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Ion-implantation Induced Defects in ZnO Studied by a Slow Positron Beam

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Abstract. Introduction and annealing behavior of defects in Al^+-implanted ZnO have been studied using an energy variable slow positron beam. Vacancy clusters are produced after Al^+-implantation. With increasing ion dose above 10^{14} Al^+/cm^2 the implanted layer is amorphized. Heat treatment up to 600 ^oC enhances the creation of large voids that allow the positronium formation. The large voids disappear accompanying the recrystallization process by further heat treatment above 600 ^oC. Afterwards, implanted Al impurities are completely activated to contribute to the n-type conduction. The ZnO crystal quality is also improved after recrystallization.

Introduction

ZnO is now a promising material for applications as short wavelength optoelectronic devices because of its wide band gap (3.4 eV) and large exciton binding energy (60 meV) [1]. To fabricate these devices, effective doping methods which enable to control both n- and p-type conduction should be established. Ion implantation is an effective way of doping in semiconductors. However, ion implantation always introduces severe damage. Hence, understanding the production and recovery of implantation damage is necessary. Up to now defects induced by implantation in ZnO have not been adequately studied [2]. In this paper, we investigated the production and recovery process of damage in Al^+-implanted ZnO single crystals using a slow positron beam [3].

Experiment

Hydrothermally grown (0001) ZnO single crystals (undoped n-type) were purchased from SPC Inc. Prior to implantation the crystals were annealed at 900 ^oC in a nitrogen ambient for two hours to reduce grown-in defects [4]. Aluminum ions were implanted with multiple energies from 50 to 380 keV so that a box-like implantation profile is formed. The ion dose ranged from $10^{13}/cm^2$ to $10^{15}/cm^2$. Isochronal annealing was performed for the implanted samples in a nitrogen ambient from 200 to 900 ^oC for 30min. Doppler broadening of annihilation radiation measurements were performed using an energy variable slow positron beam. Positron lifetime spectra were also measured using a pulsed slow positron beam. The electrical and optical properties of the samples after implantation were characterized by Hall and cathodoluminescence measurements.

Results and Discussion

Figure1 shows the *S-E* curves for the Al^+-implanted ZnO with different doses. Before implantation, the S-parameter shows decrease with increasing positron energy and becomes constant after E >5 keV. This is a typical change of the positron state from surface to the deep bulk state. After implantation, we can observe a plateau area in the energy range of 3-11 keV. The S-parameter in this area increases with increasing ion dose and attains nearly 1.08 at the highest dose. This indicates the

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introduction of defects in the Al^+-implanted box layer. The predominant defects are possibly vacancy clusters. The average S-parameter in the implanted layer is obtained by summing the spectra measured in the energy range of 5-9 keV. The change of the S-parameter as a function of the annealing temperature is shown in Fig.2. It shows similar change for all the samples, i.e., it increases with annealing temperature until 600 ^oC, and then decreases to the bulk value after further annealing. The S-parameter increases to very high values for the two samples implanted at higher doses, i.e., about 1.26 and 1.14 at 600 ^oC, respectively. It might be due to the formation of positronium (Ps) [5].

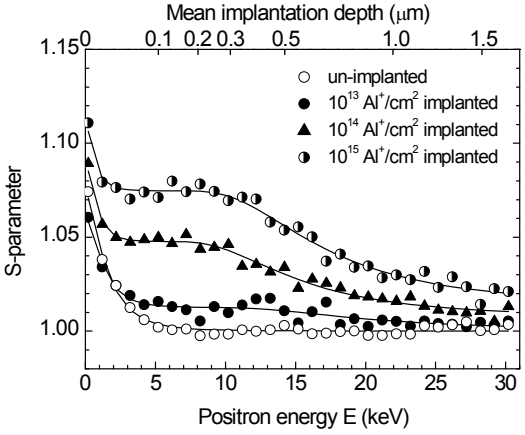

Fig.1 S-E curves measured for the ZnO before and after Al^+ implantation with different doses.

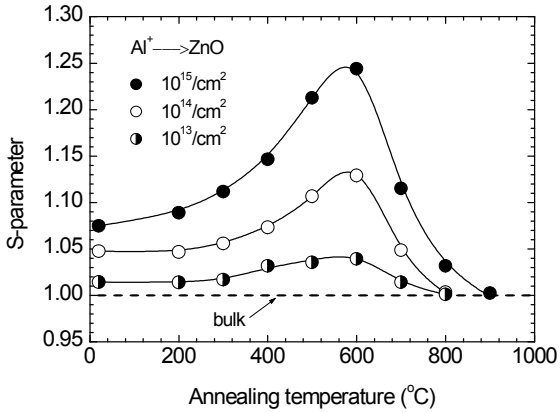

Fig.2 Annealing behavior of the S-parameter in the implanted layer for the Al^+- implanted ZnO.

