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Effect of nitrogen ion implantation on the sprayed ZnSe thin films

Mustafa Öztaş, Metin Bedir *

University of Gaziantep, Department of Engineering Physics, 27310-Gaziantep, Turkey

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Abstract

The ZnSe thin films were deposited onto glass substrates by the spray pyrolysis method using mixed aqueous solutions of $ZnCl_2$ and SeO_2 at the substrate temperature 430 °C. These films were implanted with 130 keV nitrogen ions to various doses from 1×10^{16} to 1×10^{17} ions/cm^2. We have analysed the properties of the nitrogen ion-implanted ZnSe thin films using X-ray diffraction and optical transmittance spectra. The values of optical bandgap have been determined from the absorption spectra. The bandgap of the N^+ doped films decreased from 2.70 eV for undoped film to 2.60 eV for maximum doping probably due to band-tailing, whereas the absorption coefficient values increased with the increase of the implantation dose.

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Keywords: ZnSe; Thin film; Spray pyrolysis; Ion implantation

1. Introduction

Semiconducting thin films have been found to be useful in the fabrication of a number of solid state devices such as thin film transistors, solar and photoconductive cells and electroluminescent cells. Thin films can be prepared by various techniques including vacuum evaporation, spray pyrolysis, sputtering, molecular beam epitaxy, vapour phase epitaxy, chemical vapour deposition, solution growth, screen printing, and electrophoresis. A great deal of effort has been expended in the development of simple and low-cost methods for the deposition of thin films suitable for device applications [1,2]. These simple methods normally produce polycrystalline films which are considered to be prime candidates for solar cell production. Among the thin films, zinc selenide (ZnSe) has been regarded as materials with many attractive properties, such as large bandgap, low resistivity, remarkable photosensitivity, etc. Consequently, this compound offers an important number of applications (ultrasonic transducers, photodetectors, solar cells, semiconductor diode lasers, blue light-emitting devices, etc.) [3,4]. Many efforts are currently directed to a new generation of photodiodes based on wide bandgap compound semiconductors. ZnSe meets this requirement because it has a wide bandgap (direct bandgap, $E_g=2.7$ eV) and is capable of emitting light in the blue-green region. In the last years, a variety of methods has been employed for the growth of high-quality ZnSe thin films such as molecular beam epitaxy, solution growth, organometallic chemical vapour deposition, spray pyrolysis, physical vapour deposition under vacuum, etc. [5–9].

One of the properties of semiconductors which is very important for device applications is the bandgap. The best values of the bandgap are obtained by optical absorption. If the bandgap energy is sufficiently small, thermal excitation can promote an electron from the valence band to the conduction band. If impurities are present in the bandgap, thermal excitation can also be used to excite an electron from an impurity level to the conduction band. Thus, the measurements of electrical resistance of the specimen as a function of temperature can be used to determine the bandgap or activation energy of the specimen. Ion implantation is increasingly being used in the fabrication of semiconductor devices, as it has several advantages over the more conventional diffusion techniques [10]. Ion implantation is technologically important in the fabrication of semiconductor devices requiring controlled dopant profiles. During ion implantation in semiconductors, it is possible to expect three types of changes: (i) the electrical property of the material due to the introduction of implanted species; (ii) the lattice disorder in

* Corresponding author.
E-mail address: bedir@gantep.edu.tr (M. Bedir).

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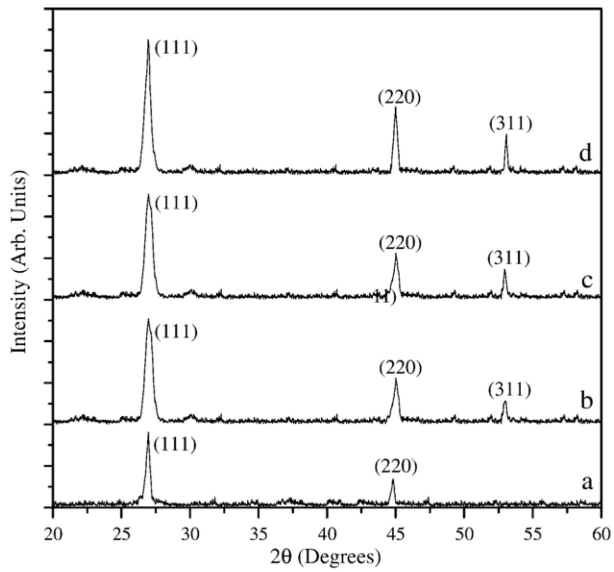

Fig. 1. X-ray diffractogram patterns of the ZnSe thin films with: (a) as-deposited, (b) 1×10^{16} ions/cm^2, (c) 5×10^{16} ions/cm^2, and (d) 1×10^{17} ions/cm^2 doses.

its structure; (iii) the optical bandgap and optical transparency. In this study, the sprayed ZnSe thin films have been implanted with N^+ ions, and the effect of ion implantation on the structural and optical properties of the films are discussed on the basis of lattice disorder.

