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Influence of Mercaptoethanol Concentration on the Structural, Surface, Optical and Electrical Properties of <Ag/Melt Growth Polished p-Si/n-CdZnS/Ag> Hetero p-n Junction high voltage Range Tunable Short Diodes

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Abstract

n-CdZnS thin films have been prepared by our in-house designed and developed chemical bath deposition (CBD) instrument using 2-mercaptoethanol as capping agent. The structural properties were investigated through X-ray diffraction (XRD) analysis which results the obtained CdZnS thin films are of hexagonal phase. The surface morphology and surface texture of the fabricated CdZnS thin films were characterized by scanning electron microscopy and atomic force microscopy. Room temperature photoluminescence (PL) spectra recorded the optical properties of CdZnS deposited on p-Silicon<100> substrates, which showed obvious blue shift relative to the CdZnS bulk materials. Electrical properties of the grown p-Si/n-CdZnS hetero-junctions were characterized by current-voltage (I-V) measurements.

Keywords: p-Si/n-CdZnS, Chemical Bath Deposition, Mercaptoethanol, Thin Films, Photoluminescence, Current-Voltage Measurement

Introduction

Metal chalcogenides (sulphides, selenides and tellurides) have been studied intensively over the past 25 years in view of their actual and potential applications as photoconductive cells, photovoltaic cells and other optical devices. These materials can be obtained in a thin film form by various methods [1] such as chemical vapor deposition, laser ablation; thermal evaporation, hydrothermal process, and template-based method have been employed to prepare low dimensional semiconductor nanomaterials [2–8]. Among them, the chemical methods, i.e. bottom to up approach, provide a more promising direction to synthesize low dimensional nanostructures due to their cost-effective, high efficiency and potential for large-scale production.

Semiconductor nanocrystals have received more attentions for both fundamental research and technical application, owing to their strong size-dependent properties and excellent chemical processibility [8]. As CdS, ZnxCd1−xSe are the most important II–VI group semiconductors, having vital optoelectronic applications for laser light-emitting diodes and optical devices based on nonlinear properties [9-11], many routes have been exploited to synthesize CdS semiconductor particles and particle arrays [12, 13]. The effects of four critical factors including temperature ramping-up rate, hydrothermal temperature, capping molecules, and sulfur source on the shape of CdS nanostructure formed by hydrothermal process was reported [14].

The control of the composition of CdxZn1-xS nano particles may lead to the development of ideal materials for short wavelength diode laser applications. Semiconducting CdZnS materials and also the related ternary compounds are promising materials for high density optical recording and for blue or even UV laser diodes. These applications are based on the structure of CdxZn1-xS which exhibit fundamental absorption edges that can varied from green to UV [15-20]. In solar cell systems, where CdS films have been demonstrated to be effective, the replacement of CdS with the higher band gap CdxZn1-xS alloys has led to a decrease in window absorption loss and an increase in the short circuit current [21-23]. Effect of annealing, substrate influence, additive concentration and Zn ion concentration on the structural, surface, optical and photoluminescence emission properties of CdZnS thin films [24-27].

Herein, we report the controllable growth of CdZnS thin films by CBD process using 2-mercaptoethanol as capping agent. Comparing to as grown CdZnS thin films, the action of lower 2-mercaptoethanol concentration on the formation of p-Si/n-CdZnS is revealed. The mechanism for the formation of p-Si/n-CdZnS structures with different 2-mercaptoethanol concentration has been preliminary presented. The presence of the band to band transition in PL spectra of synthesized samples showed the improved crystalline and surface property of CdZnS thin films. The obtained CdZnS thin films on p-Si substrates were smooth, highly adherence, specularly reflective and clear in a visible range. In present paper, characteristics like conduction mechanism of p-Si/n-CdZnS hetero-junction grown by CBD technique are reported.

