Vacancy cluster in ZnO films grown by pulsed laser deposition

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Undoped and Ga-doped ZnO films were grown on c-sapphire using pulsed laser deposition (PLD) at the substrate temperature of 600 °C. Positron annihilation spectroscopy study (PAS) shows that the dominant Vzn-related defect in the as-grown undoped ZnO grown with relative low oxygen pressure P(O2) is a vacancy cluster (most likely a Vzn-nVo complex with n = 2, 3) rather than the isolated Vzn, which has a lower formation energy. Annealing these samples at 900 °C induces out-diffusion of Zn from the ZnO film into the sapphire creating the Vzn at the film/sapphire interface, which favors the formation of vacancy cluster containing relatively more Vzn. Increasing the P(O2) during growth also lead to the formation of the vacancy cluster with relatively more Vzn. For Ga-doped ZnO films, the oxygen pressure during growth has significant influence on the electron concentration and the microstructure of the Vzn-related defect. Green luminescence (GL) and yellow luminescence (YL) were identified in the cathodoluminescence study (CL) study, and both emission bands were quenched after hydrogen plasma treatment. The origin of the GL is discussed.

Zinc oxide is a wide band gap semiconductor having a direct bandgap of 3.33 eV that finds a variety of potential applications involving ultra-violet (UV) optoelectronic, spintronic, sensor and photovoltaic technologies. ZnO has a high exciton density due to its large binding energy (~60 meV). Consequently ZnO is considered to be an excellent optoelectronic material for fabricating light emitting diodes and laser diodes operating in the UV spectral wavelength range. However, the development of ZnO-based optoelectronic devices is hindered by the asymmetric doping difficulty in ZnO, where the growth of n-type is straightforward while p-type remains a considerable challenge. Recent studies suggest that p-type conductivity could be achieved in ZnO using intrinsic point defect complexes as shallow acceptors rather than the usual atomic substitution by dopants. Implementation of this approach requires the development of fabrication procedures that provide precise control of the growth environment and a detailed knowledge of native point defects in ZnO. However, the nature of intrinsic point and complex defects in ZnO is poorly understood and remains controversial to date. For example, most first principal calculations report that V0 is a deep negative-U donor, but there is disagreement on whether V0 is present in n-type ZnO (ref. and references therein). In undoped ZnO, Vzn is shown to be a dominant compensating acceptor in the as-grown material. Consequently, the incorporation of Vzn, V0 and their defect complexes should significantly change the electrical, optical and magnetic properties of ZnO. Conversely, ZnO films doped with group III metals like Ga and Al can have low electrical resistivity and high optical transmittance, thus are excellent candidates for the transparent electrode applications in photovoltaics, optoelectronics and transparent electronics. Recent studies show that the degenerate doping of Ga in ZnO induces the formation of a high concentration of Vzn-related defect acceptor due to lower Vzn formation energy, which leads to the self-compensation of the n-type doping. There are also theoretical and experimental reports on the formation of shallow acceptor complex (AsZnVzn) in As-doped ZnO and similar complexes in P and Sb doped ZnO. Additionally, the Vzn and V0 has been suggested to be associated with the room temperature ferromagnetism observed in undoped ZnO and transition metal doped ZnO. However, there are relatively few reports on the study of vacancy clusters in ZnO. Significantly the majority of these studies identified vacancy cluster induced during ion-implantation and the subsequent annealing in the ZnO samples, rather than in both as-grown and annealed non-irradiated samples.

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Two control samples with moderate electron concentrations and higher P(O$_2$) were also fabricated. One is the co-doped ZnO sample grown by the target with Cu content 0.02% and Ga content 1% in weight ratio) and ZnO:Ga:Cu (Ga and Cu contents = 1% and 2% respectively in weight) with P(O$_2$) = 0.02 Pa. Two control samples with moderate electron concentrations and higher P(O$_2$) were also fabricated. One is the Cu-doped ZnO sample grown by the target with Cu content = 2% weight ratio at P(O$_2$) = 0.02 Pa. The other control sample is the Ga-Cu co-doped ZnO sample grown with the same weight ratio of Ga and Cu as the degenerate Ga-Cu co-doped but with high P(O$_2$) = 0.5 Pa and this yielded a Ga-Cu co-doped ZnO sample with moderate electron concentration. Isochronal annealing was carried out in a tube furnace for the time period of 40 minutes in Ar atmosphere over a temperature range of 700 °C to 900 °C. The XRD measurements were performed using a Siemens D5000 diffractometer with the CuK$_\alpha$ line. Room temperature Hall effect measurements were made using the Accent HL-5500PC system. High resolution transmission electron microscopy (HRTEM) and a JEOL 2010F HRTEM was used to study the film/substrate interface of the sample.

