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Investigation of V_O–Zn_i native donor complex in MBE grown bulk ZnO

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Abstract

In this paper, we have experimentally investigated the theoretical predictions of V_O–Zn_i to be a native donor in ZnO. Intrinsically zinc-rich n-type ZnO thin films having $N_D \sim 6.23 \times 10^{18}$ cm^{-3} grown by molecular beam epitaxy on Si (0 0 1) substrate were annealed in oxygen environment at 500–800 °C, keeping a step of 100 °C for 1 h, each. Room temperature Hall measurements demonstrated that free donor (V_O–Zn_i) concentration decreased exponentially and Arrhenius plot yielded activation energy to be 1.2 ± 0.01 eV. This value is in agreement with theoretically reported activation energy of V_O–Zn_i donor complex in ZnO. We argue; this observation can be explained by two-step process: (i) incoming oxygen fills V_O of V_O–Zn_i complex leaving behind Zn_i; (ii) Zn_i releases its energy and moves to a lower energy state with respect to the conduction band minima and/or occupies an inactive location. Consequently, Zn_i–V_O complex loses its donor role in the lattice. Our experimental data supported theoretical predictions of V_O–Zn_i to be a native donor. Results from photoluminescence spectroscopy carried out on Zn-rich ZnO additionally justify the existence of V_O–Zn_i complex.

(Some figures may appear in colour only in the online journal)

1. Introduction

ZnO is a promising material for short wavelength electronic and optoelectronic devices due to its direct wide bandgap of 3.37 eV and large exciton binding energy of 60 meV at room temperature [1, 2]. Like other wide bandgap semiconductors, ZnO is naturally an n-type material but the origin of its n-conductivity is still an unresolved issue. A variety of donors referred to as hydrogen, Zn-interstitials and/or oxygen vacancy have been proposed in literature but the origin lacks theoretical support [3–5]. For example, oxygen vacancy is the most reported shallow donor in ZnO [6, 7], but theoretically it is proved that oxygen vacancy is a deep donor and cannot play a role in the n-type conductivity of ZnO [8, 9]. Similarly Zn-interstitial is a shallow donor [10], but it has high formation energy in n-type ZnO, hence the required conductivity of ZnO is not possible [11, 12]. Moreover, simulation study has also been performed on the intrinsic donor nature of complexes and it was found that V_O–Zn_i complex, in particular, has the lowest formation energy in n-type ZnO [13]. For example Kim *et al* [14] theoretically calculated the formation energy of V_O–Zn_i complex as a strong candidate for native shallow donor in ZnO lattice. Furthermore, Kim *et al* [15] theoretically proposed that V_O–Zn_i complex might be the real origin of n-type conductivity of ZnO but no experimental evidence is available in the literature so far.

In this paper, we explored the response of V_O–Zn_i complex when ZnO samples annealed under oxygen- and zinc-rich environment. A series of experiments revealed that free donor concentration of ZnO annealed in oxygen, decreased exponentially. In comparison with the available theoretical calculations, we understand that V_O–Zn_i complex could be

the real origin of intrinsic n-type conductivity of ZnO. In the following experimental details, results, and discussion with concluding remarks are described in sections 2–4, respectively.

2. Experimental

ZnO thin films were grown on a three-inch p-type Si (0 0 1) wafer by molecular beam epitaxy. Temperature of the effusion cell of Zn was deliberately maintained higher for Zn-rich growth of ZnO; further detail can be found in [16]. The thickness of the grown wafer was calculated by profilometer and was found to be 1.6 μm. After deposition a representative wafer was cut into 1 cm $\times$ 1 cm small pieces, each piece hereafter will be referred as sample A, B, C, D, E, F and G. Samples (A–D) were annealed in oxygen environment at temperature 500–800 °C keeping step as 100 °C for 1 h, respectively. Purposely, further annealing of ZnO fresh pieces (E–H) was performed at 600 °C for 1 h, under zinc vapors, vacuum, and successively in vacuum and zinc vapor environment, respectively.

For electrical measurements, indium Ohmic contacts (1 mm diameter) on four corners of size 1 $\times$ 1 cm^2 were prepared. The characterization of various samples was carried out by the following equipment; x-ray diffraction (XRD) (PANalytic^{TM}) using Cu-α radiation as x-ray source with wavelength 1.54 Å, photoluminescence (PL) (HORIBA^{TM}) using laser wavelength 325 nm, Hall measurements (Ecopia 3000 Hall measurement System^{TM}) using magnetic field 0.5 T and SEM/EDAX from Joule^{TM}.

