Optimum Metal-Semiconductor Contact for Cadmium Sulphide Thin Film

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ABSTRACT

Activation Energy is an important feature in determining the formation of ohmic contact on a semiconducting material. Activation energy depends on workfunction of the semiconductor. Thus, there is a good co-relation between the ohmicity, activation energy and workfunction. In this work, Cadmium Sulphide (CdS) thin film of 2 µm thickness is the semiconducting material fabricated using Chemical Vapour Deposition (CVD) technique at different anneal temperatures in vacuum for 2 hours. From Four-probe, photo-response and spectroscopic measurements of CdS thin films, optimum anneal temperature is obtained. Aluminium, Nickel, Silver and Copper are the metallic contact points deposited on these fabricated films using Physical Vapour Deposition (PVD) technique. These Metal-Semiconductor (M-S) contacts are annealed in vacuum at 200°C for 1hour. Current-Voltage (I-V) measurements are recorded for these M-S contacts at different temperatures. Electrical parameters are obtained for both un-annealed and annealed M-S contacts. Annealed M-S contacts give better results than un-annealed M-S contacts. The present paper has dealt with the estimation of optimum M-S contact on CdS thin film in the light of M-S contact parameters and activation energy.

Keywords – Activation Energy, Annealing, Chemical Vapour Deposition (CVD), Metal-Semiconductor (M-S) contacts, Ohmicity, Physical Vapour Deposition (PVD), Thin films, Workfunction

I. INTRODUCTION

II-VI compound semiconductor e.g. CdS, CdTe, ZnS and ZnTe show their potential application in electronic semiconductor device fabrication. These are stable compounds and have good photo response. However, these semiconductors suffer from ohmic contact formation as work function of these semiconductors is high and it is of the order of 5 eV to 5.3 eV. This high work function poses problem in ohmic contact formation as no metal or alloy except Pt, Pd, Ni and Se can match with such work function. Au and Pd are very costly. Se has a very high work function and at the same time the bulk resistance is very high. Ni sometimes forms good contact through work function engineering. Thus options are to form ohmic contact by tailoring the work function of the semiconductor and the contacting materials. To engineer these things series of experiments have been conducted to find out the exact activation temperature, material combinations, technology and process in contact formation.

In this work, CdS thin film of 2µm thickness is chosen as the semiconductor material and Aluminium, Nickel, Silver and Copper are the metallic contact points deposited on the fabricated films by PVD technique. Studies on these aspects indicate that an optimum temperature is essential to form a good M-S contact.

Binary metal chalcogenides of group II–VI semiconductors have been a rapidly growing area of research due to their important nonlinear optical properties [1]-[3], luminescent properties [4]-[7], quantum size effect [8]-[10] and other important physical and chemical properties [11]-[12]. Cadmium Sulphide (CdS) with a wide band gap of 2.42 eV (in bulk) is one of the most important nano-structured semiconductors that have been widely studied due to their potentiality in the possible application in optoelectronic devices and photo-catalysis. CdS in a nano-crystalline form can be prepared by a variety of methods (both physical and chemical) like sol–gel [13]-[14], electrostatic deposition [15], gas evaporation [16], micelles [17], solvent growth [12],[18]-[23], screen printing [24], sputtering [25], spray pyrolysis [26] etc. Chemical bath deposition (CBD) method has attracted much attention since it is confirmed as a simple and promising technique to obtain device quality films [27]-[29].

Ghosh et al. [30] have prepared CdS nanocrystallites using chemical route and studied the influence of annealing temperature upto 200^0C on grain growth. The crystallite size is reported to remain within 2-4 nm within that temperature range. J. Lee [31] have compared polycrystalline thin films of CdS prepared by vacuum evaporation (VE) method and chemical bath deposition (CBD) method. It was found that VE-CdS films consisted primarily of hexagonal phase, whereas CBD CdS films containing primarily the cubic form. In general, CdS films prepared at low temperatures

(<100^0C), normally show a cubic structure, and films prepared at high temperatures (>300^0C), show hexagonal structures. VE-grown films have better crystallinity than CBD-grown films. After annealing at 400^0C, the grain size of CdS film has increased regardless of deposition method. The grain size of the CBD films is smaller than the ones of VE films. VE-CdS films have exhibited relatively high transmittance in the above-gap region. Band gap for CBD film is 2.37 eV and 2.45 eV for VE films. For VE CdS films deposited at low temperature (<150^0C), the resistivity is considerably lower than that of CBD films. Generally, CBD–CdS film exhibits more stoichiometry than VE-CdS film. So, the low resistivity of VE film may be presumably due to non-stoichiometry associated with S vacancies. In addition, the resistivity of VE-CdS films has increased with the substrate temperature.

