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# Dependence of Intrinsic Defects in ZnO Films on Oxygen Fraction Studied by Positron Annihilation *

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*Defects in ZnO films grown by radio-frequency reactive magnetron sputtering under variable ratios between oxygen and argon gas have been investigated by using the monoenergetic positron beam technique. The dominate intrinsic defects in these ZnO samples are O vacancies ($V_O$) and Zn interstitials ($Zn_i$) when the oxygen fraction in the $O_2$/Ar feed gas does not exceed 70% in the processing chamber. On the other hand, zinc vacancies are preponderant in the ZnO films fabricated in richer oxygen environment. The concentration of zinc vacancies increases with the increasing $O_2$ fraction. For the oxygen fraction 85%, the number of zinc vacancies that could trap positrons will be smaller. It is speculated that some unknown defects could shield zinc vacancies. The concentration of zinc vacancies in the ZnO films varies with the oxygen fraction in the growth chamber, which is in agreement with the results of photoluminescence spectra.*

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In recent years, zinc oxide (ZnO) has attracted extensive attention due to its many excellent properties. The combination of a large direct band gap ~3.4 eV and exciton binding energy 60 meV at room temperature makes ZnO a promising material for applications to the ultraviolet light emission source.[1−3] In addition, ZnO is quite resistant to displacement damage, as compared to the situation in Si and GaAs. This fact suggests that this material should be useful for space applications in which particle irradiation is strong.[4]

Undoped ZnO usually exhibits n-type conductivity, and the reason to account for the prevalence of n-type conductivity in undoped ZnO is suggested as those shallow donor defects such as Zn interstitials ($Zn_i$) and O vacancies ($V_O$).[5] However, the fabrication of p-type ZnO is quite difficult. This is attributed to several reasons such as low thermal excitations into the energy level of acceptor impurities, low solubility of dopants, and the introduction of point defects acting as compensators.[5,6] Many groups have made intense efforts to attain high quality p-type ZnO.[6−10] Tüzemen and his collaborators have reported that ZnO films deposited by reactive sputtering of a Zn target in $O_2$/Ar atmosphere produce n-type ZnO at low oxygen partial pressure and p-type ZnO at higher oxygen pressure.[11,12] When oxygen proportion in the growth chamber is 55%, the transition of the conductivity occurs. They considered that a change in oxygen pressure corresponds to a change in the oxygen chemical potential $\mu_O$.[12] Raising the chemical potential of the oxygen, such as by electronic excitation to a dissociated state, will raise the formation enthalpy of the donor $V_O$ and lower the formation enthalpy of the acceptor $O_i$. Hence, the concentration of donor defects ($V_O$) significantly decreases, while the concentration of acceptor defects ($V_{Zn}$, $O_i$) corresponds to grow up and become predominant, thus the shift of n-type to p-type realizes. The types of defects in ZnO films will change with oxygen ratio, and subsequently the majority carrier transits from electrons to holes. However, to date there is no direct experimental proof to back this understanding. Thus it is very interesting in studies to observe the change of defects under variable oxygen fraction conditions.

Positron annihilation spectroscopy (PAS) with slow-positron beam is a powerful and sensitive technique to detect open-volume defects in metals, semiconductors, polymers and nanomaterials.[13,14] When a positron is implanted into the condensed matters, it annihilates with an electron mainly into 511 keV $\gamma$ quanta. The momentum of the positron–electron pair causes a Doppler shift in the energy of the annihilation photons. In the material containing defects, a freely diffusing positron can be readily localized or trapped at open-volume defects as a result of the missing positive-ion cores at these defects. The trapping will lead to a narrowing of the momentum distribution of the positron–electron pair and in the annihilation photons, which is reflected in the shift of the Doppler broadening spectrum. The change of the Doppler broadening spectrum is characterized by the $S$ parameter and $W$ parameter. Parameters $S$ and $W$ demonstrate the fraction of the positron–electron pair with low-momentum and high-momentum respec-

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tively. Higher $S$ value for a particular material suggests more annihilations with low-momentum electrons implying greater positron trapping in defects.

