Optical and Electrical Properties of Vacuum Deposited $(p)Bi_2S_3/(n)Bi_2O_3$ Thin Film Heterojunction

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Abstract— Thin film $(p)Bi_2S_3/(n)Bi_2O_3$ heteojunctions (N_d=3.001x10^{14}cm^3, N_a=6.688x10^{15}cm^3) have been prepared by vacuum evaporation technique. The junctions exhibited rectifying *I-V* characteristics and low photovoltaic effect. Different junction-parameters such as ideality factors, built in potential, short-circuit current, open circuit voltage etc. were determined from *I-V* characteristics of the heterojunction. Temperature variation ideality factors have been found to decrease with the increase of temperature in (308-330) K range. Proper doping, annealing and hydrogenation are necessary to reduce the series resistance so as to achieve high carrier efficiency. More works are being carried out in this direction.

Keywords— Barrier height, Heterojunction, Ideality factor, Open circuit voltage, PV effect, Series resistance, Short circuit current.

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1 INTRODUCTION

THE photovoltaic solar energy conversion for large scale application has assumed special significance in recent years [1]. Bismuth sulfide (Bi_2S_3) thin films have been receiving great attention since its band gap (1.2-1.7)eV [2,3,4] lies close to the range of theoretically maximum attainable energy conversion efficiency [3] and strongly absorbs light of wavelength shorter than 900nm[4]. The optical band gap of our Bi_2S_3 sample was found to be 1.45eV. It is an important member of chalchogenides because of its use to form liquid [5,6,7] and solid [8] state junction solar cells. Preparation of $W/Bi_2S_3/W$, $Ag/Bi_2S_3/W$ and $Cu/Bi_2S_3/W$ (W-tungsten substrate) structure and their non-linear *I-V* characteristic [9] and formation of heterojunction by chemically deposited Bi_2S_3 thin films with other materials have been reported [10,11,12]. The chemically deposited Bi_2S_3 thin films have been reported to be n-type in nature [5,6,7,13]. The $CuBiS_3$ films reported to be p-type in nature [14]. The Bi_2S_3 have also been used in polymer solar cells [15, 16]. The primary function of a window layer in a heterojunction is to form a junction with a absorber layer and at the same time admitting maximum amount of light to the junction region and absorber layer. Bismuth trioxide (Bi_2O_3) thin films are highly transparent. The physical properties of Bi_2O_3 thin films vary with the variation of phase compositions of the samples, which is strongly dependent on the preparation technology. The optical gap of Bi_2O_3 thin film varies from about 2eV to 3.96eV [17, 18, 19]. The optical band gap of our Bi_2O_3 thin film sample was found as 3.329eV. It shows either p-type or n-type behavior depending on its phase. There are few reports of preparation of heterojunction on Bi_2O_3 thin films [20,21]. The band gap of Bi_2O_3 is closed to that of CdS and ZnO which are used as window material in semiconductor heterojunction devices [22, 23, 24]. This paper describes recent work on thin film $(p)Bi_2S_3/(n)Bi_2O_3$ heterojunction.

2 EXPERIMENTAL

Three tick films of Nickel (Ni), each of width 1mm and length 25mm were first deposited by vacuum evaporation on a chemically cleaned glass substrate (3x3cm^2 size). Above these Ni films, Bi_2S_3 (SIGMA ALDRICH) powder and 7.21% Indium (In) was simultaneously deposited from two different sources by thermal evaporation technique covering an area (1.5x1.5cm^2). It has been observed that Bi_2S_3 highly decomposes during vacuum evaporation [25]. Therefore, special care is taken in depositing Bi_2S_3 thin films. The films then annealed in air inside an oven for five hours at temperature 438K. These films were found to behave as p-type. Same technique was used to deposit Bi_2O_3 powder and 5.63% Tin (Sn) over the (p) Bi_2S_3 films. Then the composite film was again annealed at 438K for 5 hours in air inside an oven. It was observed that Sn doped Bi_2O_3 annealed films behave as n-type semiconductor. Over the composite film three Aluminium (Al) films each of width 1mm and length 25mm were vacuum deposited horizontally making crossed with the Nickel films. Thus 9 $(p)Bi_2S_3/(n)Bi_2O_3$ heterojunctions each of equal area (1mm^2) were obtained on the same substrate. The Ni (work function = 5.01eV) films connected to $(p)Bi_2S_3$ (work function = 4.93eV)[26] film were used as the lower electrode and Al (work function = 4.08eV), films deposited over the $(n)Bi_2O_3$ was used as the upper electrode. They form ohmic contact with the respective semiconductors. During all depositions, substrates were kept more or less at room temaparature (300K) and pressure was maintained at 10^{-5} Torr.

