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# Effect of $N^{5+}$ ion implantation in CVT grown ZnSe single crystals

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ABSTRACT

The ZnSe single crystals were grown by chemical vapor transport (CVT) technique using iodine as a transporting agent. As grown ZnSe single crystals have been implanted by $N^{5+}$ ion at 45 keV energy in room temperature with various fluences of $1\times10^{15}$, $5\times10^{15}$, $1\times10^{16}$ and $5\times10^{16}$ ions/cm$^2$. The lattice constants of the as grown and implanted ZnSe single crystals are 5.57 and 5.45 Å respectively. The photoluminescence studies reveal that $N^{5+}$ implanted ZnSe has the band edge emission at 468 nm (2.64 eV) and broad luminescence peak due to defect level green emission at 551 nm (2.25 eV) and yellow emission 592 nm (2.09 eV). The as grown ZnSe crystal has the absorption cut off at 483 nm whereas the cut off increases from 489 to 524 nm with an increase in ion fluences. The frequency of vibration for as grown ZnSe crystal is 504 cm$^{-1}$ and for implanted ZnSe samples, the frequencies are 657–677 cm$^{-1}$ (N–Zn bending mode) and 2337–2353 cm$^{-1}$ (N–Se stretching mode) which are due to bond formation of N.



## 1. Introduction

Recently, there has been a great deal of interest in wide band-gap II–VI compound semiconductors. Considerable interest exists in the fabrication of *p–n* junction light-emitting diodes (LEDs), lasers diodes (LDs), and integrated optoelectronic devices [1]. The band-gap energy of ZnSe is 2.67 eV at room temperature, which permits one to use this material in the fabrication of blue and green electroluminescent devices [2,3].

ZnSe single crystal always appears to be *n*-type. It has been extremely difficult to produce a good *p*-type material by means of usual bulk growth techniques or equilibrium diffusion processes. Fortunately, ion implantation offers a powerful tool to realize type conversion of this material. Several impurities, such as P, Li, Na, B, F and N have been incorporated into ZnSe by ion implantation [3,4]. Long-life blue LEDs based on ZnSe have still not been achieved. A main problem is the difficulty of producing stable low-resistive *p*-type ZnSe. Jifeng Wang et al. [4] reported that nitrogen has been found to be the best dopant in preparing *p*-type ZnSe. Park et al. [5] studied the photoluminescence properties of nitrogen doped ZnSe and achieved the low resistive *p*-type ZnSe. Chung et al. [6] performed nitrogen ion implantation, and made electroluminescent *p–n* junction diodes. However, very little is known about the properties of nitrogen impurities in ZnSe [7].

The single crystals of ZnSe of dimension of $9\times7\times5$ mm$^3$ were grown by chemical vapor transport (CVT) techniques and the grown crystals were implanted with 45 keV of $N^{5+}$ ion. The projected range of ZnSe single crystals has been calculated using SRIM-2008 computer program. The effect of $N^{5+}$ ion implantation on structural and optical properties of ZnSe single crystals has been studied.

## 2. Experimental procedure

### 2.1. Growth of ZnSe single crystals

ZnSe single crystals have been grown by chemical vapor transport (CVT) technique using iodine as a transporting agent. A two zone horizontal resistive heating furnace was used for growth of ZnSe single crystals [8,9]. The zinc (99.5%) and selenium (99.9%) powders in the ratio of 1:1 were used as starting materials. The ZnSe polycrystalline powder was synthesized at 1100 °C for 24 h in vacuum sealed quartz ampoule. 3 g of polycrystalline ZnSe powder was loaded in quartz ampoule of length 15 cm with diameter 1.4 cm. 2 mg/cm$^3$ of iodine was added to the compound as the transporting agent. A pressure of $1\times10^{-5}$ m bar was achieved and the ampoule was vacuum sealed. The sealed ampoule was placed inside the furnace connected with the Eurotherm temperature controllers having the accuracy of $\pm0.1$ °C. A reverse temperature profile was developed across the ampoule with growth zone in higher temperature for 24 h to remove the sticking powders from growth zone of the ampoule and to diminish the active sites. During the growth, the temperature difference between the two zones was

