Preparation of Cd_xIn_xS nanocomposite film by electron beam deposition

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المستخلص

تم تحضير غشاء الكادميوم سلفايد (CdS) بوساطة طريقة التبخير بالحزمة الالكترونية على ارضيات من الزجاج وبدرجة حرارة الغرفة . تم تشويب الاغشية بواسطة الانديوم ولدنت عند درجات حرارية مختلفة لمدة ساعتين تحت الفراغ لتحضير المركب كادميوم سلفايد انديوم (Cd_xIn_xS). تم دراسة الخصائص التركيبية والكهربائية بوساطة حيود الاشعة السينية (XRD) و التوصيلية المستمرة و تاثير هول. بينت قياسات الاشعة السينية تحول CdS الى Cd_xIn_xS. توصيلية غشاء CdS كانت بين 0.288 و 0.215 $(\Omega.cm)^{-1}$ وللاسماك 0.5 و 1 mm . التوصيلة للغشاء ذي السمك 1 والمشوب بالانديوم وعند مختلف دراجات حررة التلدين 473, 523, 573 and 623 K كانت 12.18, 3.32, 2.74 and 2.82 $(\Omega.cm)^{-1}$ وطاقة التنشيط كانت 0.24, 0.3, 0.63, 0.52 eV على التوالي. من خلال النتائج التي تم الحصول عليها تبين انه يمكن انتاج اغشية ذات مواصفات جيدة لاغشية CdxInxS بوساطة طريقة التشويب بالانتشار الحراري.

Abstract

Cadmium sulfide (CdS) films were prepared by electron beam evaporation on glass substrates at room-temperature, doped with indium (In) and annealing at different temperatures for two hours under vacuum. Structural and electrical properties were studied by X-ray diffraction (XRD), d.c. conductivity and Hall effect. XRD shows transformation of CdS into Cd_xIn_xS. The conductivity of CdS at 300 K was found to be 0.288 and 0.215 $(\Omega.cm)^{-1}$ corresponding to the thickness 0.5 and 1 µm. The conductivity of 1 µm thickness of CdS doped with indium and heat treatment at 473, 523, 573 and 623 K were 12.18, 3.32, 2.74 and 2.82 $(\Omega.cm)^{-1}$ respectively. The activation energy was 0.24, 0.3, 0.63 and 0.52 eV for the same temperature ranges. The results show that possibility to fabricate high quality films of CdxInxS by thermal diffusion doping.

Keywords: CdS, CdInS, Electrical transport, Indium,

Introduction

II–VI compound semiconductors have drawn considerable interest due to their potential applications in photovoltaic devices, photo-resistors, electroluminescent layers and as photocatalysts for hydrogen production at a visible region (1, 2). Cadmium sulfide (CdS) is known to be an excellent heterojunction partner of p-type cadmium telluride (CdTe) or p-type copper indium diselenide ($CuInSe_2$) due to its high electron affinity and direct band gap. CdS has a wide-band gap which emerged 2.42 eV at 300 K, and it behaves as an n-type semiconductor. CdS is a widely used substance with many advanced technological applications (1,3, 4).

CdS polycrystalline films can be prepared by various physical techniques(5-6) or chemical methods (7-9). The physical evaporation technique is the best way for preparing uniform films with high growth rate and excellent crystallinity. In addition, impurities incorporated during the chemical deposition process strongly affect the electrical, structural and optical properties of the deposited films (10).

It is difficult to produce undoped CdS films with good properties by changing the preparation conditions. Many methods were used to improve CdS properties by increase the Cd or incorporate foreign atoms as donors. CdS doping can be achieved using different materials, but indium (In) is the best one. This is because indium is very similar to cadmium (Cd) in terms of atom size. Thus, In can replace Cd in CdS lattice (11,12). At the same time, (In) reduces the barrier height between the crystal grains of the film. Many chemical methods can be used to prepare CdInS composite depending on the reaction between CdS and In_2S_3 (13). In this work a new technique to synthesis the CdS composite is introduced. The composite was fabricated on glass substrate by an electron beam evaporation technique and annealed at different temperatures. The effect of indium diffusion on the structural and electrical properties of CdS is discussed in detail. The most important thing that we wish to highlight the reported work here as the best of our pioneering work knowledge in the synthesis of CdInS composite using electron beam evaporation technique