Experimental

The CdCl2, ZnCl2 and NH2-CS-NH2 were used as the source materials for Cd2+, Zn2+ and S2- ions, respectively. A catalyst mixture was prepared by dissolving the appropriate amount of CdCl2 (analytical grade) and ZnCl2 (analytical grade) in distilled water. The CdZnS ternary thin film was co-precipitated by slowly adding aqueous solution of NH4OH to the mixture of CdCl2 and ZnCl2 aqueous solution, which was kept stirring with constant 60 rpm through out the reaction. Before making the final solution for the preparation of the films, each of the elemental solutions was stirred for 30 min to obtain homogeneity among the constituents of the solution for uniform coating. For the preparation of good quality films, the concentration of (0.12M) CdCl2, (0.12M) ZnCl2, (0.2M) NH4Cl and (0.4 M) NH2-CS-NH2 were optimized and used as stock solution. The

appropriate amount of CdCl2, ZnCl2 and NH2-CS-NH2 solutions were mixed in a 100 ml beaker, and made alkaline by the addition of NH4OH solution. The mixture was again stirred to form a homogeneous mixture. An appropriate amount of 2-mercaptoethanol (capping agent) was added to control the growth kinetics on the formation of CdZnS thin films. The p-Si substrates having a size of 1x1 cm2 are cleaned by using hydrofluoric acid (HF) and nitric acid (HNO3) having the ratio 1:3 volume ratio for 10 min at room temperature and placed vertically inside the solution with the help of a teflon disc. The disc was attached with the constant rotator rotating at 60 rpm and was kept immersed inside the chemical bath.

The deposition was carried out for 1 hour at a bath temperature of 80ºC. The NH4OH solution controlled the precipitation of metal ions to reduce the free metal ion concentration. The deposition of a thin film takes place through the condensation of the metals and sulfur ions on the initial layer, which acts as a catalytic surface. The reaction mechanism for the fabrication of CdZnS ternary thin films can be described as follows. Ammonia solution is added to the Cd and Zn salt solution to form the cadmium tetraamine ions [Cd(NH3)42+] and zinc tetraamine ions [Zn(NH3)42+], respectively. [Cd (NH3)42+] + [Zn (NH3)42+] + S2- + NH3 CdZnS + Remaining product.

The deposition of the CdZnS thin films are based on the precipitation followed by condensation. After 35 minutes, the coated substrates are removed and washed with deionized water to remove loosely adhered CdZnS powder. Our fabricated CdZnS films are yellow, uniform, transparent and highly adherent on to the p-Si substrate.

Results and discussion

X-ray Diffraction Analysis

Fig. 1(a, b, c) shows the XRD pattern of the CdZnS samples prepared by CBD technique for 35 min using 2 ml and 4 ml (capping agent) 2-mercaptoethanol, respectively. All the peaks can be indexed to hexagonal CdZnS with lattice constants of a = 4.137 A°, and c = 6.715 A°, which are consistent with the literature data of JCPDS 49-1302.

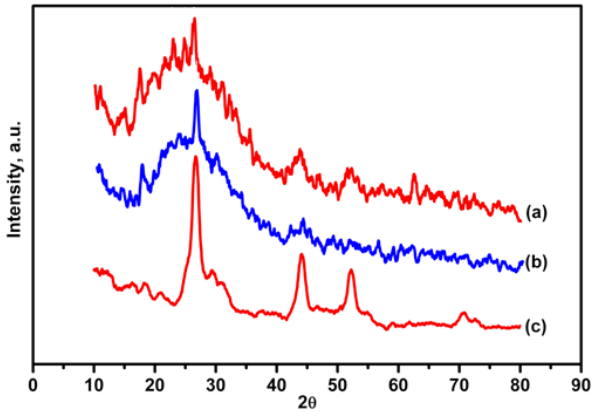

Figure 1 (a, b, c) Powder X-ray Diffraction (XRD) Pattern of (a) Without, (b) Lower and (c) Higher 2-mercaptoethanol Functionalized CdZnS Thin Films

Compared with the standard card, the (002) diffraction peaks, the second strongest peak in bulk hexagonal CdZnS, were usually strong and broad, which may be ascribed to the preferential growth along (002) of hexagonal CdZnS crystallites. The relatively broad peaks probably resulted from the small dimensions of the CdZnS crystallites. It's noted that the peaks revealed some differences among the samples prepared with different dosages of 2-mercaptoethanol, especially

the (002), (110) and (201) peaks. The FWHM of (002) peak in Fig. 1 was smaller than the other two, which indicated that the CdZnS sample prepared using 4 ml 2-mercaptoethanol showed the best orientation growth than the lower (2 ml) and with out 2-mercaptoethanol concentration in the chemical bath.