The electron concentrations for the as-grown ZnO films (undoped, Cu-doped, Ga-doped and Cu-Ga co-doped) grown at different oxygen pressure are presented in Table 1. The undoped ZnO films grown with P(O$_2$) = 0 to 5 Pa and the Cu-doped film (2 wt% in the deposition target) grown with P(O$_2$) = 0.02 Pa have electron concentrations of 3–8 × 10$^{18}$ cm$^{-3}$ (±1 × 10$^{18}$ cm$^{-3}$). For the Ga-doped (1 wt%) and Ga(1 wt%)-Cu(2 wt%) co-doped ZnO films grown at P(O$_2$) = 0.02 Pa, the electron concentration is much higher, n$^+$ = 4 × 10$^{18}$ cm$^{-3}$ since Ga is a shallow donor in ZnO. However, growing the Ga(1 wt%)-Cu(2 wt%) co-doped ZnO samples at a higher P(O$_2$) of 0.02 Pa. Figure 2 shows the electron concentration (n) and mobility (μ) of the undoped ZnO samples grown with P(O$_2$) = 0 and 1 Pa as a function of the annealing temperature. For the sample grown without oxygen, the electron concentration, n, is 6 × 10$^{18}$ cm$^{-3}$ for the as-grown sample, and it decreases to 2 × 10$^{17}$ cm$^{-3}$ after annealing at 650°C. No significant change in the carrier concentration was observed with increasing annealing temperature.
up to 800 °C. However, further increase of the annealing temperature to 900 °C was found to increase the carrier concentration to ~4 × 10^{18} \text{ cm}^{-3}. The electron mobility, \( \mu \), was observed to increase from ~35 cm\text{V}^{-2}\text{s}^{-1} for the as-grown sample to ~70 cm\text{V}^{-2}\text{s}^{-1} after annealing at 700 °C. No change in the mobility was found when the annealing temperature was increased to 800 °C, however, an increase to 81 cm\text{V}^{-2}\text{s}^{-1} occurred at 900 °C. Similar changes in n and \( \mu \) with increasing annealing temperature were found in the undoped ZnO sample grown with P(O_2) = 1 Pa.

PAS is selectively sensitive to Zn-vacancy related defects in ZnO\textsuperscript{16}. Depth profiling of S and W-parameters were conducted on the ZnO films fabricated with different P(O_2), annealed with different temperatures and with different dopings. Typical S-parameter versus positron incident energy (S-E) plots for the undoped ZnO grown with P(O_2) = 0.02 Pa, the Ga-doped (1%) ZnO grown with P(O_2) = 0.02 Pa and the sapphire substrate, are shown in Fig. 3. The mean positron implanted depth is given by \( x = A E^{1/2} / \rho \), where \( \rho \) is the materials density and \( A = 4.0 \)

| Oxygen Pressure (Pa) | n (cm\textsuperscript{-3}) |
|----------------------|--------------------------|
| ZnO                  |                          |
| 0                    | 6 × 10\textsuperscript{18} |
| 0.02                 | 6 × 10\textsuperscript{18} |
| 1                    | 3 × 10\textsuperscript{18} |
| 5                    | 8 × 10\textsuperscript{18} |
| Cu-doped ZnO (2%)    |                          |
| 0.02                 | 3 × 10\textsuperscript{18} |
| Ga-doped ZnO (1%)    |                          |
| 0.02                 | 6 × 10\textsuperscript{18} |
| Cu, Ga co-doped ZnO (Cu 2%, Ga 1%) | 0.02 | 4 × 10\textsuperscript{18} |
| Cu, Ga co-doped ZnO (Cu 2%, Ga 1%) | 0.5 | 8 × 10\textsuperscript{18} |

