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Electrochemical Studies of Yttrium Sulphide Films

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ABSTRACT: The electrochemical characterization of yttrium sulphide thin films by forming the electrochemical cell has been studied. The I-V characteristics are obtained at different temperatures in dark. By using simple diode equation, junction ideality factor is calculated and conductivity type of deposited material is decided. Barrier height can be calculated from Richardson's equation. The flat band potential and type of semiconductor are confirmed from Mott-Schottky plot.

KEY WORDS: Electrochemical cell, Junction ideality factor, Barrier height, flat band potential, Mott-schottky plot.

I. INTRODUCTION

The interest in semiconductor liquid junction has parallel to the development of solid state junction [1, 2]. The experiment of Honda and Fujishima gave birth to this new type of junction, the semiconductor – electrolyte junction, like a metal - Schottky junction. The explosion of interest in solid state semiconductor junction devices, which was constantly fueled by the exponential growth in the volume and diversity of the practical applications of these devices in the electronic and related industries, have left their liquid junction counterparts behind. The probability of new kinds of practical devices have awakened the interest of many and made available enough resources to investigate the fundamental physics and chemistry at the semiconductor – liquid interface and to develop techniques and method for inside characterization of these interfaces. Now, when the interest in solar energy conversion is not at its peak, new applications are being constantly conceived sufficient to maintain basic research in this area. Various aspects of the semiconductor electrolyte interface are being emphasized for device applications and for materials characterization for whatever the final use might be.

Bose et al [3] summarized the measurements that may be employed for characterization of semiconductor electrodes using electrochemical techniques. Sikander et al [4] reported rare earth based solar cells, Bi_2X_2 ($\text{X} = \text{S}, \text{Se}, \text{Te}$). A model for the I-V characteristics of electrochemical photovoltaic devices was suggested by S.J. Fonash and S. Ashok, for the study the performance of semiconductor electrodes [5]. Gelderman et al [6] reported experimental determination of flat band potential from Mott-Schottky equation. J. M. Shah [7] reported experimental analysis and new model of high ideality factor in GaN- based diodes. It was suggested that near the metal -semiconductor interface, the Fermi level in the semiconductor is pinned near an effective gap center, which is related to Schottky barrier heights [8]. Now a day's research has a wide scope in semiconductor Nanoarchitectures and liquid junction solar cells [9-11]. In this paper the electrochemical characterization of Y-S thin film by forming electrochemical cell is reported. The I-V characteristics are obtained at different temperatures in dark. By using simple diode equation, junction ideality factor is calculated. Barrier height can be calculated from Richardson's equation. The flat band potential is obtained using Mott-Schottky equation. The type of deposited material is decided from the slope of Mott-Schottky plot.

II. EXPERIMENTAL DETAILS

The yttrium sulphide films are prepared by the method of electrodeposition, onto a stainless steel substrate from a non-aqueous formaldehyde bath.

$0.05\text{M Y}(\text{NO}_3)_3 - 0.05\text{M CH}_3\text{CSNH}_2 - 0.05\text{M CH}_3\text{COONa}$

Electrodeposited Y-S film is used as anode and the graphite plate (cathode) is used as a counterelectrode. Different electrolytes are prepared in doubly distilled water by taking chemicals of analytical grade. A corning glass tube was modified for the cell. A saturated calomel electrode (SCE) was used as a reference electrode.

By forming the electrochemical cell with different electrolytes, the films are tested for their current-voltage characteristics in dark in the temperature range from room temperature to 50°C. The water filter was interposed between the lamp and the cell. The junction ideality factor, barrier height, flat band potential, conductivity type etc. are determined.

