Electrical Study of Al/n-ZnS Schottky Junction on Polymer Substrate

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Abstract: A study has been made on the behaviour of Al/n-ZnS thin film junction on Polyethylene terephthalate (PET) grown using thermal evaporation method. Current-Voltage (I-V) characteristics of this junction show that the Aluminium (Al) makes Schottky contact with n-ZnS (Zinc Sulfide). Intrinsic and contact properties such as saturation current, barrier height, ideality factor and series resistance were calculated from the I-V characteristics. The conduction seems to be predominantly due to thermoionic emission-diffusion mechanism. An effort has also been made to carry out the optical study of ZnS thin film using spectrophotometer. Band gap of n-ZnS thin film is determined through absorption spectra using the Tauc's extrapolation. A band diagram of Al/n-ZnS has been proposed using the so obtained data.

Keywords: Schottky barrier, Optical properties, Thermionic emission, Polyethylene terephthalate, Band gap.

INTRODUCTION

Recently, the II-VI compounds semiconductor thin films (e.g. CdS, ZnS, CdSe, ZnSe) have received an intensive attention due to their application in thin film solar cells, optical coatings, optoelectronic devices, and light emitting diodes [1-4]. Among these metal chalcogenides, ZnS is an important semiconductor material because of its broad, direct band gap energy (~3.6 eV) at room temperature [5]. Various techniques have been employed to fabricate ZnS thin films, such as, electrodeposition [6], pulsed-laser deposition [7], chemical vapor deposition (CVD) [8], molecular beam epitaxy (MBE) [9], spray pyrolysis [10], and chemical bath deposition (CBD) [11]. Among these methods thermal evaporation is one of the suitable method for depositing large area thin film for solar cell application. The development of ZnS films on flexible substrates is gaining interest due to the light weight and damage free nature of the devices.

Metal/ZnS interfaces play an important role in optoelectronic device such as solar cells. A clear understanding of the physical principles underlying the properties of these interfaces is therefore essential in order to develop practical devices based on this semiconductor material. Thus efforts have been made to study the properties of the interfaces through the measurements of I-V characteristics in Au-ZnS junction by Salma M. Shaban *et al.* [12]. However, very little efforts have been made to study the properties of interfaces in the case of Al/ZnS junction.

In view of this, in the present study Al/n-ZnS junction is fabricated using thermal evaporation method on Polyethylene terephthalate (PET) substrate to get a flexible Schottky junction. Analysis of current–voltage (I–V) characteristics of this Schottky junction allows us to understand different aspects of current transport. The junction parameters such as barrier height, ideality factor, series resistance and saturation current have also been calculated from I–V characteristics of this junction at room temperature.

EXPERIMENTAL

Thin Film Junction Preparation

ZnS thin film of area 2.25 cm^2 was prepared on PET substrate using evaporation of ZnS powder (99.999% pure, from Alfa Aesar) in a residual pressure of 10^{-5} Torr. Cleaned PET film of 20 µm (from Good Fellow Cambridge Limited, England) thick was used as substrate and it is kept at room temperature in the vacuum chamber. The boat is made of molybdenum in which evaporator material is filled. The ZnS powder is loaded in the boat for deposition over PET film. At the time of deposition the equipment was in the mode of HT (High Tension). The evaporation temperature of ZnS is around 150°C in the vacuum chamber therefore the current and voltage applied to the boat are 3 Ampere and 120 Volt respectively to evaporate the ZnS molecules. The thickness of ZnS film is of the order of 200 nm, which was measured by Quartz crystal

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E-ISSN: 1929-5995/13

thickness monitor (Model CTM 200) with the deposition rate of 20 nm per second. After the deposition of ZnS film over PET substrate, vacuum is broken. Than aluminium (aluminium single crystal disc, from Aldrich Chemical) is loaded in the boat and again the same order (10^{-5} Torr) of vacuum is obtained for the deposition. The evaporation temperature of Al is around 100°C in the vacuum chamber therefore the current and voltage applied to the boat are 2 Ampere and 100 Volt respectively to evaporate the Al particles. Al film of area 0.5625 cm^2 is deposited over the ZnS film. The thickness of Al-film deposited over the ZnS film is 200 nm. Indium electrodes have been obtained over ZnS and Al films by the deposition of Indium at the same order of vacuum and same parameter of equipment as in deposition of Al so that it can be used as electrical contacts as shown in Figure **1**.

