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## Influence of Dopants in ZnO Films on Defects

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*The influence of dopants in ZnO films on defects is investigated by slow positron annihilation technique. The results show  $S$  that parameters meet  $S_{Al} > S_{un} > S_{Ag}$  for Al-doped ZnO films, undoped and Ag-doped ZnO films. Zinc vacancies are found in all ZnO films with different dopants. According to  $S$  parameter and the same defect type, it can be induced that the zinc vacancy concentration is the highest in the Al-doped ZnO film, and it is the least in the Ag-doped ZnO film. When Al atoms are doped in the ZnO films grown on silicon substrates, Zn vacancies increase as compared to the undoped and Ag-doped ZnO films. The dopant concentration could determine the position of Fermi level in materials, while defect formation energy of zinc vacancy strongly depends on the position of Fermi level, so its concentration varies with dopant element and dopant concentration.*

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In recent years, zinc oxide has attracted a great deal of interest because of its many excellent properties and performance. As a large direct band gap of 3.37 eV semiconductors, ZnO has a substantial potential in the optoelectronic area, and the 60 meV exciton binding energy at room temperature makes it be an important application to the ultraviolet light emission source.<sup>[1–3]</sup> In order to attain the potential offered by ZnO, both high quality n- and p-type ZnO are indispensable. It is known that n-type ZnO is easily available even without intentional doping, due to native point defects, such as oxygen vacancies, zinc interstitials and the presence of hydrogen.<sup>[4]</sup> However, it is very difficult to obtain p-type ZnO. The difficulties are 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.<sup>[5]</sup> Many groups have made great efforts to attain high quality p-type ZnO by doping different elements, such as group-V elements (N, P, and As) to substitute O sites,<sup>[6–9]</sup> a Co-doping method of N and group-III elements (Ga, Al),<sup>[5,10]</sup> group-I elements (Li, Na, and K) to substitute Zn sites.<sup>[8]</sup> Group-I elements could be better p-type dopants than group-V elements in terms of shallowness of acceptor levels, however, group-I elements prefer to occupy the interstitial sites rather than substitutional sites, caused by their smaller ionic radii than Zn ionic radius; therefore they act mainly as donors. Moreover, significantly larger bond length for Na and K than ideal Zn–O bond length (1.93 Å) induces lattice distortion, increasingly forming native defects such as vacancies which compensate for the dopants.<sup>[3]</sup> These are among the many causes leading to difficulties in attaining p-type doping in ZnO. A

similar size mismatch occurs for group-V elements except for N. Thus the best candidate for p-type doping in ZnO is N among the group V impurities. However, theoretical studies indicated that the acceptor level of N is so deep that it is difficult to explain the activity of N acceptors at room temperature.<sup>[8,9]</sup> In addition, the doping efficiency of N is limited due to the compensation effect.<sup>[11]</sup>

According to Yan *et al.*'s calculation,<sup>[12]</sup> Ag could be a better candidate for producing p-type ZnO than N. The recent experimental and theoretical studies revealed that Ag, one of group IB elements, could act as an acceptor on substitutional Zn sites in ZnO. Kang's group reported that Ag-doped ZnO films deposited at a certain temperature range exhibited p-type conductivity.<sup>[13,14]</sup> At the same time, Duan *et al.* reported that the ultraviolet emission in Ag-doped ZnO films is over ten times stronger than that of pure ZnO films.<sup>[15]</sup> Hence Ag is a better dopant in ZnO films in terms of conductivity and luminescence performance.

Although n-type ZnO is easily available, when the n-type semiconductor is doped with different elements, many interesting properties can be induced, such as electronic and optical properties. The optical bandgap of ZnO films is widened in proportional to the Al-doping concentration.<sup>[16]</sup> The electrical conductivity and the mobility are substantially improved in Al doped ZnO films.<sup>[17]</sup> Al-doped ZnO films, as a transparent conductive electrode oxide, are considered as a potential to replace indium tin oxide (ITO) due to low cost, nontoxicity and stability in H<sub>2</sub> plasma atmosphere. When Al atoms are doped in ZnO, they act as donors by substituting for Zn sites.<sup>[18,19]</sup>

According to the above description, many proper-

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ties have strongly something to do with dopant elements and their concentration. Dopants have a direct effect on the position of the Fermi energy level, while the defect formation energy is a function of the Fermi energy level.<sup>[20]</sup> Here we have observed native defect evolution in different dopant environments. Although the defects can be detected by electrical and optical characterization technique, their atomic structures remain very often unresolved. This goal could be reached for vacancy-type defects by utilizing positron annihilation technique.<sup>[21]</sup>

