Review Article

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Photoconductivity of ZnS Thin Films Deposited by Solution-Processing Techniques

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ABSTRACT

We have explored various solution- processing techniques to produce ZnS thin films on conducting (ITO) and silicon substrates along with ZnS-porous silicon composite films. All these samples obtained from different methods and chemical recipes were annealed under fixed ambient conditions and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and ultraviolet photocurrent response. Various characterizations reveal that the fabrication conditions and intrinsic defects of ZnS play a vital role in optoelectronic performance.

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Introduction

ZnS has attracted increasing attention as a potential material for optoelectronic devices such as low threshold blue/UV lasers, solar cells, LEDs, sensors, display devices and photodetectors. In recent years, various attempts were made to fabricate nano/mesa-scaled ZnS for further enhancing opto/electrical performance [1-3]. While many top-down fabrication approaches were followed, solution-based techniques turned out to be the most efficient and low-cost for the production of high quality nano and micro structured ZnS thin films. Electrochemical deposition is a true bottom-up technique, with the convenience of completely filling the interstitial spaces of templates, such as polymer microsphere templates, liquid crystal templates and porous (such as porous alumina) templates, from metal to semiconductor varieties. Similarly, electrospinning has been widely recognized as an electro- hydrodynamic method to produce nano to micro sized fibers from solutions containing the desired materials. However, the optoelectronic properties of ZnS are critically affected by the preparation conditions such as the fabrication method, types of substrates, thickness and annealing conditions. Therefore, it is necessary to optimise the fabrication conditions of the aforementioned techniques for desired applications [4-6].

The direct electrochemical deposition of semiconductors, such as ZnS, on a silicon substrate is difficult due to conductivity issues as well as a large mismatch in thermal expansion coefficients and the high reactivity of silicon toward oxygen [7]. Porous silicon (PS) has been established as the most fascinating material for diverse optoelectronic applications, especially for photonic composites where the nano sized pores can be filled with different materials using simple solution-processing techniques [8].

In this paper, we have explored various solution- processing techniques to produce ZnS thin films on conducting (ITO) and

silicon substrates along with ZnS-porous silicon composite films. All these samples obtained from different methods and chemical recipes were annealed under fixed ambient conditions and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and ultraviolet photocurrent response. All films obtained from various chemical recipes were essentially in the form of Zn(OH)₂ after preparation, and to obtain ZnS, the samples were annealed at 400°C for 12 h under ambient conditions. Various characterizations reveal that the fabrication conditions and intrinsic defects of ZnS play a vital role in optoelectronic performance.

Experimental

In the literature, brief information is given about the technology of obtainment of ZnS thin layers only precipitated from the aqueous solution and about some properties. A complex physical-technological study of these layers, their the energy spectrum of local centers and purposeful management of the recombination process, depending on the technological environment, a comprehensive study of photoelectric properties is not provided. Negative photoeffects were not studied in ZnS thin layers. Metal-semiconductor obtained by the method of chemical deposition, Complex studies of MDR and isotope heterocycles have not been performed. The obtainment of materials under investigation, the technology of producing various structures of electric transition on their basis, as well as structure of the samples and the methods of investigation of parameters were studied.

The technological mode of removal of thin layers by chemical deposition method has a significant impact on their physical properties. Selection of the deposition regime of the thin layers is determined by their composition, concentration of components and molar ratios, as well as temperature and duration of deposition. Here in this work are the improvements in the method of obtaining thin layers. Thermodynamic calculations show that as the temperature of the solution increases, the amount of alkali in the solution should be reduced and temperature should be within 80°C.

However, it has been used ammonium as a complex creator in the case of recombination editing; As the ammonia is alkaline, it reduces the rate of disintegration of the components. The addition of 3-5 ml of ammonia in the solution leads to an increase in the concentration of small dispersion particles. It also increases the thickness of the precipitated layer. Thus, the concentration of Zn^{2+} ions in the solution decreases due to the increase of concentration of $\text{Zn}(\text{NH}_2)_2$ complex ions. As a result, the amount of matter in the layer decreases with the speed of the reaction, which in turn increases the thickness of the layer.

The thin layers of different chemical and percentage composition, depending on the properties (crystallographic, electrical, photoelectric and optical) and where they are applied (in the preparation of resistors, diode structures, photocell), have been obtained on different types of surface morphology, orientation and type (metal, semiconductor or oxide) pallets (Al, sital, glass/ SnO_2 , glass/ In_2O_3).

The synthesis of nanocrystals of $\text{A}^{\text{II}}\text{B}^{\text{VI}}$ type compounds is carried out in the teflon cell. For this purpose, the pre-prepared solutions are added to the silica in turn and mixed continuously. Synthesis is carried out on the following reactions:

The ZnS thin films were deposited by Chemical Bath Deposition Technique on glass substrate. The glass substrates were first washed with liquid detergent and rinsed thoroughly in double distilled water and then it is placed in boiled water for a few minutes. They were finally immersed into acetone for 15 minutes and then dried in an oven. The materials used for deposition of ZnS nanocrystalline thin films are lead acetate as source material of lead ion, thiourea as the source of Sulphur ion and cadmium acetate as the source of cadmium ion respectively. The lead acetate solution of 0.1M was prepared with double distilled water stirring separately at 50°C until a clear solution is obtained. The pH value of lead acetate solution is maintained at 10 by adding the ammonia solution to it drop by drop slowly.

