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SOL GEL DERIVED NANOCRYSTALLINE PBS THIN FILMS FOR GAS SENSING APPLICATIONS

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ABSTRACT
We demonstrate correlation between gas sensing properties of nanocrystalline lead sulphide thin films grown on glass substrates by using sol gel spin coating techniques properties with structural, optical and electrical transport. The X-ray diffraction and SEM analysis showed that the thin films grown by this method have good nanocrystalline cubic crystal structures and homogeneous surfaces. The dc electrical conductivity found in the range of 10^{-5} to 10^{-6} $(\Omega\ cm)^{-1}$. The optical studies revealed that the high absorption coefficient ($\approx 10^{4}\ cm^{-1}$) with direct energy gap of 1.41 eV. The CdS sensors showed the maximum response of 26% upon exposure to 100 ppm NO_2 at operating temperature 100 ^{o}C.

KEY WORDS: PbS, sol gel method, spin coating technique, XRD, SEM

INTRODUCTION

Nanometer sized semiconductor particles have attracted much attention over the past few years because of their novel electrical and optical properties originating from quantum confinement. The emphasis has been mainly given on the synthesis of semiconductor particles belonging to II-VI and III-V groups, which show significant quantum confinement effects. Semiconductor nanoparticles exhibit size –dependent electronic band gap energies (Brus *et al.* 1984), melting temperatures (Goldstein *et al.* 1992), solid state phase transition temperatures (Qadri *et al.* 1999) and pressures (Chen *et al.* 1999). In addition to these, doped semiconductors nanoparticles have tremendous potential for use in light emitting applications. For examples PbS is an important material for a variety of applications such as, electroluminescent devices, solar cells, gas sensors and other optoelectronic devices. Hence, there has been growing interest in developing techniques for preparing semiconductor nanoparticle films. The sol gel synthesis method is simple and inexpensive alternative to more complex physical and chemical vapour deposition.

The physical methods (Alivisators *et al.* 1998) that are commonly used for the fabrication of low dimensional solids have some resolution limits that restrict these techniques from reaching to nanometer scale. On the other hand, colloid chemistry route offers a simple means to synthesize such particles with good control of size and size distribution. I n the past few years there have been various reports of synthesizing nanometersized PbS (Nanda *et al.* 2000; Bhattacharjee *et al.* 2002) particles by chemical process using suitable capping or surf ace passivating agents to control the size of the particles. This paper reports on investigations of structural, morphological, electrical and optical properties of nanocrystalline PbS by sol gel spin coating technique first time.

MATERIALS AND METHODS

We have synthesized nanocrystalline PbS by sol gel method without using any capping agent. To prepare nanocrystalline PbS powders, we have taken two types of solution. Solution –I was prepared by dissolving lead acetate in 40 ml methanol. In solution II, thiourea was dissolved in 40 ml methanol. Solution II was added to the solution I drop wise. The mixed solution was stirred, heated at 60 ^{0}C for about 1 hrs. After 1 hrs the dark chocolate color powder of PbS is formed. The powder was thoroughly washed several times with methanol and then dried in vacuum. The PbS powder was annealed at different temperatures (100, 200, 300 ^{0}C).

To prepare thin films, 1 gm of annealed PbS nanopowder was mixed with 24 ml of m-cresol. Thin films were deposited on glass substrates using spin coating technique. Figure 1 shows a flow diagram of synthesis of nanocrystalline PbS by sol gel spin coating technique. The structural properties of nanocrystalline PbS was studied by X-ray diffraction (XRD) (Philips PW3710, Holland) using filtered CuKα radiation (λ=1.5406 A^{0}). The surface morphologies of the PbS thin films were observed by scanning electron microscope JEOL JSM 6360 operating at 20 kV.

