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# Enhancement of thermoelectric properties of MBE grown un-doped ZnO by thermal annealing

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**Abstract.** In this paper, we have reported an enhancement in thermoelectric properties of un-doped zinc oxide (ZnO) grown by molecular beam epitaxy (MBE) on silicon (001) substrate by annealing treatment. The grown ZnO thin films were annealed in oxygen environment at $500^{o}$C-$800^{o}$C, keeping a step of $100^{o}$C for one hour. Room temperature Seekbeck measurements showed that Seebeck coefficient and power factor increased from 222 to 510 $\mu$V/K and $8.8\times10^{-6}$ to $2.6\times10^{-4}$ $Wm^{-1}K^{-2}$ as annealing temperature increased from 500 to $800^{o}$C respectively. This observation was related with the improvement of crystal structure of grown films with annealing temperature. X-ray diffraction (XRD) results demonstrated that full width half maximum (FWHM) of ZnO (002) plane decreased and crystalline size increased as the annealing temperature increased. Photoluminescence study revealed that the intensity of band edge emission increased and defect emission decreased as annealing temperature increased because the density of oxygen vacancy related donor defects decreased with annealing temperature. This argument was further justified by the Hall measurements which showed a decreasing trend of carrier concentration with annealing temperature.

**Keywords:** ZnO; MBE; thermoelectric properties; annealing temperature; crystal structure

## 1. Introduction

Due to huge demands of clean energy in the word, researchers are trying to develop renewable energy sources like solar energy, wind energy, nuclear energy and thermoelectric (Shakouri 2011, Dmitriev and Zvyagin 2010). Among these, direct conversion of heat into electrical energy (Thermoelectric) is gaining substantial interest due to simplicity of technology and environment friendly (Sootsman *et al*. 2009). Furthermore thermoelectricity has some advantages over other energy sources like high reliability, no moving parts involved and low noise performance (Sales 2007, Yanzhong *et al.* 2011, Alam and Ramakrishna (2011). The efficiency of any thermoelectric material can be determined by a dimension less quantity figure of merit and can be written as (Li *et al*. 2009)

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$$ZT = \frac{S^2\sigma}{k}T \quad (1)$$

Where $S$ is Seebeck coefficient, $\sigma$ is electrical conductivity and $\kappa$ is electrical conductivity. Many materials such as Si-Ge alloy, Skutterudites, Clatherates and complex Chalcogenides (Bera *et al.* 2006, Tritt and Subramanian 2006) have been reported as thermoelectric material but all these materials suffered from low stability at elevated temperatures (Park *et al.* 2008). On the other hand oxide semiconductors are good for high temperature thermoelectric applications because they are stable at high temperatures and are highly resistive to oxidation (Synder and Eric 2008). In this class of oxides, zinc oxide (ZnO) has direct band gap of 3.37 eV and exciton binding energy 60 meV at room temperature (Asghar *et al.* 2013, Asghar *et al.* 2012). It has partial covalent character when compared with other oxide semiconductor, therefore emerging as promising candidates for high temperature thermoelectric properties (Kinemuchi *et al.* 2007). The best thermoelectric properties are reported for doped (Al, Ga, Sb) ZnO, but as grown has poor thermoelectric properties. It is also reported that crystal quality, carrier concentration and defect density in ZnO is strongly depended upon the annealing temperature (Søndergaard *et al.* 2013). Therefore the study to enhance thermoelectric properties of un-doped ZnO has significant importance and annealing would be very helpful to modulate thermoelectric properties, defect density and carrier concentration.

In this paper, we have demonstrated the effect of annealing temperature on the thermoelectric properties of molecular beam epitaxy (MBE) grown ZnO. Thin films of ZnO were annealed at different temperature from 500 to 800℃ keeping a step of 100℃ in oxygen environment for one hour. It was observed that Seebeck coefficient and power factor increases with annealing temperature. The observed increasing trend of Seebeck coefficient and power factor was explained in detail in results and discussion section.

