

DIELECTRIC PROPERTIES OF LEAD SULPHIDE THIN FILMS FOR SOLAR CELL APPLICATIONS

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Thin films of lead sulphide (PbS) were deposited on a glass substrate at room temperature using spin coating technique. X-ray diffraction (XRD) is used to establish the structure and crystallite size of these films and scanning electron microscopy is used to study the particle size and morphology. The dielectric properties of PbS thin films were studied in the different frequency range of 50Hz-5MHz at different temperatures. The frequency dependence of the dielectric constant and dielectric loss is found to decrease with increase in frequency at different temperatures. In addition, the electronic properties like valence electron plasma energy, average energy gap or Penn gap, Fermi energy and electronic polarizability of the PbS thin films are also calculated.

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1. 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. Nanotechnology deals with nanometer size objects. Size dependence new physical aspect has been generating a continuous thrust for new practical applications [1]. In recent years, there has been increasing interest in the size dependent electrical and optical properties of semiconductors. In nanocrystallites, the electrons confined in a narrow potential well, exhibit extraordinary characteristics in the optical and electrical properties [2]. When the width of such confining potential is very small, i.e., of the order of few hundred angstroms, a quantum size effect arises [3]. During the last few years, the research on the growth of nanoparticle PbS films has increased, for its technological applications in photo resistance, laser diodes, decorative coatings and optoelectronic devices [4]. In addition to these, doped semiconductor nanoparticles have tremendous potential for use in light emitting applications. In semiconductors, the electrical properties are sensitive to the impurity content and doping [5]. Inorganic semiconductors are characterized by covalent bonding between ions of the crystal. Electrons can be excited optically or thermally, promoting free electrons into the conduction band and leaving holes in the valence band. Under an applied electric field, the free charge carriers are transported causing conduction. The dielectric constant behaviour as a function of energy loss and photon energy (frequency) was over looked to some extent. In semiconductor thin film IR detector integrated circuits (for which high capacitance in small area is required), capacitors are grown by sputter techniques. To use lead sulphide thin film circuits, it is necessary that their dielectric and energy losses be understood so as they have appropriate value ranges.

The dielectric coefficient of a thin film (capacitance) is an important practical parameter for assessing the expected behaviour of any thin film device. This makes it necessary to

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study the effect of energy, dielectric losses and (photon energy) frequency on thin films for any device fabrication. The dielectric behavior of thin film devices depends not only on their material properties but also on the method and conditions of preparation. Fringing effects at the edges of thin film dielectrics is usually negligible because the thickness of the dielectric is usually very small and uniform compared to its lateral dimensions.

In the present investigation, we report the synthesis and characterization of PbS thin films. The PbS thin films subjected to study are characterized by X-ray diffraction, scanning electron microscopy (SEM) and dielectric studies. The scope of the present work is to study the dielectric properties of PbS thin films as a function of the frequency and the temperatures. The electronic properties such as valence electron plasma energy, average energy gap or Penn gap, Fermi energy and electronic polarizability of the PbS thin films required for the device application is also determined.

2. Experimental Methods

The synthesis of nanocrystalline PbS is carried out by sol gel method. Two solutions are prepared to produce nanocrystalline PbS powders. Solution (I) is prepared by dissolving lead acetate in 50 ml methanol. The solution (II) is prepared by dissolving thiourea in 50 ml methanol. The mixed solution is stirred and heated at 50 °C for one hour to form dark chocolate coloured powder of PbS. The powder is thoroughly rinsed several times with methanol and then dried in vacuum. To prepare thin films, 1 gm of annealed PbS nanopowder is mixed with 24 ml of m-cresol. Thin films are deposited on glass substrates using spin coating technique.

3. Results and discussion

3.1. Powder X- ray diffraction analysis

In order to determine the size and to study the structural properties of the synthesized PbS thin films, the powder XRD analysis was performed. Structural identification of PbS films was carried out with X-ray diffraction in the range of angle 2θ between 10° to 60°. Figure 2 shows the XRD patterns for PbS thin films, which were nanocrystalline in nature. The observed broad hump in XRD pattern is due to amorphous glass substrate. The well defined (111), (200), (220), and (311) peaks were observed in the XRD patterns.