Experimental details

Glass substrates were initially cleaned ultrasonically in a series of solutions including alcohol, chromic acid, acetone and distilled water. CdS films were obtained by electron beam evaporation which evacuated to ~ $2x10^{-5}$ torr. Edward Vacuum Coating machine model E306 was utilized to grow CdS film at two thicknesses, 0.5 and 1μm. 20 nm of indium was evaporated on the CdS films as a dopant then annealed under vacuum at various temperatures in the range of 473- 623K to synthesize Cd_xIn_xS composite. Siemens D-5000 with Cu-K line (λ=1.54 Å) was used to X-ray diffraction in the 2θ range of 20º-60º. The resistance (R) of the synthesized films as a function of temperature was measured by two probes method. By measuring current and voltage, the conductivity (σ) of the films was calculated. Carrier mobility and concentration of the films were determined at room temperature based on conductivity and Hall's measurements.

Results and discussion

Structural analysis

The crystal structures of the composite films were studied via X-ray diffraction (XRD). Fig. 1 shows the XRD patterns of CdS film without any doping at room temperature and the film after doping at 623 K. XRD spectra of CdS film is deposited in Fig 1(a). The main peak appears at 2θ equals 26.58º matching (002) the crystal plan of hexagonal CdS perfectly(10). Simultaneously, small peak at angles of 29.9º, 36.22º, 43.22º and 49.5º are trends corresponding to planes (101), (102), (110) and (112). These peaks match the cubic structure of CdS. The II-VI compounds are seen to form either

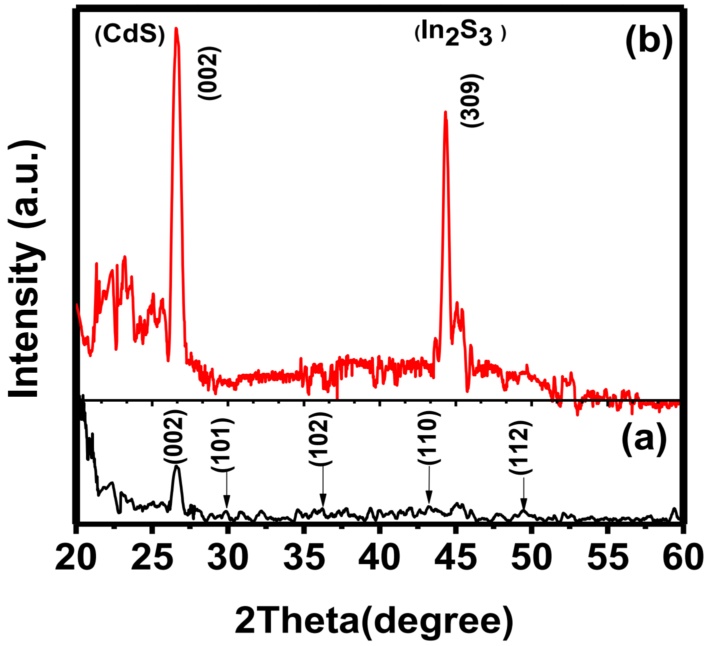

Figure (1): X-ray spectra of (a) CdS film and (b) CdInS at 623 K

sphalerite (cubic) or wurtzite (hexagonal) structures. There also show the appearance of broad humps. These peaks are due to nanocrystalline nature and low density. The grain size of the films which is calculated of the plane (002) for CdS is 99.62 and for planes (002) and (309) for CdxInxS is 98.3 and 59.7 respectively. That change in crystal size of the CdS films after doped by In maybe is resulted from diffusion of indium throw CdS films and replace Cd atoms by In. Fig. 1(b) shows CdS spectrum after doping with In and annealed at 623 K. There are two dominant peaks, CdS and In_2S_3, which is in agreement with other work (12). This means that the transformation of CdS into Cd_xIn_xS has occurred. The indium has diffused into CdS films and replaced the cadmium in the CdS lattice. Cd_xIn_xS composite film is a polycrystalline with well-defined diffraction peaks. This corresponds to the hexagonal phase of CdS and the cubic phase of In_2S_3 confirming a formation of Cd_xIn_xS. That no peaks of In and In_2O_3 are observed, It indicates that In has completely merged into the CdS lattices.