The p-Si plaques and layers, which are used as a base, during use in next step (when thin layers are precipitated) before entering the reaction at a room temperature in (1:4) solution stored for 1-2 hours, and after it is washed with bidistyle chloride and dried with nitrogen and quickly absorbed in the cold iodine solution. It was then introduced into the chemical solution as extracted therefrom. Used as a base and mainly used for the study of optical properties of thin layers glass/n- In_2O_3 (1 smx1 sm or 0.5 smx1 sm measure), glass/ITO (In_2O_3 and SnO_2 system solid solution) (1 smx1 sm or 0.4 smx0.6 sm measure), glass/n- SnO_2 and (1smx1sm or 0.4smx0.6sm measure) $\sim 100\text{-}500$ nm thickness thin layers 4×10^{-4} - 8×10^{-3} Omxsm had special resistance. The oxide pallets were cleaned from physical and chemical contamination.

Results and Discussion

The obtained ZnS thin films from various solution processing methods show considerable variation in structural, optical and optoelectronic properties on deposition parameters and conditions. Since the annealing condition for all the films was same (400°C for 12 h in air), in the present study the structural and optical properties of various films are compared and analyzed. As shown in Fig. 1, the XRD patterns were recorded for all annealed ZnS thin films obtained from (1) electrodeposition from ZnCl_2 onto a silicon substrate, (2) electrodeposition from $\text{Zn}(\text{NO}_3)_2$ solutions

onto an ITO substrate, (3) chemical deposited ZnS from a $\text{Zn}(\text{Ac})_2$ solution onto an ITO substrate, and (4) a ZnS-PS nanocomposite. Asterisks (*) indicate the XRD peaks of silicon. All the films were showing strong XRD peaks of wurtzite crystalline structure, with traces of substrate (Si) related diffraction peaks.

Figure 1: (a) XRD patterns of ZnS (1) electrodeposited from ZnCl_2 and (2) electrodeposited from $\text{Zn}(\text{NO}_3)_2$ solutions, (3) chemical deposited ZnS from $\text{Zn}(\text{Ac})_2$ solution and (4) ZnS-PS nanocomposite. The asterisk (*) indicates XRD peaks of silicon.

Steady-state and transient photocurrent measurements were performed on all ZnS films made from different solution processing techniques. Here the ZnS films were exposed to a UV laser (2 mW, 337 nm) and the photocurrent was monitored using the wet electrode method. Figure 2(a) shows the normalised photocurrent response, when the illuminated light was switched ON and OFF at different bias conditions. The data represents the ZnS thin films obtained from (1) electrochemical deposition from ZnCl_2 , (2) electrochemical deposition from $\text{Zn}(\text{NO}_3)_2$ solutions, (3) chemical deposited film from a $\text{Zn}(\text{Ac})_2$ solution and (4) a ZnS-PS nanocomposite. As seen, the photocurrent varies linearly with the increase in the bias voltage. While all films show more or less similar responses, the photocurrent efficiencies measured under similar conditions are different. Here, the photocurrent efficiency is defined as $\text{QE} = \frac{I_{\text{photo}}}{I_{\text{dark}}} \times 100\%$, where the I_{dark} and I_{photo} are the photocurrents when the light is OFF and ON, respectively. The QE for ZnS obtained from chemical deposited film from $\text{Zn}(\text{Ac})_2$ solution is 50 whereas for ZnS-PS the nanocomposite is only

Figure 2: (a) Normalised photocurrent ON–OFF response of ZnS films prepared from various methods. (b) Transient photocurrent response of ZnS deposited from various methods, the Si detector response is shown as a reference. Labels 1-4 represent the same as Fig. 1 (a).

To study the transient photocurrent behaviour, the resultant photocurrent response obtained from the excitation of a nanosecond UV laser (337 nm, 5 ns, 100 Hz) was monitored through a digital oscilloscope using a commercial silicon detector as a photocurrent response reference (Figure 2(b)). Essentially all films show a fast photocurrent rise followed by an oscillatory decay. The photocurrent decay is composed of two components: a fast fall followed by slow fall of an oscillatory nature.

While ZnS obtained from electrodeposition shows both exciton as well as defect related PL, the ZnS obtained from chemical deposited shows dominant excitonic related features in both absorption as well as PL, indicating the minimum influence of defects (Figure 3).

Figure 3: Wavelength dependent photocurrent response of ZnS electrodeposited thin films obtained from $\text{Zn}(\text{NO}_3)_2$, $\text{Zn}(\text{Ac})_2$ and ZnCl_2 solutions.

Therefore, the transient photocurrent response rise time is due to the desorption of O_2 . Whereas, the photocurrent fast fall is due to the transit time taken by the carriers, which is inversely proportional to the electron mobility and bias voltage. The oscillatory slow decay phenomenon is the result of persistent photoconductivity effects attributed to the presence of oxygen-related hole-trap states at the surface, which prevent charge-carrier recombination and prolongs the photocarrier lifetime. Similar behavior has been observed for the ZnS fabricated from various other methods. While the ZnS grown from various aforementioned methods shows a good crystalline quality, the origin of oxygen defects on the surfaces could be from both deposition conditions as well as annealing in an air atmosphere. However, in the present case, though solution processing recipes are different, the obtained ZnS may be compared since the annealing conditions for all the ZnS films are the same. Hence, these results broadly suggest that the photocurrent response of ZnS could be related to its structural and surface properties, essentially to the process induced intrinsic defects of ZnS. Figure 3 shows the wavelength (200–500 nm) dependent photocurrent characteristics of ZnS thin films fabricated from various precursors. The spectral response shows a distinct broad peak centred at about 360 nm, which corresponds to the band gap of ZnS.

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