Metin & Esen [32] have investigated the change in band gap of CBD grown CdS films. They have annealed the CdS films at 200^0C, 300^0C & 500^0C in nitrogen atmosphere for one hour. Their observation is increased crystallite size and more ordering with annealing, containing both hexagonal (Wurtzite) and cubic (Zincblende) structures as a mixture. These crystallites are surrounded by amorphous tissue. They have also observed that the energy gap of the CdS film has decreased with annealing from 2.42 eV to 1.90 eV for 0.7 µm thick films and from 2.42 eV to 1.50 eV for 0.45 µm thick films. This effect is reported by other authors as well [33]. The temperature-dependent parameters that affect the band gap are reorganization of the film, sulfur evaporation and self-oxidation of the film.

Chaure et al. [34] have attempted to study the electronic quality of chemical bath deposited CdS layers (about 100 to 200 nm thick) on glass/CG substrates, using DC conductivity and Schottky barrier measurements. They have used indium and gold to produce ohmic and Schottky contacts respectively to CdS, with measured variation (due to heat treatment at 450^0C) of ideality factor between 1.5 and 1.7, barrier height between 0.92 and 1.02 eV, series resistance between 33 and 20 ohm. The grain sizes in their case increased from 340 to 420 nm by annealing in air for 20 min. The band gap is found to reduce from 2.42 eV to 2.25 eV after heat treatment.

Lepley et al. [35] have investigated the behaviour of Cu-CdS Schottky barrier and they have found that Cu-CdS contact is ohmic just after the copper is deposited. After two days the Schottky barrier is set up with barrier height of 0.55 eV, ideality factor near unity (typically1.12). They have also found from the photoresponse the evidence of formation of copper sulphide phase at the Cu-CdS interface as a result of heat treatment. They have showed that the increase of the width of the depletion layer caused by copper diffusion is suppressed by illumination, the effect of which is to neutralize the copper acceptor centres. Several other researches on Cadmium Sulphide (CdS) thin films are reported in [36]-[39].

II. MATERIALS AND METHODS

In this work, 2 µm Cadmium Sulphide (CdS) thin films are fabricated on clean sodalime glass substrates and Indium Tin Oxide (ITO) glass substrates using chemical vapour deposition (CVD) technique at a pressure of about 10^{-6} mbar and the films are annealed in vacuum (~10^{-3} mbar) at temperatures ranging from 200^0C to 450^0C for durations of 2 hours. Corresponding sheet resistivities of the resulting structures are measured using four-probe technique (model DFP-02, Scientific Equipment) and the influence of temperature on the degree of inter-diffusion is observed. Photoresponse of these films is studied to study the photosensitivity and photo-resistance decay.

Aluminium, Copper, Silver and Nickel are the contact points deposited by Physical Vapour Deposition (PVD) technique on the CdS thin films deposited on Indium Tin Oxide (ITO) glass substrates. These metal-semiconductor (M-S) structures are then annealed in vacuum (~10^{-3}mbar) at 200ºC for 1hour. The ideality factor 'n', the reverse saturation current 'Io', the barrier height 'Φ_B', the series resistance 'R_s', the contact resistance 'R_c' and the activation energy 'E_a' are determined from the I-V characteristic data, recorded using Keithley-5A source meter (model no. 2440). These parameters are studied for the thin films to identify the optimum anneal temperature for estimating the activation energy in contact formation in CdS thin film, the selected II-VI compound semiconductor.

Also the transmission spectra of the thin films of CdS are recorded by 'Hitachi spectrophotometer' over the wavelength range 300–700 nm. The energy band gap of these films are calculated from transmission spectra to study the effect of anneal temperature on the band gap.

III. RESULTS AND DISCUSSIONS

From four probe measurements on CdS thin films, fabricated on clean sodalime glass substrate, un-annealed and annealed in vacuum (~10^{-3} mbar) at 200ºC and 450ºC respectively for a duration of 2 hours, the plots showing the variation between bulk resistivity and temperature are obtained and these are shown in Fig.1(a), Fig.1(b) and Fig.1(c) respectively. Activation energy obtained from these plots is tabulated in Table-1.

