DEPOSITION AND CHARACTERIZATION OF Bi$_2$S$_3$ FOR PHOTOELECTROCHEMICAL SOLAR CELL APPLICATION


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AN INTRODUCTION

In recent decades thin film Semiconductor materials have become technologically very important. This is because the importance of coatings and synthesis of new materials for industry have resulted in tremendous increase of innovative thin film processed technology (Buba and Adelabu, 2009). Some examples are Microelectronics, Integrated circuits, Magnetic Storage System, Optical Sensors, Photo electrochemical cells (PEC), photoconductors, Anti-reflection coatings, Interference items, Polarizers, Narrow Band Filters, Infrared (IR) detectors, Waveguide Coatings, Temperature Control of Satellites, Photo thermal Coatings, etc. Thin films can be synthesised using different techniques. These may be physical or chemical methods. In physical methods, the thin film is moved from target source with some form of energy to the substrate (Pathan and Lokhande, 2004). This method is widely used in one- compound films, under which we have Vacuum evaporation and Sputtering, where the deposition has been transferred to gaseous state by either evaporation or an impact process (Pathan and Lokhande, 2004). Whereas, the chemical method involves chemical reaction and the precursors are mostly components undergoing reactions at the substrate surface or in vicinity of the substrate (Pathan and Lokhande, 2004). Under chemical methods we have the gas phase chemical processes. For the gas phase chemical processes we have the conventional Chemical Vapour Deposition (CVD), Laser CVD, Metal Organo-Chemical Vapour Deposition (MOCVD) and Plasma enhanced Chemical Vapour Deposition (PECVD) (Pathan and Lokhande, 2004), while the Liquid Phase Chemical techniques includes; Electro-deposition, Chemical Bath Deposition (CBD) (Buba and Adelabu, 2013), Successive Ionic Layer Adsorption and Reaction (SILAR) (Ubale and Bargal, 2011), Spray Pyrolysis (Ubale et al., 2014) etc. The Chemical Bath Deposition (CBD) technique has become very popular. In recent decades, especially for thin film deposition because of its simplicity, it does not require expensive and sophisticated equipment, it is very easy to handle and it is applied to many compounds such as Sulphides, Oxides and Selenides (Buba and Adelabu, 2009; 2013). The CBD technique has been used extensively (Inderjeet et al., 1980; Chopra et al., 1982; Nair et al., 1991;
1993; Ndukwu, 1993; 1995; Eze and Okeke, 1997; Fajinmi, 2000; Usoh and Okuajagu, 2014; Karabulut et al., 2014; Mosiori et al., 2014) for the deposition of group (II-VI) and group (IV-VI) Compound Semiconductors. It has also been exploited successfully for the deposition of oxides films. Bismuth Sulphide (Bi$_2$S$_3$) belong to group (V-IV) Compound Semiconductor materials occurring naturally in grey crystalline form and referred to as “Bismuth glance” or Bismuthinite (Pathan and Lokhande, 2004). Its crystallinity, both in natural and artificial form belongs to orthorhombic crystalline structure. Bi$_2$S$_3$ is a promising low cost and non-toxic semiconductor material which is used for conversion of solar energy into electrical energy by means of photo electrochemical cell (PEC) process as its forbidden energy gap lies between 1.25eV and 1.90eV (Killedar et al., 2000).

The electrical resistivity of Bi$_2$S$_3$ is of the Order of 10$^{-4}$ - 10$^{-5}$ cm$^{-1}$ in the visible region. Bismuth Sulphide (Bi$_2$S$_3$) thin films have been deposited using various methods by different researchers such as Chemical Bath Deposition (Man et al., 1999; Ahire et al., 2001; Ahire and Sharma, 2006), Electrodeposition (Killedar et al., 2000), Hydrothermal/Solvothermal route (Sambhaji et al., 2012), Spray Pyrolysis (Ubale et al., 2011), Successive Ionic Layer Adsorption and Reaction (Ubale et al., 2011) etc. In the present work thin films of Bismuth Sulphide (Bi$_2$S$_3$) were deposited onto fluoride doped Tin Oxide (FTO) coated glass substrates by Chemical Bath Deposition (CBD) technique. The films were characterized for their photo electrochemical properties with Bi$_2$S$_3$ film as electrode and carbon as counter-electrode.