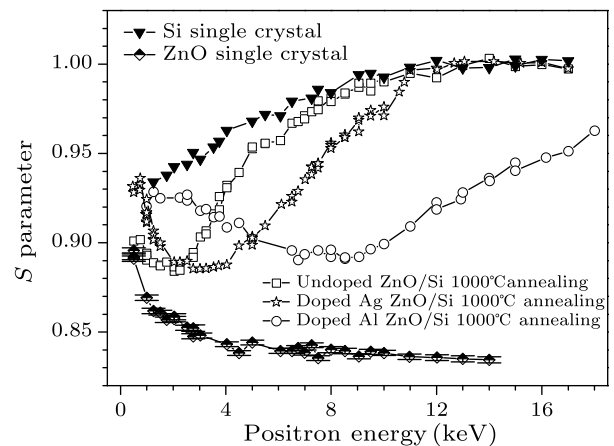
Positron annihilation spectroscopy (PAS) is a powerful and sensitive technique to detect open-volume defects in metals, semiconductors, polymers and nanomaterials.<sup>[22]</sup> When a positron is implanted into the condensed matters, it annihilates with an electron mainly into 511 keV  $\gamma$  quanta. 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  $S$  parameter and  $W$  parameter. Parameters  $S$  and  $W$  demonstrate the fraction of positron-electron pair with low-momentum and high-momentum, respectively. Higher  $S$  value for a particular material suggests more annihilation with low-momentum electrons implying greater positron trapping in defects.

The ZnO films were deposited on (100)-oriented silicon substrates with resistivity of 20–30  $\Omega$ ·cm by dc reactive sputtering. The substrate was first degreased and cleaned by a standard cleaning procedure, then it was outgassed within the growth chamber. The sputtering ambience was O<sub>2</sub> and Ar atmosphere. During the course of sputtering, Ag and Al dopants were doped, respectively. Finally the grown ZnO films were annealed at 1000°C for one hour in oxygen atmosphere.

Variable energy positron measurements were performed for samples at room temperature. 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 <sup>85</sup>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.

Figure 1 reveals the normalized  $S$  parameters as a function of the positron incident energy  $E$  for ZnO films with different dopants, Si single crystal and undoped ZnO single crystal. In Fig. 1, for Si single crystal the  $S$  parameters first monotonically increase with positron implantation energy, then they keep constant at the range of 12–17 keV, so it can be normalized using the medial  $S$  parameters corresponding to 12–17 keV. While for ZnO single crystal  $S$  parameters firstly monotonically decrease, then they keep constant. For the ZnO/Si samples,  $S$  parameters firstly descend in the low energy region, and subsequently reach a platform, and finally ascend with energy rising for each sample. In a low-energy region, a part of the positrons implanted could form some positronium near the sample surface, resulting in the  $S$  parameter growing. At the highest incident energy range,  $S$  parameters increase with the positron incident energy increasing. This arises from some positrons can annihilate at the interface between the ZnO film and the Si substrate, even in the Si substrate because of so wide positron implantation profile corresponding to high incident energy. Due to the effect of surface, the interface between the ZnO film and the Si substrate,  $S$  parameter will increase. Therefore the  $S$  parameters on the bottom platform for each film are least affected by these factors, they could be looked upon as most positrons annihilation in the ZnO film. The average of  $S$  parameters on the bottom platform is 0.888 ( $S_{un}$ ), 0.893 ( $S_{Al}$ ) and 0.887 ( $S_{Ag}$ ) for undoped, Al-doped and Ag-doped ZnO films, respectively.

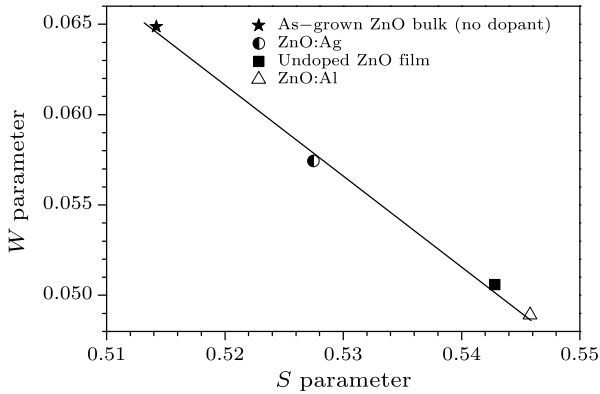


**Fig. 1.** Normalized  $S$  parameter as a function of positron implantation energy for ZnO films with different dopants, Si single crystal and undoped ZnO single crystal.

Although the  $S$  parameter for Ag-doped sample is the minimum among all the ZnO films, it is still larger than 0.834, the average of  $S$  parameter on the flat for

ZnO single crystal. This indicates that some positron trapping centres are present in all ZnO films.

The relationship between  $S$  and  $W$  parameters is shown in Fig. 2. The number of different vacancy-type defects trapping positron in materials can be investigated by the linearity between the annihilation parameters  $S$  and  $W$ .<sup>[21]</sup> 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 is clearly seen that the type defect in ZnO films is the same as ZnO single crystal.