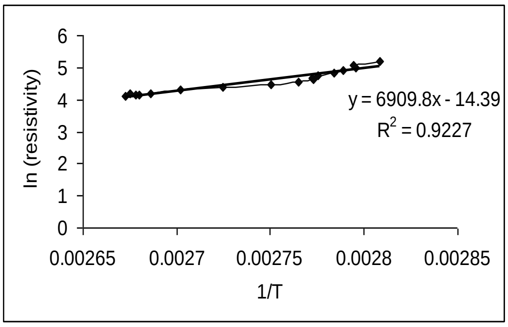

Fig.1 (a): Variation of bulk resistivity with temperature for un-annealed CdS film

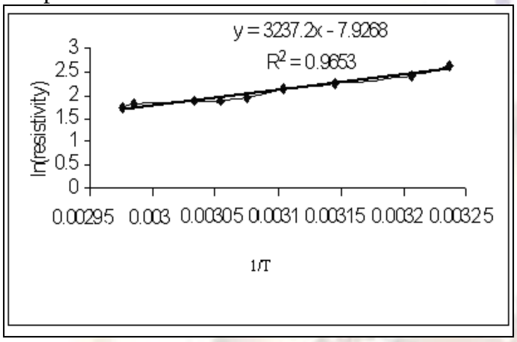

Fig.1 (b): Variation of bulk resistivity with temperature for CdS film annealed in vacuum at 200ºC

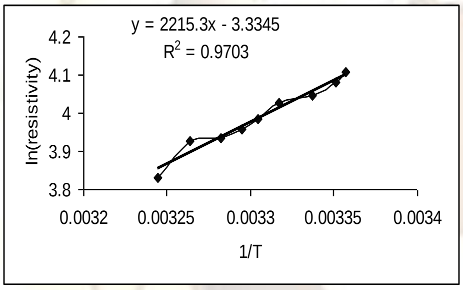

Fig.1 (c): Variation of bulk resistivity with temperature for CdS film annealed in vacuum at 450ºC

Table 1: Activation Energy and Anneal Temperature

Anneal Temperature (ºC)	Activation Energy (eV)
Un-annealed	0.5942
200	0.2784
450	0.1905

Fig. 2(a), Fig. 2(b) and Fig. 2(c) present the plots showing the photo-response for the CdS thin films fabricated on sodalime glass substrate, un-annealed and annealed in vacuum ($\sim10^{-3}$ mbar) for a duration of 2 hours at 200ºC and 450ºC respectively. Time constants are calculated from these plots and these are tabulated in Table-2.

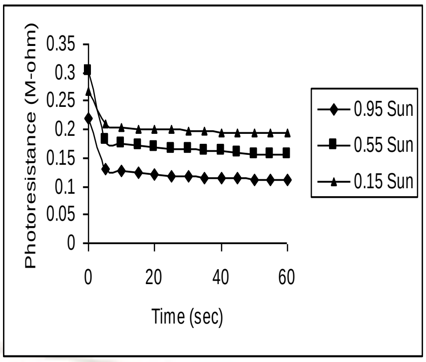

Fig. 2(a): Photo-resistance decay of un-annealed CdS thin films

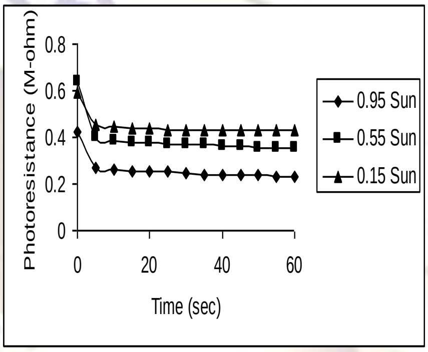

Fig. 2(b): Photo-resistance decay of CdS thin films annealed in vacuum at 200ºC

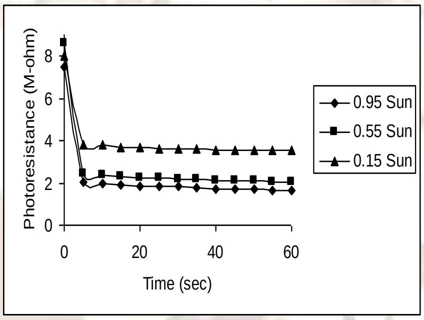

Fig. 2(c) Photo-resistance decay of CdS thin films annealed in vacuum at 450ºC

Table 2: Time constants at different illumination levels for un-annealed and annealed CdS Thin Films

Anneal Temperature (ºC)	Time Constants (sec)		
CdS Thin Film	0.95 Sun	0.55 Sun	0.15 Sun
Un-Annealed	>1min	>1min	>1min
200	>1min	>1min	>1min
450	4.2sec	4.4 sec	>1min

Fig. 3(a), Fig. 3(b) and Fig. 3(c) are the plots obtained from the spectroscopic studies of CdS thin films fabricated on sodalime glass substrate, un-annealed and annealed in vacuum ($\sim10^{-3}$ mbar) for 2 hours at 200ºC and 450ºC respectively. Band gaps are calculated from these plots and these are tabulated in Table-3.