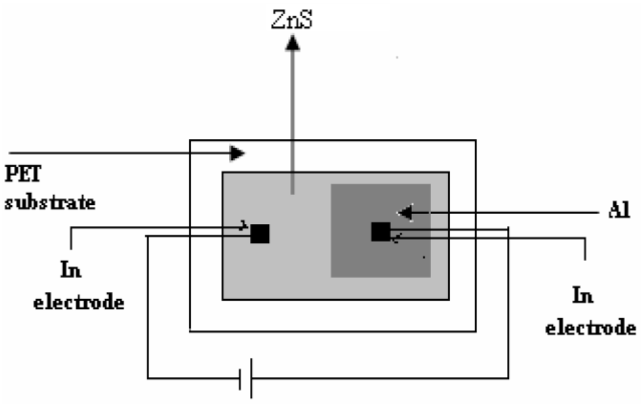

Figure 1: Schematic diagram of Al/n-ZnS junction.

Techniques Of Characterization Studies

Structural study of ZnS-PET film was done using X-ray diffraction pattern performed with Philips X'pert X–ray diffractometer at a scanning rate of 3° per minute between 10 to 60°. The source used throughout this study was Cu, Kα (λ = 1.5406Å) operated at 40 mA and 45 kV.

I-V characteristics of Al/n-ZnS Schottky junction were carried out by Keithley Electrometer/High Resistance meter 6517 A at room temperature. Keithley Electrometer has an in built capacity of output independent voltage source of ±1000 volt. The voltage is applied across the sample to measure the current through the sample.

The optical absorption spectra of ZnS thin film was recorded over the wavelength range 375 to 575 nm using an USB 2000 spectrophotometer at room temperature. In this spectrophotometer, absorption spectra are obtained directly through the computer using OOI Base 32 software. The light source is a deuterium lamp. Light falling on the sample is normal to the surface of film. From the absorption spectra, the optical band gap of ZnS thin film was determined.

RESULTS AND DISCUSSION

Figure **2** shows the X-ray diffraction patterns of PET and ZnS-PET films. These patterns show the semicrystalline nature of PET film and also contain a peak of ZnS material in ZnS-PET film. It reveals that ZnS has hexagonal structure with primitive lattice having cell parameters of a = 3.800Å, c = 6.230Å and preferred (002) [13] orientation of micro crystallites. The grain size of the crystallites (G) has been estimated using the following relation [13]:

$$G = k\,\lambda/(\beta\cos\theta) \tag{1}$$

where k is shape factor (≈1), λ is the wavelength of X-ray used, θ is Bragg's angle and β is the full width at half maximum (FWHM) of the peak. Here all the variables have their SI units. The grain size (G) of ZnS particle is found to be of the order of 17 nm.

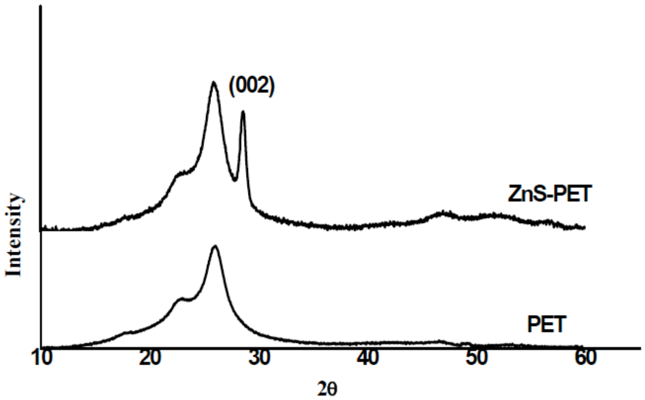

Figure 2: XRD pattern of PET and ZnS-PET film.