The samples used in the present experiment were undoped ZnO films grown on oriented (100) silicon substrates by rf reactive magnetron sputtering. The substrate was first degreased and cleaned by a standard cleaning procedure, then it was outgassed within the growth chamber, metal zinc with a purity of 99.99% acts as a target at $O_2$/Ar atmosphere.[15] The evaluation of film thickness is performed by scanning electron microscope (SEM). The information about all samples is listed in the Table 1.

Table 1. Samples grown for experiments.

| Sample | Substrate temperature (°C) | $O_2$ Fraction | Film thickness (nm) | rf power (W) |
|---|---|---|---|---|
| A | 350 | 50 | 105 | 110 |
| B | 350 | 60 | 180 | 110 |
| C | 350 | 65 | 210 | 110 |
| D | 350 | 70 | 250 | 110 |
| E | 350 | 75 | 280 | 110 |
| F | 350 | 85 | 400 | 110 |

Variable energy positron measurements were performed for samples at room temperature with University of Science and Technology of China (USTC) slow positron beam equipment.[16] Doppler broadening spectra of annihilation radiation were measured with a high purity Ge detector system (ORTECGEM-1075), which has an energy resolution of 1.2 keV (FWHM) at 514 keV rays for $^{85}$Sr. Spectra with a total count number of $5 \times 10^5$ were measured for every value of energy $E$. The defect sensitive line parameter, $S$ parameter is defined as the ratio of the integral of ray counts in central energy region at the 511 keV to the total counts of spectrum. In the same way, the $W$ parameter is the ratio of the wing area to the total area under the spectrum, and it gives the information of high-momentum electrons.

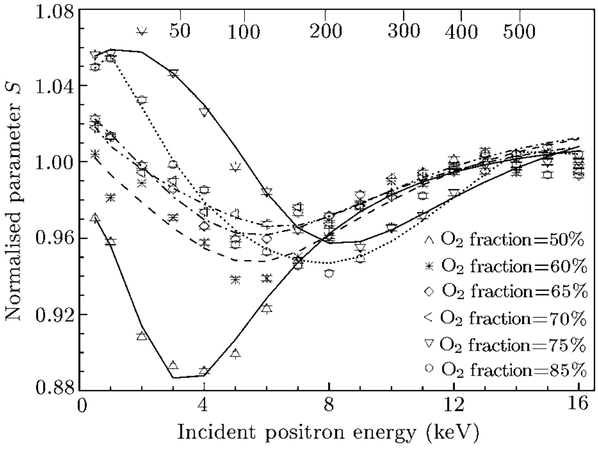

**Fig. 1.** Parameter $S$ versus positron energy for various samples, the solid lines are the fitted curves.

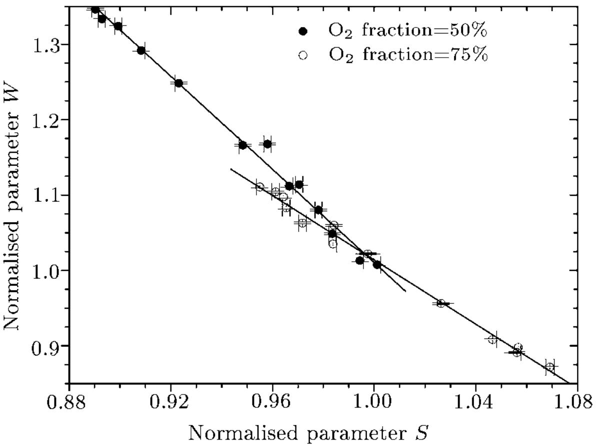

**Fig. 2.** Electron-momentum parameters $S$ and $W$ in various ZnO samples. For the $O_2$ fraction larger than 70%, parameters $S$ and $W$ fall on a line. For the $O_2$ fraction smaller than 70%, the parameters can fall on another line.