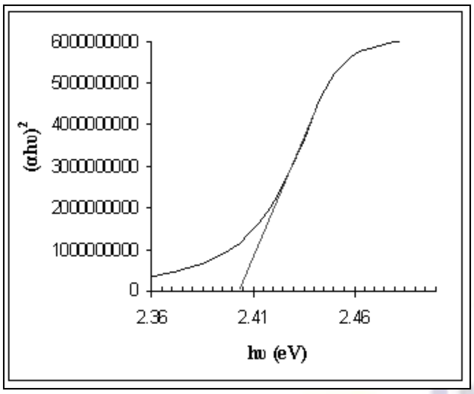

Fig. 3(a): Plot obtained from spectroscopic study of un-annealed CdS thin film

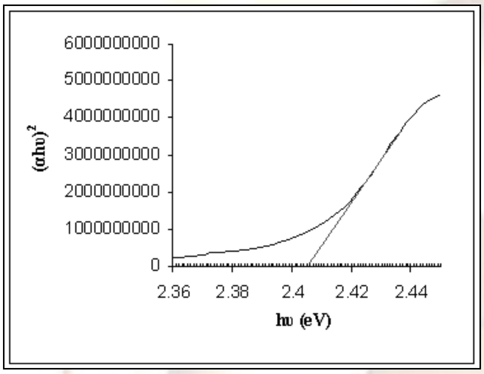

Fig. 3(b): Plot obtained from spectroscopic study of CdS thin film annealed at 200ºC

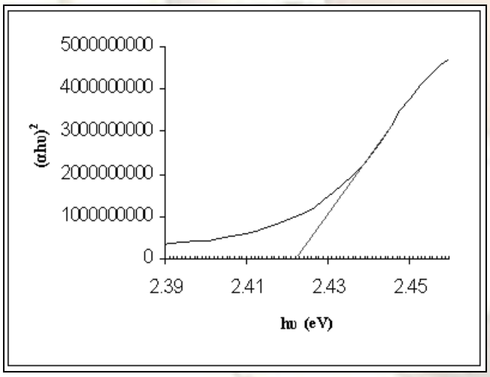

Fig. 3(c): Plot obtained from spectroscopic study of CdS thin film annealed at 450ºC

Table 3: Band gap for un-annealed and annealed CdS Thin Films

Substrate Anneal Temperature (ºC)	Band-Gap (eV)
Un-Annealed	2.403
200	2.405
450	2.422

From Table-3 it is observed that there are changes in the band-gap with the changes in anneal temperatures. The effect of anneal temperature can be explained as: due to the inter-atomic diffusion, the absorption coefficient changes and this fact is reflected in the changes in the values of band gaps at different anneal temperatures. Interatomic diffusion of Cd and S atoms may have incorporated additional stress. Impact of stress may have changed the band gaps. Thin oxide layer formation may be another cause for the change in the band gaps.

Electrical parameters Rs, Io(FB), Io(RB), n(FB), and n(RB) are obtained from the I-V characteristic data recorded from thin film of CdS fabricated on ITO glass substrate, annealed at 200ºC, 450ºC and unannealed with Al, Cu, Ag and Ni as the un-annealed (UAC) and annealed (AC) contact points. The parameters, Rs, n(FB), and Io(FB) are found to be less for AC than UAC for all the metallic contacts considered in this study i.e. Al, Cu, Ag and Ni and these parameters are found to be predominantly less for CdS thin film on ITO glass substrate, annealed at 450ºC as the anneal temperature. Also from Table 1, it is observed that activation energy is minimum at 450ºC as the anneal temperature. Here, Rs represents Series resistance; Io represents Reverse saturation current; FB represents Forward bias; RB represents Reverse bias and n represents Ideality factor. From the series of experimental observations it can be commented that 450ºC is the optimum anneal temperature or the optimum activation temperature for good contact formation.