3. Results and discussion

3.1. X-ray diffraction

XRD, Raman scattering, energy dispersive spectroscopy (EDS) and PL are well known diagnostic techniques for structural characterization of as-grown layers. Figure 1 demonstrates typical XRD pattern of a representative as-grown ZnO layer: three peaks were observed and associated with (0 0 2), (1 0 1) and (0 0 4) planes of hexagonal ZnO structure preferably oriented along *c*-axis i.e. (0 0 2) [17]. Full-width half- maximum (FWHM) of all samples annealed in oxygen environment at different temperatures for 1 h was calculated and the plot of annealing temperature verses FWHM of (0 0 2) plane of ZnO is shown in the inset of figure 1. The crystal quality improved with annealing temperature as the FWHM decreased as annealing temperature increased from 500 to 800 °C.

3.2. PL measurements

Figure 2 displays PL spectra of various samples annealed at different temperatures in oxygen environment. The legend lists various annealing temperatures. The spectrum revealed a peak at 3.28 eV related with band-edge emission [18]. As a matter of fact, the intensity of band-edge emission is directly related with the quality of grown film [19]. Most of the oxygen vacancy related defects are compensated with incoming oxygen as the

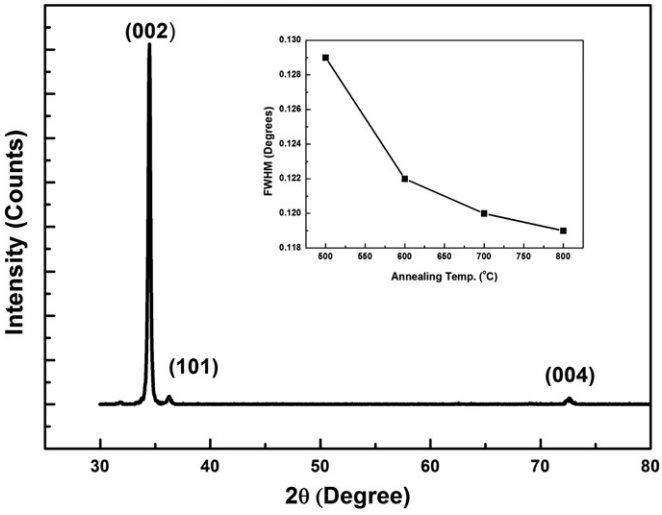

Figure 1. A typical XRD pattern of the as-grown ZnO layer (0.5 μm thick). The (0 0 2) peak is dominant, showing that growth is along *c*-axis. Inset shows the relationship of annealing temperature and FWHM of ZnO (0 0 2) plane.

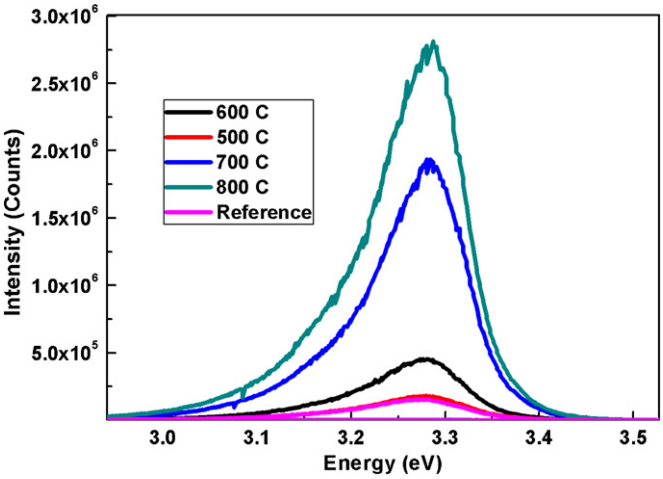

Figure 2. Photoluminescence spectra of samples annealed in oxygen environment for 1 h at different temperatures recorded at room temperature. The spectrum shows strong dependence of band-edge emission on annealing temperature.

annealing temperature increases from 500 to 800 °C, therefore the intensity of band-edge emission increased and crystal quality improved.

3.3. Hall measurements

Kim *et al*, using theoretical calculations, suggested that V_O–Zn_i complex could be the actual source of n-type conductivity and/or free electron carriers (N_D) in bulk ZnO layer. To reconcile with the theoretical calculations, electrical parameters e.g., free carrier concentration (N_D), mobility (μ) and resistivity (ρ) are useful. We used Hall measurements (four probe method) to extract these parameters from our ZnO samples labeled as A–G purposely, annealed under specific environments. Out of seven, four similar samples (A–D) of ZnO were separately annealed in oxygen environment at

Table 1. Effect of annealing environment on carrier concentration, mobility and resistivity of MBE grown Zn-rich ZnO annealed at 600 °C for 1 h.