I-V characteristic of Al/n-ZnS junction on PET substrate is shown in Figure **3**. The I-V characteristic shows the rectification behaviour, which indicates the formation of Schottky contact between Al and ZnS film.

At low voltage, the current varies exponentially (Figure **4**) suggesting conduction by thermionic emission [14]. The current through the Schottky junction under low bias voltage (0.0-3.0 V) is given by the following relation

$$I = I_S[\exp(eV/nk_BT) - 1] \tag{2}$$

and

$$I_S = A^* T^2 \exp(-e\Phi_b/k_BT) \qquad (3)$$

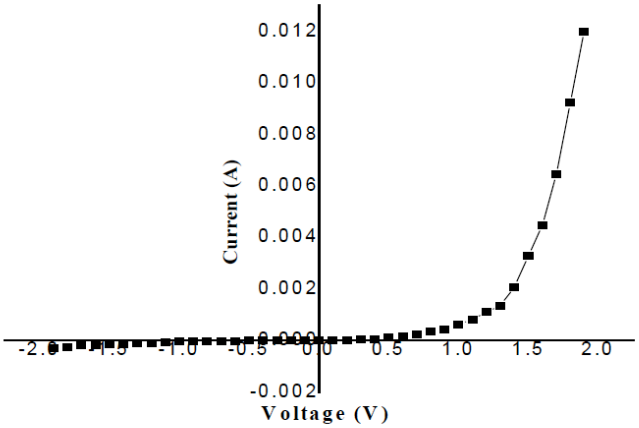

Figure 3: I-V characteristic of Al/n-ZnS Schottky junction at room tempetrture.

where e is the charge on electron, V is the applied voltage, n is the diode ideality factor, k_B is the Boltzmann constant, T is the temperature, Φ_b is effective barrier height, A* is effective Richardson constant and I_S is the reverse saturation current. All the variables have their SI units.

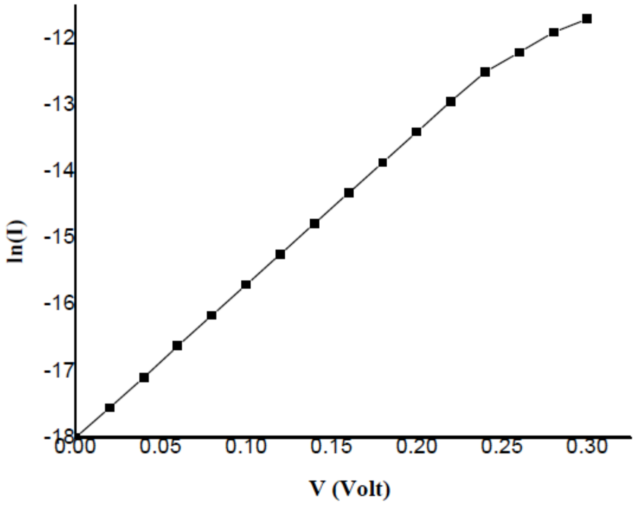

Figure 4: ln I vs. V curve of Al/n-ZnS junction at lower voltages.

The reverse saturation current (I_S) is determined by interpolation of exponential slope of I at V=0. The barrier height and ideality factor has been calculated using equations (2) and (3) respectively. It has been found that the reverse saturation current (I_S), barrier height (Φ_b) and ideality factor of Al/n-ZnS junction is 5.14 x10^{-6} A, 0.75 eV and 1.36 respectively. The value of ideality factor greater than unity is associated with Fermi-level pinning at the interface [15-17]. Interfacial oxide layer may also be the possible cause for a higher ideality factor [18]. Surface defects produce electronic energy levels in the band gaps of ZnS semiconductor. These levels can pin the Fermi energy at metal-semiconductor interfaces and cause Schottky-barrier formation [19]. The value of series resistance (Rs) has also been calculated, which is 102.6 Ω for Al/n-ZnS junction.