## 2. Experimental procedure

ZnO thin films were grown on a three-inch p-type Si (001) wafer by MBE. Temperature of the effusion cell of Zn was deliberately maintained higher for Zn-rich growth of ZnO, further detail can be found in reference (Asghar *et al.* 2011). After deposition a representative wafer was cut into 1 cm×1 cm small pieces and were annealed in oxygen environment at temperature $500^{o}$C-$800^{o}$C keeping step as $100^{o}$C for one hour. For Seebeck and electrical measurements, indium Ohmic contacts (1mm diameter) on four corners of size 1×1 $cm^2$ of 1.6 $\mu$m ZnO layer were prepared. The characterization of various samples was carried out by the following equipments; X-ray diffraction (PANalytic™) using Cu-$\alpha$ radiation as x-ray source with wavelength 1.54 Å, Photoluminescence (HORIBA™) using laser wavelength 325 nm, Hall measurements (Ecopia 3000 Hall measurement System™) using magnetic field 0.5T and homemade Seebeck Effect.

## 3. Results and discussion

### 3.1 Thermoelectric properties

Fig. 1 shows the temperature difference dependence of thermo-electromotive force of MBE

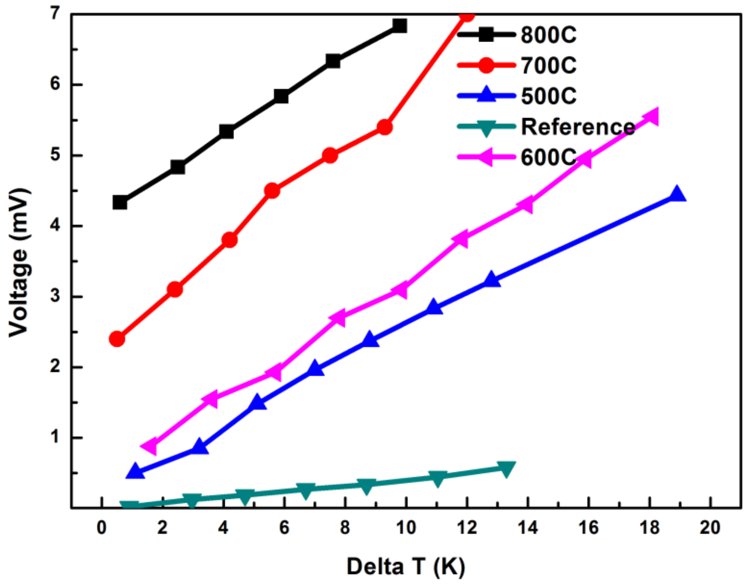


Fig. 1 Graph between temperature difference and Seebeck voltage of MBE grown ZnO annealed at different temperatures in oxygen environment for one hour

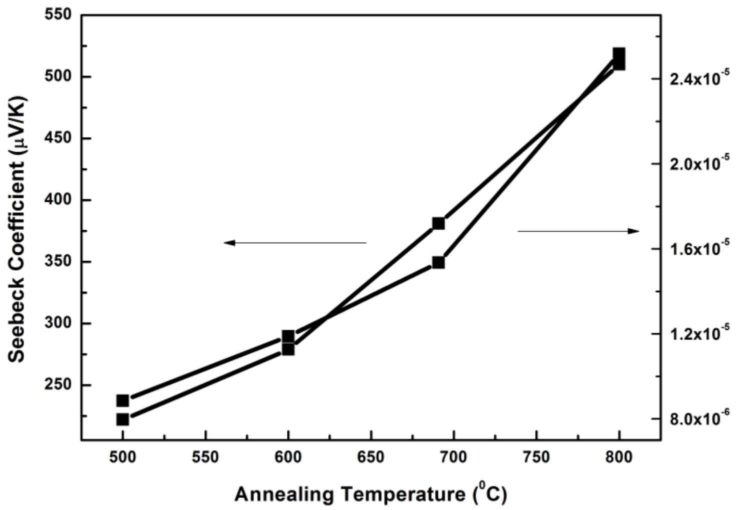


Fig. 2 Effect of annealing temperature on Seebeck Coefficient and power factor. Graph shows that Seebeck Coefficient increases with annealing temperatures

grown ZnO annealed at different temperature in oxygen environment for one hour. It demonstrated that electromotive force increases linearly as the temperature difference between cold and hot end of sample increased. All the thermo-electromotive forces are negative which confirm that electrons are major carriers in grown samples. The Seebeck coefficient was obtained by the slope of this graph and the power factor was calculated by the following formula

$$P=S^2\,\sigma \tag{2}$$

Where $S$ is Seebeck coefficient and $\sigma$ is electrical conductivity. The value of electrical resistivity measured by Hall data increased from 5 to 12 ohm-cm as the annealing temperature increased from 500 to 800℃. Similar trend of decreasing electrical conductivity with increasing annealing temperature was also observed by Park *et al*. (2006), Park and Lee (2008).

