

Full Length Research Paper

Effect of dielectric constant on energy losses in lead sulphide thin films grown by solution method at room temperature

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Thin films of lead sulphide (PbS) were deposited using chemical bath deposition (CBD) at different lead ion concentrations. A mixture of sodium hydroxide, varied concentrations of lead nitrate, triethanolamine (TEA), ammonia solution, thiourea, di-ionized and distilled water were used. A dip time of 120 min and pH of 9 at room temperature were maintained. It was found out that dielectric constants of the films varied from a maximum value of 12 to a minimum value of 2.3 in the photon energy range of 1.0 to 4.8 eV. Energy losses in the thin films were also found to be dependent on the concentration of lead ions in the bath and also this energy losses decreased as dielectric constants increased. It was concluded that the films could be used in photoconductivity, capacitance and solar cell absorber applications.

Key words: dielectric constant, thin films, lead sulphide, temperature.

INTRODUCTION

Semiconducting thin films and particularly lead chalcogenides have been widely studied owing to their interesting switching property (Prakash and Ashokan, 2004). These materials are used to fabricate a variety of electronic devices, which arises when the material is cast into thin film form. It is also observed that most physical properties reported on chalcogenides have been investigated using polycrystalline pellets or electrodeposits (Bresser et al., 1996; Lade et al., 1994). A good amount of work on DC conduction (Sagbo et al., 1994), contact capacitance (Simashkevin et al., 1994), spectral properties (Vidourek et al., 1995), AC conduction (Giuntini et al., 1995), and structural and magnetic properties (Dauoudi and Ekpunobi, 1996) has also been reported. However, dielectric constant behaviour as a function of energy loss and photon energy (frequency) has been 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 either evaporation or sputter techniques. When large-area capacitors are required, then the appropriate method of choice of growing them could be chemical bath method (CBD). 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 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

Table 1. Parameters for depositing PbS thin films.

Conc. Pb ⁺² (mol.)	Vol. Pb ⁺² (cm ³)	Vol. 1M NaOH (cm ³)	Vol. 1M TU (cm ³)	Vol TEA (cm ³)
0.3	5	5	6	2
0.4	5	5	6	2
0.5	5	5	6	2
0.6	5	5	6	2
0.7	5	5	6	2

dimensions. The magnitude of its geometrics and measured influence of dielectric capacitance gains or losses may differ if the electric field at the thin film/metal insulator interface varies with the insulator over a certain region. For given material the film thickness alone establishes the capacitance density which in turn can be used to determine the area needed for a particular capacitance value. Since most capacitors utilize constant and uniform thickness then much concern is not only based on thickness but also on dielectric and energy losses in capacitor performance. The dielectric loss as part of the energy of an electric field is dissipated without recovery as heat in the dielectric material and is comprised of two parts; the first part arises due to lead resistance and electrode resistance. This part is frequency dependent. It is effective and very influential at higher frequencies or photon energies. It is minimized using high conducting metal electrodes. The other part arises due to material property and is also frequency dependent (Maissel and Glang, 1970). Dielectric strength is found to reduce rapidly below about 100 nm wavelength as the presence of pinholes or discrete defects in thin films increases. To the best of our knowledge, little or no reports is available on the study of dielectric properties of lead sulphide (PbS) thin films deposited by chemical bath at room temperature. In this paper, an attempt is made to report some of the dielectric properties of solution deposited PbS thin films for solar cell, charge storage/detection applications. In all the thin films used in this study, thickness thin film was kept at about 103 nm to minimize the inherent defects and pinholes.

METHODOLOGY

The chemical bath deposition technique was used. Glass substrate (microscope slides) which had been previously degreased in concentrated nitric acid for 24 h, cleaned in cold water with detergent, rinsed with di-ionized water and dried in clean dry air to provide better surface nucleation for growth of the films were used. A mixture of 1 M sodium hydroxide, 0.3 – 0.7 M lead nitrate solutions, 7.4 M triethanolamine (TEA), 14 M ammonia, 1 M thiourea, di-ionized and distilled water, microscopic glass slides and beaker were used. 5 ml of lead nitrate was poured into a 100 ml beaker followed by 5 ml of 1 M sodium hydroxide and then thoroughly stirred to obtain a milky solution. 6 ml of 1 M thiourea and 2 ml of 1 M tri-ethanolamine were immediately added, the mixture thoroughly stirred with a glass rod before glass slides was

vertically introduced into the beaker. The dip time was kept at 120 min, and pH at 9 and at room temperature. Lead nitrate concentration was varied for the subsequent films from 0.4-0.7 M PbS as illustrated in Table 1. The grown samples were removed, rinsed with distilled water and allowed to dry before they were analyzed and characterized.