The observed experimental (Schottky) behavior of Al/n-ZnS junction is largely attributed to the existence of an electric dipole at the interface of junction [20], which is explained by the proposed band diagram of this junction as shown in Figure **5** using tunneling-induced dipole effects. The probability of tunneling electrons in ZnS material is less due to high work function difference therefore forward current in Schottky junctions with ZnS is low in comparision to Schottky junctions with CdS at the same voltage. The possibility of tunneling of electrons in ZnS material can be related with effective work function model (EWF) [21]. This model suggests that the Fermi level at the surface (or interface) is not fixed by surface states but rather is related to the work functions of microclusters of the one or more interface phases resulting from either oxygen contamination or metal-semiconductor reactions which occur during metallization. The theory requires that when a metal is deposited, or an oxide is formed, the interface formed between them, contains a mixture of microclusters of different phases, each having its own work function. Therefore effective work function (Φ_{eff}) is an appropriately weighted average of the work functions of the different interface phases. Hence it may be possible that the effective work function of ZnS becomes less than the standard value which decreases the work function difference at metal-ZnS interface and may lead to tunneling of electrons from metal to ZnS material.

Since the Fermi level of metal is higher than that of semiconductor (shown in Figure **5a**), therefore it is possible that some electron just below the Fermi level in metal can tunnel through the interface into the forbidden gap of semiconductor leaving behind a positive charge on the metal side in the neighborhood of interface. These electrons penetrate a short distance in the semiconductor forbidden band before being reflected back and leave negative charge into the ZnS. This creates an electric dipole at the interface for a very short distance, resulting, an upward bending in ZnS bands as shown in Figure **5b**. To attain equilibrium in this case, electrons move from the conduction band of the semiconductor to the lower available states in the metal. As the electrons leave the semiconductor, they leave behind ionized donors, which shift the semiconductor energies downward until the Fermi levels line up. The charge region of the junction then consists of tunneling-induced dipole layer, a depletion region in the semiconductor and a thin region of charge at the surface of the metal and extends into the metal only to a short distance. Because of relative charge densities in the two materials, virtually the entire voltage drop and space charge region lies within the semiconductor. The barrier for electrons going from the semiconductor to metal is different from the barrier for electrons going from the metal to the semiconductor.

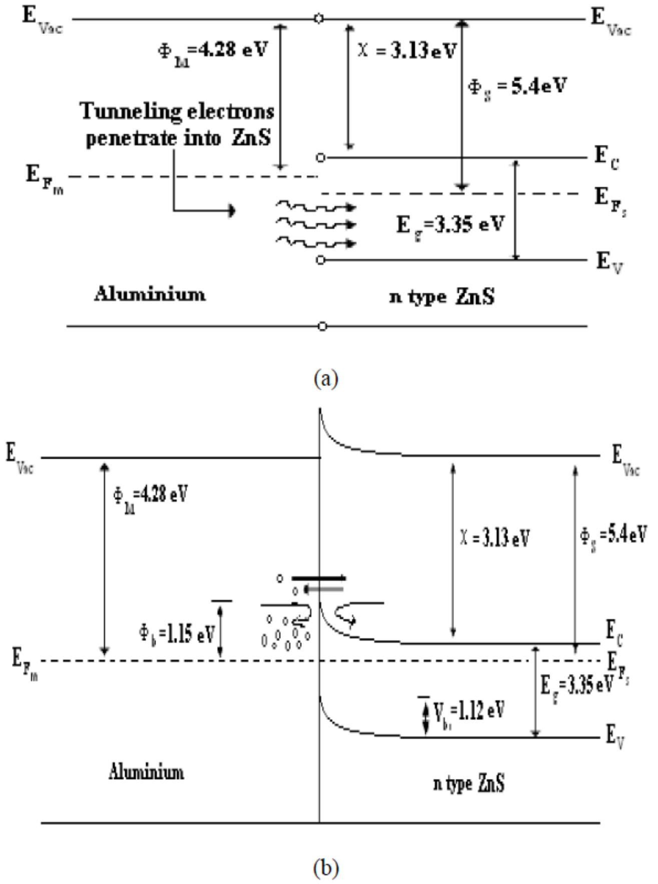

Figure 5: The energy band diagram of Al/n-ZnS Schottky junction including tunneling-induced dipole effect: (**a**) neutrality (**b**) equilibrium.