Table 1. The electron concentrations of the as-grown undoped ZnO, ZnO:Cu(2%), ZnO:Ga(1%) and ZnO:Ga(1%):Cu(2%) samples grown with different oxygen pressures.
The $S$-curves of the two ZnO/sapphire samples decreased with increasing $E$ for small $E < 2.5$ keV. This is because as $E$ increases, fewer positrons annihilate at the surface and more positrons annihilate in the ZnO film, and the $S$-parameter of the surface is larger than that of the film. For $2.5$ keV $< E < 7$ keV, the $S$-$E$ curves show a plateau indicating that all the implanted positrons annihilated in the film. A further increase of $E$ decreases the $S$-parameter and finally the $S$-parameter saturates at $E \approx 2$ keV, signifying that all positrons are now annihilated inside the sapphire. The average positron implanted depth at the positron incident energy $E = 5$ keV is $\sim 140$ nm. As the film thickness is $\sim 200$–$300$ nm, the leveling off at $\sim 5$ keV of the $S$-$E$ data for the three samples as seen from Fig. 3 characterize the $S$-parameters of the annihilation gamma radiation predominately coming from the corresponding films. Consequently, the $S$ and $W$-parameters obtained for each of the samples were normalized against those acquired from the ZnO single crystal and the $W$-parameters were plotted against the $S$-parameter as shown in Fig. 4. The positron lifetime spectrum of the bulk single crystal used for the normalization reference was well fitted by a single lifetime component of 166 ps, indicating that the sample is close to defect free.$^6,18–20$.

The positrons with energy of 5 keV implanted into the samples are rapidly thermalized inside the film, and undergo diffusion in the delocalized state. Subsequent trapping by a neutral or negatively charged open volume defect, if the defect exists, can then occur annihilating the positron with either a surrounding electron in the delocalized bulk state or the localized defect state. The measured $S$-parameter is given by $S = f_b S_b + \sum_i f_{d,i} S_{d,i}$, where $f_b$ is the fraction of positron annihilating in the delocalized bulk state and $S_b$ is its characteristic $S$-parameter. $S_{d,i}$ and $f_{d,i}$ are respectively the characteristic $S$-parameter and the fraction of positron annihilating in the $i$-th defect state. Similar relation also holds for the $W$-parameter, i.e. $W = f_b W_b + \sum_i f_{d,i} W_{d,i}$. If a single type of defect

Figure 2. Carrier concentrations as a function of the annealing temperature for the undoped ZnO samples grown with $P(O_2) = 0$ and $1$ Pa.

Figure 3. The $S$-parameter versus positron implantation energy ($S$-$E$) plots of the sapphire substrate, the undoped and Ga-doped (1 wt%) ZnO films grown on sapphire with $P(O_2) = 0.02$ Pa.
VZn-related defects other than V1.

Square symbols in Fig. 4) as well as that of the ZnO single crystal lay on a straight line. Linear regression analysis of these data gave a fitted slope of reasonable to conclude that samples belonging to this series result from the same type of VZn-related defect, i.e. (DBS), isolated VZn, VZnVO divacancy, the VZn-rich 2VZn-VO and 4VZn-VO are not easily differentiated by this region.

Doppler broadening parameters (W, S) W-S implies that if there is single type of defect, the W-S lines for VZn-nVO (n=1,2,3) with different configurations are close and lay within the red region.

Figure 4. The W-S parameter plots of the different ZnO films and the error bars of the W-S data are shown at the lower right hand corner. The S and W-parameters are normalized against those of the ZnO single crystal (data included in the figure), which is close to defect-free. The (W,S) data for the as-grown and 750 °C annealed undoped ZnO samples grown with relatively low P(O2) ≤ 1.3 Pa (dark open square) all lay on the straight line V1 (dark line) with excellent fitted R-square (0.99). The (W,S) data of the undoped ZnO samples grown with P(O2) ≤ 1.3 Pa and annealed at 900 °C are denoted by red solid square and are statistically distinguishable from V1 (argument given in text). The (W,S) data of the different Ga and Cu-doped ZnO samples are also included in the figure. Line Mak1 is the characteristic W-S line for VZn-VO and 2VZn-VO given in the theoretical study of Makonen et al.27, for which they are not distinguishable by the DBS. Mak2 is the theoretical W-S line of (VZn)n.

Theoretical W-S lines for VZn-nVO (n=2,3) with different configurations are close and lay within the red region.

