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Ag diffusion in ZnS thin films prepared by spray pyrolysis

E. Bacaksiz [a,*], O. Görür [b], M. Tomakin [b], E. Yanmaz [a], M. Altunbaş [a]

[a] Department of Physics, Faculty of Arts and Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey
[b] Department of Physics, Faculty of Arts and Sciences, Rize University, Rize, Turkey

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Abstract

ZnS thin films were deposited by spray pyrolysis method on glass substrates. Diffusion of Ag in ZnS thin films was performed in the temperature range 80–400 °C under a nitrogen atmosphere. The diffusion of Ag is determined with XRF, and the obtained concentration profile allows to calculate the diffusion coefficient. The temperature dependence of Ag diffusion coefficient is determined by the equation $D=8\times10^{-9}$ exp(−0.10 eV / kT). It was found that the as-grown undoped high resistive n-type ZnS thin films were converted to the p-type upon Ag doping with a slight increase in resistivity only by rapid thermal annealing at 400 °C in N_2 atmosphere. In addition, the band gap of the p-type film was decreased as compared with the undoped sample annealed under the same conditions. The results were attributed to the migration of Ag atoms in polycrystalline ZnS films by means of both along intergrain surfaces and intragrain accompanied by interaction with native point defect.

Keywords: ZnS thin films; Silver diffusion; Diffusion coefficient

1. Introduction

ZnS thin films are promising materials for their use in various device applications. In the opto-electronics, it can be used as light emitting diode in the blue to ultraviolet spectral region due to its band gap (3.7 eV) at room temperature. It is well known that the electrical conductivity of ZnS films is too low to act as a substrate for transistors, however it can be used as light source for display screens and buffer layers for Cu(In,Ga)$(S,Se)_2$ solar cells [1,2]. Furthermore, ZnS/Ag/ZnS multilayer films have been used as an important low emittance films such as heat mirrors [3].

It is known that the ZnS semiconductor has an n-type conductivity. Donor centers, which formed in ZnS during growth, were attributed to the native point defects caused by deviation of ZnS composition from the stoichiometry. It is very difficult to change film conductivity from the n-type to the p-type by conventional doping and diffusion processes. It was reported in the literature [4–6] that doping of ZnS by silver causes p-type ZnS layers having low resistivity under excess Zn atmosphere. The method of application of excess Zn pressure fills the Zn vacancies which are incompatible with utilization of the Zn vacancy related to the so-called blue emission for light emitting devices. Thus, the choice of proper ion impurity centers related to blue emission is quite important. Ag impurities occupying the Zn sites in ZnS are known to make the so-called blue centers [7]. It is well known that group I metals such as Ag and Cu are fast-diffusing impurities in II–VI compounds [8]. Therefore, the interdiffusion of components of Ag–ZnS bilayer structures and particularly diffusion penetrations of silver into ZnS can cause changes in physical properties of the near-interface region of ZnS and thereby in characteristics of structure.

Generally, the mechanism of diffusion in thin films is different from that in the bulk sample. Diffusion in thin films can proceed through the grain or along the grain boundaries depending upon the microstructure of films. In large grained films, diffusion is generally via the grains and analysis gives the lattice diffusion coefficients. As the grain size decreases, atomic transport also occurs preferable along the grain boundary surfaces and analysis yields grain boundary diffusion parameters [9]. According to our knowledge, the thermal diffusion behavior of silver in ZnS films has not been reported. In this

* Corresponding author.
E-mail address: eminb@ktu.edu.tr (E. Bacaksiz).

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work, we have investigated the diffusion of silver into ZnS and its influence on the structural, electrical and optical properties of ZnS thin films.

2. Experimental

ZnS thin films (d=3 μm) are obtained by spray pyrolysis in air atmosphere on the glass substrate. The initial solution is prepared from zinc chloride $ZnCl_2$ (98% purity) at 0.1 M concentration and 0.1 M concentration thioure $(NH_2)_2CS$ (99% purity) in deionized water. The growth was performed with a spray rate of about 5 ml/min and growth rate of ~50 nm/min on the glass substrates cleaned in ethanol dried in vacuum. During the growth, the substrates were rotated with a speed of 10 rev/min at a temperature of 500 °C and in atmospheric pressure in order to produce homogenous films [10]. The obtained films had good adhesion to the substrate surfaces. The thickness of these films measured by the SEM method is found to be about 3 μm. Silver diffusion into ZnS thin films was carried out for 3 min using the vacuum evaporated layer of Ag on the open surface of the film. The diffusion annealing of the films with the deposited layer of silver was performed under a nitrogen atmosphere in the temperature range 80–400 °C with 80 °C steps. The undoped films (without silver layer) were annealed under the same conditions. After the annealing, the rest of the Ag layer on the upper ZnS surface was removed by using HNO_3:H_2SO_4:H_2O (5:5:90) solution and lateral sides of the ZnS films were cleaned by grinding. By measuring the surface electrical conductivity it was tested whether the whole remaining metallic Ag layer was removed from the ZnS film by the etching in a HNO_3:H_2SO_4:H_2O solution. The concentration distributions of Ag atoms in the ZnS thin films were analyzed by the successive removal of thin layers from the sample by using a HF:H_2O (1:2) solution and by measuring the energy dispersive X-ray fluorescence (EDXRF) intensity of the Ag-K_α peak. The thickness of the film after the removal of each layer by etching in HF:H_2O (1:2) was measured by forming a series of 10 equal etching steps and measuring the total decrease in the thickness by SEM and then finally calculating the decrease in the thickness for each etching step. For the excitation of silver atoms, an annular Am-241 radioisotope source (50 mCi) emitting 59.543 keV photons was used. Intensity measurements of the Ag peaks were detected with a Si (Li) solid-state dedector [11].