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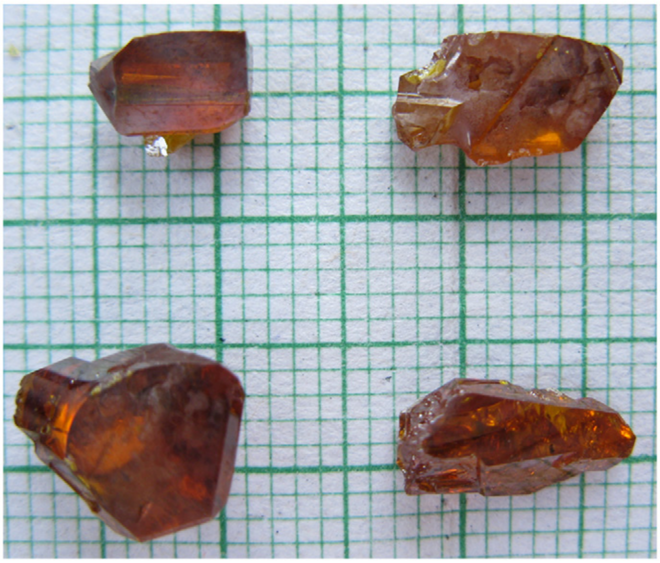

**Fig. 1.** As grown ZnSe single crystals using source temperature of 900 °C and growth temperature of 850 °C.

**Table 1**
Theoretical SRIM calculation of $N^{5+}$ ion implantation in ZnSe single crystals.

| Ion energy (keV) | d*E*/d*X* (Elec) | d*E*/d*X* (Nucl) | Projected range (nm) | Longitudinal straggling (nm) | Lateral straggling (nm) |
|---|---|---|---|---|---|
| 45 | 0.3734 | 0.1954 | 73.9 | 52.3 | 40.6 |

maintained at 50 °C with the source temperature of 900 °C and growth temperature 850 °C. The growth period was about 15 days. After the furnace was cooled to room temperature at the rate of 30 °C/hour, the crystals were obtained with different dimensions and morphology. The maximum dimension of the ZnSe single crystal was $9\times7\times5$ mm$^3$. The as grown ZnSe single crystals are shown in Fig. 1.

The ZnSe single crystal has been studied by single crystal X-ray diffraction. The single crystal XRD analysis was done by ENRAF (BRUKER) NONIUS CAD4 single crystal X-ray diffractometer. The crystal belongs to cubic structure with space group F43m. The unit cell parameter values of as grown ZnSe is $a=b=c=5.57$ Å and interfacial angle $\alpha=\beta=\gamma=90^\circ$. This unit cell parameter values are similar to that of the reported value $a=b=c=5.66$ Å [8].

### 2.2. $N^{5+}$ ion implantation in ZnSe single crystals

$N^{5+}$ ion implantation was performed in as grown ZnSe single crystals using electron cyclotron resonance (ECR) plasma ion source at room temperature with 45 keV energy. The ion fluences during implantation were $1\times10^{15}$, $5\times10^{15}$, $1\times10^{16}$ and $5\times10^{16}$ ions/cm$^2$. During implantation, the chamber pressure was maintained at $2.6\times10^{-6}$ Torr and beam current of 2.5–5 μA was maintained. Using theoretical SRIM-2008 computer program the projected range of $N^{5+}$ ion implantation in ZnSe single crystal was determined to be 73.9 nm. The results are tabulated in Table 1.