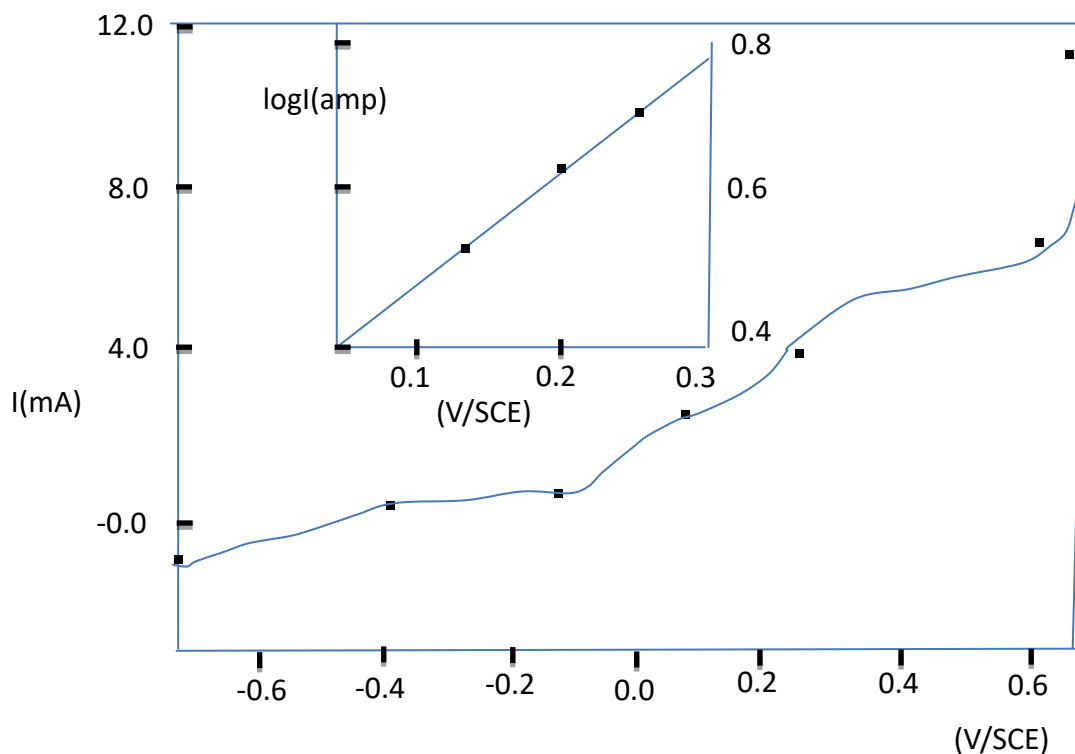


Fig.1: I-V characteristics of Y-S / 0.1 M [(K₃ Fe (CN)₆ – K₄ Fe (CN)₆]/ C cell. (Inset shows log I versus V of the same

III. RESULTS AND DISCUSSION

The yttrium sulphide films are tested in various electrolytes. The electrolyte, 0.1 M [(K₃ Fe (CN)₆ – K₄ Fe (CN)₆], PH =7.0, found to be reliable in which films remains stable and no significant weight loss is observed. Therefore, further studies have been carried out in ferri-ferro cyanide electrolyte.

a) Current-Voltage (I-V) Characteristics:

Electrochemical cell with the configuration: Y-S / 0.1 M [(K₃ Fe (CN)₆ – K₄ Fe (CN)₆] / C is formed. It is observed that even in the dark, cell gives some voltage, V_D and current I_D with Y-S film is as a positive electrode and graphite rod as a negative electrode. The polarities of the voltages are positive towards the Y-S electrode. The origin of these is attributed to the difference two half cells in the electrochemical cells which can be written as,

$$E = E_{\text{graphite}} - E_{\text{Y-S}}$$

E_{graphite} and E_{Y-S} are the half cell potentials when dipped in the electrolytes. From above observation, one can write'

$$E_{Y-S} < E_{\text{graphite}}$$

Fig.1 shows I-V characteristics of electrochemical cell Y-S as an anode and graphite as a cathode. It is observed that in the forward flow of current, junction acts as a diode in a reverse direction, current gets saturated. Hence it is concluded that Y-S is the P-type semiconductor.

b) Junction Ideality Factor (n):

The value of junction ideality factor can be calculated by simple diode equation

$$I = I_0 \exp. (qV/nKT)$$

Where, n is junction ideality factor. The plots of log I versus V at room temperature for electrochemical cell formed with Y-S film electrode (shown as inset in fig.1) show linear behavior. From this junction ideality factor n was calculated to be 35.1. This value is much larger than ideal value, which indicates that our semiconductor (Y-S film) form nonideal junction with ferri-ferro cyanide electrolyte.