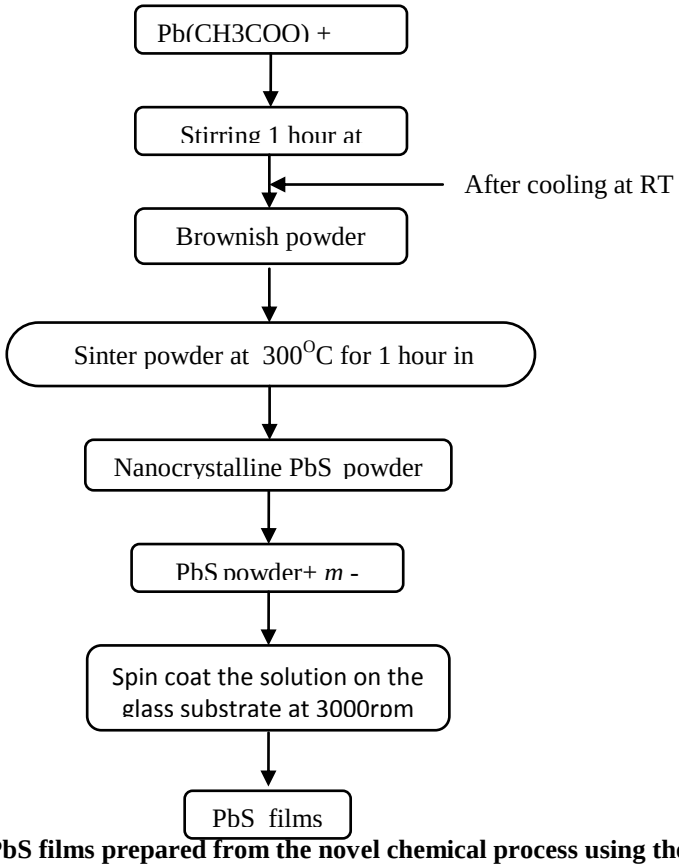

Figure 1. Flow diagram for PbS films prepared from the novel chemical process using the spin- coating method

RESULTS AND DISCUSSION

X ray diffraction analysis

X-ray diffraction pattern of nanocrystalline PbS is shown in Fig.2.

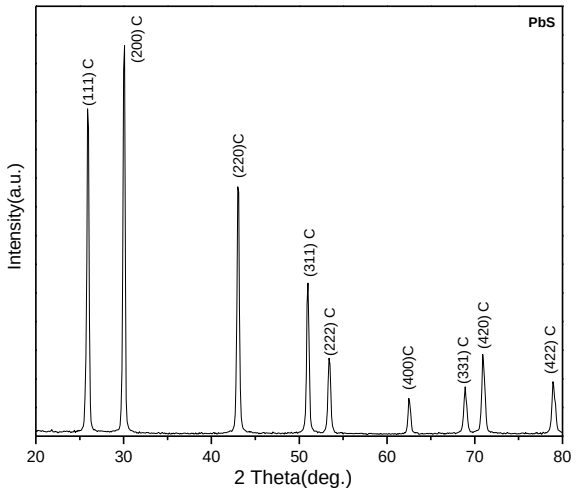

Figure 2. X-ray diffraction of PbS films

Figure 2 shows that different diffraction peaks at 2θ values of 25.94^0, 30.24^0,43.08^0, 51.05^0, 53.47^0, 62.56^0, 68.85^0, 70.96^0 and 78.93^0. The peaks were identified to originate from (111), (200), (220), (311), (222), (400), (331), (420) and (422) planes of bulk cubic zinc blende phase of PbS respectively. The information on strain and the particle size was obtained from the full widths at half maximum (FWHM) of the diffraction peaks.