2. Experimental details

The ZnSe thin films were prepared by spraying an aqueous solution of $ZnCl_2$ (Merck, purity 99.99%) and SeO_2 (Merck, purity 99.99%) on a glass substrate kept at 430 °C. ZnSe thin films were spray deposited from an aqueous solution containing 0.05 mol/l $ZnCl_2$ and 0.05 mol/l SeO_2. A 100 ml spraying solution was prepared at the same ratio (Zn:Se = 1:1), the spray flow rate was adjusted to about 0.3 ml per min and the distance between the nozzle (head of the sprayed source) and the substrate was kept at 20 cm. A 150 keV ion implanter has been used to irradiate the ZnSe thin films with mass analysed 130 keV nitrogen ions to different doses (10^{16}–10^{17} ions/cm^2). The beam current was maintained around 0.8 mA to avoid excessive heating of the sample during ion implantation. The implantation was carried out at room temperature in a vacuum of the order of 10^{-7} mbar. A Philips X-ray generator (Model PW 1390) with a Ni filter and CuKα radiation ($\lambda = 1.5418$ Å) at 40 kV and 20 mA in the 2θ range 20–60° was employed for the structural analysis of the films. Optical properties were studied by transmittance and optical absorption at room temperature, in the spectral range between 300 and 900 nm, by using a UV–VIS double beam spectrophotometer.

3. Results and discussion

3.1. Structural studies

The X-ray diffraction (XRD) patterns indicate that the samples are polycrystalline and have a cubic (zinc blende) structure. For the as-deposited ZnSe thin films, the crystallites are preferentially oriented with the (111) planes parallel to the substrate surface (Fig. 1a). The diffractograms indicating the presence of all the prominent peaks of ZnSe are arising from (111) and (220) reflections from which all the ZnSe thin films are polycrystalline having f.c.c cubic zinc blende structure. And also it is observed that the XRD patterns of all ZnSe thin films show a most preferred orientation along (111) plane. The (111) direction is the close-packing direction of the zinc blende structure.

Table 1
Values of FWHM for (111) and (220) peaks and the bandgap values of the as-deposited and N^+ ion-implanted ZnSe thin films

Dose (ions/cm^2)	(111) Peak	(220) Peak	E_g (eV)
As-deposited	0.409	1.230	2.70
1×10^{16}	0.416	1.075	2.66
5×10^{16}	0.455	0.984	2.62
1×10^{17}	0.473	0.967	2.60

Fig. 1 also shows the X-ray diffraction patterns of the N^+ implanted films. The XRD patterns of the implanted films (b, c and d) are shifted along the intensity axis for clarity. The most intense peak representing cubic structure with a preferential (111) orientation appears at XRD patterns for the implanted films as in the case of the as-deposited ZnSe thin films. The diffractograms indicating the presence of all the prominent peaks of ZnSe are arising from (111), (220) and (311) reflections from all the ZnSe thin films are polycrystalline having f.c.c cubic zinc blende structure. The full width at half maximum (FWHM) values of the (111) and (220) peaks of this film are calculated to be 0.409 and 1.230, respectively. In the ion-implanted film it is seen that the FWHM of the (111) peaks is higher (Table 1) than that of the as-deposited film. But, in the case of the (220) peak, the FWHM is found to decrease with the increase of implantation dose. This may be due to the implantation-induced lattice damage resulting in the decrease of the fraction of (111) orientation and the increase of the degree of orientation along the (220) plane. For all the implanted films, only one extra peak appeared. This extra peak might be due to the implantation-induced (311) cubic orientated grains. On nitrogen ion implantation, there is a possibility for the decomposition of ZnSe monolayers to its elemental components zinc and selenide. So there may be a possibility for the loss of selenide atoms and the excess zinc could precipitate in

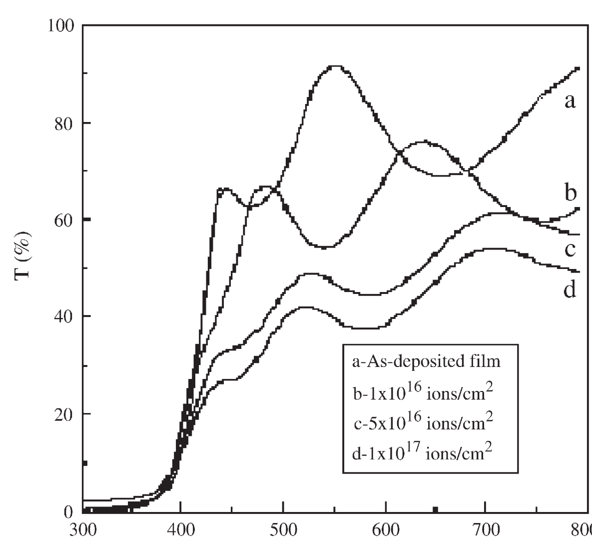

Fig. 2. Transmittance versus wavelength of N^+ ion-implanted ZnSe thin film.