Electrical properties of Nano crystalline $Zn_xCd_{1-x}S$ thin films prepared by CBD technique

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Abstract

Nanocrystalline zinc cadmium sulfide ($Zn_xCd_{1-x}S$) thin films were deposited on glass substrate by chemical bath deposition (CBD) technique using the mixed aqueous solution of zinc chloride (($ZnCl_2$), cadmium chloride ($CdCl_2$), thiourea ($CS(NH_2)_2$) and ammonia solution (NH_4OH). The as deposited films were characterized by high quality instrument type (HMS-3000). The results show that all the prepared films have n-type conductivity; this is concluded from the Hall measurements. The electrical conductivity is found to decrease with increasing x, while the activation energies are found to be increasing from (0.458 to 0.860 eV) as x increase from (0.1 to 0.9).

Keywords: Nanostructures, II-VI Thin films, Chemical bath deposition technique.

الخصـــــائــــص الكهربـــائيــــة لأغشيـــــــة $Zn_xCd_{1-x}S$ النانـــويــــــة المحضـــــرة بتقنيـــــة الترسيـــب بالحمـــام الكيميـــائــي

الخلاصـــة

تم ترسيب اغشية كبريتيد خارصين- كادميوم ($Zn_xCd_{1-x}S$) النانوية على ارضيات زجاجية بتقنية الترسيب بالحمام الكيميائي باستخدام محلول كلوريد الخارصين ($ZnCl_2$) ، كلوريد الكادميوم ($CdCl_2$) ، الثايوريا ($CS(NH_2)_2$) ومحلول الامونيا (NH_4OH). تم فحص الاغشية المحظرة باستخدام جهاز نوع (HMS-3000) حيث بينت النتائج باستخدام جهاز هول ان الاغشية المحظرة ذات توصيلية من النوع السالب (n-type) وان التوصيلية الكهربائية تتناقص كلما زادت قيمة x ، بينما طاقات التنشيط تزداد من 0.458 الى 0.860 الكترون- فولط عندما تزداد قيمة x من 0.1 الى 0.9

الكلمات المفتاحية: التراكيب النانوية، الاغشية الرقيقة II-VI ، تقنية الترسيب بالحمام الكيميائي.

INTRODUCTION

Semiconductors with dimensions in the nanometer realm are important because their electrical, optical and chemical properties can be tuned by changing the size of the particles. These nanostructures have attracted much interest due to their fundamental importance in bridging the gap between bulk matter and molecular species [1]. Since novel properties of nanomaterials depend on their size, structure and shape, a new direction for synthetic methods and an understanding of the mechanisms by which the size, structure and shape of the nanocrystals can be easily varied are key issues in nanoscience [2]. Nano crystalline semiconductors exhibit changes in the energy band structure, resulting in quantum size effects. Since the energy levels are confined to potential wells of small dimensions, the spacing's

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between the energy levels increase as the crystal becomes smaller [3]. The quantum size effect is theoretically classified into two types: one is the exciton confinement effect and the other is the independent confinement effect of electron and hole. When the radius of the microcrystal is sufficiently larger than the exciton Bohr radius, the exciton confinement effect occurs. On the other hand, when the radius is comparable or smaller than the exciton Bohr radius, the independent confinement of electrons and holes takes place [4]. The II-VI binary semiconducting compounds (CdS, ZnS, CdSe) are considered to be very important materials for a wide spectrum of optoelectronic applications as having specific physical properties such as direct band-gap widths, high absorption coefficients in the visible and infrared part of the solar spectrum, good electrical properties (e.g. carrier mobility and lifetime) and increased capability in obtaining adjustable n- or p-type conductivity by doping [5]. An alloy is a combination, either in solution or compound, of two or more elements. The resulting alloy substance generally has properties significantly different from those of its components. Ternary alloy is an alloy made up of three different chemical elements; usually two cations and an anion and their band gap is a continuous function of composition [6,7]. Ternary compounds are found to be promising materials for optoelectronic device applications such as green light emitting devices and expected to improve the performance of thin film solar cells and photo electrochemical energy conversion[8,9]. $Zn_xCd_{1-x}S$ compound has a band gab between CdS (2.42 eV) and ZnS (3.66 eV) and the value of the band gab depends onto Cd and Zn ratio [10]. In solar cell systems, where CdS films have been demonstrated to be effective, the replacement of CdS with the higher band gap $Zn_xCd_{1-x}S$ alloys have led to a decrease in window absorption loss and an increase in the short circuit current [11,12]. The aim of this work is to study the electrical properties such as Hall measurements and electrical conductivity of the as-depositd $Zn_xCd_{1-x}S$ thin films on glass substrate by CBD technique.