Jundale [12] has formed electrochemical cell with samarium chalcogenide films and a junction ideality factor has been reported, which are much larger than ideal value. Similarly the values of junction ideality factors for polymer based junctions are also higher [13].

c) Temperature Effect Studies:

The interface between the semiconductor and an electrolyte is a key element of the electrochemical cells. The theoretical dependence of current components on temperature in solid junction solar cells has been discussed by Wysocki and Rappaport [14]. Many reports on solid junction solar cells show that both the efficiency and fill factor decreases with an increase in the temperature [15, 16]. However, very little data are available on electrochemical cells [17-19].

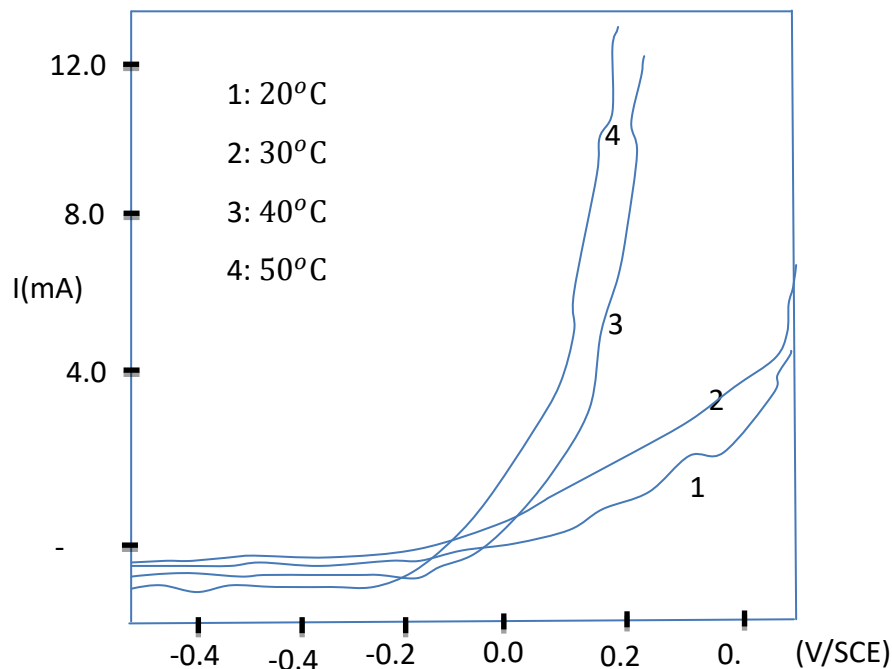


Fig.2: I-V characteristics of Y-S / 0.1 M [(K₃ Fe (CN)₆ – K₄ Fe (CN)₆]/C cell at different temperatures.

The junction ideality factor ‘n’ and barrier height ‘ ϕ_B ’ are affected by the temperature of the junction formed between semiconductor and electrolyte [16, 17]. The behavior of the junction at different temperatures can be known from the study of current voltage (I-V) characteristics of electrochemical cell at different temperatures. I-V characteristics of electrochemical cell in the temperature range from 20^oC to 50^oC under both forward and reverse bias conditions are studied. Fig. 2 shows I-V characteristics of Y-S / 0.1 M [(K₃Fe (CN)₆ – K₄Fe (CN)₆] / C cell. At increase in temperature under forward bias, the current increases rapidly and shows poor rectification above 50^oC.

d) Barrier height ‘ ϕ_B ’ between Y-S and ferri-ferro cyanide electrolyte:

The reverse saturation current, I_o is given by the relation,

$$I_o = A^* T^2 \exp (-\phi_B/KT)$$

Where A^* is the Richardson’s constant and ‘ ϕ_B ’ is the barrier height, the reverse bias current I_o , was estimated at different temperatures (T).