VZnrich 4VZn-VO is (~0.75,1.1) which is also adjacent to the line Mak1. The W-S data of the different Ga and Cu-doped ZnO samples are also included in the figure. The (W,S) data of the undoped ZnO samples grown with different oxygen pressures and subjected to different post-growth annealing treatments. It also contains the W-S data points of the ZnO single crystal, the as-grown Cu-doped(Zn%), Ga(1%-doped and Ga(1%) Cu(2%)-co-doped ZnO samples with moderate and degenerate electron concentrations. The experimental error of the S and W-parameter are indicated by the error bars at the lower right-hand corner of Fig. 4. This graph shows that the data points of the as-grown and 750 °C-annealed undoped ZnO films grown with relatively low P(O2) = 0 Pa, 0.02 Pa and 1.3 Pa (black open square symbols in Fig. 4) as well as that of the ZnO single crystal lay on a straight line. Linear regression analysis of these data gave a fitted slope of ~1.88 ± 0.04 with an adjusted R square value of 0.99. Accordingly, it is reasonable to conclude that samples belonging to this series result from the same type of VZn-related defect, i.e. the V1 center. For samples grown with the same P(O2), annealing at 750 °C has the effect of moving the W-S data point along the V1 straight line (i.e. decreasing the S-parameter and increasing the W-parameter), indicating a decrease in the V1 concentration without any change in the defect microstructure.

The W-S data points are observed to move below the V1 straight line (the solid red square symbols in Fig. 4) in these undoped samples grown with relatively low P(O2) when annealed up to 900 °C. The other series of samples, namely the undoped ZnO samples grown with high P(O2) = 5 Pa with different annealing treatments (solid dark circles), and the n+ Ga-doped and Ga-Cu-doped ZnO samples (red solid triangles) also have their W-S data away and below the V1 straight line. As it is noticed that these data points though away from the V1 line but still only marginally separable while considering the experimental error, it is valuable to analyze the corresponding W-S line slopes while joining with the defect-free ZnO single crystal (W,S) data. The W-S data of these samples while joined with the single crystal W-S data have straight lines with slopes between ~2.03 and ~2.20, which is statistically different from that of V1 (~1.88 ± 0.04). It is plausible to conclude that these samples contain VZn-related defects other than V1.

Makonen et al.27 carried out the theoretical study of Doppler broadening on VZn and its relevant clusters in ZnO. It is worthy to compare the present data and the theoretical characteristic W-S lines of the various vacancy clusters. A theoretical W-S straight line of VZn is plotted in Fig. 4 and labelled Mak1, using its characteristic Doppler broadening parameters (W,S)=(0.82,1.06), which was obtained from the W-S plot in ref. 27. It is also found that the theoretical (W,S) data points of the vacancy clusters VZn-VO and 2VZn-VO are closely positioned to those of VZn. The (W,S) values of the VZn-rich 4VZn-VO is ~ (0.75,1.1) which is also adjacent to the line Mak1. Therefore taking into account the resolution (see error bars in Fig. 4) of the Doppler broadening spectroscopy (DBS), isolated VZn, VZn-VO divacancy, the VZn-rich 2VZn-VO and 4VZn-VO are not easily differentiated by this technique. The effect of adding VO to the vacancy cluster would horizontally shift the (W,S) point to the right side (i.e. an increase of S-parameter), while adding a VZn moved the (W,S) point vertically down (i.e. decrease of W-parameter). The 4VZn vacancy cluster has (W,S)=(1.08,0.71) and its corresponding line is included as Mak2 in
nescence at 2.4 eV (shown in Fig. 5(b)). Heating the film at 700 °C reduced the intensity of the YL relative to the annealing at 900 °C (Fig. 1). The Zn out-diffusion from the ZnO film to the sapphire substrate would inevitably on the film/substrate interfaces of the undoped ZnO samples confirm the inter-diffusion at the interface after position (ALD), metalorganic chemical vapor deposition and molecular beam epitaxy (MBE). The vacancy create VZn on the film side. Consequently the VZn-rich environment would lead to the vacancy cluster with micro-

\[ \mu \] theoretical line of VZn-nVO (n = 2,3). It is plausible to suggest that the V1 is the VZn-nVO with n = 2,3.