Experimental details

Analytical grade cadmium chloride (0.1M $CdCl_2$), zinc chloride (0.1M $ZnCl_2$) and thiourea (0.1M $CS(NH_2)_2$) are used for prepared nano crystalline $Zn_xCd_{1-x}S$ thin films. The pH adjusts at 10 (i. e. PH =10) and the temperature fixed at 75±2 ºC. The experimental details of the five different concentrations in the formation of chemical bath to deposit $Zn_xCd_{1-x}S$ thin films are present in the table (1). For more experimental details one can see reference [13].

Table (1) Experimental details for prepared $Zn_xCd_{1-x}S$ thin films.

Samples	$ZnCl_2$ (ml) (0.1M)	$CdCl_2$ (ml) (0.1M)	Bath conditions
$Zn_{0.1}Cd_{0.9}S$	2	18	Vol. of $CS(NH_2)_2$= 20 ml of (0.1 M) Deposition time =2 hour Temperature = 75±2 ^oC PH=10
$Zn_{0.3}Cd_{0.7}S$	6	14	
$Zn_{0.5}Cd_{0.5}S$	10	10	
$Zn_{0.7}Cd_{0.3}S$	14	6	
$Zn_{0.9}Cd_{0.1}S$	18	2	

The four-point probe (vander pauw geometry at room temperature) method is the most widely used technique for electrical profile measurement of the materials. The shape of $Zn_xCd_{1-x}S$ film is square (1cm×1cm) and four symmetrically aluminum (high purity) electrodes is evaporated to the corners of each sample by using thermal vacuum evaporation system (type Edwards) as shown in figure (1). Contacts between the electrodes and silver wires are made with silver paste.

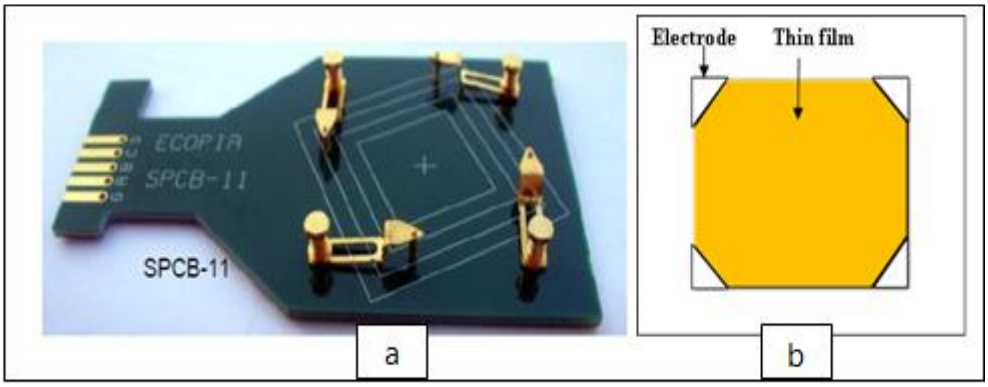

Figure (1): (a) Base of the sample. (b) Thin film with deposited electrodes.

