

## Nature of Native Defects in ZnO

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This study revealed the nature of native defects and their roles in ZnO through positron annihilation and optical transmission measurements. It showed oxygen vacancies are the origin for the shift in the optical absorption band that causes the red or orange coloration. It also revealed experimental evidence that the donor nature of oxygen vacancy is  $\sim 0.7$  eV. In addition, this work showed the Zn interstitial was not the donor in the as-grown ZnO and supported recent calculations that predicted hydrogen in an oxygen vacancy forms multicenter bonds and acts as a shallow donor.

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ZnO and, in general, wide band gap semiconductors have experienced difficulties in both  $n$  and  $p$  type doping. There is normally one type of doping which is difficult to achieve. These difficulties have been attributed to the compensation by native point defects or to lattice relaxations that cause the dopants to have deep energy level [1]. The location of dopants atoms on interstitial sites has also been suggested to be the origin of the doping difficulties in some cases [2]. ZnO, with its wide band gap, has numerous potential applications [3] that have been hindered by the lack of control over the electrical conductivity and the resistance to the formation of  $p$  type. Despite the number of studies on ZnO (e.g., [4–9]), many fundamental issues remain unresolved. The reason behind the difficulty of obtaining shallow acceptors remains unresolved. The nature of native shallow donors in ZnO and the dependence of luminescence and optical absorption on the environmental conditions are still subjects of controversy [7–11]. Oxygen vacancies ( $O_v$ ), Zn interstitials ( $Zn_i$ ), and hydrogen background impurities have been suggested as candidates for the native donors in ZnO. The role of hydrogen as a shallow donor has been supported by theoretical and experimental evidence [7,10]. Electron irradiation study has suggested Zn interstitial is the dominant native donor in ZnO [8]. The role of  $O_v$  as a shallow donor has been widely discussed [9,11], but no agreement has been reached. First-principles calculations [12] predicted that while isolated  $O_v$  are relative deep donors in ZnO, they are not the major shallow donor and not responsible for the  $n$ -type conductivity. However, no clear experimental evidence has supported this prediction.

Research at Washington State University has identified the defects associated with heating of ZnO in different environments and investigated their potential as the dominant native donor in ZnO. Experimental evidence is presented to demonstrate  $O_v$  are the source for the shift in the optical absorption band that causes the red coloration in ZnO crystals after heating in Zn vapor [5]. From the present measurements, it is consistent this shift in the absorption band is  $\sim 0.7$  eV which indicated  $O_v$  are deep

donors in ZnO. This was consistent with the first principle calculations [12]. Data also suggested  $Zn_i$  cannot be accountable for the  $n$ -type conductivity in ZnO and supported recent calculations [13] that predicted hydrogen may occupy an oxygen sublattice and act as a shallow donor. Research also demonstrated different types of vacancies can be generated and controlled which may facilitate the doping process. In this investigation, optical transmission measurements were applied with positron annihilation spectroscopy (PAS) [14] which is well suited to identify neutral or negatively charged vacancy type defects in semiconductors. Because of the lack of positive ion cores, vacancy type defects form an attractive potential that traps positrons and leads to characteristic changes in the measured annihilation parameters.

Commercial undoped ZnO single crystals were used. The as-grown samples were clear. Samples were sealed in an evacuated quartz ampoule with Zn, Ti, or Zr metal and heated to temperatures ranging from 900–1100 °C for various times. Annealing with Zn at 1100 °C caused the ZnO samples to turn orange or red as previously reported [5]. Figure 1 shows the optical transmission spectra for the as-grown and annealed samples measured at room temperature. The edge shifted from 390 to 500 nm after heating in Zn vapor and caused the red coloration. Depth resolved measurements of PAS Doppler broadening [14] were performed to investigate the source of the shift. The 511 keV annihilation peak was recorded using a HPGe detector. The  $S$  parameter [14], which is sensitive to the annihilation fraction with low momentum valence electrons, was used to characterize the annihilation peak. It was obtained by dividing the counts in the central region to the total counts in the peak. Trapped positrons at defects are more likely to annihilate with low momentum valence electrons causing an increase in  $S$ .  $S$  is displayed in Fig. 2 as a function of incident positron energy ( $E$ ) and mean implantation depth.  $S$  is normalized to the minimum  $S$  bulk obtained for defect free ZnO single crystals. The high values of  $S$  at low energies ( $E < 5$  keV) were associated to positronium formation at the surface.  $S$  in the bulk

