Energy Variable Slow Positron Beam Study of Li^+-Implantation-Induced Defects in ZnO

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(Received 30 November 2005)

ZnO films grown on sapphire substrates are implanted with 100-keV Li ions up to a total dose of 1×10^{16} cm^{-2}. Vacancy-type defects, mostly vacancy clusters, are observed by positron annihilation measurements after implantation. Upon annealing, they first have an agglomeration process which leads to the growth in the vacancy size. After annealing at about 500°C, vacancy clusters grow into microvoids, which is indicated by the positronium formation. With annealing temperature increases to above 500°C, the microvoids begin to recover, and finally all the implantation-induced vacancy defects are removed at 1000°C. No Li nanoclusters can be observed after Li^+ implantation.

PACS: 61.80.Jh, 61.72.Ji, 78.70.Bj

Since the successful growth of large area ZnO single crystals, there has been a growing interest in this material.[1] Due to the wide band gap (3.4 eV) and large exciton binding energy (60 meV), it has promising applications in the blue and ultraviolet light emitting devices.[2,3] However, previous studies have shown that in ZnO, there are always various kinds of defects, which affect both electrical and optical properties. For example, the native defects such as Zn_i or V_O can act as donors, and cause intrinsic n-type conductivity in the undoped ZnO.[4] They may compensate acceptors and cause unexpected p-type doping problem.[5] The defects can also act as nonradiative recombination centres, and deteriorate the light emitting efficiency. Therefore, understanding the behaviour of defects in ZnO is a very important subject.

Positron annihilation is a new and powerful method for studying vacancy-type defects in semiconductors.[6] Zn vacancies have been identified in the as-grown and electron irradiated ZnO.[7–9] More complicated defects such as vacancy clusters were also observed after ion implantation.[10] In this Letter, we study the defects induced by Li implantation in a ZnO film using an energy variable (0.2–30 keV) slow positron beam. Lithium is a light ion, however, our results show that the implantation-induced vacancies have a sufficient increase in the size and grow into microvoids after annealing, which might be due to the chemical effect of the Li ions.

ZnO films were grown on Al_2O_3 $(11\bar{2}0)$ substrates using the pulsed laser deposition method. A pulsed KrF excimer laser (248 nm, 10 Hz) was irradiated on a sintered bulk ZnO (purity 99.99%). The Al_2O_3 substrate was kept at 500°C. The oxygen partial pressure was about 10^{-2} Torr. X-ray diffraction and Raman scattering measurements show successful growth of c-axis oriented ZnO layer.[11] The thickness of the film is about 1 μm. Lithium implantation was performed at room temperature using a 400-keV implanter. The ion energy was 100 keV, and the total ion dose was 1×10^{16} cm^{-2}. The implanted samples were annealed in nitrogen ambient to study the thermal recovery of the defects. Doppler broadening of positron annihilation was measured for the ZnO film as a function of the incident positron energy. The spectra were analysed using the S parameter which is defined as the ratio of the central region to the total area of the 511-keV annihilation peak.

The S parameters as a function of positron incident energy ($S - E$ curve) measured for the ZnO film before and after Li^+ implantation and annealing are plotted in Fig. 1. The upper x-axis shows the average positron implantation depth. A defect free ZnO bulk crystal grown by the hydrothermal method was also implanted and studied simultaneously. The results of the film and bulk crystal show high repeatability. The S parameter shows a relatively higher value at low positron energy of 0–5 keV, which is due to the positron annihilation at the surface. For the as-grown ZnO film, the S parameter keeps constant at about 1.01 with $E > 5$ keV, indicating that no positron diffusions return to the surface, and all the positrons annihilate in the ZnO bulk region. In this study, the S parameters are all normalized to that for the ZnO single crystals. Therefore, $S = 1.01$ means that there are a small number of vacancy defects in the as-grown ZnO film. The decrease of S parameter above 15 keV is due to positron annihilation in the Al_2O_3 substrate.