Using the VEPFIT source code, the effective positron diffusion lengths, L, for these undoped ZnO samples were obtaining by fitting their S-E data with a two-layer model, giving respectively L = 12 to 23 nm (with errors of ±1 nm) depending on P(O2) and annealing temperature. The fitted boundary position coincides well with the physical thicknesses of the films (200–300 nm depending on P(O2)). The defect concentrations, C\text{\textsubscript{D}}, can be estimated by the equation \[ C\text{\textsubscript{D}} = \left( \frac{L_\text{bb}}{L_\text{bb}} \right)^2 - 1 \mu_\text{\textsubscript{T}}, \] where \[ \mu_\text{\textsubscript{T}} \] is the positron diffusion length of the defect free material, \[ \tau_\text{bb} \] is the characteristic bulk lifetime and \[ \mu \] is the positron trapping coefficient. Although \[ \mu \] for VZn-nVO with n = 2,3 is not known precisely, an estimate of the order of magnitude of the VZn-nVO concentration can be obtained using a representative value of \[ \mu \text{\textsubscript{\textit{typ}} = } 10^{18} \text{s}^{-1} \] while \[ \mu \text{\textsubscript{\textit{typ}}} \] is reported to be 3 × 10^{15} s^{-1} for V1 in GaN. Using \[ \tau_\text{bb} \text{ as 166 ps, which is value of the positron lifetime of the single component of the positron lifetime spectrum of our ZnO single crystal, and L,}_\text{bb} \text{~70 nm (values obtained from the ZnO single crystal sample and references 18–22),} \]

\[ C\text{\textsubscript{D}} = \text{\textsubscript{VZn-nVO}} \text{\textsubscript{found in these samples} } \sim 3 \times 10^{17} \text{cm}^{-3} \text{ for taking L,}_\text{bb} \text{~18 nm.} \]

VZn has also been identified in as-grown undoped ZnO single crystals, ZnO films grown by atomic layer deposition (ALD), metalorganic chemical vapor deposition and molecular beam epitaxy (MBE). The vacancy cluster concentration as found in the as-grown PLD grown sample in this work is higher than those found in the single crystal (10^{17} cm^{-3}), but comparable to the films grown by ALD, MOCVD and MBE (10^{17} cm^{-3}). For the undoped ZnO samples grown with relatively low P(O2) (≤ 1.3 Pa) annealing these samples at 900 °C have the effect of shifting the (W,S) points on the V1 line downward into the yellow shaded region. According to theoretical results, this indicates the presence of vacancy clusters having more VZn as relative to the original VZn-nVO after the 900 °C annealing process. Annealing induces diffusion of the Zn vacancies. Once mobile, the Zn vacancy can move to a sink (for example the surface) and vanish or alternatively it can diffuse to another vacancy to form a vacancy cluster. Zn out-diffusion from the ZnO film to the Al2O3 side across a ZnO/Al2O3 interface during annealing has been observed experimentally. Furthermore, our HRTEM and EDXS studies on the film/substrate interfaces of the undoped ZnO samples confirm the inter-diffusion at the interface after annealing at 900 °C (Fig. 1). The Zn out-diffusion from the ZnO film to the sapphire substrate would inevitably create VZn on the film side. Consequently the VZn-rich environment would lead to the vacancy cluster with micro-structure containing more VZn as relative to V1 thus pulling the (W,S) data point vertically down after annealing at 900 °C.

For the ZnO sample series grown with higher P(O2) = 5 Pa (as-grown and annealed, dark circles in Fig. 4), the (W,S) points are all below the V1 straight line and are also located in the yellow shaded region. High P(O2) during O-rich growth may lead to the formation of vacancy cluster with more VZn and less VO, thus pulling down the experimental (W,S) data point. It is worthy to point out that the observed (W,S) parameters in the yellow region do not coincide with any of the theoretical characteristic lines of vacancy clusters. It may be the effect of co-existence of V1 and other VZn-richer vacancy cluster, but of course we cannot exclude the possibility of formation of defects not studied in the theoretical study.