**Experimental Details**

The deposition of Bi$_2$S$_3$ thin films onto FTO glass substrates took place under room temperature from the solution containing (20ml) 0.03M Bi(NO$_3$)$_3$ solution, used as cationic precursors with pH~10 and (16ml) 0.1M of thioacetamide [CH$_2$CS-NH$_2$] used as anionic precursor with pH~11 which was raised by addition of hydrazine hydrate as demonstrated by Ahire and Sharma (2006). The FTO glass substrates were immersed in the cationic precursor solution of [Bi (NO$_3$)$_3$] for 30 seconds on which the Bi$^{3+}$ ions were absorbed, after the substrates were taken out, and then immersed into distilled water for one minute to cater for ion exchange in order to remove unabsorbed ions from the surface of the substrates. Thereafter, the substrates were then immersed into the ionic precursor of [CH$_2$CS-NH$_2$] solution for another 30 seconds in which the S$^{2-}$ ions from the thioacetamide solution reacted with Bi$^{3+}$ ions already absorbed by the FTO glass substrates in the cationic precursor.

This was again followed by rinsing in distilled water for one minute to remove the unreacted S$^{2-}$ions on the surface of the substrates which completes the deposition cycle of the Bismuth Sulphide (Bi$_2$S$_3$) thin films. For optimal quality the deposition cycle was repeated up to thirty times on the glass substrates. A Photo electrochemical cell (PEC) was formed having two electrodes consisting of Bi$_2$S$_3$ film already deposited on the FTO glass substrate as the working electrode, graphite as a counter electrode and 0.3M polysulphide (Na$_2$S-S-NaOH) solution as electrolyte. The Current-Voltage (I-V) characteristics of the PEC cells were measured in the dark and under illumination using 200W tungsten filament as demonstrated by Ahire and Sharma (2006) and Mane et al., (1999). The heating of the PEC cells by the tungsten lamp was prevented by interposing a water filter between them. The intensity of the illumination was measured by Lux meter and found to be at 80mW/cm$^2$. The spectral response of the cell was recorded using monochromator in the wavelength range of 350nm-1050nm. Transient photo response and Capacitance-Voltage (C-V) characteristics of the cell were used to calculate other photo electrochemical properties of the cell.

**Theoretical Considerations and Calculations**

A Photo electrochemical Cell (PEC) is a device in which one or both electrodes is a photo responsive Semiconductor (SC) such that the Semiconductor with light of $h\nu \geq E_g$ the band gap of the Semiconductor, results in the flow of current in an external circuit (Aruchamy et al., 1982). The photo effect responsible for the current flow occurs at the Semiconductor/electrolyte interface in which the light absorption takes place in the Semiconductor to produce excess charge carriers. At the interface, when a Semiconductor whose Femi level (electrochemical potential, $E_F$) is brought into contact with an electrolyte whose electrochemical (redox) potential is $E^\circ$, an equilibrium of electrochemical potentials of the two phases is established by transfer of electrons across the interface. This leads to a potential Barrier for the further flow of charge carriers. The Semiconductor electronic bands near the surface are bent due to the depletion of majority charge carriers near the surface. The magnitude of the height of the potential Barrier (also the extent of band bending), $E_B$ is equal to the difference in the electrochemical potentials (Fermi levels) of the two phases (Semiconductor and electrolyte) before contact given by:

$$E_B = |E_F - E^\circ|$$

(1)

The correlation between charge density and electrostatic potential has been derived for various conditions of space charge layers (Aruchamy et al., 1982). The differential capacity $C_{dc}$ for fairly large band gap Semiconductor is given by the Mott-Schottky equation (Gerischer, 1970):

$$\frac{1}{C_{dc}^2} = \frac{2}{\varepsilon \varepsilon_0 N_D (E - E_F - K^*/q)}$$

(2)

Where $N_D$ is the concentration of donors (for n-type Semiconductors), $\varepsilon$ an $\varepsilon_0$ are dielectric constants of the vacuum and the Semiconductor, $E$ is the electrode potential, $E_F$ is the flat band potential of the Semiconductor, $K$ is the Boltzmann constant, $T$ is the absolute temperature and $q$ is the charge on the electron. The relationship between the current and potential of Shottky-type Barrier for a Semiconductor/electrolyte interface can be obtained, and the consideration becomes valid particularly when the reaction kinetics is ignored. The reaction kinetics is generally described by the Butler-Volmer equation:

$$i = i_s \left[ \exp \left( \frac{\Delta FE_F^*}{KT} \right) \right] - \left[ \exp \left( - \frac{\Delta FE_F^*}{KT} \right) \right]$$

(3)

Where $i_s$ is the exchange current density, $E_F$ is the over potential required to derive a current through the electrode, F
is the Faraday constant and $\alpha$ transfer coefficient (<1.0). For $I \ll I_p$, the over potential is negligible and the reaction kinetics do not limit the process. When $I = I_p$ reaction kinetics will become the rate limiting the process (the over potential at the counter electrode can minimised by having a large surface area). For a Semiconductor photoelectrode the charge transfer reaction is driven by the over potential (Butler, 1977):

$$E_a = E_a - \Phi - E_D$$  \hspace{1cm} (4)

