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Changing vacancy balance in ZnO by tuning synthesis between zinc/oxygen lean conditions

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The nature of intrinsic defects in ZnO films grown by metal organic vapor phase epitaxy was studied by positron annihilation and photoluminescence spectroscopy techniques. The supply of Zn and O during the film synthesis was varied by applying different growth temperatures (325–485 °C), affecting decomposition of the metal organic precursors. The microscopic identification of vacancy complexes was derived from a systematic variation in the defect balance in accordance with Zn/O supply trends. © *2010 American Institute of Physics.* [doi:10.1063/1.3462394]

Zinc oxide (ZnO) attracts considerable attention on behalf of its unique physical properties, offering a variety of multifunctional applications in optoelectronics, transparent electrodes, and sensors.[1–3] Several methods to fabricate ZnO thin films have been demonstrated so far,[4] among which metal organic vapor phase epitaxy (MOVPE) has been studied as a function of reactor type, growth conditions, and substrate variations for the attainment of high quality material.[5] Note, the microscopic understanding of the intrinsic defects in ZnO is important because of its potential to resolve the p-type doping problem in ZnO.[6] A method providing direct means of vacancy-type defect identification in semiconductors and ZnO in particular is positron annihilation spectroscopy (PAS).[7] To date PAS studies have mostly addressed defect formation in bulk ZnO with only a few reports on MOVPE-ZnO films,[8,9] partly because of a lack of high quality material until recently and also more complicated interpretation of the annihilation data in thin films. On the other hand, vacancy-type defects in ZnO thin films have been extensively studied using photoluminescence (PL),[10] although the exact correlation of deep-level emission (DLE) peaks with specific intrinsic defects still remains a matter of ongoing discussions.[1,5,11] In this respect, a combination of PAS/PL measurements might be capable to reveal the nature of the dominating intrinsic defects in MOVPE-ZnO films. To make such identification conclusive, it is essential to provide samples exhibiting systematic variations in the intrinsic defect balance. In the present work, we have prepared such samples by varying MOVPE-synthesis temperature (325−485 °C), which resulted in different amounts of Zn and O supplied to the reaction zone in the process of the precursor decomposition.[12] Thus, the defect concentration balance in the films was influenced in a controlled way, allowing for direct correlation of characteristic PAS/PL signatures as well as their microscopic assignment.

ZnO films used in this study were grown on r-axis oriented sapphire (r-Al$_2$O$_3$) substrates by MOVPE. Diethylzinc (DEZn) and tertiarybutanol (t-BuOH) were used as precursors for Zn and O reagents, respectively. Both DEZn and t-BuOH were carried by N$_2$ and introduced into the chamber through separated injectors over a rotating platen holding the substrates.[13] Effectively, the substrates are alternately "dosed" with certain amounts of Zn/O reagents attached to the surface as a function of the growth temperature. The DEZn/t-BuOH flow rate ratio (1/1) and growth time (90 min) were kept constant resulting in 400–600 nm thick ZnO films. In addition, we have conducted tests employing flow rate variations in order to alter DEZn and t-BuOH delivery to the chamber in a more "direct" way. However, changing the flow rates will affect the partial pressures influencing precursor decomposition rates and a combination of these factors with temperature variation may result in a complicated trend. Importantly, the same II/VI molar ratio will in practice provide completely different amounts of Zn/O reagents depending on the growth temperature because of different degrees of precursor decomposition as a function of temperature.[12] Based on a set of preliminary experiments we understood that employing the temperature variation only we will cover a wide variation in the Zn/O reagent supply and decided to keep the flow rate constant for the rest of the experiment. All samples demonstrated similarly high crystalline quality as confirmed by ~0.15° full width at half maximum broadness of the (002) x-ray diffraction peak.

PL properties of the samples were investigated at 10 K temperature by employing 325 nm wavelength of cw He–Cd laser as an excitation source. In this work, we focus primarily on the spectral region of DLE and employ deconvolution techniques to analyze intensities and positions of the characteristic bands referring to data reported in literature[5,11] as well as to the trends resolved in our PAS measurements. The essence of the vacancy identification with PAS is in positron trapping at neutral and negative vacancy defects, which modifies the annihilation characteristics. The Doppler broadening of the 511 keV annihilation line was measured at room temperature using a variable energy positron beam in the 0–30 keV range. We characterized the Doppler spectra by
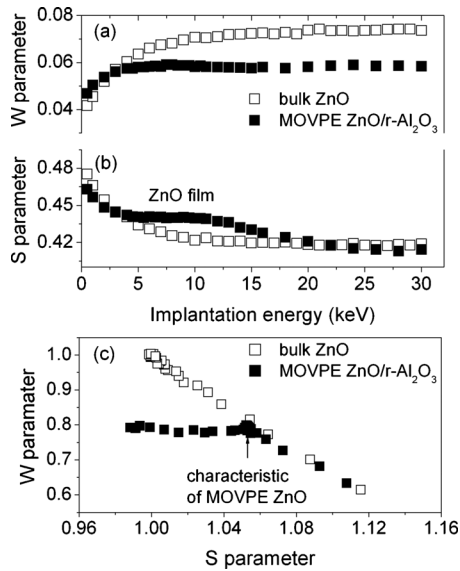
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FIG. 1. Typical PAS data for the bulk ZnO reference sample and MOVPE-ZnO/r-Al$_2$O$_3$ structure grown at 385 °C. W and S parameters vs energy profiles are shown in panels (a) and (b), respectively, while panel (c) is the normalized to the bulk (S, W) plot.