Figures 1 and 2 illustrate the results of positron annihilation. Figure 1 reveals the $S$ parameter as a function of the positron incident energy $E$. The mean implantation depth is shown on the upper axis. The relationship between $S$ parameters and energy $E$ could analysed by VEPFIT, which is a software package developed by van Veen.[17] The linear $S$ parameter could be expressed as a linear superposition of the contributions from the different positron state, weighted with annihilation fraction $f$, for the corresponding state as[5,18]

$$S = S_s f_s + \sum_i S_i f_i + S_{\rm sub} f_{\rm sub}, \qquad (1)$$

where $S_s$, $S_i$, and $S_{\rm sub}$ are the $S$ parameters corresponding to the surface, the $i$th slab, and the substrate respectively; and $f_s$, $f_i$, and $f_{\rm sub}$ are the fractions of positrons annihilated at the surface, in the $i$th block, and in the substrate ($f_s + \sum f_i + f_{\rm sub} = 1$). The experimental $S$ versus $E$ curves have been analysed in terms of Eq. (1) using VEPFIT program.

In Fig. 1, it is demonstrated that $S$ parameters firstly descend in the low energy region, and subsequently ascend with energy rising for each sample. In a low-energy region, a part of the positrons implanted could form some positroniums near the sample surface, resulting in the $S$ parameter growing.[19] Then they annihilate in ZnO films with incident positron energy rising. In the high-energy region, there is a clear indication of the character of positrons annihilated in silicon substrate. When positron energy is over 13 keV, the $S$ parameters almost keep constant, so it can be normalized using the medial $S$ parameters corresponding to 13–16 keV. In the fitting procedure, two layers fittings are tried; treating ZnO films and silicon substrate as if there were no interlayer existing, the fitted data are poor and unacceptable. Three layers fitting is tried, assuming a transition block presence, and satisfactory results could be obtained. Moreover, the formation of a transitional layer at the ZnO/Si interface is reported.[20] Thus we consider that an interlayer appears between the epilayer and substrate. The fitted $S$ parameters and effective diffusion length $L_{\text{eff}}$ of positron are listed in Table 2.

Table 2. The fitted $S$ parameters and effective diffusion length $L_{\text{eff}}$ of ZnO films.

| Sample | $O_2$ fraction | S parameter | $L_{\text{eff}}$ (nm) |
|---|---|---|---|
| A | 50 | $0.484 \pm 0.001$ (68.3%) | $64 \pm 1.6$ (68.3%) |
| B | 60 | $0.493 \pm 0.002$ (68.3%) | $63 \pm 2.7$ (68.3%) |
| C | 65 | $0.502 \pm 0.002$ (68.3%) | $61 \pm 2.0$ (68.3%) |
| D | 70 | $0.515 \pm 0.002$ (68.3%) | $54 \pm 4.3$ (68.3%) |
| E | 75 | $0.523 \pm 0.003$ (68.3%) | $38 \pm 3.2$ (68.3%) |
| F | 85 | $0.518 \pm 0.002$ (68.3%) | $46 \pm 2.0$ (68.3%) |

From Table 2, it can be seen that the effective diffusion length of positron in all samples is not more than 64 nm, and these results are in agreement with the values obtained in ZnO grown on sapphire by Zubiaga *et al.*[21] However, the typical value of effective diffusion length $L_{\text{eff}}$ of positron in semiconductors such as Si, Ge, and GaAs is 200–300 nm, and that in metals such as Ni and Cu is 150–200 nm. It is obvious that $L_{\text{eff}}$ in the ZnO samples is much shorter than the typical value of $L_{\text{eff}}$ in defect-free materials, which reveals that positrons are trapped or scattered by open volume defects. Uedono *et al.*[5] have reported the presence of Zn interstitial ($Zn_i$) or O vacancy ($V_O$) in ZnO single crystals. Interstitials are unlikely to affect the $S$ parameter, but these defects act as scattering centres in the course of positrons diffusing in the lattice, so short effective diffusion length could be attained. Tuomisto and his co-workers[22] utilized the positron lifetime and observed Zn vacancies ($V_{\text{Zn}}$) in n-type ZnO.