SEM Analysis

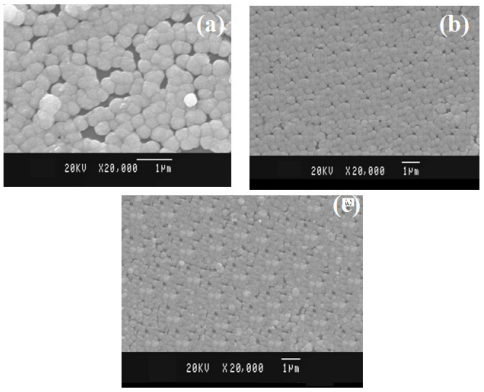

Figure 2 (a, b, c) SEM Images of (a) Without, (b) Lower and (c) Higher 2-mercaptoethanol Assisted CdZnS Thin Films

Fig. 2 (a, b, c) shows the SEM surface images from the CdZnS films with and without 2-mercaptoethanol concentration. The as-grown CdZnS film consists of a dense layer of small crystallites, some large particles are embedded in the surface and more number of granules was observed with in 1μm range. Those particles are quite likely colloidal CdZnS particles formed on the p-Si<100> substrate during the growth of the films. A gradual change is observed in the surface morphology from the capping agent added sample, which displays the highly agglomerated granules like morphology.

AFM Analysis

The morphological characteristics of CdZnS thin films on p-Si substrate were determined by AFM analysis. 4 μm×4 μm areas of the surfaces of CdZnS thin films were imaged. A typical AFM topographic image of a CdZnS thin film with and without 2-mercaptoethanol added chemical route is shown in Fig. 3 (a, b, c).

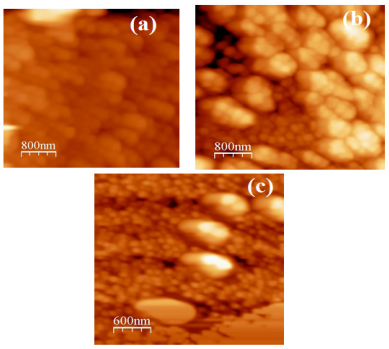

Figure 3 (a, b. c) AFM Images of (a) Without, (b) Lower and (c) Higher 2-mercaptoethanol Assisted n-CdZnS Thin Films

The AFM image of CdZnS (Fig. 3 (a)) shows that the grain size varies between 100 and 300 nm and the surface roughness is about less than 100 nm which are extracted from the reported AFM software [28]. The sizes of individual grains and the surface roughness of the CdZnS thin film vary between 60, 100 and 200 nm, respectively, as shown in Fig. 3 (b) and 3 (c). By means of the capping agent assisted chemical bath deposition method, CdZnS thin films have been obtained in desired surface roughness and grain sizes.

Photoluminescence Analysis

Photoluminescence behaviour of semiconductor nanoparticles could give information on the energies and dynamics of photo generated charge carriers as well as on the nature of the emitting states. Emissions from semiconducting nanoparticles originate from electrons in the conduction band, excitonic and trap states [29–34]. It is well known that emission and efficiency are very sensitive to nature of nanoparticles surface, due to the presence of gap surface states arising from surface non-stoichiometry and unsaturated bonds [35 - 41]. Surface trap states allow non-radiative recombination and enhance luminescence efficiency. Broad low energy PL spectrum is usually attributed to trap state emissions arising from surface defect sites [42 - 46]. For certain particle size distribution, both spectral position and yield of the crystallite fluorescence can be modified by changing the chemical nature of the CdZnS thin film through the addition of 2-mercaptoethanol.

The PL spectra of the fabricated CdZnS thin films (figure 4 a–c) prepared with 2-mercaptoethano l 0 ml, 2 ml and 4 ml, respectively are shown in Fig. 4. The luminescence intensity changes drastically in the fabricated CdZnS thin film with 2-mercaptoethanol. Also, the peak position is blue-shifted indicating decrease in particle size in agreement with the blue-shift of band edge emission.