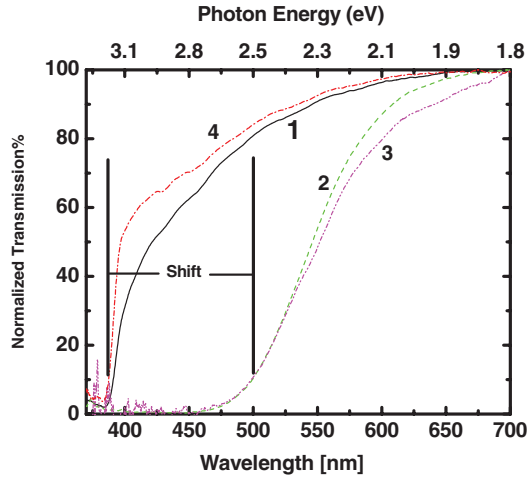


FIG. 1 (color). Optical transmission spectra measured at room temperature for ZnO single crystals annealed in various environments. Curve 1: as-grown, curve 2: Zn-vapor anneal, curve 3: Ti-vapor anneal, curve 4: Zn anneal followed by O anneal. The spectra are normalized to the transmission at 700 nm.

region ( $E > 15$  keV) did not exhibit any increase after heating in Zn vapor which indicated those defects created by annealing (the defects associated with the appearance of red color) were not effective positron traps. This would be consistent with isolated  $O_v$ ,  $Zn_i$ , or Zn antisites on the oxygen sublattice. A Zn vacancy with its negative charge state is an effective trapping center for positrons [15]. If there were zinc vacancies ( $Zn_v$ ) in the as-grown sample, they would be filled with Zn after annealing in Zn vapor, which would lead to a decrease in  $S$  bulk [6,15]. Since Fig. 2 showed similar  $S$  bulk before and after annealing in

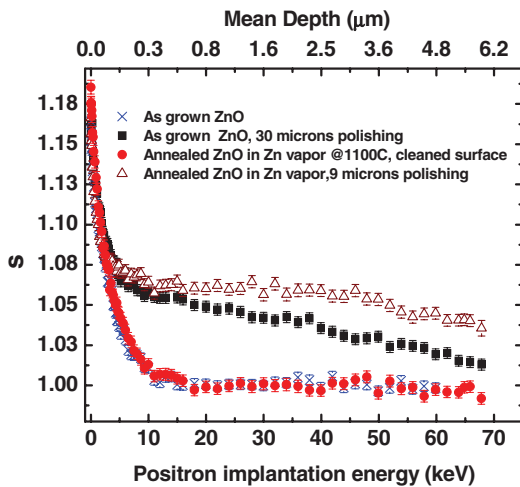


FIG. 2 (color). Open-volume defect parameter ( $S$ ) as a function of positron implantation energy ( $E$ ), which is associated with the mean implantation depth [14].  $S$  is normalized to the minimum  $S_{\text{bulk}}$  obtained for defect free ZnO single crystals. Polishing was carried out to create open-volume defects including  $Zn_v$ .

Zn, it was concluded  $Zn_v$  was not present in the as-grown sample or its concentration was below the detection limit by positrons. The detection limit is reported to be  $2 \times 10^{15} \text{ cm}^{-3}$  for  $Zn_v$  in ZnO [6].