After Li^+ implantation, the S parameter shows a great increase up to around 1.05 at 5–15 keV. This re-

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veals that vacancy defects are introduced, and most of them are vacancy clusters. Upon annealing, the $S-E$ curves show considerable changes, which reflects the thermal evolution of defects. After final annealing at 1000°C, the $S-E$ curve recovers to that in the as-grown state. The average S parameter in the energy range of 8–11 keV contains the defect information in the central implanted region. Figure 2 shows its value as a function of annealing temperature. It first increases continuously with annealing temperature, and attains a high value of nearly 1.17 at 500°C. This increase is mostly due to the agglomeration of the vacancy clusters, which results in the increase of their size. After further annealing above 500°C, the S parameter begins to decrease, and at 1000°C, it reaches almost the bulk value for the as-grown sample. This indicates the recovery process of the vacancy clusters, and all the vacancy defects induced by implantation are annealed out at 1000°C.

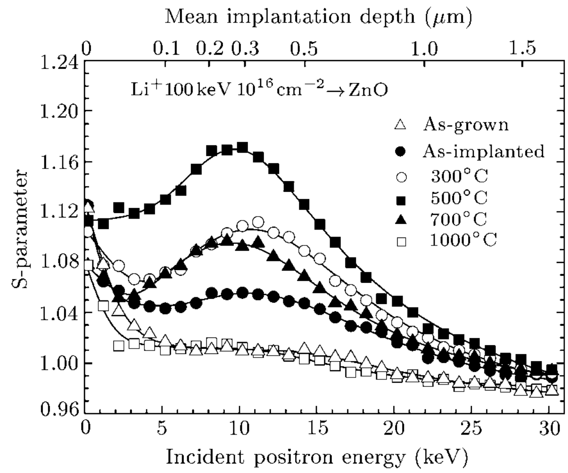

Fig. 1. $S-E$ curves measured for the Li^+-implanted ZnO before and after annealing.

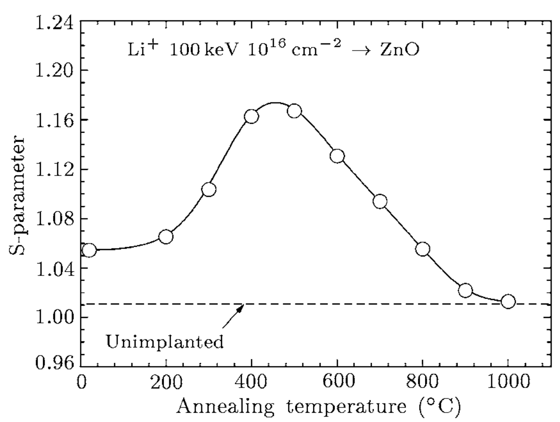

Fig. 2. Average S parameter in the energy range of 8–11 keV as a function of annealing temperature for the Li^+-implanted ZnO.

The high S parameter at 500°C suggests that the vacancy clusters have grown into a very large size. Possibly microvoids have been formed, and the high S parameter might be due to the formation of positronium in the microvoids. The para-positronium (p-Ps), which has very narrow momentum distribution, will result in a sufficient increase of the S parameter. In order to verify the formation of positronium, we analysed the Doppler broadening spectra using a multiple gaussian fitting procedure.[12] For the as-grown and as-implanted ZnO samples, only two wide gaussian components (about 2.8 keV and 5.1 keV in full width at half maximum) are observed, which reflect the momentum distribution of the valence and core electrons, respectively. After annealing the implanted sample at 500°C, a narrow component of about 1.4 keV appears with intensity of 16%. This is obviously the p-Ps annihilation peak.[11,12] For this 500°C annealed sample, we also measured the coincidence Doppler broadening spectrum which both improves the energy resolution and reduces the background. After a deconvolution procedure, a narrow peak can be clearly seen, which is shown in Fig. 3. This further confirms the formation of p-Ps.