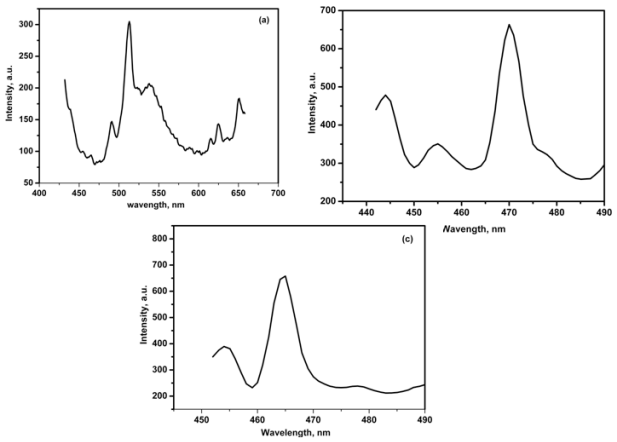

Figure 4 (a, b, c) Room Temperature Photoluminescence Emission of (a) Without, (b) Lower and (c) Higher 2-mercaptoethanol Assisted n-CdZnS Thin Films

The optimum amount of defects concentration at which PL intensity is maximum occurs at the higher 2-mercaptoethanol assisted CdZnS thin film.

Current-Voltage Characteristics

Silver paste has been confirmed for the formation of ohmic contact with both p-Si and n-CdZnS. The typical I-V characteristics of p-Si/n-CdZnS hetero-junction are shown in the figure 5 (a, b, c).

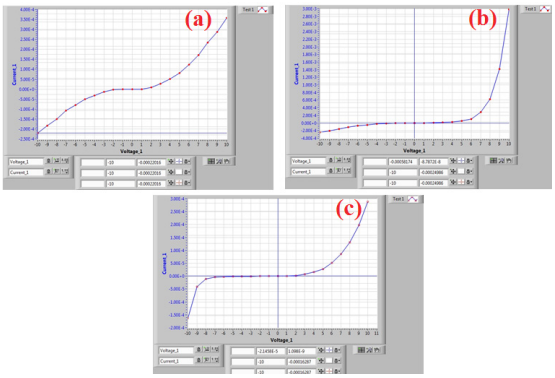

Figure 5 (a, b, c) Voltage – Current (V-I) Characteristics of (a) Without, (b) Lower and (c) Higher 2-mercaptoethanol Assisted Ag/p-Si/n-CdZnS/Ag High Voltage Range Diode Structure

A detailed analysis of I-V characteristics has been made to explain the current flow mechanism. The plot of ln I vs. V for the junction at higher voltages is shown in the figure 6.

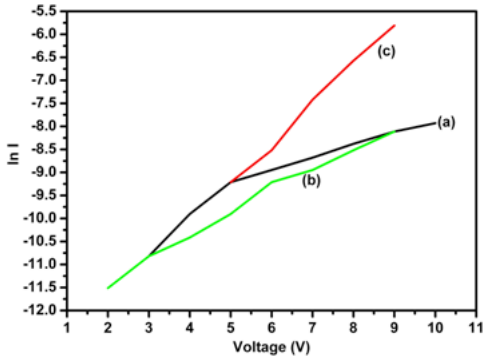

Figure 6 (a, b, c) ln I Against V at Higher Voltages for p-Si/n-CdZnS Hetero-Junctions

Non-linearity in the plot at higher voltage region rules out the current conduction by recombination mechanism in this region. At higher voltages, current varies as square of the voltage (figure 7).

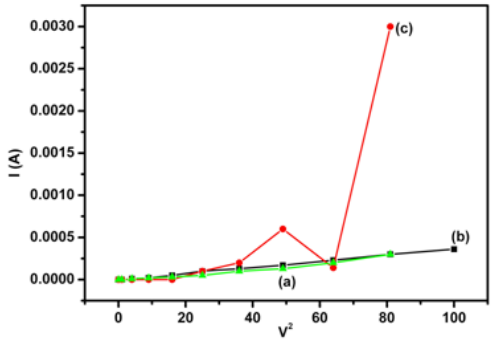

Figure 7 (a, b, c) I against V2 for p-Si/n-CdZnS hetero-junctions at higher voltages

This suggests that, in this region, current is controlled by space charge limited conduction (SCLC) and allows us to use space charge limited (SCL) theory for I-V analysis.

Conclusions

The improved crystallinity was observed in the CdZnS thin film fabricated on p-Si substrate at higher 2-mercaptoethanol concentration than the lower and with out 2-mercaptoethanol added CdZnS thin films. Relatively smooth surface morphology and surface texture was observed in the CdZnS thin film fabricated on p-Si substrate at higher 2-mercaptoethanol concentration than the lower and with out 2-mercaptoethanol added CdZnS thin films. The fabricated p-Si/n-CdZnS hetero-structures show good rectification characteristics. High intense room temperature photoluminescence emission was observed in the higher 2-mercaptoethanol added film than the other films.

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