Fig. 2 demonstrated the effect of annealing temperature on the Seebeck coefficient and power factor of ZnO thin films grown on Si by MBE. The Seebeck coefficient and power factor increases from 220 to 510 $\mu$V/K and $8.8\times10^{-6}$ to $2.6\times10^{-4}$ $Wm^{-1}K^{-2}$ respectively (detail can be shown in table 1) as the annealing temperature increases from 500 to 800℃. This result can be explained as: when the annealing temperature increases, the stress in the grown film decreased and crystal structure improved significantly. It is accepted fact that ZnO has high density of intrinsic defects such as oxygen vacancies and zinc interstitials (Park and Lee 2008). These donor defects form a complex ($V_O$-$Zn_i$) which justifies the intrinsic n-type conductivity of ZnO (McCluskey and Jokela 2009). Annealing in oxygen environment fills the available oxygen vacancies and breaks the donor complex. As a result crystal structure of annealed film improved which results in the improvement of electrical conductivity. To strengthen our argument we have performed a number of characterization techniques like XRD, photoluminescence (PL) and Hall measurements.

Table 1 Effect of annealing temperature on the Seebeck Coefficient, power factor, FWHM of XRD (002) peak and FWHM of PL NBE peak of MBE grown ZnO on Si (001) substrate

| Annealing Temperature (°C) | Seebeck Coefficient ($\mu VK^{-1}$) | Power Factor ($Wm^{-1}K^{-2}$) | FWHM of XRD (002) Peak (Degree) | FWHM of PL NBE peak (eV) |
|---|---|---|---|---|
| Un-annealed | 43 | $1.7\times10^{-7}$ | 0.50 | 0.133 |
| 500 | 222 | $8.8\times10^{-6}$ | 0.40 | 0.129 |
| 600 | 279 | $1.1\times10^{-5}$ | 0.39 | 0.122 |
| 700 | 381 | $1.4\times10^{-5}$ | 0.38 | 0.120 |
| 800 | 510 | $2.6\times10^{-4}$ | 0.37 | 0.119 |

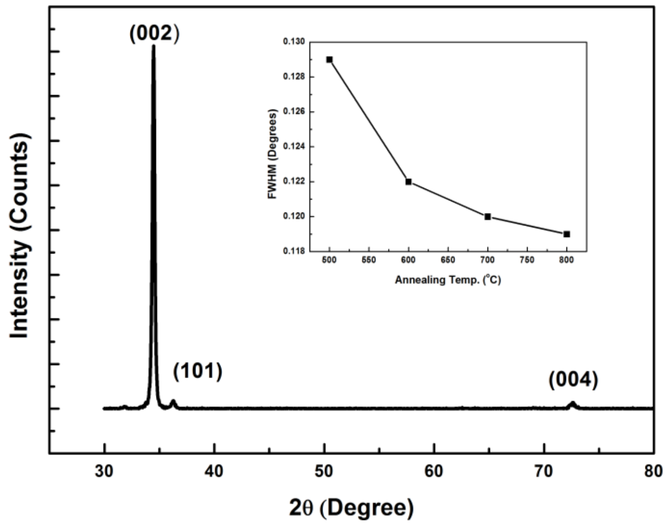


Fig. 3 XRD spectra of representative sample of MBE grown ZnO. The (002) plane is dominant showing that growth is along c-axis. The Inset shows the effect of annealing temperature on FWHM of (002) plane

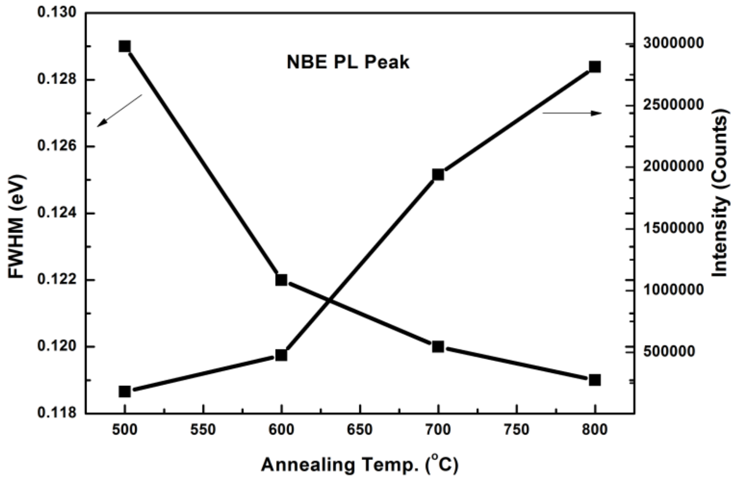


Fig. 4 Effect of annealing temperature on the intensity and FWHM of band edge emission of PL peak of MBE grown ZnO