FIG. 2. W-S plot for MOVPE-ZnO synthesized at different temperatures. The reference annihilation states (bulk and V$_{Zn}$) are labeled by open squares. Open circles denote (S, W) trend points revealed in previous ion implantation experiments.

conventional line shape parameters representing the fractions of annihilations with low-momentum (S) and high-momentum (W) electrons.[8]

Figure 1 shows a typical example of the PAS results in MOVPE-ZnO, while the data obtained in the bulk ZnO reference are shown for comparison. The reference sample contains only two annihilation states—surface and lattice [see open squares following a linear trend in Fig. 1(c)]. In contrast, the MOVPE sample contains more annihilation states (in part because of the different natures of the film and the substrate). As seen from Fig. 1(a) low energy positrons (0–3 keV) annihilate at surface states in the MOVPE structure similar to those in the reference sample, while 4–11 keV positrons annihilate in the ZnO film. At higher implantation energies, positrons start to annihilate in the substrate and are not considered in the further analysis. The characteristic values for S and W parameters detected in ZnO films [e.g., S =1.05 and W=0.79 in Fig. 1(c), representing the constant region at 4–11 keV in Figs. 1(a) and 1(b)] are used in further analysis.[8]

Figure 2 is a W-S plot containing characteristic (S, W) values of the MOVPE-ZnO films grown at different temperatures. In addition, reference parameters corresponding to the ZnO lattice and V$_{Zn}$ (Ref. 14) are included in Fig. 2. First, we see that positron annihilation at open volume defects dominates in the films based on the high S-values in Fig. 2. Second, the position of the (S, W) values of the samples grown at 350 and 385 °C in the plot resembles saturation trapping of positrons and subsequent annihilation predominantly at defects related to the V$_{Zn}$. Reducing the growth temperature to 325 °C moves the data horizontally toward higher S-values in the plot, indicating formation of vacancy clusters, while increasing the synthesis temperature to ≥420 °C results in a clear trend for S(W) parameters to increase (decrease), indicating the formation of vacancy clusters of a different nature than those at the lowest growth
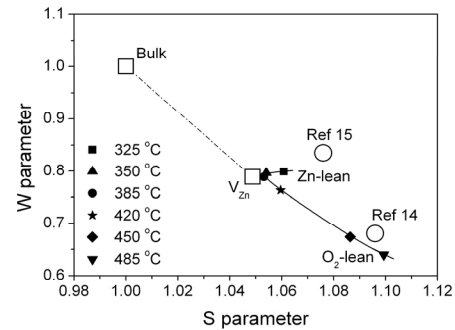
temperature. It should be noted that the positron diffusion length (L^+) (Ref. 8) decreases monotonically from about 20 nm to about 10 nm in the samples grown at ≥385 °C, indicating that no saturation trapping at V$_{Zn}$ occurs in the samples grown at 350 and 385 °C. This means that in addition to V$_{Zn}$ there are other annihilation states—vacancy clusters giving significant contributions to the positron data in these samples. Moreover, the reduction in L^+ implies that the positron trapping rate and hence the defect concentration (not only the size of the vacancy clusters) increases when the growth temperature is increased. Interestingly, the (S, W) parameters of the sample grown at 325 °C approach those of the vacancy clusters observed in Li-implanted and flash-annealed ZnO,[15] correlated with the characteristic 2 eV optical emission in Ref. 11.

PL results for the films synthesized at different temperatures are summarized in Fig. 3. Two distinct DLE components centered at around 2 and 2.5 eV can be readily observed, allowing for satisfactory deconvolution of all DLE spectra. The relative intensity of the green and red spectral signatures apparently correlates with the synthesis temperatures. Similar DLE components were observed by
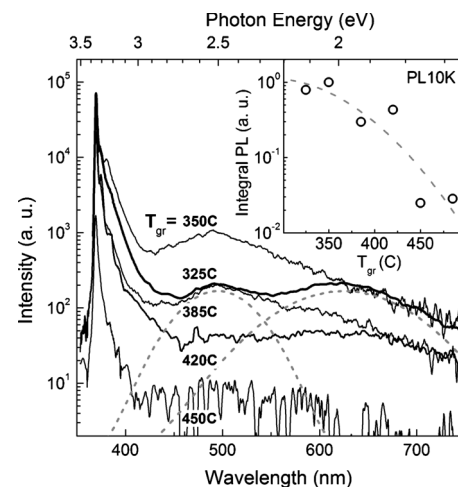

FIG. 3. PL spectra at 10 K for MOVPE-ZnO films grown at different temperatures (T$_{gr}$). Gaussian dotted curves are guides for eyes indicating two dominant deep-level emission components. The inset shows the evolution of the total PL yield integrated over entire emission spectrum as a function of growth temperature.