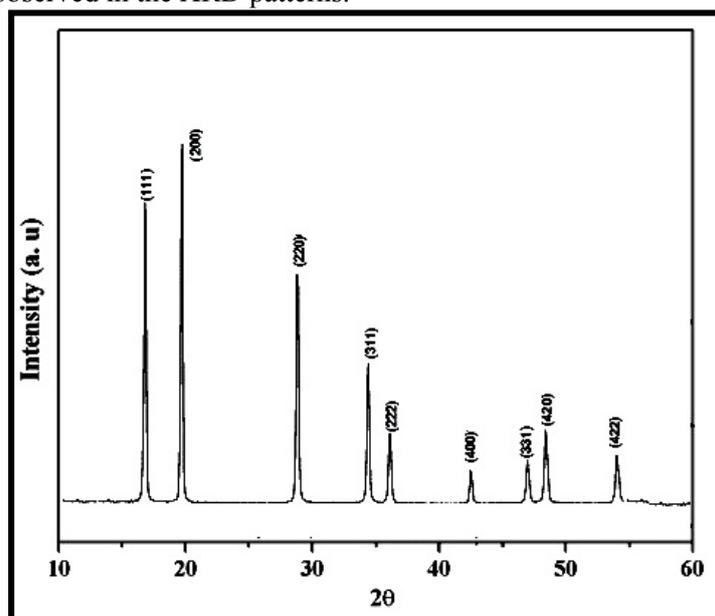


Fig.1.XRD spectrum of PbS thin films

3.2 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) was used for the morphological study of PbS thin films. Fig. 2 shows the SEM images of the PbS thin films. The PbS thin films formed were highly agglomerated. The cube crystallites which have a mean particle size of ~ 12 nm are visible through the SEM analysis.

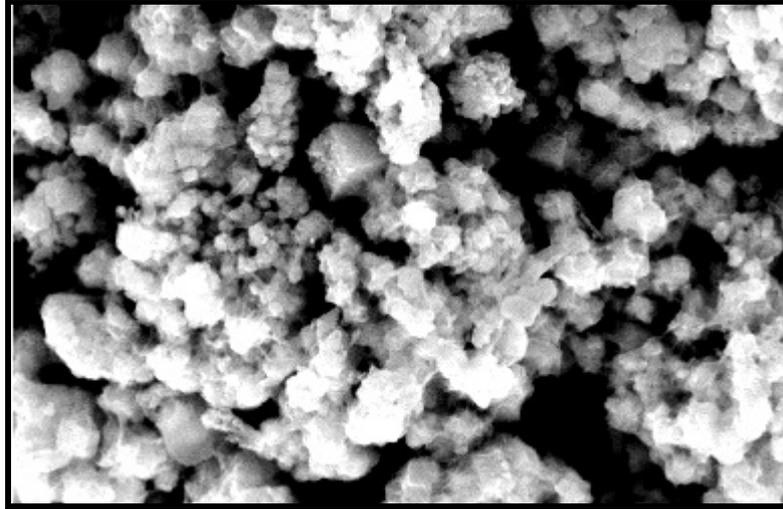


Fig. 2. SEM Image of the PbS thin films

3.3 Clausius - Mossotti relation for dielectric permittivity

Consider a molecule of a dielectric medium situated in a uniform electric field E . The total electric field acting on this molecule E_{loc} will have three main components- E_1 , E_2 , and E_3 . Here E_1 is the applied electric field E , E_2 is the field from the free ends of the dipole chain, and E_3 is the near field arising from the individual molecular interactions. In solids we have to consider the actual effective field acting on a molecule in order to estimate the dielectric permittivity. For electronic and ionic polarization, the local field for cubic crystals and isotropic liquids can be given by the Lorentz field, as

$$E_{loc} = \frac{1}{3\epsilon_0} P \quad (1)$$

By assuming that the near field E_3 is zero, Clausius and Mossotti derived a relation for the dielectric constant of a material under electronic and ionic polarization.

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} (N_i \alpha_i + N_e \alpha_e) \quad (2)$$

Here, ϵ_r is the relative permittivity at low frequencies, α_i is the effective ionic polarizability per ion pair, N_i is the number of ions pair per unit volume, α_e is the electronic polarizability and N_e is the number of ions (or atoms) per unit volume exhibiting electronic polarization. The atomic/ionic polarizability α_i and the electronic polarizability α_e cannot be separated at low frequencies, and hence, they are represented together as the induced polarizability α_{ind} . Hence, equation 8 can be written as:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} (N_m \alpha_{ind}) \quad (3)$$

This is known as the Clausius – Mossotti equation for non polar dielectrics. Above the frequencies of ionic polarization relaxation, only electronic polarization will contribute to the relative permittivity, which will be lowered to $\epsilon_{r\infty}$ (relative permittivity at optical frequencies).

$$\frac{\epsilon_{r\infty} - 1}{\epsilon_{r\infty} + 2} = \frac{N_e \alpha_e}{3\epsilon_0} \quad (4)$$

By using the Maxwell relation for a lossless (non-absorbing), non magnetic medium,

$$n^2 = \epsilon_{r\infty} \quad (5)$$

where n is the index of refraction of the material, equation (10) can be rewritten as:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N_e \alpha_e}{3\epsilon_0} \quad (6)$$

In this form, it is known as the Lorentz-Lorenz equation. It can be used to approximate the static dielectric constant ϵ_r of non polar and non magnetic materials from their optical properties. In the case of dipolar materials we cannot use the simple Lorentz field approximation, and hence the Clausius–Mossotti equation cannot be used in the case of dipolar materials.