Annealing environment	Carrier concentration (cm^{-3})	Mobility ($cm\ V^{-1}\ s^{-1}$)	Resistivity (Ω cm)	Conduction type
Un-annealed	6.23×10^{18}	0.52	1.90	N
Oxygen	3.97×10^{17}	2.397	6.55	N
Vacuum	7.89×10^{18}	6.88	1.48×10^{-1}	N
Zinc	1.56×10^{19}	23.55	1.699×10^{-2}	N
Vacuum + Zn	5.11×10^{19}	2.255	5.41×10^{-2}	N

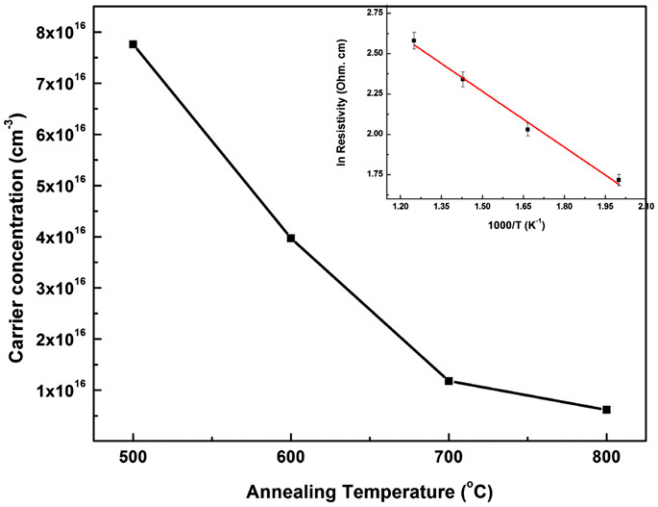

Figure 3. Dependence of carrier concentration on the annealing temperature. The carrier concentration decreases as annealing temperature increases from 500 to 800 °C with steps of 100 °C. The linear fit of 1000/T versus log Resistivity is shown in the inset, which gives the binding/dissociation energy of V_O–Zn_i complex.

temperatures 500 °C, 600 °C, 700 °C and 800 °C, respectively. Hall measurements demonstrated all samples to have n-type conductivity. Temperature-dependent data of N_D and ρ were seen to decrease exponentially with the increase of temperature from 500 to 800 °C. It is pertinent to mention here that as the grown ZnO films are n-type and Si substrate is p-type, therefore, a p–n junction is developed at the interface which acts as an insulating layer, which is why using Si substrate will not affect Hall measurements and/or could be in the tolerance limit [20].

Figure 3 displays the effect of annealing temperature on the carrier concentration. The carrier concentration decreased from 6.23×10^{18}–$6.15 \times 10^{16}\ cm^{-3}$ as annealing temperature increased from 500–800 °C. Understandably, the carrier concentration is directly related to Zn_i–V_O complex. As the concentration of this complex increases, the carrier concentration is also increased. The observed result can be explained by two-step process: (i) incoming oxygen fills V_O of V_O–Zn_i complex leaving behind Zn_i; (ii) Zn_i releases its energy and moves to a lower energy state with respect to the conduction band minima and/or occupies an inactive location. This type of interaction is also supported by literature [21, 22]. The physical mechanism of the formation of Zn_i–V_O complex was explained by Kim *et al* [15]. They theoretically proved that there is a strong interaction between two donor-like defects i.e. Zn-interstitials and O vacancies. The driving force for this attractive interaction between two donors is the quantum mechanical hybridization between the electronic orbitals of their deep and shallow states, described by Kim *et al*. This attractive interaction results in large reduction of total energy of the system ZnO leaving behind a large amount of Zn_i–V_O complex to explain the high n-type carrier concentration N_D. Furthermore, literature indicates that under oxygen environment, because oxygen vacancies are supposed to be filled 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, subsequent decrease in N_D is acceptable which is consistent with Kim *et al* calculations. To strengthen our results, we prepared Arrhenius plot of logarithm (resistivity) as a function of 1000/T and worked out activation energy (shown in the inset of figure 3) of the intrinsic defect associated with V_O–Zn_i complex which surprisingly happened to be the reported activation energy of V_O–Zn_i complex i.e. 1.22 eV [15]. This result confirms theoretical predictions related with V_O–Zn_i complex involvement in free carrier concentration in ZnO lattice.

