ELECTRICAL PROPERTIES OF THERMALLY ANNEALED CdS THIN FILMS OBTAINED BY CHEMICAL BATH DEPOSITION

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Abstract–*Electrical conductivity and the Hall-effect are investigated in the temperature interval (80-400) K on thermally annealed in H_2 CdS thin films obtained by chemical bath deposition. Different characters of the temperature dependence of conductibility are observed in the CdS films annealed at different temperatures. The Hall measurements allow calculating the values of the N_A, N_D, n_{ex} and E_D. According to Hall measurements the CdS films show several donor levels at different energetic depths in dependence of the annealing temperature. The sample annealed at high temperatures than 350^{o}C proves to be compensated with a sharply decreasing electrical conductivity with the temperature decrease.*

Keywords: *CBD method, CdS thin films, conductivity, Hall coefficient.*

1. INTRODUCTION

In CdTe thin-film PV devices, which are grown on CdS substrates to form an active heterojunction, the chemical bath deposition (CBD) process for CdS films has produced high efficiencies. The growth of CdS thin films by CBD with predetermined electrical properties is extremely difficult. Annealing treatment in H_2 atmosphere could shift Fermi level of CdS film to higher position and consequently improve the CdS/CdTe junction and performance of solar cells. Knowledge about the effect of the thermally annealing in H_2 on the electrical properties of CdS thin films obtained by CBD is lacking. In previous papers [1, 2] were presented structural and optical properties of thermally annealed in H_2 CBD CdS layers. Therefore this paper is focused on electrical properties of thermally annealed in H_2 CdS thin films in the temperature range 80-400 K.

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2. EXPERIMENTAL DETAILS

The CdS thin films were deposited on glass slides from a chemical bath containing water solution of $CdSO_4$ (1 mM), NH_4OH (0.2 M), $(NH_4)_2SO4$ (0.03 M) and relative to Cd 0.001 at. % NH_4Cl. When the solution reached 85 °C thiourea (10 mM) was added. $CdCl_2$ formation occurs during the introduction of NH_4Cl dopant in the deposition solution. The deposition process of the layer takes 30 min. CdS thickness 350 – 400 nm was achieved with three times repeated deposition. Then CdS were subjected to H_2 annealing process in pre-heated furnace between 200-450°C. Details about technological process of deposition and annealing are widely presented in papers [1, 2]. XRD investigations of the films were performed using a Rigaku X-ray diffractometer with $Cu_{K\alpha}$/40 kV/40 mA radiation (λ = 1.54056 Å). The ohmic contacts on all the films were made by evaporating high purity indium under high vacuum. The samples were mounted in a Dewar-vessel cryostat and Hall-effect and conductivity measurements were made over the temperature 80 – 400 K. Hall measurements were made in magnetic inductions up to ~ 1 T. The dark conductivity was made using the method of four contacts. Input impedance of the used devices was more than 10^6 Ω. Due to limitations of our measurement setup, we did not succeed in measuring the conductivity and carrier concentration of the as deposited and annealed at 450^{o}C CdS films. A constant current is applied to the sample of thickness *d*, the voltage *U* perpendicular to the current is measured in the eight possible configurations of current and magnetic field *(B)* directions. The average Hall voltage U_H is related to the Hall coefficient R_H by

$$R_H = \frac{U_H d}{I \cdot B} \qquad (1)$$

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

XRD studies show that CdS layers are formed by crystallites with size ~ 40 nm forming granules with size ~ 150 nm [3]. In the Fig. 1 is shown behavior of crystallites size depending on the treatment temperature for two different times: 20-30 minutes and 60 minutes. The crystallites sizes first increase with increase of the annealing temperature for both times and then tend to a reduced size with increasing temperature. SEM analysis shows that all CdS layers have sulfur deficiency. The CdS thickness is 300-400 nm

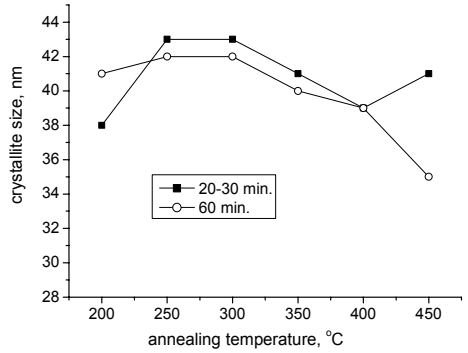


Fig. 1. Crystallites size of CdS layers in dependence on heat treatment temperature at two different times.

