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Physical properties of ZnSe films prepared by two-source evaporation and a study of post doping effect

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Abstract

Two-source thermal evaporation method was utilized to prepare hard ZnSe thin films, the films were then immersed in silver nitrate solution for different time periods. The optical properties of the films were measured from the transmittance spectra. X-ray pattern of the films were also included. Final compositions of the resulting films were measured by EMPA method and comparisons between compositions by EMPA vs. optical absorbance were also reported. The dc electrical conductivity increased and a small shift in the optical band gap was also observed.

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1. Introduction

ZnSe is one of the group II–VI semiconductors and it has a direct optical band gap of ~2.7 eV, which makes it suitable material for variety of the optoelectronics applications in the blue–green wavelength region, including light emitting diodes and lasers [1–9]. Fabrication of ZnSe LEDs requires the formation of p–n junctions through controlled substitutional doping [2]. Because of wide band gap and transparency over a wide range, ZnSe is also suitable as window layer for thin films solar cells [10,11].

Many efforts were reported for producing low resistive p-type ZnSe, the main elements used for p-type dopant of ZnSe were Li and nitrogen [3,12,13]. ZnSe thin films have been grown using different techniques including pulsed laser deposition [14–16], molecular beam epitaxy [12,17–19], closed space sublimation [11], hot wall evaporation [20] and metal oxide chemical vapor deposition [21].

The transition metal Ag introduces acceptor level in II–VI semiconductors, when introduced substitutionally on cation site. Ag was concluded to be a conventional d^{10} acceptor in ZnSe [22].

The two-source evaporation is suitable for preparing compound semiconductors to control the film quality [23]. In addition to that the ion exchange process has also been utilized as a simple technique for post doping of the II–VI semiconductor films, such as CdS [24–26], ZnTe films [27,28]. In this work we report our results for ZnSe films prepared by two-source thermal evaporation and post immersed in $AgNO_3$ solution.

2. Experimental

Highly pure Zn and Se (99.99+) materials were used for evaporation. Se and Zn were filled into two separate graphite crucibles in powder and pellet forms (to avoid scattering of the material), respectively. These crucibles were heated

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separately by quartz lamps. The crucibles were heated independently by 500 W quartz lamps connected to the main through temperature controller with K-type thermocouples inserted into the graphite crucibles. An IR heater was used for substrate heating. All the evaporation processes were carried out under vacuum of $\sim 10^{-6}$ mbar in Edward E306A vacuum system.

The source temperature of Zn was kept at 540 °C, which was pre-checked to yield evaporation rate of ~2.5 nm/s on cold surface. In case of selenium, source temperature was kept at 300 °C to get evaporation rate of ~2.5 nm/s. The substrate temperature was kept at 400 °C. These parameters were selected from the pre-checked experiments to get the best hard films, which could stay in hot solution for comparatively longer time without detaching from the substrate.

After deposition the films were immersed in $AgNO_3$ solution (0.1 g $AgNO_3$/100 ml of distilled water) at temperature of 50 °C for different time periods, these films were then cleaned by distilled water, and then heated in vacuum for 1 h at a temperature of 400 °C to ensure the diffusion of silver into the sample [27]. Pre-experimental results showed no sharp effects of the solution concentration for speeding the ion exchange process, while solution temperature had more critical effect.

The optical transmission was recorded by Perkin Elmer Lambda 900 spectrophotometer using UV-WinLab software. X-rays from CuKα source were used to study the structure of the films. EMPA attached to SEM was utilized to measure the Ag ratio in different films. The dark dc resistivity was measured at room temperature for all the samples (i.e. as deposited, immersed and heat treated).

3. Results and discussion

The films prepared with Se source temperature of 300 °C and Zn of 540 °C were highly transparent yellowish green in colour and were very difficult to scratch and could sustain in solution of $AgNO_3$ (0.1 g $AgNO_3$/100 ml) for comparatively longer time. The colour of the films turned brownish after immersion in $AgNO_3$ solution.