## 3. Results and discussion

### 3.1. X-ray diffraction analysis

Fig. 2 shows the X-ray diffraction spectra of as grown and $N^{5+}$ ion implanted ZnSe single crystals. The XRD spectra were recorded using BRUKER D8 ADVANCE X-Ray Diffractometer. The stronger diffraction peak at (111) plane confirms the formation of ZnSe crystalline phase. The crystal belongs to cubic structure of primitive lattice with space group F43m. From the (111) plane, the calculated lattice parameter value of as grown ZnSe is 5.57 Å whereas the reported value is 5.60 Å [10]. The position of peak corresponding to (111) plane is slightly shifted by 0.25° for the implanted ZnSe single crystals. The calculated lattice parameter value of the implanted ZnSe is 5.45 Å. The increase in $N^{5+}$ ion fluence decreases intensity of the diffraction peaks. The full width at half maximum (FWHM) of the as grown ZnSe is 0.11° and for the implanted samples at $1\times10^{15}$, $5\times10^{15}$, $1\times10^{16}$ and $5\times10^{16}$ ions/cm$^2$ of ZnSe crystals the FWHM values are 0.17°, 0.18°, 0.20° and 0.25° respectively. The calculated values of lattice parameters and the full width at half maximum (FWHM) are tabulated in Table 2. The value of FWHM is found to increase with increase of the ion fluences. The increasing FWHM values and a decrease in lattice parameter values may be due to the structural deformation of induced lattice disorder in implanted ZnSe crystals. The decrease in lattice constant due to

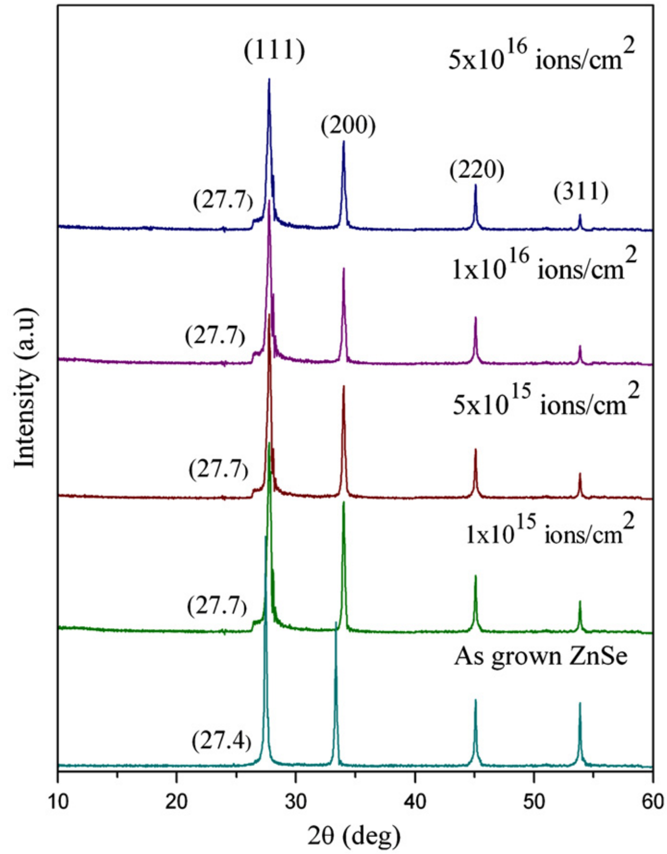


**Fig. 2.** X-ray diffraction studies of as grown and $N^{5+}$ ion implanted ZnSe single crystals.

**Table 2**
The calculated lattice parameters and FWHM values of as grown and $N^{5+}$ ion implanted ZnSe single crystals.

| Samples | (111) plane (2$\theta$) (deg.) | Lattice parameter $a$ (Å) | FWHM (deg.) |
|---|---|---|---|
| ZnSe (As grown) | 27.71 | 5.57 | 0.11 |
| *$N^{5+}$ion implanted ZnSe* ($1\times10^{15}$, $5\times10^{15}$, $1\times10^{16}$ & $5\times10^{16}$ ions/cm$^2$) | 27.45 | 5.45 | 0.17, 0.18, 0.21 & 0.25 |