3.2. Studies of Electrical Conductivity a nd Hall Effect

The variation of dark conductivity with temperature for annealed at different temperatures CdS thin films were measured in the temperature range of 80-400 K. Typical log (σ) versus 10^3/T curves is illustrated in Fig.2 for samples treated at different temperatures and times. It is found that the conductivity in all the samples decreases weakly as temperature decreases and shows a tendency towards saturation at low temperatures. The slope is not constant, also decreases with decreasing temperature, too. The conductivity of the CdS films annealed at 250°C and 350°C is found to be much compared to that annealed at 400°C. The results can be explained with an increase of crystallite sizes and improvement of contact between them till 350°C. The X-ray diffraction spectra show that the crystallites size decreases with increasing treatment temperature. Presumably, this can be explained due to greater thermal shock and greater force, leading to decomposition of hydroxide group, probably incorporated into the CdS lattice during the growing from solution. These effects contribute to destruction of CdS crystallites. Also, this can be connected, may be, with the fact that in such short time, even at temperature higher than 350°C, the recrystalization is not yet well started. Another important feature of the results is that in the CdS films annealed at 400 °C at higher temperatures the increase in conductivity with temperature is comparatively sharper.

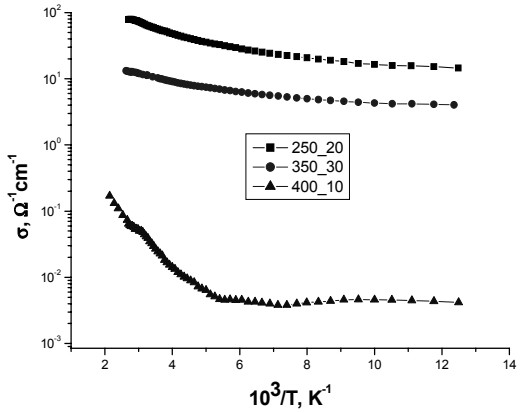


Fig. 2. Temperature dependence of the electrical conductivity in CdS thin films.

An exponential increase of σ with temperature has been observed in high temperature region. We suppose that the well-known exponential law can describe the temperature dependence of the electrical conductivity

$$\sigma = \sigma_o \exp\left(\frac{E_a}{kT}\right) \qquad (2)$$

where σ_o is a parameter depending on the sample characteristics (thickness, structure), E_a denotes the thermal activation energy of electrical conduction, and k is Boltzmann's constant. At low temperatures, conductivity of as deposited samples increases slightly with temperature. After 200 K conductivity starts to increase much sharply with increasing of the temperature. As shown in Fig.2 log(σ) versus 10^3/T plots show

several linear slopes in the temperature region 200-380 K for all samples.

Temperature dependencies of the Hall coefficient are shown in Fig. 3.

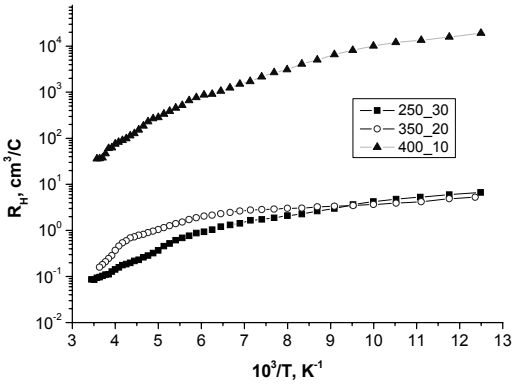


Fig. 3. Temperature dependence of the Hall coefficient for CdS thin films.