To investigate the possibility of forming  $Zn_i$  by heating in Zn vapor, the following procedure was conducted. A few samples were polished to roughen the surface and create subsurface damage and the positron measurements were repeated. The large increase in  $S$  after polishing (Fig. 2), for the two samples (as-grown and Zn-vapor annealed), indicated the introduction of subsurface open-volume defects, not associated with single  $O_v$ , which do not trap positrons. Polishing generated dislocations and vacancy typed defects. The generation of a high density of intrinsic point defects resulting from dislocation motion has been reported for GaN [16]. The formation of  $Zn_v$  in ZnO after mechanical polishing has been previously confirmed [17] and believed to be induced from dislocation motions. The current measurements showed the creation of vacancy type defects after polishing including  $Zn_v$  (effective traps for positrons). Figure 2 shows the extension of those defects to  $5 \mu\text{m}$  depth. In addition, fitting of the data points indicated that those damage induced by polishing extend in the bulk up to  $30 \mu\text{m}$ . Annealing in a vacuum at  $200^\circ\text{C}$ ,  $400^\circ\text{C}$ , and  $500^\circ\text{C}$  was performed on the two polished samples (as-grown and Zn-annealed). Further annealing in N at  $500^\circ\text{C}$ ,  $700^\circ\text{C}$ , and  $800^\circ\text{C}$  was performed on the Zn-annealed polished sample.  $S_{\text{bulk}}$  at room temperature was almost the same [Fig. 3(a)] before and after annealing to  $450^\circ\text{C}$  for the polished as-grown (clear) sample. Figure 3(a) also displays the  $S$ - $E$  curves measured at  $200^\circ\text{C}$  and  $450^\circ\text{C}$ . It can be seen that  $S$  had higher values below  $20$  keV at  $450^\circ\text{C}$ . This was an indicator the depth profiling of the induced damage by polishing was temperature dependent. Defects moved towards the surface at high temperature. Movement started at  $300^\circ\text{C}$  (not shown in the graph) which is the reported annealing temperature for some point defects in ZnO [15]. The Zn-annealed polished (red) sample showed a different behavior [Fig. 3(b)]. A large nonlinear increase of  $S$  with annealing temperature was indicated. This large increase was associated with positron annihilation at increasing vacancy clusters with rising temperature. Vacancies diffused and formed vacancy clusters and reached its maximum size at  $500^\circ\text{C}$ . Recovery of those clusters started at  $700^\circ\text{C}$ . We have confirmed the formation of  $Zn_v$  in this sample after polishing. If Zn interstitials were present in the sample and accounted for the red color, annealing at high temperature in a vacuum or N would allow them to diffuse,  $S$  would decrease. However,  $S$  showed an increase with annealing temperature. As seen from Figs. 3(a) and 3(b), the formation of vacancy clusters after heating was only significant in the damaged Zn-annealed sample. This may be explained by the presence of high concentrations of both  $O_v$  and metal (Zn) vacancies that diffuse and form clusters at high tem-