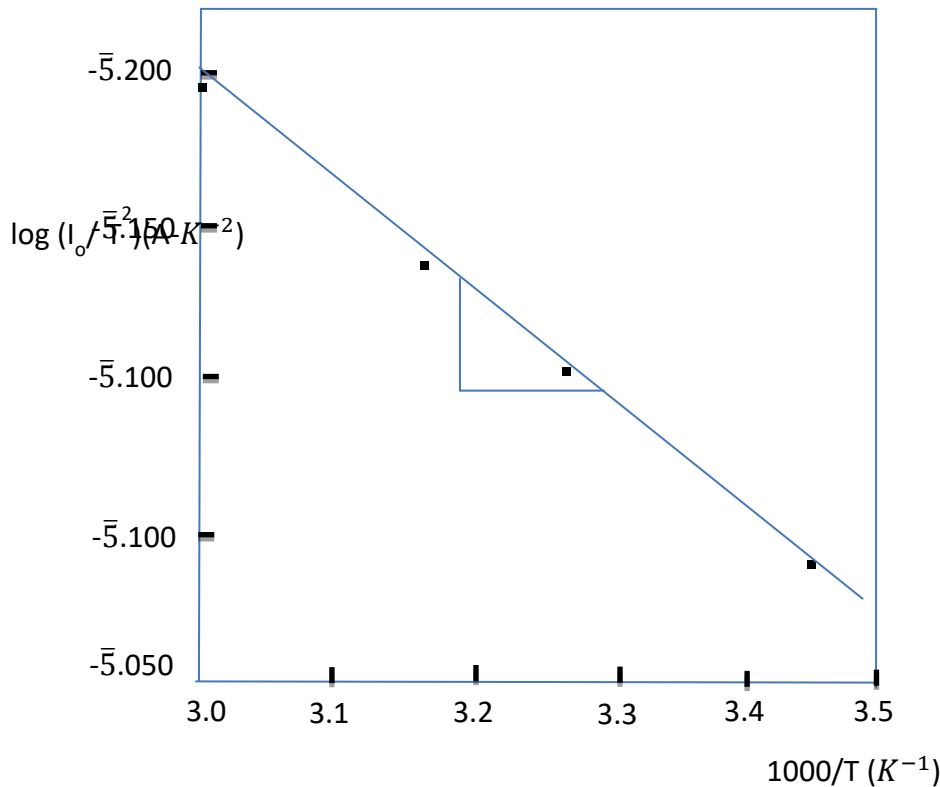


Fig.3: The plot of $\log (I_o / T^2)$ versus T^{-1} for Y-S / 0.1 M [(K₃Fe (CN)₆ – K₄Fe (CN)₆] / C cell.

The plot of the $\log (I_o / T^2)$ against T^{-1} is linear in nature. Fig. 3 show the plot of $\log (I_o / T^2)$ against T^{-1} of the cell Y-S / 0.1 M [(K₃Fe (CN)₆ – K₄Fe (CN)₆] / C. The slope of the plot gives the value of ‘ ϕ_B ’ is to be 0.33.

e) Capacitance-Voltage Characteristics (Mott-Schottky plots):

The relation between capacitance and electrode potential is given by Mott-Schottky equation,

$$I/C^2 = 2/(q\epsilon\epsilon_0N_D) [V - V_{fb} - kT/q]$$

Where, V_{fb} is the flat band potential, and N_D is ionic donor density and other symbol have their usual significance. Therefore a plot of I/C^2 versus electrode potential V , called as Mott-Schottky plot, is a straight line. Its intercept on the voltage axis gives the value of ' V_{fb} ' and the slope gives the donor concentration. Fig.4 show the Mott-Schottky plot of the cell Y-S / 0.1 M $[(K_3 Fe (CN)_6 - K_4 Fe (CN)_6)] / C$.