**Fig. 2.** Dependence of  $W$  on  $S$  for ZnO films with different dopants.

To accurately identify the defect type, positron lifetime in ZnO single crystal was carried out. The positron lifetime spectroscopy of ZnO single crystal was measured using a fast-fast coincidence lifetime spectrometer. The second lifetime component is  $232(\pm 6.1)$  ps, decomposed from the measured spectrum. This value is in good agreement with the result of Tuomisto *et al.*<sup>[23]</sup> Moreover, the positron lifetime around the zinc vacancies is 235 ps, given by the theoretical calculation. Thus zinc vacancies are present in ZnO single crystal. Combined with Doppler broadening measurements and the positron lifetime result, it can be deduced that the trapping centres to positrons in ZnO films are zinc vacancies.

As mentioned above, the average of  $S$  parameters on the bottom platform is considered as positron annihilation in ZnO films. The  $S$  parameter in the ZnO film 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  $S = S_b f_b + S_d f_d$ , where  $S_b$  and  $S_d$  are the  $S$  parameters corresponding to the ZnO perfect lattice and the ZnO defect respectively; and  $f_b$  and  $f_d$  are the fractions of positrons annihilated at the ZnO perfect lattice and around the defects ( $f_b + f_d = 1$ ). The defect type for all ZnO films is the same, so the  $S$  parameter around the defects  $S_d$  is a constant. According to  $S_{Al} > S_{un} > S_{Ag}$ ,

$S_b = \text{const}$  and  $S_d = \text{const}$ , it is deduced that the annihilation fraction  $f_{Al}$  in Al doped ZnO films is the largest for all ZnO films. The annihilation fraction is given by  $f = \mu C_v / (\lambda_B + \mu C_v)$ , then  $C_v = \lambda_B f / \mu (1 - f)$ , where  $\mu$  is the specific trapping rate due to the vacancies,  $C_v$  the concentration of the vacancies and  $\lambda_B$  the annihilation rate of positrons from bulk state.<sup>[24]</sup> Since the defect type is the same and all films are ZnO films,  $\mu$  and  $\lambda_B$  are the same for different-dopant ZnO films. Thus vacancy concentration is determined by the  $f$  value. The larger the value of  $f$ , the greater the concentration  $C_v$ . According to  $f_{Al} > f_{un} > f_{Ag}$ , the vacancy concentration meets the expression  $C_{v,Al} > C_{v,un} > C_{v,Ag}$ . It means that zinc vacancy concentration in Al doped ZnO films is the largest compared with undoped and Ag-doped ZnO films. In addition,  $S_{Ag}$  is less than  $S_{un}$ , but the difference between both the values is little, which means that the vacancy concentration in undoped ZnO film is slightly higher than that in Ag-doped ZnO film.

Usually undoped ZnO films exhibit n-type conductivity, when Al atoms are doped in ZnO films, Al atoms act as donors, then electron density increases. This leads to Fermi energy level rising. In ZnO the formation enthalpies of native acceptor defects of  $V_{Zn}$  can be written<sup>[25–27]</sup>, as

$$\Delta H^{(2-, V_{Zn})} = \Delta E^{(2-, V_{Zn})} + \mu_{ZnO} - \mu_O - 2eE_F, \quad (1)$$

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,  $\mu_{ZnO}$  and  $\mu_O$  represent the chemical potential of ZnO and oxygen, respectively, and  $E_F$  is the Fermi energy level. With the Fermi energy increasing, the defect formation energy of zinc vacancies decreases in n-type ZnO, which has been reported by Oba *et al.*<sup>[20]</sup> Thus the concentration of Zn vacancies in Al-doped ZnO films is greater than that of undoped and Ag-doped ZnO film.

When Ag atoms are doped in the ZnO film, they could substitute Zn sites, and  $Ag_{Zn}$  acts as acceptors, so ZnO films show p-type conductivity, and p-type conductivity has been shown by  $I$ - $V$  curve.<sup>[15]</sup>  $E_f$  lowers in p-type semiconductor, so the defect formation energy of zinc vacancies increases, which results in the concentration of zinc vacancies reduced in Ag-doped ZnO films. Ag-doped ZnO is similar to Mg-doped GaN. Mg atoms act as acceptors in GaN. Saarinen *et al.* reported that the concentration of Ga vacancies decreases with Mg concentration rising.<sup>[21]</sup> As mentioned above, the vacancy concentration in undoped ZnO films is slightly higher than that of Ag-doped ZnO films. It may be ascribed to dopant difficulty and weak p-type conductivity.<sup>[14,28]</sup>

The influence of dopants on defects in ZnO films

has been investigated. The results demonstrate that Zn vacancies are found in all ZnO films with different dopants. The concentration of Zn vacancy is the least in Ag-doped ZnO films compared with Al doped and undoped ZnO films. The defect formation energy could be adjusted by different dopants, due to the shift of Fermi energy levels after doping.

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