The M-S contact points are subjected to temperatures, varying from room temperature of 27ºC to 75ºC. Fig. 4(a), Fig. 4(b), Fig. 4(c) and Fig. 4(d) present the plots showing the relationships between reverse saturation current, Io and temperature, T for the CdS thin films on clean ITO glass substrate annealed at 450ºC with the contact points Al, Cu, Ag and Ni respectively. Activation energy of the M-S contacts is obtained from the slope of these plots and these results are tabulated in Table-4.

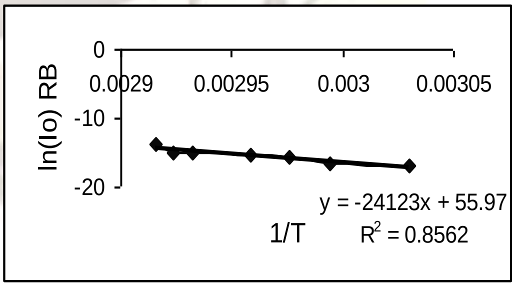

Fig. 4(a): Relationship between reverse saturation current, Io and temperature, T for the CdS thin film on clean ITO glass substrate annealed at 450ºC with the Al as the contact point

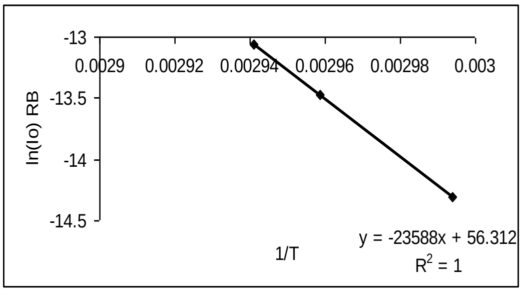

Fig. 4(b): Relationship between reverse saturation current, Io and temperature, T for the CdS thin film on clean ITO glass substrate annealed at 450ºC with the Cu as the contact point

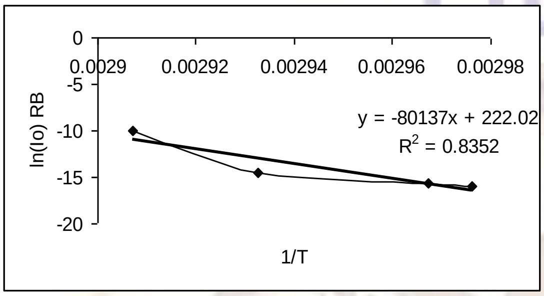

Fig. 4(c) Relationship between reverse saturation current, Io and temperature, T for the CdS thin film on clean ITO glass substrate annealed at 450ºC with the Ag as the contact point

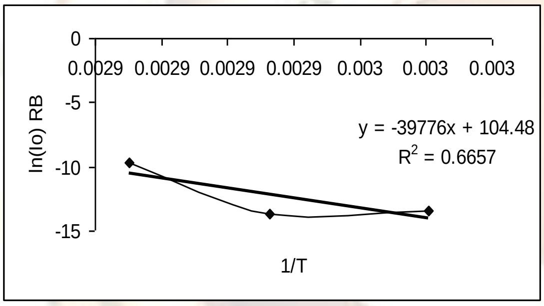

Fig. 4(d) Relationship between reverse saturation current, Io and temperature, T for the CdS thin film on clean ITO glass substrate annealed at 450ºC with the Ni as the contact point

Table 4: Activation Energy for different metallic contacts deposited on CdS thin film annealed at 450ºC

Metallic Contact Types	Activation Energy (eV)
Al	2.074578
Cu	2.028568
Ag	6.891782
Ni	3.402736

Fig. 5(a) and Fig. 5(b) show the relationships between voltage and current obtained from the forward and reverse characteristics of the I-V measurement recorded for CdS thin film on ITO glass substrate annealed at 450ºC with copper as the metallic contact at 65ºC. This is presented as one of the series of experimental results of this work. Ideality factors, n and reverse saturation currents I_0 are obtained from these two plots and the results are tabulated in Table-5. Series resistance is obtained from the inverse of the slope of forward characteristic curve and the result is tabulated in Table-5. Barrier height [40] is obtained from the slope of the plot shown in Fig. 5(c). The plot shown in Fig. 5(c) is obtained from the reverse characteristics portion of the I-V measurement recorded for CdS thin film on ITO glass substrate annealed at 450ºC with copper as the metallic contact at 65ºC.