For measuring *I-V* of the junctions, the sample was mounted on a specially designed sample holder fitted inside a vacuum chamber. Electrical and optical measurements were

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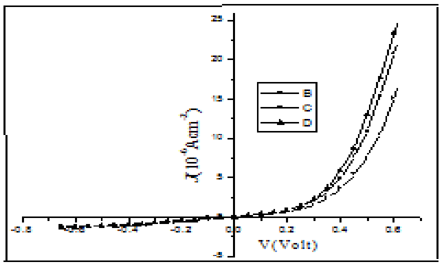

Fig.1 *I-V* characteristic of three typical (p)Bi_2S_3/(n)Bi_2O_3 heterojunctions in dark condition.

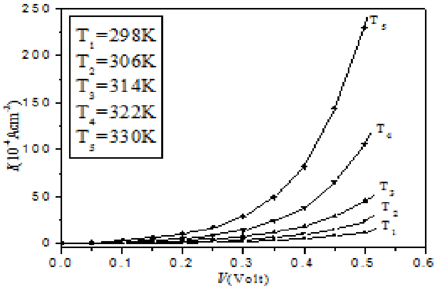

Fig. 2.*I-V* characteristics of a typical (p)Bi_2S_3/(n)Bi_2O_3 heterojunction in dark and at different temperature.

performed at room temperature as well as at elevated temperature using a specially designed electronic temperature controller. To measure *I-V* under illumination, the junction inside the chamber was illuminated using white light from tungsten halogen lamp (500W) through a glass window. The light was incident from the "Al" side. The input intensity of the light was measured with a Lux meter (Luxmat -300ED; Research Ins ND-110028, India). The types of carrier concentrations were determined by hot probe method. The capacitance of the junction was measured by 4-digit auto compute LCR-Q meter (Aplab-4910).The monochromator (Oriel 77022) fitted with a grating 1200 per cm, blazed at 35nm (Oriel 77233) was used to study the spectral response of the junctions. The input and output slits were set at 3mm. A tungsten halogen lamp was used to illuminate the entrance slit of the monochromator; Output of the monochromator was carefully allowed to fall on the junction for spectral response measurement. All electrical measurements were performed at pressure 10^{-2} Torr.

3. Results and Discussion

3.1 Study of *I-V* characteristic

I-V characteristics of three typical (p)Bi_2S_3/(n)Bi_2O_3 heterojunctions at room temperature (300K) in dark is shown in Fig.1. The curves show rectifying nature. The rectification has been also observed to increased with the increase in temperature (Fig.2). Assuming thermoionic emission over the heterojunction barriers to be dominant mechanism, current density-voltage relation is given by the relation [27].

$$J = qA^{*}TV_{bi}/k\left[\exp\left(-qV_{bi}/kT\right)\left\{\exp\left(qV_a/nkT\right)-1\right\}\right] \quad (1)$$

$$= J_s\left[\exp\left(qV_a/nkT\right)-1\right]$$

$$\approx J_s\left[\exp\left(qV_a/nkT\right)\right] \qquad (1)$$

after approximation, neglecting higher terms for conditions $V_a 3KT/q$, where V_a is the applied voltage and

$$J_s = \left(qA^{*}TV_{bi}/k\right)\left[\exp\left(-qV_{bi}/kT\right)\right] \qquad (2)$$

is the reverse saturation current density and V_{bi} is the built in potential of the junction. Well known diode equation

$J = J_s \exp\left(-{}^{qV}\!/_{nkT}\right)$ was used to calculate the diode ideality factor *n* and saturation current density J_s from the slop and Intercept of *InJ* vs *V* plots. Fig.3 shows linear portion of such plots at different temperature for a typical junction. The

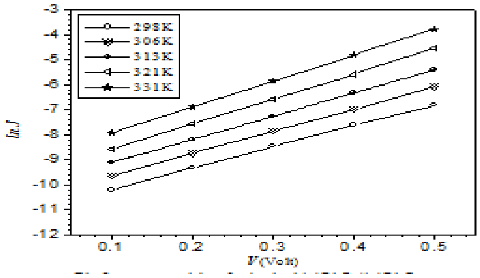

Fig.3 *lnJ* versus *V* plots of a typical (p)Bi_2S_3/(n)Bi_2O_3 heterojunction at different temperature.