On the other hand, annealing of samples E, F and G in Zn, vacuum and successively in Zn environment under vacuum, respectively, resulted in an increase in N_D as shown in table 1, which means that incoming Zn ions might have found inactive V_O to form more V_O–Zn_i complex entities in the structures. This argument is in line with the peculiar ZnO structure, where a lot of space is available to accommodate foreign species [3] and hence N_D increases. Furthermore, theoretical calculations appearing the in literature revealed that oxygen vacancies are deep donors in the bandgap of ZnO with lowest formation energy among the intrinsic defects in n-type ZnO [5]. While Zn-interstitials defects are shallow donors but their formation energy in n-type ZnO is very high [16], therefore, intrinsic n-type ZnO would have high density of V_O together with a small density of Zn-interstitials. Hence, a small increase in carrier concentration with annealing in vacuum and about two orders increase in carrier concentration when annealed in Zn are justified.

To verify our results, we prepared four samples of ZnO with Zn/O atomic percentage ratio 52/48, 53/47, 54/46 and 55/45 and hereafter called samples H, I, J and K, respectively, not shown here. It is pertinent to mention here that all samples (H–K) exhibited well-defined structures of ZnO as explored using XRD, PL and Raman scattering techniques. As ZnO has hexagonal structure with half of the tetrahedral sites occupied by Zn atom, whereas all the octahedral sites are empty, hence,

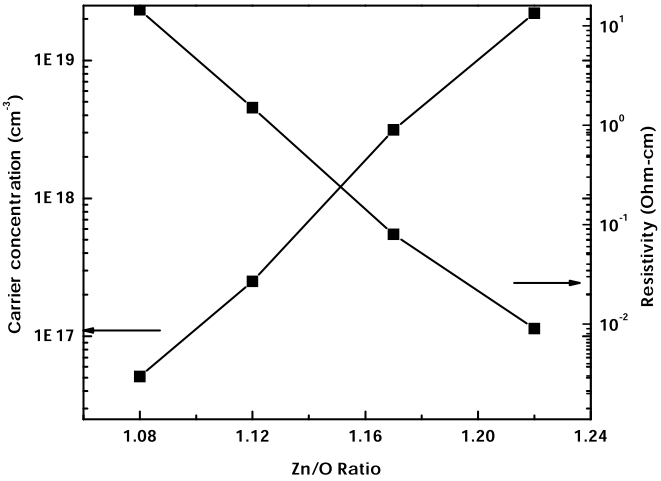

Figure 4. The plot shows the dependence of carrier concentration and resistivity on Zn/O ratio. The graph is evidence that with increasing Zn/O ratio, the carrier concentration increases and resistivity decreases.

there are plenty of sites for ZnO to accommodate intrinsic (Zn-interstitials, O-vacancy and/or Zn-antisite) [23] and extrinsic defects as well. Zinc, being in larger quantity in all samples (H–K), demonstrated by EDX measurements (not shown here) therefore, occupies the interstitials sites referred as Zn_i [24]. Thereafter, Zn_i forms a complex with V_O and therefore the density of V_O–Zn_i complex increases with Zn/O ratio.

Figure 4 above demonstrates the effect of Zn/O ratio on carrier concentration and resistivity of samples in the measurement range. With increasing Zn/O ratio in the samples, the carrier concentration increases and resistivity of samples decreases. The carrier concentration increased from $5.0 \times 10^{16}\,\mathrm{cm}^{-3}$ to $2.2 \times 10^{19}\,\mathrm{cm}^{-3}$ and resistivity decreased from 14.4 to 0.009 Ω cm for samples with increasing Zn/O ratio from 1.08 to 1.22, respectively. These Zn-interstitials in combination with V_O form (V_O–Zn_i), which gives conduction electrons to conduction band, therefore carrier concentration increases significantly.

4. Conclusion

In this paper we investigated and explored the response of V_O–Zn_i complex when ZnO samples were annealed under oxygen and zinc environment. A series of experiments revealed that free donor concentration of ZnO annealed in oxygen, decreased exponentially. This observation was further strengthened by annealing representative pieces of sample (ZnO) under Zn, vacuum and vacuum and Zn environments at 600 °C and interestingly found an increase in the free electron concentration. Similar results were found in samples having sequentially larger Zn/O ratios. This observation is attributed to the increase of V_O–Zn_i complex involving extrinsic Zn and intrinsic inactive V_O and/or generation of new V_O possibly because of out-diffusion of O. In comparison with the available theoretical calculations, we conclude that V_O–Zn_i complex could be the real origin of intrinsic n-type conductivity of ZnO.

Acknowledgments

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