The curves illustrated in Fig. 3 are typical for semiconductors having several electrically active impurity levels. For a semiconductor partially compensated by acceptors with concentration N_A and having only one type of donor with concentration N_D, the temperature dependence of the electron concentration n in the conduction band can be expressed as [4]

$$\frac{n(N_A+n)}{N_D-N_A-n}=\frac{2\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2}}{g}\exp\left\{-\frac{E_D}{kT}\right\} \quad (3)$$

where g is the impurity state degeneracy factor, m^* and E_D is the electron effective mass and the activation energy of the donor impurity, respectively. As follows from the equation (3) for the determination of the n_{ex}, N_D, N_A and E_D is enough to plot the dependence $\left(\frac{\lg[(n_{ex}-n)T^{3/2}}{n(N_A+n)}\right)$ versus *1/kT* and to choose two parameters $n_{ex}=N_D-N_A$ and N_A. Taking into account that n_{ex} acts only in the high temperature region of the curve in the Fig.4, this dependence has been plot for annealed at 250_30 CdS films and has showed how to select N_A. The obtained values of the N_A, N_D, n_{ex} and E_D parameters are presented in Table 1.

With temperature increase, R_H decreases due to electron activation from the shallowest impurity level *(E_{D1})* and the curves tend to saturation at different temperatures in dependence of the annealed temperature of the CdS film due to exhaustion of the impurity level.

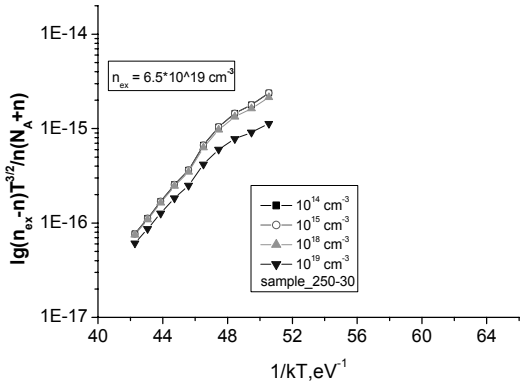


Fig. 4. The dependence $\left(\frac{\lg[(n_{ex}-n)T^{3/2}}{n(N_A+n)}\right)$ versus *1/kT* for CdS thin films.

The increase of temperature above (170-230) K leads again to an exponential decrease of R_H with a sharper slope due to the activation of electrons from the second shallow *(E_{D2})* impurity level. The slopes of the exponential part of the curves give the energies of the corresponding impurity levels. Table 1 show as a result of the lack of compensation, that the values of activation energy of electrons from shallow impurity level (E_{D2}) vary more in comparison with the values of the activation energy of the (E_{D1}) impurity level. As one can see the conductivity of the 400°c annealed CdS film at all measurements temperatures shows the lowest value (Table 2). The sample proves to be compensated with a sharply decreasing electrical conductivity with the temperature decrease. The state of the electron gas in the investigated samples is determined by the temperature dependence of the Fermi level (Fig 5), which was calculated from expression

$$E_F = kT\ln\frac{n}{N_c} \quad (4)$$

where N_c density states in conduction band.

The electron gas in the sample annealed at 400°C is in a nondegenerated state, since the Fermi level is situated at a depth not lower than 2kT from the conductance band in the all investigated temperature interval. With the decrease of the annealing temperature of the samples the Fermi level is situated in the conductance band.

Table 1. Electrical parameters of CdS thin films annealed at different temperatures

Sample No	n, cm^{-3} 300 K	n, cm^{-3} 80 K	N_D, cm^{-3}	N_A, cm^{-3}	$k = \frac{N_A}{N_D}$	n_{ex}, cm^{-3}	E_D, meV
250_30	$3.9 \cdot 10^{19}$	$1.1 \cdot 10^{18}$	$7.5 \cdot 10^{19}$	$1.0 \cdot 10^{19}$	0.13	$6.5 \cdot 10^{19}$	84 (160- 230K) 310 (230-290 K)
350_20	$4.2 \cdot 10^{19}$	$9.4 \cdot 10^{17}$	$5{,}1 \cdot 10^{20}$	$1.0 \cdot 10^{18}$	0.1	$5{,}0 \cdot 10^{20}$	80 (130-170 K) 144 (170-290 K)
400_10	$9.7 \cdot 10^{16}$	$3.3 \cdot 10^{14}$	$3.0 \cdot 10^{19}$	$1.0 \cdot 10^{19}$	0.33	$2.0 \cdot 10^{19}$	91 (105-190 K) 210 (190-290 K)