Dong *et al.*[11] in depth resolved cathodoluminescence (DRCL) experiments, with the 2 eV emission reportedly in a direct correlation with the vacancy cluster signals measured by PAS. Such association also appears consistent with the present PAS data, specifically considering clear dominance of the 2 eV emission in the films grown at 325 °C comparing to the rest of the samples in Fig. 3. It should also be noted that the overall luminescence yield, including both DLE and near-band-edge emission, notably decreases in the samples grown at elevated temperatures, as can be seen in the inset in Fig. 3, implying an increasing competition from the nonradiative recombination channels.

The trends presented in Figs. 2 and 3 can be explained in terms of changes in the Zn/O reagent supply due to variations in DEZn/t-BuOH thermal decomposition.[12] Indeed, the pyrolysis of DEZn starts at 300 °C and is not completed until the temperatures are well above 350 °C. Consequently, the 325 °C synthesis would result in Zn lean material which is consistent with detecting vacancy clusters formed of two or more missing Zn atoms in this sample in Fig. 2 as well as the 2 eV signature in Fig. 3. Please note that in spite the II/VI flow rate ratio was constantly maintained at ~1, the Zn/O reagent supply was effectively ≪1 because insufficient decomposition of DEZn at "low" temperatures. Accounting that oxidizing properties of t-BuOH does not change in the range of 325–385 °C,[12] we can readily explain the transformation happening at 350 and 385 °C—more Zn is supplied in the reaction zone consistently with decreasing the S parameter (interpretable as a decrease in the cluster size) and changing annihilation parameters toward those of V_{Zn}. However, this initial trend breaks because of changing in oxidizing conditions at higher temperatures. Indeed, the presence of stable oxonium ion is responsible for Zn oxidation when using t-BuOH as an oxidizer.[16] However, the relative abundance of oxonium ion decreases drastically due to pyrolysis of t-BuOH which starts at elevated temperatures, likely >385 °C in our growth conditions.[12] Thus, the growth at temperatures >385 °C results in insufficient oxidation and formation of another kind of vacancy cluster with the W parameter clearly lower comparing to that observed in the Zn-lean case. Interestingly, these points follow a trend similar to that observed in high-dose 2 MeV O^+ irradiated ZnO samples.[14] Taking into account the magnitude of the W parameters (which is determined by annihilations with high-momentum Zn 3*d* electrons) we conclude that there should be more Zn atoms present around annihilation states in samples grown at 325 °C. This can be readily interpreted as the vacancy clusters being of considerably smaller size in the Zn-lean sample.

The transformation happening when changing from Zn-lean to O-lean conditions is also confirmed by the evolution in PL data in Fig. 3. The 2 and 2.5 eV emissions coexist already in the sample grown at 325 °C and also the maximum of the DLE changes from 2 to 2.5 eV when increasing the growth temperature from 325 to 350 °C. This correlates with the PAS result that zinc vacancy related defects are the main positron traps strongly indicating involvement of zinc vacancies in the PL processes. Further, no (or only weak) DLE signals are observed for samples grown in O-lean conditions in Fig. 3 which is interpreted in terms of the formation of bigger clusters reducing radiative recombination in the DLE range. Assuming the defect evolution scenario discussed above and accounting that zinc lean conditions implies the formation energy of V_{Zn} to be lower that of V_o,[1] we may tentatively correlate 2.5 eV emission in Fig. 3 with V_{Zn}.[1,5]

In summary, an interpretation for the nature of vacancy-type defects in MOVPE-ZnO is suggested based on systematic variation in Zn/O lean conditions during synthesis in spite of generally complicated defect balance in the samples. The samples grown at 325 °C (most Zn-lean condition studied) are found to be enriched with vacancy clusters and the assignment of the 2 eV emission with V_{Zn}-clusters is confirmed. Samples synthesized at higher temperatures corresponding to O-lean conditions are found to contain bigger vacancy clusters responsible for damping of defect related radiative transitions in ZnO. In addition a characteristic 2.5 eV emission band is found to dominate at intermediate synthesis temperatures (350–385 °C) and is tentatively associated with radiative transition involving V_{Zn}.

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