In this band diagram, work function of aluminium (Φ_M) 4.28 eV and work function of n-type ZnS material (Φ_S) 5.4 eV have been taken as a standard value, whereas the electron affinity (χ) of ZnS is 3.13 eV determined using the relation $\chi = \Phi_M - \Phi_b$. The built-in potential V_{bi} is the height of Schottky barrier on the semiconductor side, which is equal to the difference between the work function of metal and semiconductor. In this case the value of V_{bi} is 1.12 eV. The band gap of ZnS as obtained from optical measurements is 3.35 eV, and is explained below.

From optical absorption spectrum of ZnS the band gap was calculated using the Tauc relation [22] given by equation (6).

$$(\alpha h \nu) = A (h \nu - Eg)^m \quad (6)$$

where m = ½ for allowed direct transition and A is a constant.

The energy band gap is obtained by plotting a graph between $(\alpha h \nu)^2$ (as ordinate) and hν (as abscissa) as shown in Figure **6**. The value of band gap of ZnS film is estimated by extrapolating the linear portion of the curve to $(\alpha h \nu)^2 = 0$. The energy band gap of ZnS film is found to be 3.35 eV. The presence of PET film does not affect the absorption spectrum of ZnS because it is taken as reference material for the absorption spectrum of ZnS film.

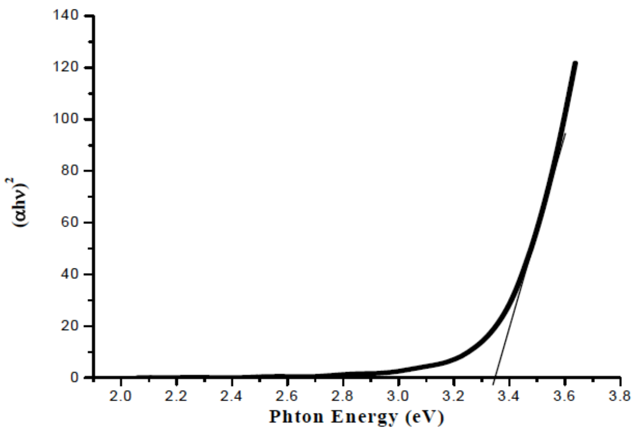

Figure 6: Energy band gap determination of ZnS thin film.

CONCLUSION

Room temperature deposited ZnS film on PET substrate is hexagonal in structure with preferred (002) orientation of micro – crystallites. Al makes Schottky contact with n-ZnS. The contact properties such as saturation current, barrier height, ideality factor and series resistance of this junction are 5.14 x10^{-6} A, 0.75 eV, 1.36 and 102.6 Ω respectively which helps in the fabrication of Al/n-ZnS Schottky junction of particular thickness for their use in electronic devices. At lower bias voltages, current conduction is by thermionic emission. A band diagram for Al/n-ZnS at equilibrium is proposed using tunneling-induced dipole effect at the interface.

ACKNOWLEDGEMENTS

One of the authors Sandhya Gupta is thankful to UGC for providing financial assistance during this work.

Author would also like to thank Ms. Deepika, Ms. Manasvi Dixit and Mr. Mahesh Baboo, Mr. K.S. Rathore, Mr. Vishal Mathur for their help in various ways during the course of this work.

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Received on 02-05-2013 Accepted on 18-06-2013 Published on 26-06-2013

DOI: http://dx.doi.org/10.6000/1929-5995.2013.02.02.4