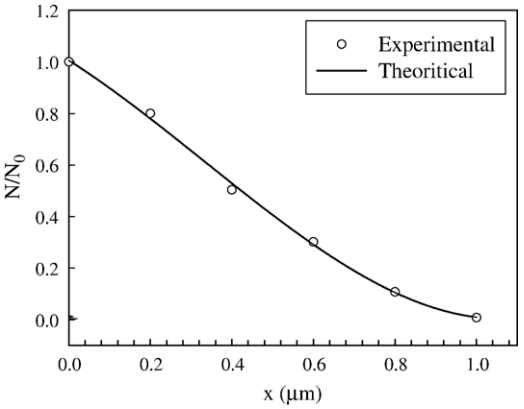

Fig. 2. Concentration profiles of Ag in ZnS films T=320 °C for 180 s (the full curve is calculated according to (2)).

The X-ray diffraction (XRD) data of ZnS and ZnS/Ag films were taken using a Rigaku D/Max-IIIC diffractometer with CuK_α radiation over the range 2θ=3–70° at room temperature. The surface morphology was studied by using JEOL JST-6400 scanning electron microscope. The absorption spectra of undoped and Ag-doped ZnS films were measured by Perkin-Elmer Lambda 2SUV/Vis Spectrometer with 190–1100 nm wavelength range using non-polarised ligth. The resistivity of ZnS and Ag-doped ZnS films was determined by Van Der Pauw measurements at room temperature. The carrier concentration was determined by Hall effect measurements.

3. Results and discussion

The values of resistivity and charge carrier concentration for the as-grown n-type ZnS films obtained on the glass substrate with a thickness of about 3 μm were found to be 2.8×10^5 Ω cm and $n=9.5\times10^{14}$ cm^{-3} respectively. Fig. 1 shows the X-ray diffraction pattern of ZnS film grown by spray pyrolysis technique. The diffraction pattern arising from the film consisted of a single intense peak at ~28.96° due to the fcc (111) reflection. The lattice constant a is calculated from the peak

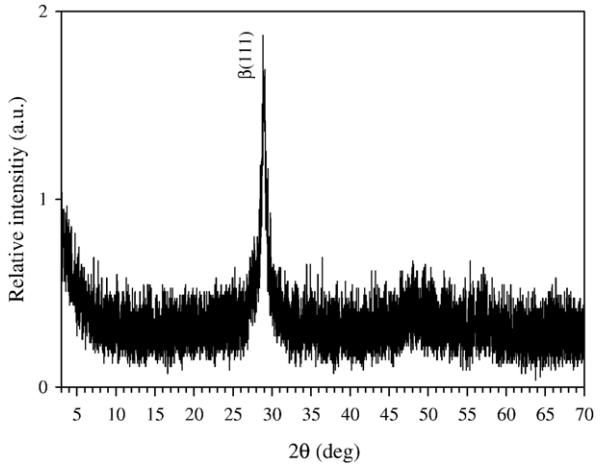

Fig. 1. The XRD pattern of undoped ZnS film.

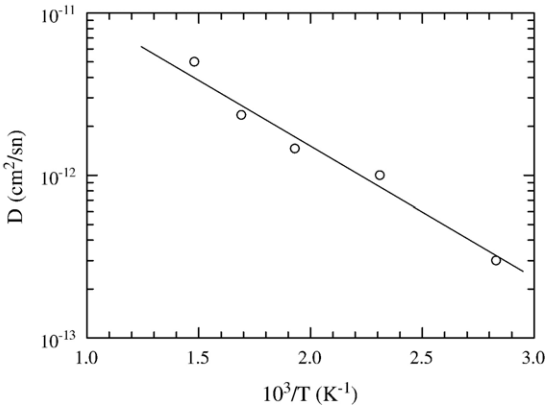

Fig. 3. The temperature dependence of Ag diffusion coefficient in ZnS films.