RESULTS

During deposition, cations and anions in the solution react to become neutral atoms, which precipitate slowly under the control of a complexing agent (TEA). With the addition of TEA, the reaction proceeded slowly so that PbS thin films of neutral atoms were formed on the substrate. The complexing agent slowed down precipitation action while ammonia served as a pH stabilizer. Sulphide ions were released by hydrolysis from thiourea and complexes formed were adsorbed onto the substrate as heterogeneous nucleation. Growth took place by ionic exchange reaction of S²⁻ with Pb²⁺ ions and by this process of ion-by-ion exchange, PbS thin films were deposited. The films were transparent, uniform and adherent though specularly reflecting. In discussing the dielectric properties of PbS thin films, a model to represent the dielectric property was used. A quantum-mechanical model to outline the characteristics of dielectrics of PbS thin films was used. The model predicts on the basis of classical mechanics. 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. This is observed in PbS thin films (they have a dielectric constant of above 8). This shows that conduction in the lower fully occupied bands is impossible since there are no un-occupied energy levels to take care of the additional energy which would be acquired by the electrons from the applied field caused photons. 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

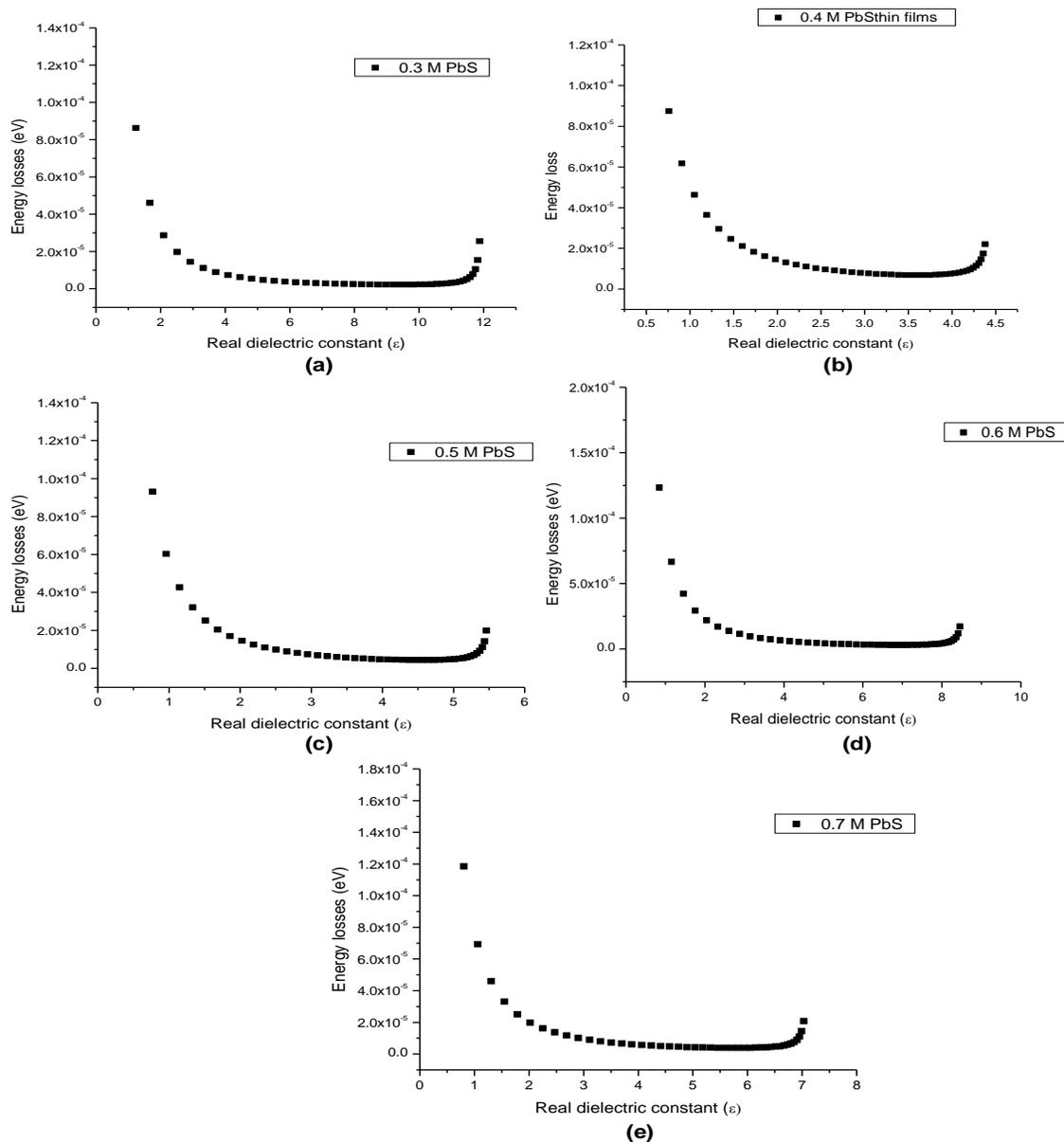


Figure 1. (a) Variation of real dielectric constant versus energy losses in 0.3 M PbS films; (b) Variation of dielectric constant against energy losses for 0.4 M PbS films; (c) Variation of real dielectric constant versus energy losses in 0.5 M PbS thin films; (d) Variation of real dielectric constant versus energy losses in 0.6 M PbS thin films; (e) Variation of real dielectric constant versus energy losses in 0.7 M PbS films.