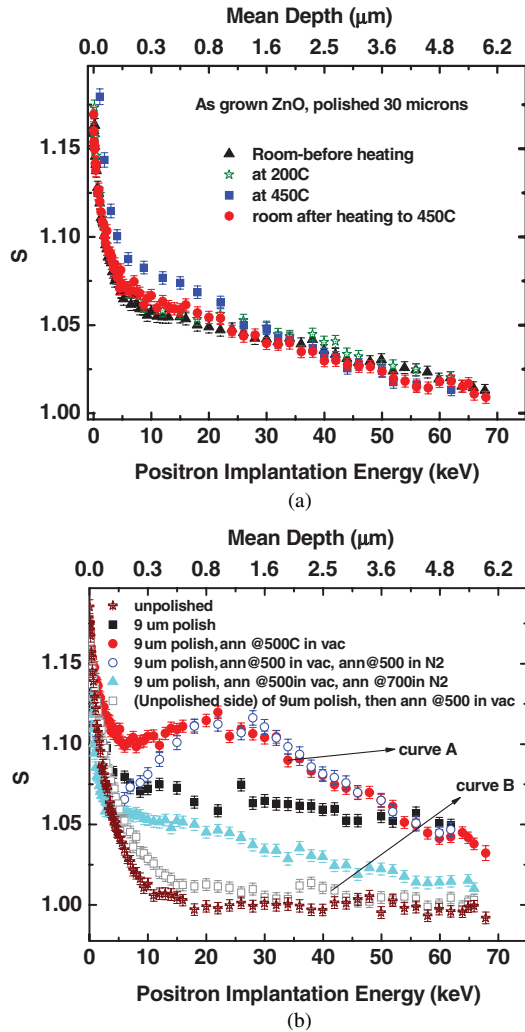


FIG. 3 (color). (a) Open-volume defect parameter ( $S$ ) for polished as-grown ZnO (clear sample) before and after annealing in vacuum at 450 °C. No significant effect of annealing up to 450 °C on the open-volume defects created by polishing. The graph also shows  $S$ - $E$  curves measured at 200 °C and 450 °C. (b) Effect of subsequent annealing on the Zn vapor annealed polished sample (red sample). Note the measurements were made at room temperature after each anneal. All of the shown samples were previously annealed in Zn vapor. Large vacancy clusters were formed during annealing up to 500 °C and started to anneal out at 700 °C. None of these changes altered the red color of the sample. Note curve A and curve B represent the polished and unpolished side for the same sample after annealing up to 500 °C. No vacancy cluster formation appeared in the unpolished side because of the absence of  $Zn_v$ .

peratures [18]. These measurements proved  $Zn_i$  were not present in the damaged ZnO layers (previously annealed in Zn vapor). Thus, the Zn-vapor anneal did not create  $Zn_i$  in those layers or in the bulk.

Annealing in O at 1100 °C for one-half hour turned the red ZnO sample to a colorless sample again which indicated  $O_v$  as the dominate candidate for the source of red color. To confirm this conclusion and exclude the possibil-

ity of the formation of Zn antisite on the oxygen sublattice, another clear as-grown ZnO sample was sealed in an evacuated ampoule with Ti metal and annealed it at 1100 °C for one-half hour. The Ti metal was changed to Ti oxide and the ZnO sample became red. Ti was added to reduce ZnO or capture evaporated O atoms leaving  $O_v$  behind in ZnO. Energy dispersive x-ray (EDX) measurements showed no traces of Ti metals in the ZnO sample after annealing. Annealing of another ZnO sample with Zr metal at 1100 °C also produced the red color and confirmed the role of  $O_v$ . The normalized optical transmission spectra of the Zn-anneal followed by the O-anneal sample and the Ti-anneal sample are shown in Fig. 1 with the as-grown and Zn-anneal samples. These measurements provide further support the edge shift in the transmission spectra is associated with the formation of  $O_v$ . This shift was  $\sim 0.7$  eV as shown in Fig. 1 and suggested an  $O_v$  has a relatively deep level below the conduction band. Annealing of as-grown clear ZnO in Ar at 1100 °C and in a vacuum at 1300 °C without Zn, Ti, or Zr that captures O atoms did not produce the red color which indicated  $O_v$  were not formed in this case.

Figure 4 compares positron measurements for 3 samples: annealed in Zn vapor, annealed in Zn vapor followed by O anneal, and annealed with Ti. The difference between the three curves at low energies was due to surface effects. This research confirmed the formation of  $O_v$  after annealing in Zn or Ti vapor. However,  $O_v$  in a positive charge state at room temperature would not trap positrons and  $S_{bulk}$  would be similar to defect-free ZnO [15]. There was an increase in  $S_{bulk}$  and a large decrease in the positron diffusion length ( $L_+$ ) after annealing in O which suggested the presence of effective positron traps ( $Zn_v$ ). Short  $L_+$  is

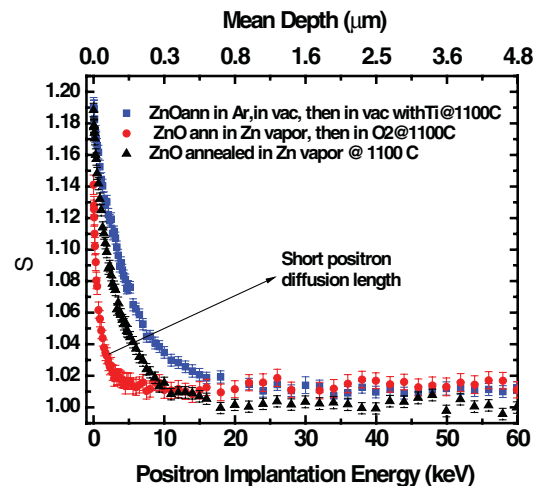


FIG. 4 (color). Effect of various annealing environments on open-volume defect parameter ( $S$ ). Annealing in Zn vapor or Ti vapor created the red color and annealing in O removed it. The graph indicates an increase in  $S_{bulk}$  and a short  $L_+$  after annealing in O, which is attributed to the formation of  $Zn_v$ .