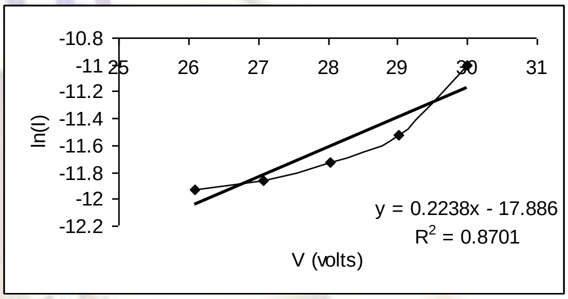

Fig. 5(a) Relationship between voltage and current obtained from forward characteristic of I-V measurement for CdS thin film on ITO glass substrate annealed at 450ºC with copper as the metallic contact at 65ºC.

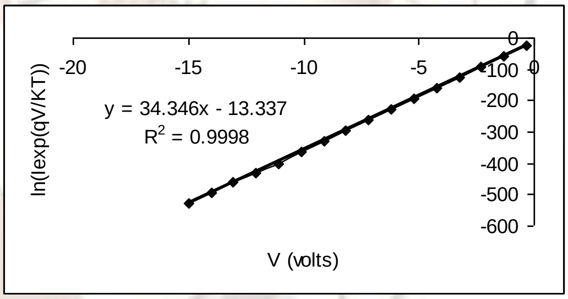

Fig. 5(b) Relationship between voltage and current obtained from reverse characteristic of I-V measurement for CdS thin film on ITO glass substrate annealed at 450ºC with copper as the metallic contact at 65ºC.

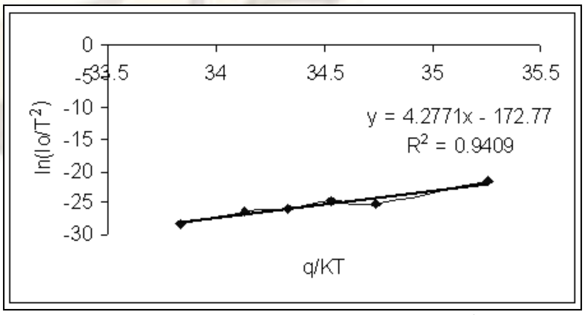

Fig. 5(c) Plot showing the variation of reverse saturation current, I_0 with temperature, T obtained from reverse characteristic of I-V measurement for CdS thin film on ITO glass substrate annealed at 450ºC with copper as the metallic contact at 65ºC.

Table 5: Electrical parameters obtained from I-V measurements of thin film of CdS on ITO glass substrate with Cu as the contact point

Temperature at M-S contact (ºC)	Ideality factor (n) RB	Reverse saturation current (Io) RB (μA)	Barrier Height (eV)	Ideality factor (n) FB	Reverse saturation current (Io) FB (nA)	Series Resistance Rs (KΩ)
65	0.99	1.61	4.28	153.3	17.07	500

Table 6: Electrical parameters obtained from I-V characteristics of thin film of CdS on ITO glass substrate with Al, Cu, Ag and Ni as the contact points

Metallic contact types	Rs (KΩ)	Io (RB) (A)	Io (FB) (A)	n (FB)
Al	50	3.66×10^{-5}	8.85×10^{-7}	240.40
Cu	11.1	6.67×10^{-7}	1.86×10^{-10}	85.14
Ag	25	2.39×10^{-5}	4.35×10^{-6}	289.34
Ni	142	4.33×10^{-5}	4.71×10^{-6}	343.01

Table-6 presents the electrical parameters obtained from the I-V characteristics of thin film of CdS on ITO glass substrate annealed for 2 hours in vacuum (~10^{-3}mbar) at 450ºC with Al, Cu, Ag and Ni as the contact points annealed at 200ºC for 1hour. From Table-6, it is observed that with respect to Rs, Io(RB), Io(FB) and n(FB), Cu is the optimum annealed contact on CdS thin film annealed for 2 hours, in vacuum (~10^{-3}mbar) at 450ºC.

From Table-4, it is seen that activation energy of Cu is the lowest amongst all other metallic contacts considered in this work. So, from the activation energy point of view Cu is found to be the optimum contact.

For all contacts and anneal temperatures, it is found that the value of n (FB), the ideality factor at FB is in the order of few hundreds while that estimated at RB is between 1 and 2. This unusual high value at FB may be attributed to the high value of forward current resulting in large number of recombination in the depletion region.

IV. Conclusion

This study infers that out of all the metallic contacts considered in this work, Copper is found to be the optimum contact annealed in vacuum (~10^{-3}mbar) at 200ºC for 1 hour on Cadmium Sulphide thin film fabricated on Indium Tin Oxide glass substrate annealed for 2 hours in vacuum (~10^{-3}mbar) at 450ºC.

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