Results and discussion

Hall Measurements

The Hall effect is used to distinguish whether a semiconductor is n-type or p-type and to measure the resistivity (ρ), the majority carrier concentration and majority carrier mobility (μ_H). The obtained results by high quality instrument type (HMS-3000) under bath conditions, (T=75 °C, PH=10, t=120 min. concentrations 0.1M) are summarized in Table (2).

Table (2) Electrical properties of $Zn_xCd_{1-x}S$ thin films.

Sample	Resistivity (Ω cm)	Conductivity (Ω cm)$^{-1}$	Mobility (cm^2/Vs)	Carrier concentration (cm)$^{-3}$	Ava. Hall coefficient (m^2/C)
CdS	3.316×10^{2}	3.016×10^{-3}	1.056×10^{5}	-1.782×10^{11}	-3.502×10^{7}
$Zn_{0.1}Cd_{0.9}S$	1.062×10^{3}	9.419×10^{-4}	6.319×10^{4}	-9.304×10^{10}	-6.709×10^{7}
$Zn_{0.3}Cd_{0.7}S$	2.506×10^{3}	3.991×10^{-4}	2.521×10^{4}	-9.882×10^{10}	-6.317×10^{7}
$Zn_{0.5}Cd_{0.5}S$	2.671×10^{3}	3.844×10^{-4}	4.625×10^{3}	-5.05×10^{11}	-1.235×10^{7}
$Zn_{0.7}Cd_{0.3}S$	5.196×10^{4}	1.925×10^{-5}	4.131×10^{2}	-2.908×10^{11}	-2.147×10^{7}
$Zn_{0.9}Cd_{0.1}S$	1.110×10^{5}	9.009×10^{-6}	6.089×10^{1}	-9.230×10^{11}	-6.759×10^{6}
ZnS	1.402×10^{5}	7.13×10^{-6}	2.298×10^{2}	-1.938×10^{11}	-3.222×10^{7}

The negative sign in Hall coefficient and carrier concentration indicates that the as-deposited $Zn_xCd_{1-x}S$ thin films have n-type conductivity. From table (2), it can be observed that the resistivity increases as the Zn^{2+} content increased. The electrical resistivity of as-deposited pure CdS in the order of 10^2 Ω-cm increased to 10^5 Ω-cm when x increase from x=0.1 to x=0.9, because the zinc incorporation increases the resistivity [14]. This result confirms that the increase in resistivity and the decrease in conductivity as the film Zn^{2+} concentration increased from (x=0.1) to (x=0.9), which leads to decreases in crystallinity of the $Zn_xCd_{1-x}S$ films. The high value of resistivity of $Zn_{0.7}Cd_{0.3}S$ and $Zn_{0.9}Cd_{0.1}S$ films might be due to the presence of amorphous clustering around the CdS nuclei at this higher Zn^{2+} concentrations, or it is attributed to dislocations and imperfections of the films and the results are in good agreement with reference[15].

D.C Electrical Conductivity

The conductivity of a semiconductor depends on two factors: (i) the number of current carriers per unit volume and (ii) the mobility of the carriers through the substance under an applied electric field [16]. For all films resistivity follows Arrhenius relation [17]:

$$\rho = \rho_o \exp (E_a / k_B T) \quad \ldots\ldots (1)$$

Where:

ρ is resistivity at temperature T, ρ_o is a constant, k is the Boltzman, constant and E_a is activation energy required for the conduction. The electrical resistivity of the deposited films was determined by equation :

$$\rho = (R\, b\, d) / l \quad \ldots. (2)$$

Where:

ρ is the electrical resistivity of the film and *l*, b and d are the length, width and thickness of the film respectively. The electrical resistivity of $Zn_xCd_{1-x}S$ thin film is measured using D.C. two point probe method, while the films are heated in the temperature interval of 323–490 K by using oven. Figure (2) shows a plot of ln (σ) as a function of reciprocal of temperature $(1/T)\times10^3$ of all as-deposited films (x=0.1-0.9).