Where $E_a$ is the band bending with the anode and cathode shorted together, for large band gap Semiconductors $E_a$ will be sufficiently large so that the reaction at the photo electrode would not be rate limiting for light intensities of at least up to 100mW/cm$^2$. Under these conditions, photo response of PEC will be determined by the behaviour of photo generated electron-hole pairs and thus the physical properties of the Semiconductor (Aruchamy et al., 1982). The photo current flowing through the interface can be given (Butler, 1977):

$$J = q\sigma_0 \left[ 1 - \exp\left(-\alpha W_c (E - E_F) / qN_D \right) \right]$$  \hspace{1cm} (5)

Where $\sigma_0$ is the photon flux, $\alpha$ is the optical absorption constant, $L_p$ is the hole diffusion length, $q$ is the electronic charge and $E$ is the electrode potential. The depletion layer width is given by:

$$W = W_c (E - E_F)^{1/2} = \frac{2E^{1/2}}{\alpha N_D} (E - E_F)$$  \hspace{1cm} (6)

Where $W_c$ is the width of the depletion layer at a potential difference of volt across it. This equation relates the photocurrent density with various parameters that is; carrier density, diffusion length, flat band potential, applied potential and optical absorption constant ($\alpha$).

Where;

$$\alpha = \frac{A(h\nu - E_a)^2}{h\nu}$$  \hspace{1cm} (7)

And A is a constant, $h\nu$ is the photon energy, $n=1$ when electronic transition is direct and $n=4$ when the electronic transition is indirect. The illumination of the Semiconductor/electrolyte junction with light of energy $h\nu = E_a$ gives rise to non-equilibrium situation in which the Fermi levels of the Semiconductor and redox electrolyte shift apart. The variation of the potential with incident light intensity is given by the exponential relation in analogy with a p-n junction (Memming, 1978) given by:

$$V_p = -kT \ln \left( \frac{I}{I_p} \right)$$

$$= \frac{kTDP}{q} \ln \left( \frac{I}{I_p} \right)$$  \hspace{1cm} (8)

Where $P_0$ is the density of holes in the bulk of the Semiconductor, $DP$ is the increase in hole density on illumination, $\gamma$ is proportionality factor and $I$ is the light intensity. The energy conversion efficiency ($\eta$) of photovoltaic devices is given (Gerischer, 1977) by:

$$\eta = \frac{E_{st}}{E_{solar}}$$  \hspace{1cm} (9)

Where $\eta$ is simply defined as the ratio of the output electrical power to chemical power from the cell to the total optical energy input, $E_{solar}$ is the threshold energy, $E_{st}$ is the stored energy, $A(E)$ is the characteristic absorbance and $N(E)$ is the flux density of the incident photons. For photovoltaic Semiconductor devices the free energy conversion efficiency depends on the band gap and reaches maximum for $E_g = 1.3 - 1.5eV$. For photo electrolysis cells which produce chemicals with an applied bias, solar energy conversion efficiency is given by:

$$\eta = \frac{(I \times V)_{max}}{100}$$  \hspace{1cm} (10)

Where the energy stored in the fuel is released when the fuel is oxidised. The optical to electrical energy conversion efficiency in a Semiconductor/electrolyte junction solar cell is given by:

$$\eta = \frac{(I \times V)_{max}}{P}$$  \hspace{1cm} (11)

Where $(I \times V)_{max}$ is the maximum power output of solar cell and $P$ is the optical power input. In addition to $\eta$ a parameter called the fill factor (FF) of a PEC is defined by:

$$FF = \frac{(I \times V)_{max}}{I_{sc} \times V_{oc}}$$  \hspace{1cm} (12)

Where $I_{sc}$ is the short circuit photo current and $V_{oc}$ is the open circuit voltage. The fill factor (FF<1) indicates the extent of departure from the ideal behaviour of the semiconductor/electrolyte junction. In addition to the overall energy conversion efficiencies two other efficiency criteria in PECs are the current efficiency and quantum efficiency.