### *3.2 Structural properties*

Fig. 3 demonstrates typical XRD pattern of a representative as grown ZnO layer: three peaks were observed and associated with (002), (101) and (004) planes of hexagonal ZnO structure preferably oriented along c-axis (Janotti and Van de Walle 2007). FWHM of all samples annealed in oxygen environment at different temperatures for one hour has been calculated and shown in the inset of Fig. 3. The crystal quality improved with annealing temperature as the FWHM of (002) peak decreased from 0.40 to 0.37 degree as the annealing temperature increased from 500 to 800$^o$C. (for detail see Table 1)

### *3.3 Optical properties*

Fig 4 displays the effect of annealing temperature on the intensity and FWHM of near band edge emission (NBE) of various samples annealed at different temperatures in oxygen environment. All samples consist of two peak at 2.5 eV and 3.28 eV related with defect and band-edge emission respectively (Asghar *et al.* 2012) (not shown here). As a matter of fact the intensity and FWHM of band edge emission is directly related with the quality of grown film (Wang *et al.* 2010), accordingly, the density of oxygen vacancy related donor defects decreases as the annealing temperature increased which results in the enhancement of NBE. To verify this argument we have also performed Hall measurements.

### *3.4 Electrical properties*

The Fig. 5 displays the effect of annealing temperature on the carrier concentration. The carrier concentration decreased from $6.23\times10^{18}$ to $6.15\times10^{16}$ cm$^{-3}$ as annealing temperature increased from 500 to 800°C. The carrier concentration ($N_D$) is directly related to $Zn_i$-$V_O$ complex as describe by Asghar *et al.* (2012). As the concentration of this complex increases, the carrier

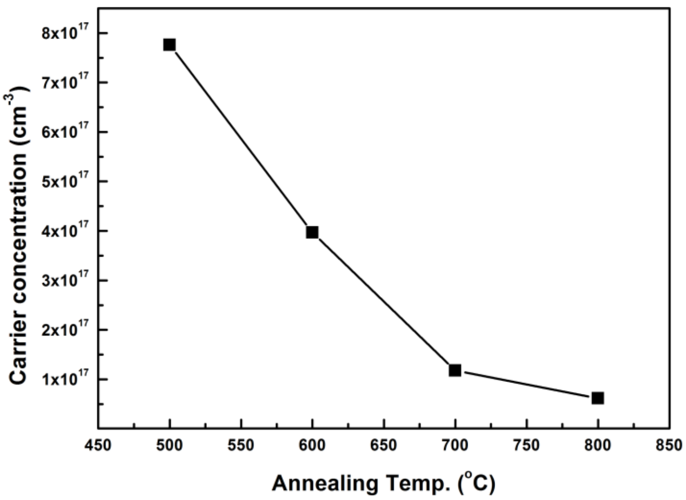


Fig. 5 Graph shows the effect of annealing temperature on the carrier concentration of MBE grown ZnO thin films

concentration also is increased. Furthermore, literature indicates that under oxygen environment, because oxygen vacancies are supposed to be filled (Hadia *et al*. 2009) with the incoming oxygen and as a result, the $V_O$-$Zn_i$ complex loses its identity and owing to the relevance of $V_O$-$Zn_i$ complex with $N_D$, and subsequent decrease in $N_D$ is acceptable. It is pertinent to mention here that as the grown ZnO films are n-type and Si substrate is p-type, there is p-n junction which act as insulating layer, therefore using Si substrate will not affect significantly on Hall measurements and will be in the tolerance limit. All these measurements confirmed that the stress in the grown films decreased as annealing temperature increased. Therefore the thermoelectric properties improved significantly.

## 4. Conclusions

In this study, we have investigated the effect of annealing temperature on the thermoelectric properties of ZnO. Thin films of ZnO were grown by MBE and were annealed in oxygen environment for one hour at different temperature from 500 to 800℃. The Seebeck coefficient and power factor were improved significantly with values 510 $\mu$V/K and $2.6\times10^{-4}$ $Wm^{-1}K^{-2}$ as annealing temperature increased to 800℃. This observation was related with the improvement of crystal structure with annealing temperature, as most of the oxygen vacancy related donor defects fills with incoming oxygen atoms.

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