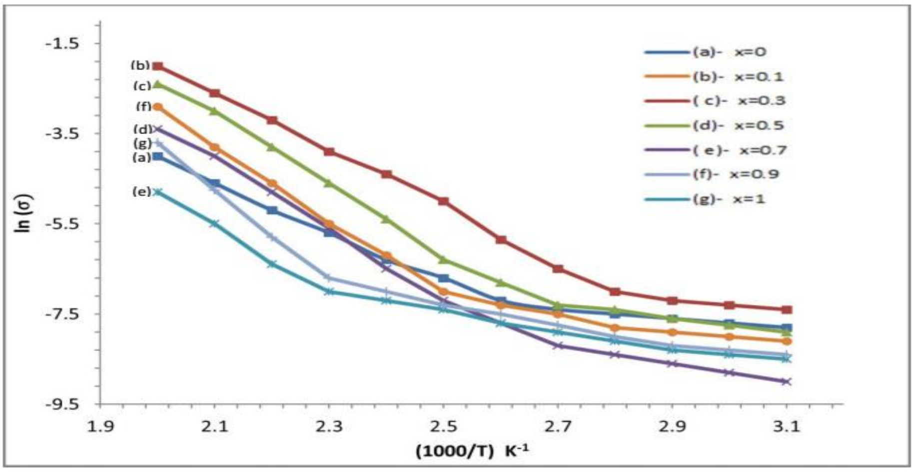

Figure (2) ln(σ) as a function of $10^3/T$ of the as deposited $Zn_xCd_{1-x}S$ thin films.

It is seen that D.C resistivity decreases with increasing temperature (conductivity increases with increasing temperature), this means that the $Zn_xCd_{1-x}S$ thin films have negative thermal coefficient of resistivity indicating semiconducting nature of the film. The straight line indicates that conduction in the film is through thermally activated process. In general, the thickness of $Zn_{0.9}Cd_{0.1}S$ film increases as Cd content increase and reaches to maximum in case of $Zn_{0.1}Cd_{0.9}S$ film, so that the resistivity decreases with the thickness. The decrease of resistivity with the thickness is due to the influence of the structural properties like grain size, lattice parameters and lattice strain. When thickness increases, the grain also increases, the grain boundaries decrease, therefore a concomitant decrease in the number of high-resistance path in the film and hence resistivity is less. From figure (2), thermal activation energies is calculated using relation (1). There are two distinct linear regions, indicating the presence of two-conduction mechanism, giving rise to the two activation energies E_{a1} and E_{a2} of higher and low temperatures respectively. The lower temperature range is characterized by small slope, while higher temperature range, the curve is characterized by large slope. The activation energies obtained from the slope of straight lines of (ln σ) vs. (1000/T) plots are included in Table (3).

Table (3) Activation energies Ea_1 and Ea_2 for $Zn_xCd_{1-x}S$ thin films.

Sample	E_{a1} (eV)	E_{a2} (eV)
CdS	0.458	0.103
$Zn_{0.1}Cd_{0.9}S$	0.537	0.114
$Zn_{0.3}Cd_{0.7}S$	0.602	0.143
$Zn_{0.5}Cd_{0.5}S$	0.616	0.167
$Zn_{0.7}Cd_{0.3}S$	0.630	0.186
$Zn_{0.9}Cd_{0.1}S$	0.705	0.215
ZnS	0.860	0.215

Conclusions

- The results shows, all the films obtained in the present investigations have resulted in n-type conductivity. The resistivity of nanocrystalline $Zn_xCd_{1-x}S$ thin films increase from (1.062×10^3-1.110×10^5 Ω-cm) for (x=0.1-0.9) respectively.
- Also, the low resistivity of $Zn_xCd_{1-x}S$ (1.062×10^3 Ω-cm), high transparency (above 80%), carrier concentration of 10^{10} carriers/cm^3 and the possibility of tuning band gap are found by varying the value of x, makes these films are in the required range for the application as window layer in solar cell fabrication.

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