3.4. Dielectric properties

Based on the wave mechanical theory of matter, a dielectric is a material which is so constructed such that the lower bands of its allowed energy levels are completely full at the absolute zero of temperature (Exclusion Principle) and at the same time isolated from higher unoccupied bands by a large zone of forbidden energy levels. The zone of forbidden energy levels is so wide that there is only a negligible probability that an electron in the lower band of allowed levels will acquire enough energy to make the transition to the unoccupied upper band where it could take part in conduction. That is why PbS thin films are poor solar cell absorber layers. When photons fall on PbS thin film layer, an electric field due to photons is impressed upon a PbS, positive and negative charges in their atoms and molecules are displaced in opposite directions causing polarization. Since the motion of charges of opposite sign move in opposite directions, they constitute an electric current called a polarization current.

In the present studies of the dielectric constant and the dielectric loss of the PbS thin films were studied at different temperatures using the HIOKI 3532 LCR HITESTER instrument in the frequency region of 50 Hz to 5 MHz. The dielectric constant was measured as a function of the frequency at different temperatures as shown in Fig.3, while the corresponding dielectric losses are depicted in Fig.4. Fig. 3 shows the plot of the dielectric constant (ϵ_r) versus applied frequency. It is observed (Fig.3) that the dielectric constant decreases exponentially with increasing frequency and then attains almost a constant value in the high frequency region. This also indicates that the value of the dielectric constant increases with an increase in the temperatures. The net polarization present in the material is due to ionic, electronic, dipolar and space charge polarizations [6]. The large value of the dielectric constant is due to the fact that PbS thin films acts as a nanodipole under electric fields. The small-sized particles necessitate a large number of particles per unit volume, resulting in an increase of the dipole moment per unit volume, and a high dielectric constant. The dielectric loss studied as a function of frequency at different temperatures is shown in Fig.4. These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field, similar to that of the dielectric constant. The dielectric loss decreases with an increase in the frequency at almost all temperatures, but appears to achieve saturation in the higher frequency range at all the temperatures. In the low frequency region, high energy loss is observed, which may be due to the dielectric polarization, space-charge and movement of electrons in rotational fashion at low frequency range.