For the Ga doped and Ga-Cu co-doped samples grown at relatively low P(O2) = 0.02 Pa having a degenerate electron concentration of n = 10^{19} cm^{-3}, their (W,S) points also lie within the yellow shaded region. However for the Cu-doped sample grown with the same P(O2) and the Ga-Cu co-doped ZnO sample grown with the higher P(O2) = 0.5 Pa which have n = 10^{18} cm^{-3}, the (W,S) points are positioned on or above the V1 straight line. This implies that with the same Ga doping level, low P(O2) leads to degenerate electron concentration and the formation of a vacancy cluster having more VZn as compared to V1 (i.e. VZn-nVO, n = 2,3). The higher tendency for forming a VZn-rich vacancy cluster in degenerate n samples may be associated with the favorability of VZn in degenerate ZnO, for which enhancement of VZn concentration has been reported in Ga-doped degenerate ZnO samples. However, we cannot exclude the possibility that the difference in the W-S data for the Ga-doped grown in different P(O2) is related to the formation of Ga\textsubscript{\textit{Zn}}-VZn, which as a deep acceptor is more energetically favorable than VZn. Electron paramagnetic resonance (EPR) studies have revealed that Al in ZnO binds with 90% of the electron irradiation induced VZn to form Al\textsubscript{\textit{Zn}}-VZn, in ZnO single crystal. Higher P(O2) during growth may result in more VZn and thus more Ga\textsubscript{\textit{Zn}}-VZn complexes, which seems to be consistent with the observed decrease of electron concentration from 10^{18} cm^{-3} to 10^{15} cm^{-3} in the Ga-codoped ZnO samples when the P(O2) increases from P(O2) = 0.02 Pa to 0.5 Pa. The observation of the (W,S) data shifting up to the V1 line could be expected if the (W,S) characteristic line of the Ga\textsubscript{\textit{Zn}}-VZn is close to V1. Nevertheless, further investigation is needed to confirm this behaviour.

Figure 5(a) shows the CL spectra of the as-grown and annealed ZnO films (grown with P(O2) = 0 Pa) with the electron energy of 5 keV (corresponding to the analysis depth of ~140 nm). Near band edge emission at 3.31 eV and defect emissions are observed in the spectra of all the three samples. Compared to the as-grown sample, the NBE intensity increases by a factor of 3 and 4 respectively after annealing at 700 °C and 900 °C. The defect emissions were fitted by two Gaussian peaks, a yellow luminescence (YL) positioned at 2.0 eV and a green luminescence at 2.4 eV (shown in Fig. 5(b)). Heating the film at 700 °C reduced the intensity of the YL relative to the GL while annealing at 900 °C strongly quenching the YL, leaving only the GL.

To study the in-depth distribution of GL and YL centres, depth-resolved CL spectra were acquired with a constant power (30 μW) by adjusting the beam current, \[ i_{\text{\textit{p}}} \] as the accelerating voltage was varied between 2 and 10 kV. Figure 6(a,b) show the I\textsubscript{GL} and I\textsubscript{YL} respectively of the fitted defect emission spectra as a function of accelerating
voltage. The depth-resolved CL measurements were interpreted by modeling the in-depth electron energy loss using the Monte Carlo stimulation software CASINO.

The measured and modeled depth-resolved CL results for the as-grown sample reveals the following: (i) the decrease of the GL and YL intensities near the ZnO surface at 2 kV for the as-grown sample suggests the presence of non-radiative recombination channels and/or a surface depletion layer due to surface band bending; and (ii) the GL and YL defect density decreases towards the sapphire interface in the as-grown sample. It is noticed that the GL intensity significantly drops after annealing at 900 °C. For the YL, its intensity significantly drops after 700 °C annealing and completely quenched at 900 °C, suggesting YL center is unstable at this temperature.

ZnO films were doped with H using a mild hydrogen plasma treatment at 200 °C. Following the incorporation of H, both the GL and YL are totally quenched (see Fig. 4(b)). As a H$^+$ is a donor in ZnO, it would favor interacting with acceptor site rather than donor site. In a previous CL study of O-rich and Zn-rich ZnO powder, two distinct GL emissions with different peak positions at 2.30 and 2.53 eV were identified which were quenched and enhanced after the H-plasma treatment respectively. By considering the excitation-power dependencies, the GL at 2.30 eV in O-rich ZnO was assigned to band-to-$V_{Zn}$ related acceptor and the GL at 2.53 eV in Zn-rich ZnO was ascribed to a band-to-$V_{O}$ related donor. The YL in ZnO has been attributed to acceptors including both

**Figure 5.** (a) The CL spectra of the as-grown, 700 °C and 900 °C annealed undoped ZnO samples grown with $P(O_2) = 0$ Pa. (b) The modelled CL spectra fitted with the yellow and green luminescence components and the experimental defect emission for the three samples in (a). The defect emission of for the 200 °C hydrogen plasma treated undoped sample is also included. The CL measurements were performed at the temperature of 80 K and the electron energy is 5 keV.
substitutional Li on Zn sites (Li\(_{\text{Zn}}\)) and oxygen interstitials (O\(_{\text{i}}\))\(^{33}\). In the present study, H quenching of the YL precludes its assignment to Li-related centers as these centers are unaffected by hydrogen doping\(^{34}\) and consequently the YL observed in our films is assigned to O\(_{\text{i}}\)-related centers.