The dependences of parameters $S$ and $W$ are shown in Fig. 2. The number of different vacancy-type defects trapping positron in the material can be investigated through the linearity between the annihilation parameters $S$ and $W$.[23] If only a single type of vacancy is present, the $W$ parameter depends linearly on the $S$ parameter when the fraction of positron annihilations at vacancies varies. From the $S-W$ plot, it clearly exhibits that two-type defects appear in low oxygen fraction and high oxygen fraction ZnO films, respectively.

In unintentionally doped ZnO, the formation enthalpies of native donor and acceptor defects of $V_O$ and $O_i$ can be written as[12,24]

$$\Delta H^{(2+,V_O)} = \Delta E^{(2+,V_O)} + \mu_O + 2eE_F, \tag{2}$$

$$\Delta H^{(2-,O_i)} = \Delta E^{(2-,O_i)} - \mu_O - 2eE_F, \tag{3}$$

where $\Delta E^{(q,\alpha)}$ is the calculated total energy of unit cell including the host material with defect $\alpha$ in charge state $q$ minus the total energy of a unit cell of the host only, and $E_F$ is the Fermi energy level. The oxygen chemical potential $\mu_O$ enters a negative sign when atoms are moved from the reservoir to the host crystal. In the rf electromagnetic field, the oxygen molecular could be excited to a dissociated state, thus raising the oxygen chemical potential, which increases the formation enthalpy of $V_O$ and correspondingly lowers that of $O_i$. According to the relation $\mu_{\text{Zn}} + \mu_O = \mu_{\text{ZnO}}$, the dependence of formation enthalpy of $V_{\text{Zn}}$ and $Zn_i$ on $\mu_O$ are expressed in the following equations:

$$\Delta H^{(2-,V_{\text{Zn}})} = \Delta E^{(2-,V_{\text{Zn}})} + \mu_{\text{ZnO}} - \mu_O - 2eE_F, \tag{4}$$

$$\Delta H^{(2+,Zn_i)} = \Delta E^{(2+,Zn_i)} - \mu_{\text{ZnO}} + \mu_O + 2eE_F, \tag{5}$$

where $\mu_{\text{ZnO}}$ is a constant. When oxygen chemical potential grows up, the formation enthalpy of $V_{\text{Zn}}$ lowers, while that of $Zn_i$ rises.

A change in oxygen fraction corresponds to a change in the $\mu_O$. The formation enthalpies of $V_{\text{Zn}}$ and $O_i$ lower with $O_2$ fraction rising; whereas those of $V_O$ and $Zn_i$ go on the opposite way. Thus the concentration of $V_{\text{Zn}}$ and $O_i$ becomes larger with the increase of oxygen ratio.

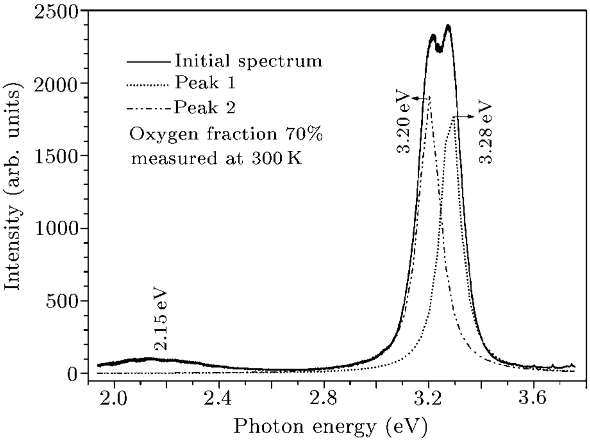

**Fig. 3.** Photoluminescence (PL) spectra of ZnO films grown at oxygen fraction 70% in mixed $O_2$/Ar gas in growth chamber.