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. This polarization causes energy losses in PbS thin films (Figure 1a to d). A charge accumulating in PbS thin film layer in an un-measurably short time referred to as the instantaneous dielectric constant or geometric dielectric constant describes the property of the medium giving rise to the effect called dielectric states (Figure 1 a-d). This is recognized by the

modern theory that identifies two distinct types of charges and charging currents that rapidly results into forming instantaneous polarizations and absorptive polarizations. PbS thin films depends on this mechanism as shown in Figure 2. The effect of chemical and physical structures in PbS dielectric constant depend on two quantities; magnitude and relaxation-time which in turn determine many of the properties of dielectric polarizations of the absorptive type. The magnitude of the polarizability (k) of PbS can be expressed in terms of a directly measurable quantity or by simulation in relation to dielectric constant

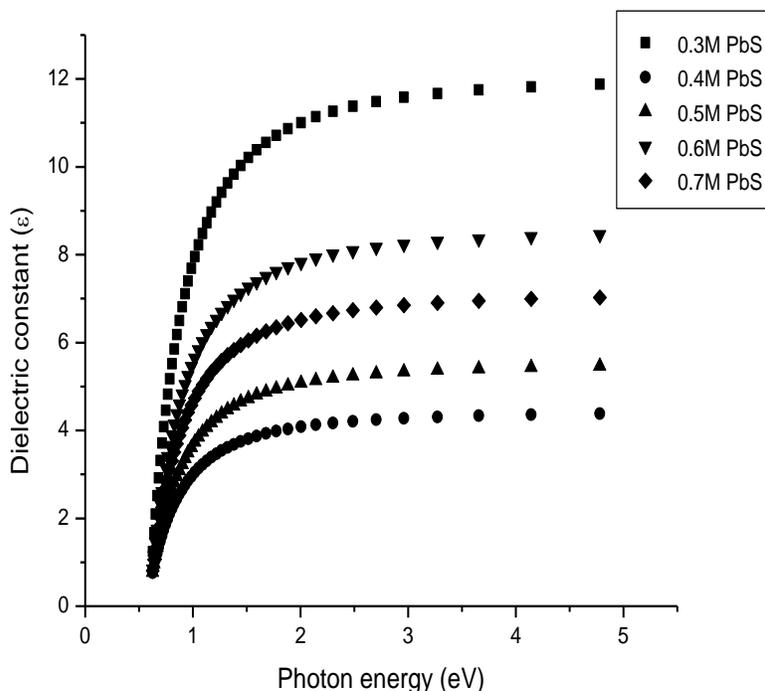


Figure 2. Variation of dielectric constants versus photon energy (eV) for PbS.

by the relation:

$$k = \frac{3(\varepsilon - 1)}{4\pi(\varepsilon + 2)} \quad (1)$$

A classification of dielectric polarization into absorptive polarization has been made based on this expression. Electronic polarizations are due to the displacement of charge within the atoms and are the most important of the instantaneous polarizations that determine the dielectric constant of PbS thin films. Polarizability per unit volume due to the electronic polarizations is considered to be a quantity which is proportional to the number of bound electrons in a unit volume and inversely proportional to the forces binding them to the nuclei of the atoms. This occurs in PbS molecules. This is depicted by the small band gap of about 0.4 eV for PbS thin films. It is known that the time required for any applied field to displace electrons within an atom to a new position with respect to their nuclei is so short that there is no observable effect of time or frequency upon the value of the dielectric constant. This is true only until frequencies corresponding to absorption lines in the visible or ultra-violet spectrum are attained (called the optical frequency range). The frequencies in the optical range corresponding to the absorption lines in the spectrum, the dielectric constant or better the refractive index changes rapidly with frequencies and till absorption starts to appear. This is why this report is justified to use refractive index (n) and dielectric constant (ε)