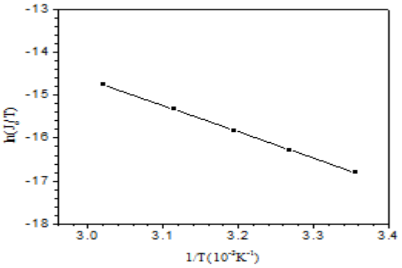

Fig.4 *InJ* versus 1/*T* plot a typical (p)Bi_2S_3/(n)Bi_2O_3 heterojunction in dark at different temperature,

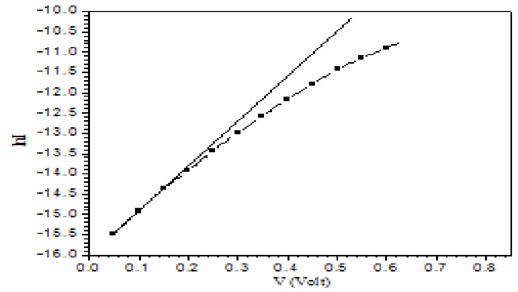

Fig.5 *lnL* versus *V* plot of a typical (p)Bi_2S_3/(n)Bi_2O_3 heterojunction in dark.

TABLE 1

VARIATION OF SOME PARAMETERS OF A TYPICAL (P)BI_2S_3/(N)BI_2O_3 HETEROJUNCTION ($N_D=3.001\times10^{14}$CM^3, $N_A=6.688\times10^{15}$CM^3) WITH TEMPARATURE IN DARK.

Temperature (K)	Ideality factor n	Saturation current density J_s(10^{-4}Acm^{-2})
298	4.5	0.143
306	4.3	0.256
314	4.0	0.428
322	3.7	0.706
330	3.4	1.285

built in potential of the junction have been calculated from *In(J_o/T) vs T^{-1}plot* [Fig.4] and found to be 0.523*eV*. The reverse saturation current density of the junctions at room temperature (298K) were found to vary (0.121-0.146)x10^{-4}Acm^{-2} in dark and (0.444-0.462)x10^{-4} Acm^{-2} under illumination(4400) Lux. The ideality factor of the junctions studied in the present case at room temperature was found to vary from 4.6 to 4.5 in dark and from 6.9 to 7.2 under illumination (4400)Lux. This may be due to increase of free carrier density which is the result of generated electron-hole pairs. The value of ideality factor n has been observed to decrease with the increase of temperature (298-330)K range, while reverse saturation current was observed to increase with the increase of temperature. The temperature variation of reverse saturation current and ideality factors have been shown in TABLE 1. The presence of interfacial layers, image force lowering of barrier height, recombination of electron and hole in the depletion region, tunneling effect and very high resistance of both Bi_2S_3 and Bi_2O_3 are the main regions for ideality factor greater than unity.

3.2 Effect of Series Resistance

For bias voltage greater than 0.3V, *Inl* vs *V* plots have been observed to deviate from linearity [Fig.5]. The deviation reveals the presence of series resistance (R_s) associated with the neutral regions of the semiconductor layers (p)Bi_2S_3 and (n)Bi_2O_3 of the junction. The series estimated from I vs ΔV plot [Fig.6] shows that the device possesses the series resistance as high as 6830Ω in dark. In the present investigation the large value of series resistance is contributed to the high resistance of (p)Bi_2S_3 and (n)Bi_2O_3 layer and the resistance offered by the interfacial layers.

3.3 Capacitance-Voltage Measurement

The carrier concentrations of both (p)Bi_2S_3 and (n)Bi_2O_3 films were measured individually at room temperature and under reverse bias condition, from the slop of C^{-2} vs V plots of (p) Bi_2S_3 and (n) Bi_2O_3 films at 1KH$_z$ (plots are not shown) respectively using the relation [27].

$$C=\left(q\varepsilon_s N_a/2\right)^{1/2}\left(V_{do}+V_r-{kT}/{q}\right)^{-1/2} \quad (3)$$

where V_{do} is the diffusion voltage at zero bias which is equal to V_r+kT/q, where V_l is the negative intercept on the V_r axis and ε_s is the permittivity of the respective materials. The carrier

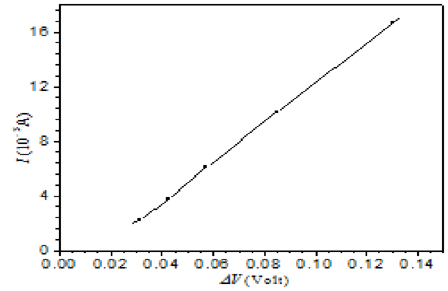

Fig.6 I versus ΔV plot of a typical (p)Bi_2S_3/(n)Bi_2O_3 heterojunction in dark.

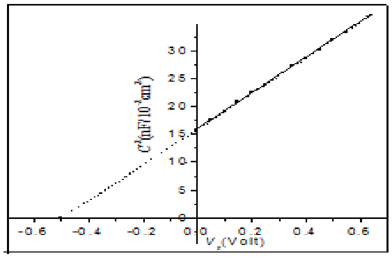

Fig.7 C^{-2} versus V_r plot of a typical (p)Bi_2S_3/(n)Bi_2O_3 heterojunction in dark.