The GL observed in this work is not associated with Cu impurities as it does not exhibit their signature fine structure at low temperature\(^{34}\). Moreover, as the GL was quenched following H-plasma treatment the involvement of V\(_{\text{O}}\) can also be ruled out, suggesting that the origin of the GL in our ZnO samples is related to acceptor-like V\(_{\text{Zn}}\)-related defects\(^{33}\). Considering the energy states of intrinsic defects and their complexes in ZnO obtained from a density functional theory based pseudopotential all-electron approach, GL has also been suggested to originate from a V\(_{\text{Zn}}\)\(\text{V}_{\text{O}}\) divacancy\(^{35}\). However, the W-S plots (Fig. 4) indicates that the GL observed in the present study cannot be produced by an isolated V\(_{\text{Zn}}\), a V\(_{\text{Zn}}\)\(\text{V}_{\text{O}}\) divacancy or a 2V\(_{\text{Zn}}\)\(\text{V}_{\text{O}}\) complex because the samples are dominated by the V\(_{\text{Zn}}\)-nV\(_{\text{O}}\), n = 2,3 (Fig. 4), and the PAS signal is clearly distinguishable from those of V\(_{\text{Zn}}\), V\(_{\text{Zn}}\)\(\text{V}_{\text{O}}\) and 2V\(_{\text{Zn}}\)\(\text{V}_{\text{O}}\). A similar negative correlation between the GL and isolated V\(_{\text{Zn}}\) has also been reported by Chen et al.\(^{18}\), who studied the electron irradiated ZnO single crystal by PAS and CL. This work argued that V\(_{\text{Zn}}\) would instead act as non-radiative recombination centers. Using hybrid density functional theory calculations, Frodason et al.\(^{36}\) reported that an isolated V\(_{\text{Zn}}\) was a deep polaronic acceptor. Furthermore using a one-dimensional configuration coordinate model to simulate the luminescence peak and lineshape for an isolated V\(_{\text{Zn}}\) it was concluded that this defect was unlikely to be the cause of the GL.

In the present study, we cannot provide an unequivocal assignment for the origin of the observed GL intensity, which is quenched by H-plasma treatment and anneals out at 900 °C (Fig. 6(a)). The latter finding is indeed correlated with the experimental PAS results showing the formation of the vacancy cluster containing more V\(_{\text{Zn}}\).
as relative to $V_{\text{zn}}$-nV$_O$ (n = 2, 3) which occurs at the same annealing temperature. These results open the door for further discussion. If the $V_{\text{zn}}$-nV$_O$ is considered to be the cause of the GL, the H-plasma treatment may incorporate the H into the $V_{\text{zn}}$ site of the $V_{\text{zn}}$-nV$_O$ cluster. The new H decorated vacancy cluster may become optically inactive and thus quenches the GL. It is also important to note that with the reduction in the GL intensity following the formation of the new vacancy cluster which is relatively $V_{\text{zn}}$ rich after annealing at 900 °C, no new defect emission is observed and the NBE emission is enhanced. This is consistent with the newly formed vacancy cluster not being optically active and no longer competing with the NBE radiative recombination pathways. Nevertheless, the origin of the GL observed in the present study cannot be assigned at this time to a specific defect center and requires further investigation.