The film stoichiometry was investigated by x-ray photoelectron Spectroscopy (XPS).[15] The results reveal that O element has higher ratio than Zn element when $O_2$ fraction is 75%, indicating Zn-deficient and O-enrichment states in ZnO films. In this way $V_{\text{Zn}}$ and $O_i$ may be the predominant defects. According to the calculated results, the formation energy of $V_{\text{Zn}}$ is less than that of other defects in oxygen-rich ambient.[25] In addition, $V_{\text{Zn}}$ could readily bind and trap positrons as they are negatively charged defects. Combined with experimental and theoretical conclusion mentioned above, it is suggested that Zn vacancies exist in richer oxygen ZnO films, and Zn interstitials or O vacancies appear in the ZnO films grown under low oxygen proportion conditions.

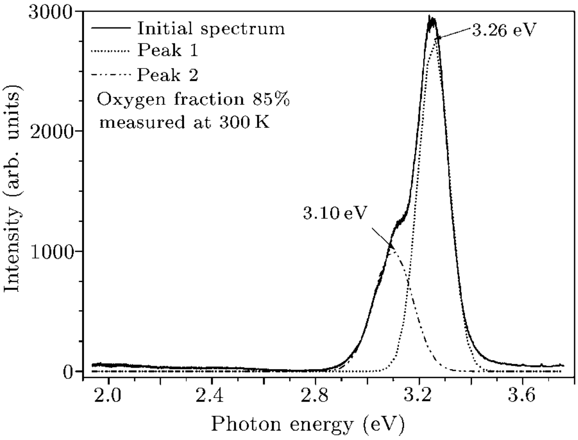

**Fig. 4.** PL spectra of ZnO films grown at oxygen fraction 85% in mixed $O_2$/Ar gas in the growth chamber.

Raising the oxygen fraction will increase the $V_{Zn}$ concentration in ZnO films. Thus the $S$ parameters listed in Table 2 observed by positrons become larger, and the effective diffusion length diminishes. This suggestion can be supported by the photoluminescence (PL) spectra. The PL spectra of the fraction composition of 70% and 85% oxygen are displayed in Figs. 3 and 4. The PL spectra exhibit the peaks at 3.20, 3.28 and 3.26 eV. In the report of Onuma *et al.*,[20] the peaks at 3.28 and 3.25 eV, which are lower than the free exciton emission energy (3.3 eV) at 300 K, were ascribed to the effect of impurities or defects in the samples. The green luminescence has been attributed to the involvement of O vacancies in ZnO films.[24,26] Comparative studies of PL spectra have suggested that green emission weakens, or even disappears, with the increase of the oxygen fraction, which implies that O vacancies decrease, corresponding to Zn vacancies growing up. However, when the ratio of oxygen ratio reaches 85%, one can find that the S parameter is lower than that of 75%, at the same time $L_{eff}$ becomes longer. There should be the highest concentration of $V_{Zn}$ and $O_i$ in the oxygen fraction 85% ZnO sample, and there may be some unknown defects around the Zn vacancies, which shield $V_{Zn}$ to trap and to annihilate positrons. Thus the $S$ parameter and $L_{eff}$ have an exceptional trend as the advance of oxygen fraction.

In summary, a monoenergetic positron beam has been used to investigate the defects in ZnO films fabricated with various oxygen fractions in combination with XPS and PL spectra. The concentration of $V_{Zn}$ rises as the oxygen fraction increases. O vacancies or Zn interstitials are dominant defects when the oxygen fraction is lower than 70%, while Zn vacancies are primary defects in the oxygen-rich films. In oxygen-fraction 85% films, there may be some unknown defects around $V_{Zn}$, which prevent $V_{Zn}$ from trapping positrons.

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