS film prepared on the substrate is single phase and polycrystalline form. The presence of hydrazine hydrate in bath can affect the rate of deposition and the microstructure of deposited lead sulfide film. Meanwhile, the orientation growth of the film is (111). Optical absorption spectrum shows a blue shift happens in the absorption peak of the spectrum.

These results confirm that the film has been formed from nanometer grains.

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