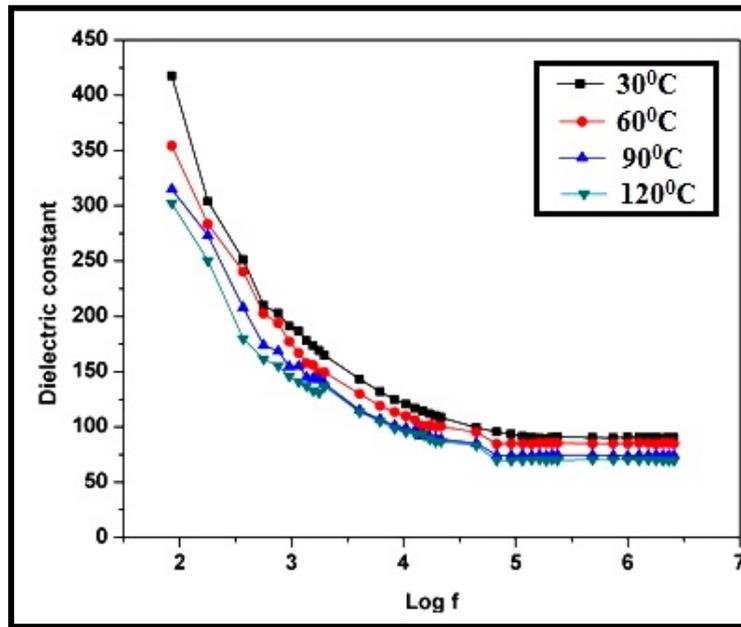


Fig.3. Dielectric constant of PbS thin films, as a function of frequency

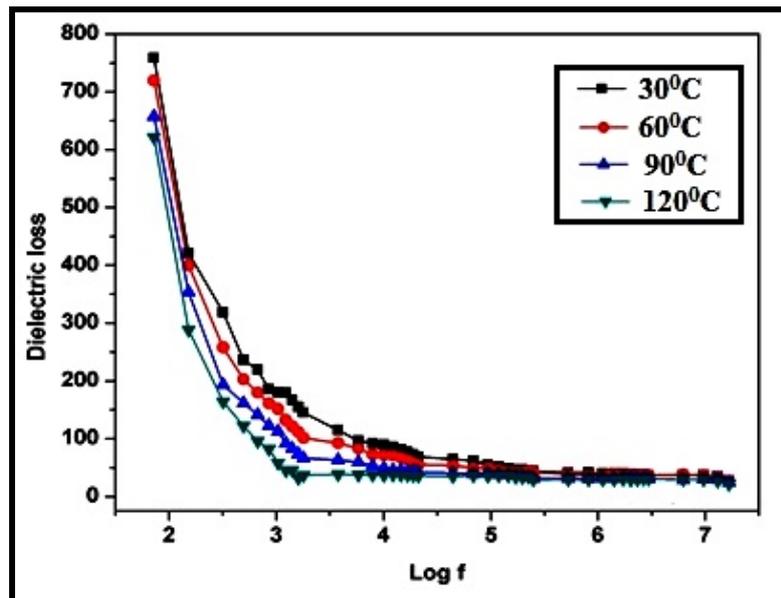


Fig.4. Dielectric loss of PbS thin films, as a function of frequency

In the proposed relation, only one parameter viz, the high frequency dielectric constant is required as input, to evaluate electronic properties like valence electron plasma energy, average energy gap or Penn gap, Fermi energy and electronic polarizability of the PbS thin films. The theoretical calculations show that the high frequency dielectric constant is explicitly dependent on the valence electron Plasma energy, an average energy gap referred to as the Penn gap and Fermi energy. The Penn gap is determined by fitting the dielectric constant with the Plasmon energy [7]. The valence electron plasma energy, $\hbar\omega_p$, is calculated using the relation [8],

$$\hbar\omega_p = 28.8 \left(\frac{Z\rho}{M} \right)^{1/2} \quad (7)$$

According to the Penn model [9], the average energy gap for the PbS thin films is given by

$$E_p = \frac{\hbar\omega_p}{(\varepsilon_\infty - 1)^{1/2}} \quad (8)$$

where $\hbar\omega_p$ is the valence electron plasmon energy and the Fermi energy [7] given by

$$E_F = 0.2948(\hbar\omega_p)^{4/3} \quad (9)$$

Then we obtained the electronic polarizability α , using a relation [9, 10],

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_p^2} \right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{ cm}^3 \quad (10)$$

where S_0 is a constant given by

$$S_0 = 1 - \left[\frac{E_p}{4E_F} \right] + \frac{1}{3} \left[\frac{E_p}{4E_F} \right]^2 \quad (11)$$

The value of α obtained from equation (10) closely matches with that obtained using the Clausius-Mossotti relation,

$$\alpha = \frac{3}{4} \frac{M}{\pi N_a \rho} \left[\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \right] \quad (12)$$

Considering that the polarizability is highly sensitive to the bandgap [11], the following empirical relationship is also used to calculate α ,

$$\alpha = \left[1 - \frac{\sqrt{E_g}}{4.06} \right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{ cm}^3 \quad (13)$$

where E_g is the bandgap value determined through the UV absorption spectrum. The high frequency dielectric constant of the materials is a very important parameter for calculating the physical or electronic properties of materials. All the above parameters as estimated are shown in Table 1.

Table.1 Electronic properties of the PbS thin films

Parameters	Value
Plasma energy ($\hbar\omega_p$)	16.53 eV
Penn gap (E_p)	2.21 eV
Fermi Energy (E_F)	12.52 eV
Electronic polarizability (using the Penn analysis)	$5.78 \times 10^{-24} \text{ cm}^3$
Electronic polarizability (using the Clausius-Mossotti relation)	$5.86 \times 10^{-24} \text{ cm}^3$
Electronic polarizability (using bandgap)	$5.18 \times 10^{-24} \text{ cm}^3$

4. Conclusion

The XRD studies show that, films prepared are in nanocrystalline range and also diffraction peaks are found. The size and morphology of the PbS thin films were characterized using scanning electron microscopy (SEM). The cubical crystallites shaped were confirmed

through the SEM analysis. The dielectric constant and dielectric loss of the PbS thin films are measured in the frequency range of 50Hz-5MHz at different temperatures. The dielectric studies reveal that both the dielectric constant and dielectric loss decrease with an increase in frequency. The dielectric characterization shows the low value of the dielectric constant at higher frequencies. Electronic properties such as plasma energy, Penn gap, Fermi energy and electronic polarizability of the PbS thin films, which are required for device application, have been calculated.

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