The sign of the slope of I/C^2 versus V plots determines the types of the majority carriers i.e. type of conductor [20]. The positive value of slope supports that Y-S is a P-type semiconductor.

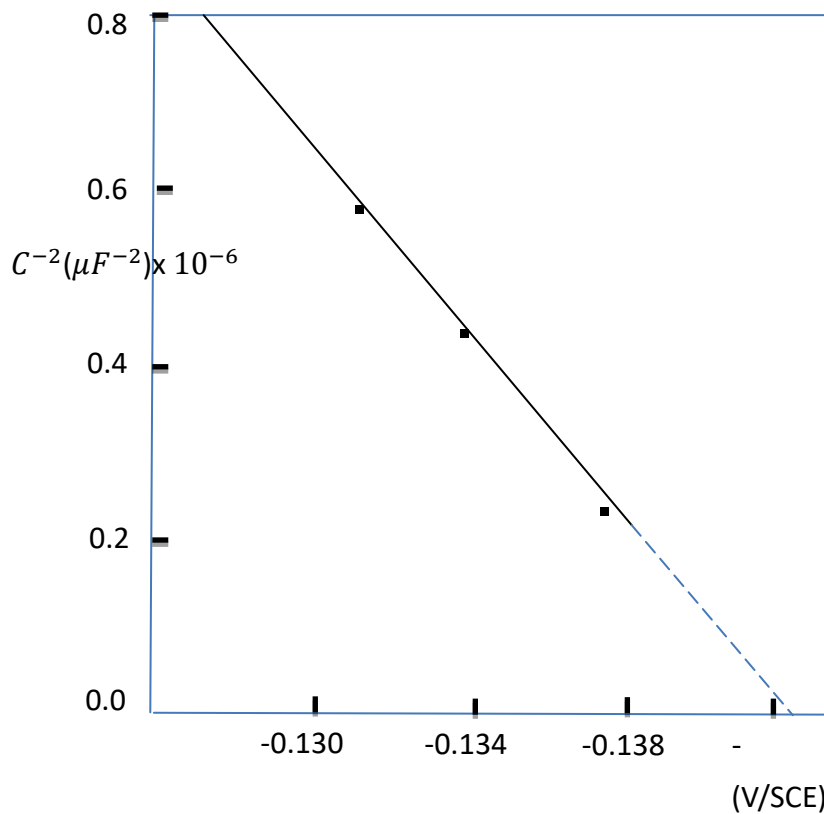


Fig. 4: The plot of C^{-2} versus V for Y-S / 0.1 M $[(K_3 Fe (CN)_6 - K_4 Fe (CN)_6)] / C$ cell.

Thus ' V_{fb} ' determines the relative Fermi levels of the electrolyte and the semiconductor and the amount of band bending at the interface. ' V_{fb} ' values have been reported for different electrolyte semiconductor pairs [12, 13, 21]. The intercept (at $I/C^2=0$) on the V (SCE) axis of Mott-Schottky plot give the value of the flat band potential and it is -0.143 for Y-S film.

IV. CONCLUSION

The electrochemical characterization of yttrium sulphide thin film is studied by forming the electrochemical cell with configuration Y-S / 0.1 M $[(K_3 Fe (CN)_6 - K_4 Fe (CN)_6)] / C$. The I-V characteristic is obtained at different temperature in dark. It is observed that in the forward flow of current, junction acts as a diode with forward bias condition and in reverse bias direction, current get saturated. From this, it is concluded that Y-S is p-type semiconductor. By using diode equation the junction ideality factor is calculated. The value of junction ideality factor



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is found to be much greater than the ideal value. From Richardson's reverse saturation current relation, the barrier height is calculated to be 0.33. Mott-Schottky plot give the value of the flat band potential is -0.143 for Y-S film.

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