Electrical properties

Hall effect mesurement is confirms that the films are n-type and the mejurity of carrers are electrones. Fig. 2 (a) illustrates the variation of d.c. conductivity (σ) with temperature for CdS and Cd_xIn_xS films for two different thickness at 0.5 and 1 μm respectively.

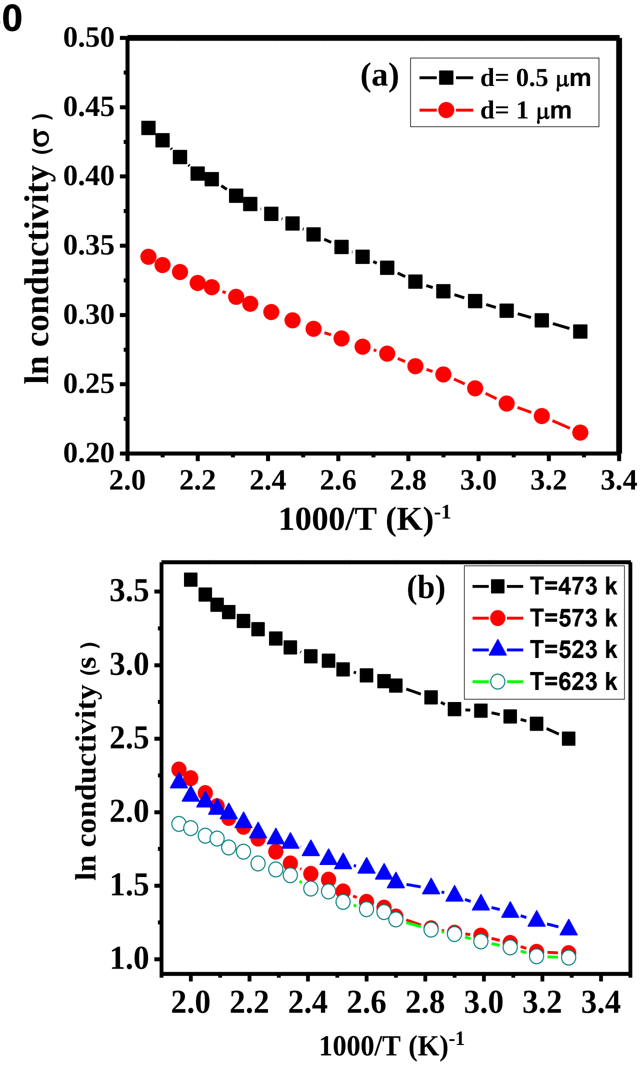

Figure (2): ln conductivity (σ) versus 1000/T of (a) CdS films and (b) CdS:In film at different heating temperature for thickness 1μm