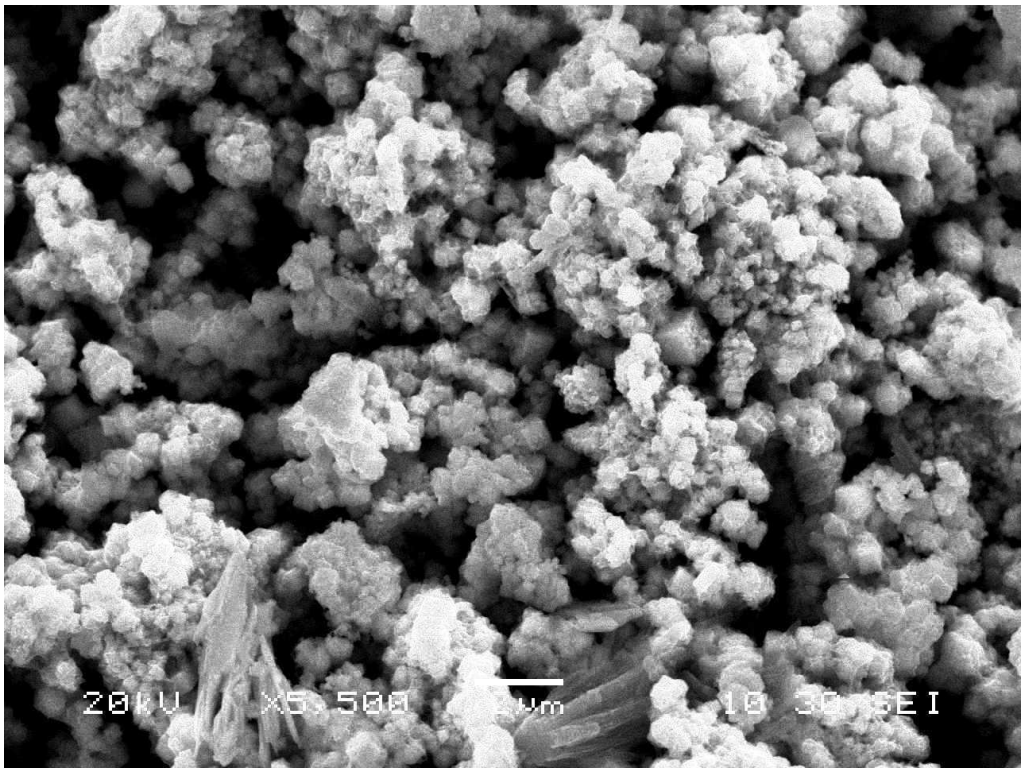

Figure 3. shows the SEM image of nanocrystalline PbS films

Electrical properties

The electrical conductivity of sol - gel derived nanocrystalline PbS thin films was measured in the 300-500K temperature range using custom fabricated two probe techniques and its temperature dependence can be expressed by usual Arrheneous equation as:

$\sigma = \sigma_o \exp(-E_{a\sigma}/KT)$

where $E_{a\sigma}$ is the conductivity activation energy; T, the absolute temperature and K, the Boltzmann constant. The room temperature electrical resistivity of this sample is of the order of $10^5\Omega$cm. Fig. 4 shows the temperature dependence of an electrical conductivity. From figure it is seen that the two distinct regions corresponding to two activation energies and it is found for low and high temperature regions are 0.45eV and 0.14 eV respectively.

Optical properties

The optical parameters namely absorption coefficient (α), energy gap (E_g) and type of the optical absorption spectrum in the 200-1000 nm wavelength range at room temperature. The energy gap is determined from the studies for this deposited PbS material. Fig.5. Shows determination of the optical gap from the (αhν) versus (hν) variation. A band gap of 1.39 eV has been determined for the as deposited PbS sample. The type of transition is band to band direct as determined from the ln (αhν) versus in ($h\nu$-E_g) variation (Bhargava *et al.* 1994).

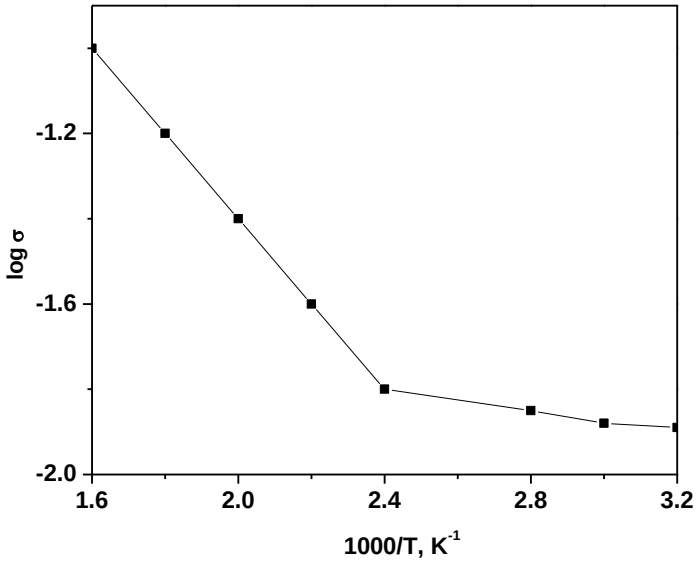

Figure 4 . The temperature dependence of an electrical conductivity of PbS film

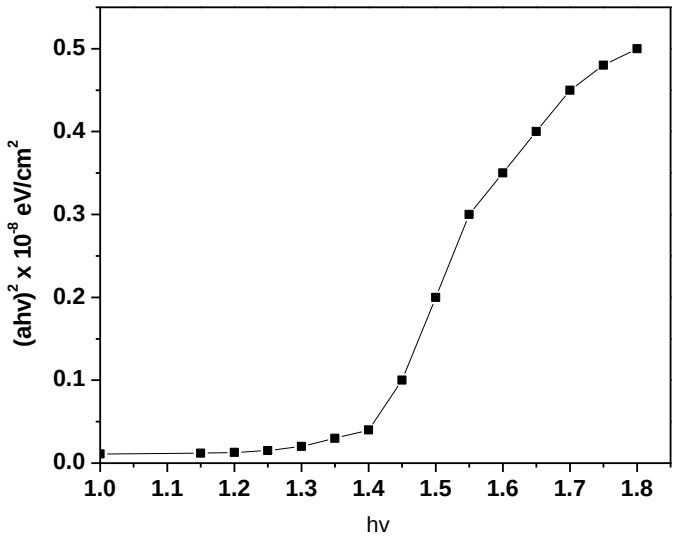

Figure 5. Variation of $(\alpha hv)^2$ versus (hv) of PbS film

Gas Sensing properties

Selectivity of PbS film

The PbS film showed more selectivity for NO_2 (26%) over NH_3 compared H_2S to at an operating temperature of 100^oC. It revealed that $NO_2$is the more selective against NH_3 and poor selective against NH_3.