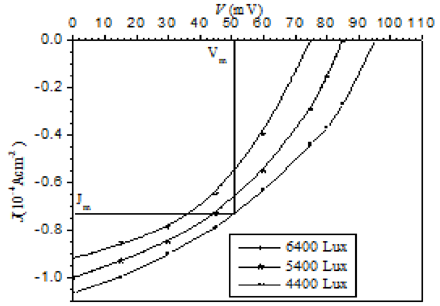

Fig.8 Photovoltaic effect of a typical (p)Bi_2S_3/(n)Bi_2O_3 heterojunction at three different illumination intensities

concentration was found as N_d=3.001x10^{14}cm^3 and N_d=.688x10^{16} cm^3. The built in potential V_{bi} of the junction was found out from C^{-2} vs V plots of (p) Bi_2S_3/(n)Bi_2O_3 junctions at 1 KHz (Fig.7). The value of built in potential V_{bi} found out of a typical junction from C^{-2} vs V plots is 0.525eV.

3.4 Photovoltaic Effect

The (p)Bi_2S_3/(n)Bi_2O_3 junctions were exposed to light intensity 50mW/cm^2 for studying photovoltaic effect. The *J-V* plots [Fig.8] under illumination reveal the photovoltaic effect of the junction. Nearly linear nature of the curve implies the existence of a large series resistance. To measure ideality factor *n* and current density J_s under illumination, the relation

$$J_{sc} = \left[\exp\left(\frac{qV_{oc}}{nkT}\right) - 1\right] \qquad (4)$$

TABLE 2

SOME PHOTOVOLTAIC PARAMETERS OF A TYPICAL (P)BI_2S_3/(N)BI_2O_3 HETEROJUNCTION AT ROOM TEMPARATURE

Symbol	Description	Value.
V_o	Open circuit voltage (mV)	150
J_{sc}	Short circuit current Density (10^{-4}A/cm^2	0.5
P_m	Maximum power out put (mW cm^2)	24.355X10^{-4}
F%	Fill factor	33.68
η%	Efficiency	0.231
R_s	Series resistance (Kohm)	5.876
Js	Saturation current density (10^{-4}A/cm^2)	0.202

was used, for this purpose, J_{sc} and V_{oc} were measured at three different levels of illumination. Then InJ_{sc} versus V_{oc} plot for the junction was plotted (not shown) and form the slop and intercept of the plot the diode ideality factor *n* and reverse saturation current J_o under illumination were calculated. Some diode parameters of a typical (p)Bi_2S_3/(n)Bi_2O_3 heterojunction under illumination have been shown in TABLE 2. It has been observed that the diode ideality factor under illumination decreases while the reverse saturation current increase. This may be the effect of generation of electron-hole pairs due to illumination.

3.5 Spectral Response

The spectral response of the (p)Bi_2S_3/(n)Bi_2O_3 junctions were studied in the wavelength range (100-1100) nm using a monochromator. Short circuit current versus spectral wavelength plot of a typical (p)Bi_2S_3/(n)Bi_2O_3 junction is shown in Fig. 9. The plot shows that the wavelength corresponding to the maximum short circuit current about 725nm which is well within the visible region of the spectrum. The value of the band edge calculated from the peak height was found to be 1.714eV which implies that the absorption is mostly within Bi_2S_3 layer of the structure.

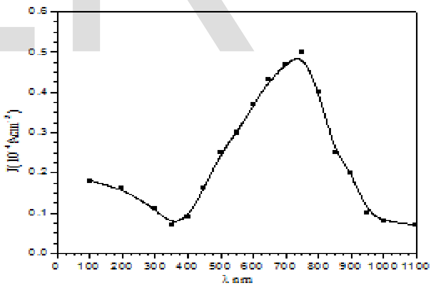

Fig.9 Spectral response of a typical (p)Bi_2S_3/(n)Bi_2O_3 heterojunction.

4 CONCLUSION

Thin films (p)Bi_2S_3/(n)Bi_2O_3 heterojunction prepared by vacuum evaporation exhibits rectifying *I-V* characterstic and poor photovoltaic effect. The very high diode ideality factor and poor photovoltaic effect possessed by the junction may be due to the high resistance of the neutral region of (p)Bi_2S_3, (n)Bi_2O_3 and interfacial layers in the neutral region. It has been observed that Bi_2S_3 highly decomposes into Bismuth and sulfur during evaporation. Sulfur reacts with base metal (counter electrode) forming sulphide compound which might be one of the main regions of creating high resistivity in the sample. Maximum carrier concentration found in our sample is N_d=3.23x10^{14}cm^3 and N_a=1.6x10^{16}cm^3. Special care is necessary to reduce decomposition of Bi_2S_3 during evaporation. More works are progress in this direction.

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