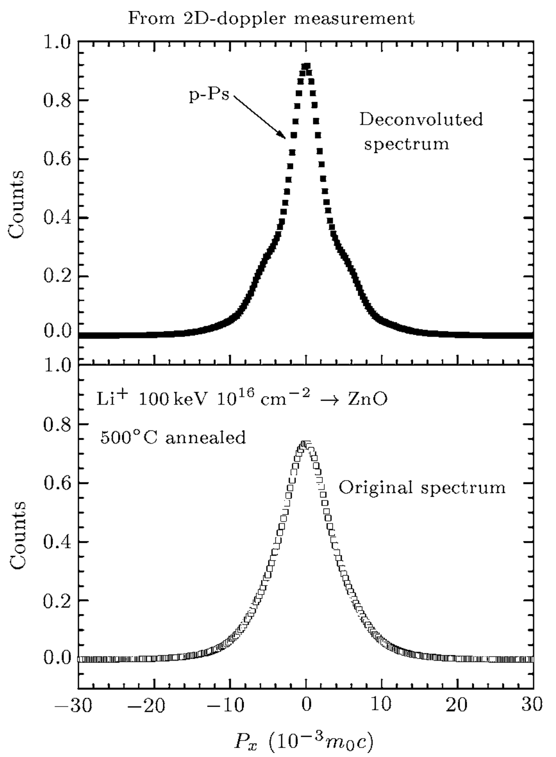

Fig. 3. Original and deconvoluted Doppler broadening spectra measured for the Li^+-implanted ZnO after annealing at 500 °C.

There is yet another possible origin for the narrow Doppler broadening peak appeared after annealing of the Li^+-implanted ZnO: that is, the Li nanocluster formation. The positron may be confined in the nanoclusters due to their strong affinity.[13] Because of the rather small Fermi cutoff,[14] the electron momentum distribution for the Li crystal is very narrow and van Huis *et al.*[15] indeed observed a narrow Doppler broadening spectrum in the Li^+-implanted MgO after annealing, and they attributed to the Li nanocluster formation. However, we believe that the large increase of the S parameter in our Li^+-implanted ZnO is not due to formation of nanoclusters. The reasons are as follows. (1) The width of the Doppler broadening spectrum of Li crystals is around 1.8–1.9 keV, which is much wider than our resolved narrow component of 1.4 keV. (2) In our experiment, the incorporated Li peak concentration is only $3\times10^{20}\,\mathrm{cm}^{-3}$, which is not enough for the nanocluster formation. (3) The nanocluster has high thermal stability, which is kept to be stable in the Li^+-implanted MgO.[15] However, in our results, the S parameter begins to decrease at 600°C. This indicates that the high S parameter is not due to the Li nanoclusters.

In order to further exclude the possibility of Li nanoclusters, we illustrate the ratio curve of the Doppler broadening spectra measured for the Li^+-implanted sample to the as-grown ZnO reference sample, as shown in Fig. 4. The ratio curve for the Al^+-implanted ZnO is also included for comparison. These two curves show completely the same structure. In the Al^+-implanted sample, we have found the p-Ps formation after annealing.[10] Therefore, this comparison also confirms that the narrowing of the Doppler broadening spectrum in the Li^+-implanted ZnO is due to the p-Ps formation in the microvoids other than the nanocluster formation.

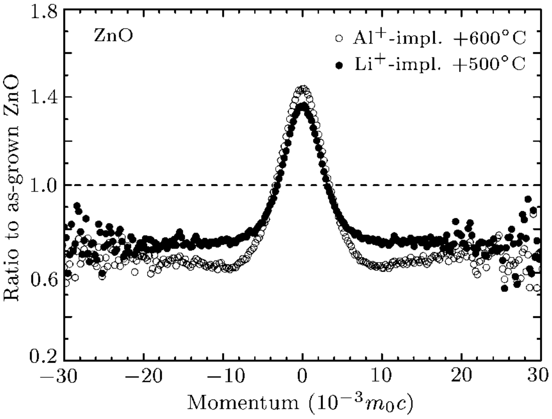

Fig. 4. Ratio of the coincidence Doppler broadening spectra for the Li^+ and Al^+-implanted ZnO to the as-grown ZnO.

The fast growth of the vacancies into microvoids after annealing of the Li^+-implanted ZnO might be due to the chemical effects of Li ions. That is, some defects are stabilized by Li ions. Actually we did not observe the microvoid formation after implantation by other ions such as N^+ and O^+, which has much heavier ion mass. The Li impurities implanted into ZnO might combine with oxygen interstitials O_i, and form Li_2O complexes. A very recent theoretical calculation[16] has predicted the formation of Li_2O included in the Li doped ZnO. Due to this complex formation, the recombination of oxygen vacancies (V_O) and O_i is suppressed. Therefore, oxygen vacancies are stabilized. When these oxygen vacancies cannot find sinks to annihilate, they possibly contribute to the microvoid formation through the agglomeration process during annealing.

In summary, positron annihilation measurements have been carried out to study the introduction of vacancy defects in the Li^+ implanted ZnO. These vacancies evolve into large microvoids during annealing. This is possibly due to the chemical effect of Li impurities, which stabilize some defects such as oxygen vacancies.

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