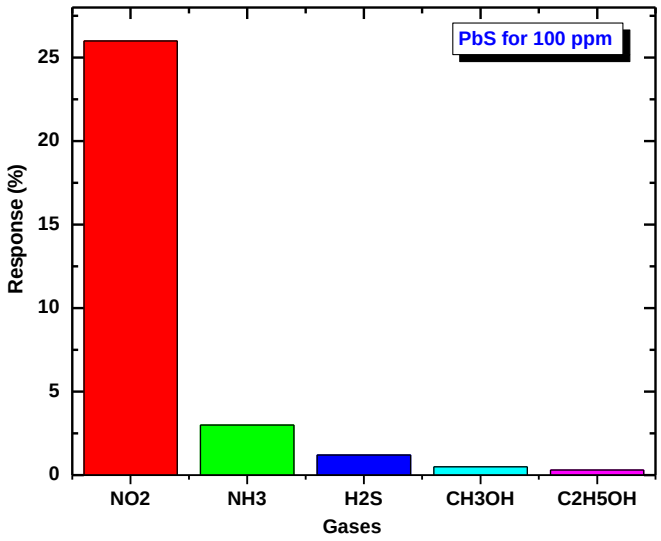

Figure 6. Selectivity of PbS film

Dynamic response transients of PbS thin film

Figure 7 shows the dynamic variation of the response of the PbS thin film with time upon exposure to 25-100ppm of NO_2 at 100 ^oC. The figure revealed that the initially the response of sensor film increase from 11 to 26 % with increasing the concentration of NO_2. At 100 ppm, the PbS film showed the maximum response of 26%. Such a higher value of response is believed to be due to the sensitivity of the semiconductor sensors mainly determined by the interactions between the target gas and the surface of the sensor (Nenov *et al.* 1996). So, it is obvious that for the materials of greater surface area, the interactions between the adsorbed gases and the sensor surface are significant (Korotcenkov *et al.* 2001).The PbS t granular morphology (fig.3)

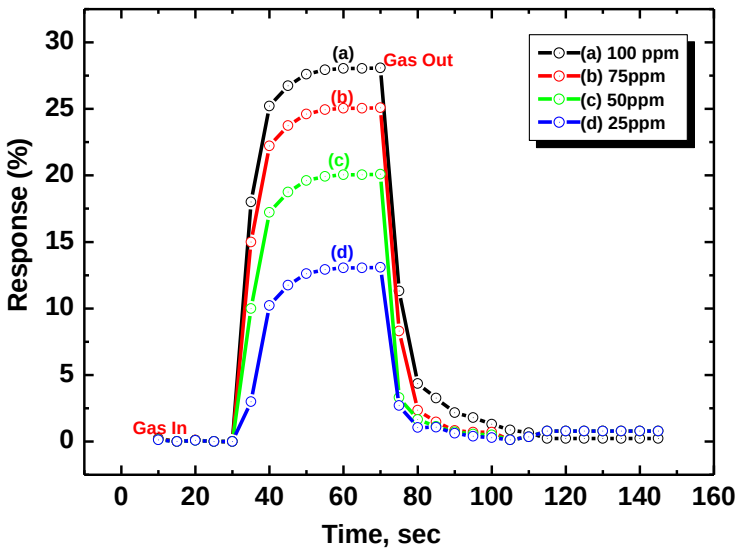

Figure 7. Dynamic variation of the response of the PbS thin film with time

CONCLUSION

We conclude that nanocrystalline PbS films, reproducible both in the electrical and optical properties, can easily be obtained with almost negligible consumption of an electrical energy and the basic starting materials. The deposits are dark chocolate in color with a room temperature resistivity of 10^5 to 10^6 Ω cm. XRD studies showed cubic structure of PbS. The SEM observations revealed nanocrystalline crystalline nature of the film. The material exhibit high optical absorption coefficient (10^4 /cm) with a direct band gap type of transition. The estimated energy gap is 1.41 eV.

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