**RESULTS AND DISCUSSION**

A PEC configuration of Bi$_2$S$_3$/ (NaOH-S-NaS)/C were formed. The cell was observed to have produced some dark voltage ($V_a$) and dark current ($I_a$) with Bi$_2$S$_3$ as the negative electrode and the carbon being the positive electrode. The difference between the two half-cell potentials in the PEC gives rise to the dark voltage written by:

$$E = E_{carbon} - E_{Bi_2S_3}$$  \hspace{1cm} (13)

Where $E_{carbon}$ and $E_{Bi_2S_3}$ are the half potentials when dipped in the polysulphide electrolyte. When the junction was illuminated, the voltage increases negatively toward the Bi$_2$S$_3$ electrode and the cathodic behaviour of the Semiconductor film was observed, indicating the conductivity of the Bi$_2$S$_3$ film to be n-type which was confirmed also by Ahire and
Sharma, (2006) and Mane et al. (1999). Fig.1 depicts the current (I) - voltage (V) characteristics of the PEC cell in dark and under illumination with Bi$_2$S$_3$ thin film being the negative photo electrode. The nature of the I-V curves is analogous with nature reported by Ashire and Sharma, (2006) and indicates the formation of rectifying junction. When the PEC cell was illuminated the curves which were in the fourth quadrant shifted their positions confirming the generation of electricity by the cell and the increase in current under illumination is attributed to the conductivity of the thin film. Also, the increase in current can be attributed to the onset of electron injection from the electrolyte (Kale et al., 1996). The rectifying junction formed acts as a diode and the information on the diode ideality factor can be obtained from the equation:

$$I = I_o \left\{ \exp \left( \frac{qV}{nKT} \right) - 1 \right\}$$  \hspace{1cm} (14)$$

Taking the log of both sides of the equation gives:

$$\log I = \log I_o + \left( \frac{qV}{nKT} \right)$$  \hspace{1cm} (16)$$

Fig.2 shows the plot of log I versus V (extracted from fig.1) using the forward bias data only. The dark ideality factor for diode is found to be 11.72 while the diode ideality factor for under illumination is 8.76 (Fig. 2). Deviation from one in ideality factor indicates that, either there are unusual recombination mechanisms taking place or that the recombination is changing in magnitude. The photovoltaic output characteristics of the Bi$_2$S$_3$ PEC cell under illumination at intensity of 80mW/cm$^2$ is given in Fig.3. The series resistance $R_S$ and the shunt resistance $R_{sh}$ were calculated from the gradients through:

$$\frac{1}{R_S} = \left( \frac{dI}{dV} \right)_{I=0}$$  \hspace{1cm} (17)$$

$$\frac{1}{R_{sh}} = \left( \frac{dI}{dV} \right)_{V=0}$$  \hspace{1cm} (18)$$

Which gives the values of $R_S$ and $R_{sh}$ to be approximately 49Ω and 59Ω respectively and the calculated fill factor (FF) of 30% and power efficiency ($\eta$) of 0.047. This results is in agreement with the report of Ahire and Sharma (2006). The low efficiency may be due to high shunt resistance of the cell and the interactive recombination resulting from interfacial states. The study on the spectral response of the PEC cell was carried out by measuring the short circuit current ($I_{sc}$) and plotting it on a graph against the wavelength ($\lambda$) which is shown in Fig.4. The Short circuit current increases with wavelength, it reaches maximum and then decrease with
The decrease in the (Isc) on the shorter wavelength side of peak may be due to absorption of light in the electrolyte and high recombination of photo generated carriers by surface states and the decrease in (Isc) on the longer side may be attributed to the transition between defect levels (Ahire and Sharma, 2006; Mane et al., 1996).

The measurement of capacitance as a function of applied voltage was carried out from which the Mott-Schottky plot of the Bi2S3 thin film PEC cell is given in Fig.5.

Fig. 4. Spectral response Bi2S3 PEC cell

Fig. 5. Mott-Schottky plot for Bi2S3 PEC cell (Capacitance Vs Potential)

The flat band potential (Vfb) an important factor in explaining the charge transfer process across the Semiconductor-electrolyte junction of the PEC cell was determined by extrapolation of the linear region of the plot on the potential axis (which is approximately equal to -0.045V). The plot is linear with negative slope indicating the n-type conductivity of the film.

Conclusions

PEC cell was formed using Bi2S3 thin film onto FTO coated glass as negative electrode and graphite as the counter electrode. The I-V characteristic of the PEC cell reveals the rectifying nature of the junction. The flat band potential of the junction is found to be -0.45V through C-V measurement. The conversion efficiency and fill factor of the cell at an illumination intensity of 80mW/cm² are respectively 30% and 0.047 which are found to be small due to low series and high shunt resistance. The Bi2S3 thin film exhibits n-type electrical conductivity. Hence, from the study, it is essential to improve the structural, optical and electrical properties of the Bi2S3 thin film so as to achieve higher conversion efficiency.

REFERENCES


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