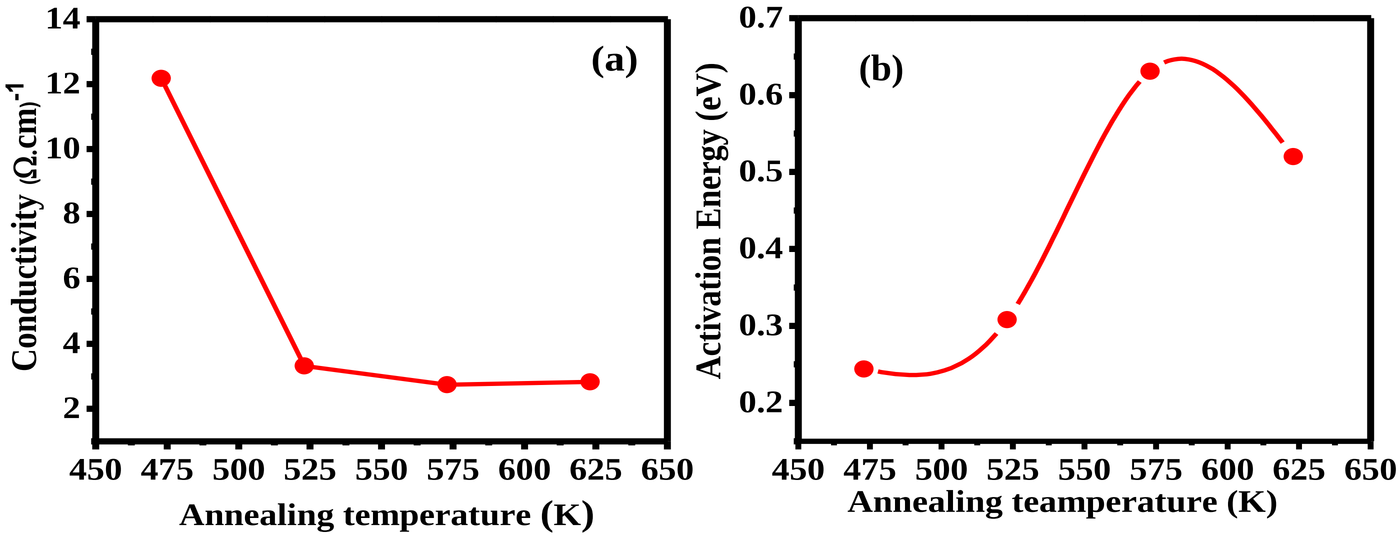

Figure (3): Variation (a) conductivity (b) activation energy with annealing temperature

The conductivity of the films is increased with temperature increases, which prove the semiconducting behavior of the films. The conductivity of the films presents non-linear variation with temperature. In addition the films have two transition mechanisms with different temperatures due to the thermally assisted tunneling of carriers through the grains boundary barrier as well as hopping transition (13). However the films have many sub levels under the conduction band attributed to sulfur vacancies (8, 13). Activation energy of the films in the temperature range (445-485K) is 0.346 eV and 0.3601 eV at thicknesses of 0.5 and 1 µm respectively.

This slight difference is attributed to the polycrystalline nature of the films and barrier height between the grains. Fig. 2(b) shows the results of CdS doped by indium at different 473 and 523 K. Generally both of curves have similar trends of conductivity with temperature, but there is a big difference between the two temperatures. It was indicated that at lower temperature, the indium has little or no effect on CdS and the temperature is not enough to diffuse it through CdS film. However when the temperature increased to 573 K, the conductivity behavior entirely changes. The reason for the fluctuation which occurs at 573K is still unknown. The presence of indium effect on the electrical transport of CdS in addition indium has merged with CdS crystal to produces of a new composite of Cd_xIn_xS.

Fig.3 demonstrates conductivity and activation energy with annealing temperature. The conductivity of the films decreases with temperature. The activation energy is found to be optimum at a temperature of 573 K, but it drastically drops at 623K. The explanation for such results can be attributed to reduction in the barrier height at grain boundaries for the annealed films and diffusion of In through the CdS. When the temperature is greater than 573 K, the In begins to replace Cd in crystallattice sites or is inserted between the atoms as an impurity. An interstitial indium acts as a recombination center, and decreasing the conductivity (13).

Conclusions

CdS thin films were evaporated by electron beam deposition method on glass substrates at room temperature and doped with indium and annealed at different temperatures to fabricate CdInS composite. The production of CdInS is confirmed by XRD characterization. CdInS thin films are composed of cubic and hexagonal phases of In_2S_3 and CdS. The electrical conductivity of CdInS is $2.82(\Omega.cm)^{-1}$. The grain size of the crystals synthesized is very small, below 100 nm. This is a pioneer work which focused on the fabrication of CdInS thin films using thermal diffusion of indium in the CdS films.

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