interchangeably for the qualitative discussion of the properties of dielectric polarization that follows the relation $\varepsilon = n^2$, which is known as Maxwell's rule based on electromagnetic theory and only applicable whenever ' ε ' and ' n ' are measured at the same frequency no matter how high or low they may be. The refractive index (n) in the visible spectrum provides the means of determining the magnitude of electronic polarizations since other types of polarizations have negligible magnitude when frequency of the impressed field lies in the visible spectrum. For materials like PbS having only electronic polarizations, dielectric properties are simply independent of frequency in the electrical frequency range and are characterized by complex dielectric behaviours. PbS thin films also experience atomic polarizations. Atomic polarizations form part of the polarization of a molecule which can be attributed to the relative motion of the atoms in a molecule which it is composed. They are attributed to perturbation by any applied field causing vibrations on atoms due to energy gained from photons. Ions having their characteristics or resonance in the infra-red range experience them and thus PbS thin films that are sensitive to infra-red and atomic polarization begin to contribute to ε or n^2 at frequencies below approximately 10^{14} seconds; that is, in the near infrared and about 10^{10} cycles per second frequency where optical and electrical frequencies ranges merge. Atomic polarizations contribute a constant amount to ε and n^2 for any given material. It is taken as the difference between polarization (measured at some low infrared or high electric frequency) and the

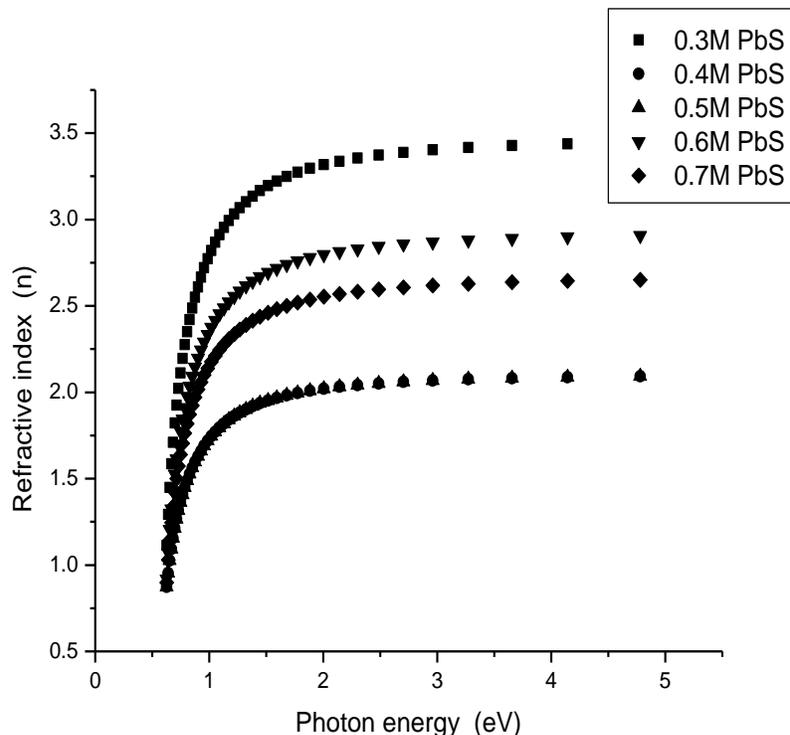


Figure 3. Variation of refractive index versus photon energy for PbS thin films.

electronic polarization as determined from refractive index measurements in the visible spectrum. When photoelectric effect causes a field to be applied, there is a tendency for molecules in a material to align themselves with their dipole axes in the direction of that field. This dipole polarization is superimposed upon electronic and atomic polarizations induced by the field. Since dipole polarization depends upon the displacement of charges within an atom, rather than upon the displacement of charges within a molecule, time required for this type of polarization to form depends on internal frictions of the material. Debye expressed time of relaxation of the dipole polarization in terms of the internal frictional force by the equation:

$$\tau = \frac{\xi}{2kT} = \frac{8\pi\eta r^2}{2kT} \quad (2)$$

where ξ is the internal friction coefficient, η is the coefficient of viscosity, r is the radius of the molecule and T is the absolute temperature. Applying this equation to the calculation of the relaxation time for PbS thin films at room temperature, τ is found to be 10^{-10} seconds assuming that PbS molecular radius is 2×10^{-8} cm and taking viscosity as 0.01 poises as they form in the bath, the result agrees with the experimental studies extending from 10^9 to 10^{11} cycles. This is what causes the dielectric constant to decrease from its highest value to a value approximately equal to the square of their refractive index

as seen in Figure 3.

Conclusion

Thin films of PbS were successfully deposited at room temperature using CBD at different lead ion concentrations. Their dielectric constant varied from a maximum value of 12 to a minimum value of 2.3 in the photon energy range of 1.0 to 4.8 eV. Energy loss was found to decrease as the dielectric constant of the thin film increases and it was concluded that the films could be used in photoconductivity, capacitor fabrication and solar cell absorber applications.

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