another indicator of positron trapping at defects [14]. It can be evaluated from the  $S$ - $E$  curves (Fig. 4). The O-anneal curve showed  $L_+$  of  $\sim 13 \pm 2$  nm, whereas the extracted  $L_+$  for the as-grown and Zn-annealed samples was in the range of 60 nm. The decrease in  $L_+$  and increase in positron trapping after O-anneal strongly indicate the formation of  $Zn_v$ . This is consistent with the predicted lower formation energy of  $Zn_v$  in O-rich conditions [19].

Based on the data and interpretation of positron measurements, annealing in Zn vapor did not generate  $Zn_i$  which led to an important conclusion.  $Zn_i$  were not formed in Zn-rich thermal environment. Instead, Zn vapor was thermodynamically favored to bind to O atoms and it formed new ZnO. This indicated they are not the dominant native donors in ZnO. By confirming a deep level below the conduction band for  $O_v$ , considering very low concentration of  $O_v$  in the stoichiometric clear ZnO, and excluding  $Zn_i$  as dominant defect in ZnO crystals, hydrogen would be the most likely candidate for the dominant shallow donor in ZnO. Hydrogen is known to be very difficult to remove from the growth or annealing environment [7]. However, it has been reported the carrier concentration and conductivity increase after Zn-vapor anneal [5]. This increase cannot be explained based on the above conclusion. Hall-effects measurements also showed a carrier concentration increase by a factor of 2 for the sample annealed with Ti. Also shown was a 50% reduction in the concentration, relative to the as-grown for the sample annealed with Ti followed by O anneal. Since Ti is known to be a strong absorber for hydrogen, it was concluded that reduction in carrier concentration can be realized by filling  $O_v$  and reducing hydrogen impurities. This behavior can be interpreted by assuming a complex of the O vacancy and hydrogen may form and act as a shallow donor. This picture is consistent with recent calculations [13] showing hydrogen forms multicenter bonds in the center of  $O_v$  with an antibonding state in the conduction state which makes this complex an active shallow donor. These calculations also showed hydrogen in this configuration is highly stable whereas hydrogen as an interstitial is unstable at high temperature.

In summary, strong evidence has been presented showing  $O_v$  are behind the shift in the optical absorption band that produces the red coloration in ZnO under Zn-rich anneals. This shift was found to be in the average of 0.7 eV confirming the relatively deep donor nature of  $O_v$ . Research also demonstrated that  $Zn_i$  are not likely to form in ZnO and cannot account for the background  $n$ -type conductivity. Hydrogen as interstitial or in vacancy is the source for this conductivity. This study also demonstrated the difficulty of creating high concentrations of  $O_v$  in stoichiometry ZnO. This might contribute to the difficulty

of  $p$  doping with N, P, and As. Although few studies have reported the formation of  $p$  type by N, P, and As doping, failure of doping by the same dopants has been also reported (e.g., [20]). This may be attributed to their incorporation as interstitials or substitutions of Zn atoms instead of substitutions of O atoms. It is suggested doping of red ZnO crystals, which contain high concentrations of  $O_v$ , with N may overcome this problem. With regard to P and As, it has been reported their incorporation on Zn sub lattices can produce  $p$  type by forming shallow acceptors of  $Zn_v$  next to the dopant [4]. Annealing in O at high temperature produces O-rich ZnO containing  $Zn_v$  which has been confirmed by the current measurements. Samples with high concentrations of  $Zn_v$  might be suitable to form the  $p$  type by Cu or Ag doping.

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