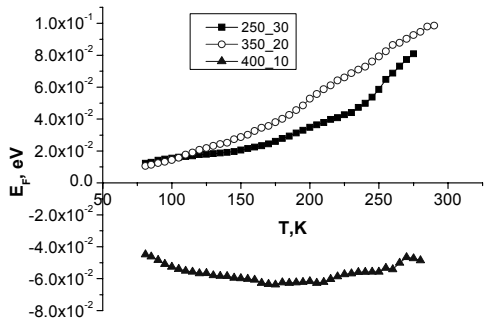


Fig. 5. Temperature dependence of the Fermi level in CdS thin films.

Table 2. Conductibility and mobility at T= 300 K and T= 80 K

Sampl No	σ, $\Omega^{-1} \cdot cm^{-1}$ 300 K	$R_H \cdot \sigma$, $cm^2/V \cdot s$) 300 K	σ, $\Omega^{-1} \cdot cm^{-1}$ 80 K	$R_H \cdot \sigma$, $cm^2/V \cdot s$ 80 K
250_30	59.3	1.6	14.8	97
350_20	10.7	5.1	4	21
400_10	0.03	0.87	0.01	80

As a working hypothesis, incorporation of cadmium hydroxychloride into CdS lattice on sulfur site in deposition process from basic ammonia solution is assumed. The hydroxide and chloride ions on sulfur site form electrically neutral defect complexes $V_{Cd}2Cl_S$ and $V_{Cd}2(OH)_S$. Increase in annealing temperature accelerates sintering of as deposited polycrystalline CdS and retention of larger quantities of chloride and hydroxide impurities, which would otherwise evaporate and decompose. Upon decomposition of two hydroxide groups in CdS lattice one water molecule will be released and one sulfur vacancy created. Annihilation of sulfur and cadmium vacancies creates two donor centers of Cl_S^+ and $(OH)_S^+$. These substitution impurities on sulfur site behave as shallow donors contributing at room temperature to the increase of conductivity. The concentration of chloride and hydroxide impurities, saved in as deposited CdS, depends on post-deposition temperature of vacuum drying. At high temperature region of annealing, due to destruction of hydroxide group and out diffusion of chlorine and removal by evaporation, the concentration of electrons decreases.

4. CONCLUSIONS

Influence of the thermal and duration of annealing in hydrogen atmosphere on electrical properties of CdS thin film have been studied, and shown that its leads to the formation of two impurity levels whose position depends on the temperature of thermal treatment and variation of concentration of electrons from $10^{19}cm^{-3}$ to $10^{16}cm^{-3}$.

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References

[1] J. Hiie, K. Muska, V. Valdna, V. Mikli, A. Taklaja, A. Gavrilov, "Thermal annealing effect on structural and electrical properties of chemical bath-deposited CdS films", *Thin Solid Films*, **516**, pp. 7008–7012, 2008.

[2] J. Hiie, F. Quinci, V. Lughi, V. Sergo, V. Valdna, V. Mikli , E. Kärber, T. Raadik, "Chlorine doping of cadmium sulfide on the example of CBD CdS", *Proceedings of Mater. Res. Soc. Symp.*, San Francisco, p. 1165, 2009.

[3] Maticiuc N., Potlog T., Hiie J., Mikli V., Põldme N., Raadik T., Valdna V., Mere A., Gavrilov A., Quinci F., Lughi V., Sergo V., "Structural changes in chemically deposited CdS: effect of thermal annealing", *Moldavian Journal of Physical Sciences*, **3-4**, pp. 279–283, 2010.

[4] Iu. Vorobiov, V. Dobrovolskii, *et al.*, *Metodi issledovania poluprovodnicov*, *Vishaia scola*, Kiev, pp. 95–120, 1988.