3.1. Optical properties

The transmission spectra of the films as deposited and after immersion in $AgNO_3$ solution and heat treated (in vacuum) for different time periods at 400 °C are shown in Fig. 1. The spectrum showed no improvement in transmission after heat treatment for 15 min, so for the rest of the films we decided that one hour will be sufficient time for heat treatment, this would ensure the diffusion of Ag in ZnSe films. Fig. 2 shows the transmittance of ZnSe films with different immersion times in $AgNO_3$ solution. It is clear that the transmittance of the films decreases with increasing immersion time, because of the Ag layer formed on the top of the films.

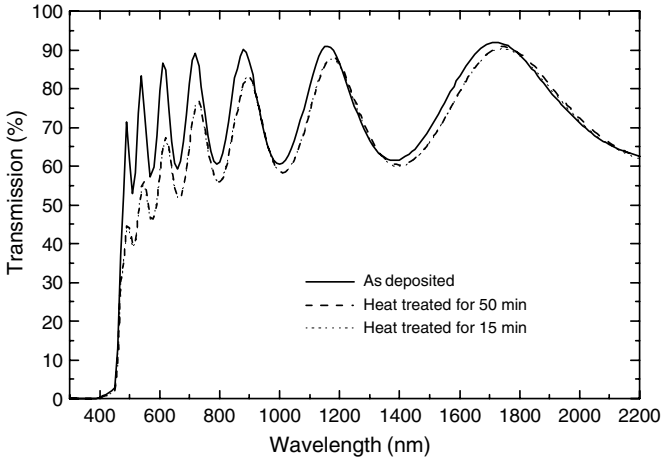

Fig. 1. The transmission spectra of ZnSe film as deposited and after immersion, in $AgNO_3$, for 5 min, along with heat treatment (in vacuum) for different time periods at 400 °C.

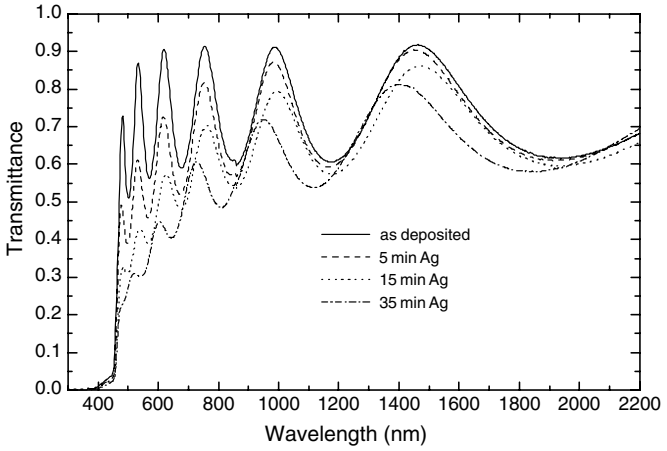

Fig. 2. Transmittance spectra of as deposited and immersed films, for different time periods after heat treatment (400 °C, 1 h).

The thickness and the refractive index of the films were calculated by fitting the transmission data to the following equation [28–30]:

$$T = \frac{Ax}{B - Cx\cos\phi + Dx^2}, \tag{1}$$

where T is the normal transmittance for the system consisting of thin film on a transparent substrate surrounded by air, and taking into account all multiple reflections at the interface for the case of $k^2 \ll n^2$, where k is the extinction coefficient of the film, which is true for this kind of semiconductor thin films [28–30]. The other variables are defined as $A = 16n^2 s$, $B = (n+1)^3(n+s^2)$, $C = 2(n^2-1)(n^2-s^2)$, $D = (n-1)^3(n-s^2)$, $\phi = 4\pi nd/\lambda$, $x = \exp(-\alpha d)$, $k = \alpha\lambda/4\pi$. Here n and s are the refractive index of the film and the glass substrate, respectively, d is the thickness of the film and α is the absorption coefficient of the film.