The formation energies of monovacancies $V_{\text{zn}}$ are lower than those of the vacancy clusters 2$V_{\text{zn}}$-V$_O$ and $V_{\text{zn}}$-2V$_O$ by 2.5–3.1 eV$^3$. However, in this work, the vacancy clusters become the dominant defect rather than the $V_{\text{zn}}$. The dissociation energy of a vacancy cluster is equal to the sum of its binding energy and the diffusion barrier of the corresponding monovacancy. For n-type ZnO, the dissociation energies for the $V_{\text{zn}}$-V$_O$, 2$V_{\text{zn}}$-V$_O$, and $V_{\text{zn}}$-2V$_O$ are high$^{47}$. This implies that once the vacancy cluster is aggregated via the diffusion of the monovacancies, they are energetically difficult to dissociate at the relatively low temperatures typically above 900 °C. In the present study, the substrate temperature is 600 °C during the PLD growth. At this relatively low growing temperature, kinetic processes on the growth surface would become dominant, which would lead to the dominance of vacancy cluster rather than monovacancy as the dissociation energy of vacancy cluster is high. The annealing of the samples at 900 °C is also not a thermodynamic equilibrium process as there is excessive $V_{\text{zn}}$ creation at the film/substrate boundary due to Zn out-diffusion. The excessive $V_{\text{zn}}$ creation during annealing may be the reason why instead of simply annealing out, vacancy cluster containing more $V_{\text{zn}}$ as relative to V1 is formed. However the exact dynamic and interaction of different kinds of vacancy type defects is not known in the present study and require further investigation.

Secondary ion mass spectroscopy (SIMS) study was conducted to obtain the hydrogen concentration of the as-grown and 900 °C annealed undoped ZnO samples. They are found to be respectively 7 × 10$^{18}$ cm$^{-3}$ and 3 × 10$^{18}$ cm$^{-3}$, which are close to the electron concentrations of 8 × 10$^{18}$ cm$^{-3}$ and 4 × 10$^{18}$ cm$^{-3}$ for the as-grown and 900 °C annealed samples. The n-type conductivity of the undoped ZnO could be due to the hydrogen impurity as it is known to be a shallow donor$^{48}$. It is also noticed that the electron concentration for the undoped sample grown with P(O$_2$) = 0 Pa increase from ∼2 × 10$^{18}$ cm$^{-3}$ to ∼4 × 10$^{18}$ cm$^{-3}$ while the annealing temperature increases from 750 °C to 900 °C (see Fig. 2). For the sample grown with P(O$_2$) = 1 Pa, similar electron concentration and mobility increase are also observed as the annealing temperature increases from 750 °C to 900 °C. It is also observed that the electron mobilities also increases upon the 900 °C annealing. The increase of electron concentration and mobility correlate with the observation in the W-S plot that the formation of the vacancy cluster with more $V_{\text{zn}}$ as relative to V1 which occurs at the same annealing temperature. This could be explained if the V1 cluster is initially a compensating defect and the newly formed defect after annealing at 900 °C is not electrical active.

Conclusion

Zn-vacancy related defects in ZnO films grown by PLD method were systemically studied using the PAS and CL. PAS study shows that vacancy cluster V1 (which is possibly $V_{\text{zn}}$-nV$_O$ with n = 2, 3) is the dominant $V_{\text{zn}}$-related defect in the as-grown undoped ZnO samples grown with relatively low P(O$_2$). Annealing at 900 °C changes the microstructure of the vacancy cluster becoming containing more $V_{\text{zn}}$ whereas excessive $V_{\text{zn}}$ are created by Zn out-diffusion at the film/substrate interface induced by annealing. Growing the undoped ZnO samples at higher P(O$_2$) would favor the formation of vacancy cluster with more $V_{\text{zn}}$ comparing to V1. The domination of vacancy cluster rather than the isolated $V_{\text{zn}}$ with lower formation energy could be due to the vacancy aggregation resulted from the vacancy diffusion and the high dissociation energies of the vacancy cluster. GL and YL were observed in the CL study of the samples and they anneal out respectively at 750 °C and 900 °C and both emissions were found to be quenched by H-plasma treatment. The GL found in this study cannot be assigned to isolated $V_{\text{zn}}$-V$_O$ or the $V_{\text{zn}}$-2V$_O$ centers.

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Author Contributions
Wang, Luo and Su were involved in the samples fabrication and treatment. Wang and Luo had the equal contribution to the work. Anwand, Wagner and Butterling were involved in the positron beam line operation and the measurements of positron annihilation spectroscopic studies. Rahman, Phillips and Ton-That performed cathodoluminescence measurements and contributed to the analysis of data. Younas carried out the transmission electron microscope measurement. Ling conceived the idea of the study, coordinated the collaboration and wrote-up of the manuscript.

Additional Information
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