To clarify this possibility, we measured the positron lifetime at E=7 keV for the implanted sample at a dose of 10^{15} Al^+/cm^2. Figure 3 shows the positron lifetime analyzed by the CONTIN program [6]. Before implantation, only one narrow peak centered at around 192 ps is seen. This indicates that very few positron traps exist in the unimplanted sample. After implantation, two peaks are observed. The second peak is around 374 ps with an integrated intensity of about 66%. This lifetime is apparently due to the positron trapping at large vacancy clusters introduced by implantation. The first peak of about 210 ps might be the average lifetime of the free and trapped positrons at small vacancies. After 600 ^oC annealing, the second lifetime increases to around 530 ps with intensity of about 40%, and it becomes rather broad. This long lifetime is due to the o-Ps annihilation. The first lifetime also shows a slight increase in spite of the Ps formation. This might be due to the positron trapping by some vacancies or vacancy clusters, of which the size or concentration increases after annealing.

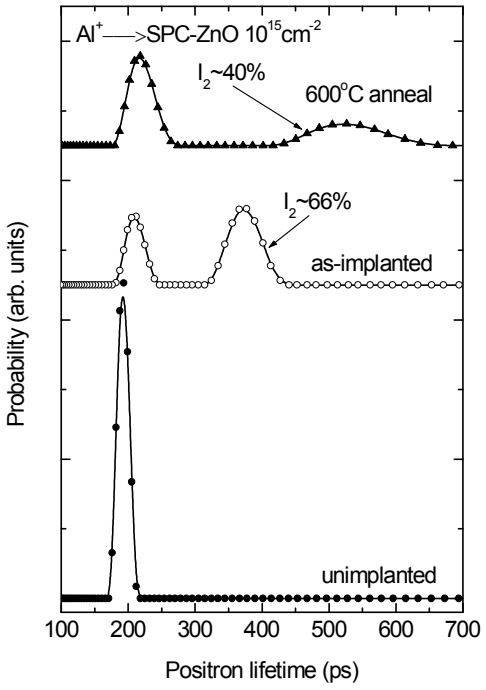

Fig.3 Positron lifetime distribution for the ZnO before and after Al^+-implantation (10^{15} Al^+/cm^2) and 600^oC annealing. The incident positron energy is fixed at 7 keV.

The formation of Ps means that large voids are formed after annealing. This suggests that the samples become amorphized or partly amorphized after implantation at doses higher than 10^{14} Al^+/cm^2. The annealing will cause agglomeration of vacancies or vacancy clusters into large voids, which is energetically more favorable. These large voids are necessary for the Ps to form and reside. Further annealing will cause the amorphous structure to transform to the crystalline structure through a recrystallization process. From Fig. 2, we can also see that the S-parameter approaches the bulk value

after high temperature annealing (800-900 °C). This means that the large voids disappear during the recrystallization process, and the implantation-induced damage is completely recovered. On the other hand, for the sample implanted at the lowest dose (10^{13} Al^+/cm^2), the increase of S-parameter is small even after annealing. This means no amorphization occurs in this sample.

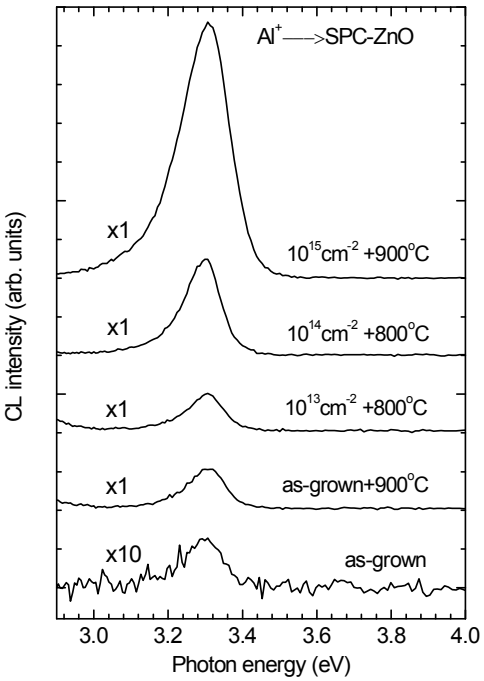

Fig.4 Cathodoluminescence spectra measured at room temperature for the ZnO samples before and after Al^+-implantation and annealing

The sample implanted at a dose of 10^{15} Al^+/cm^2 shows strong n-type conductivity after annealing. The free carrier concentration increases from $3.6\times10^{14}/cm^3$ for the unimplanted sample to $8.6\times10^{19}/cm^3$ after implantation, which is comparable to the implanted Al^+ concentration ($\sim7.5\times10^{19}/cm^3$). This means that the implanted Al^+ dopants are completely activated as donors. The electron mobility also increases from 70 $cm^2V^{-1}s^{-1}$ to 167 $cm^2V^{-1}s^{-1}$ after implantation and annealing. This confirms that the implantation damage is completely removed, and the crystal quality after recrystallization is even better than that of the unimplanted state.

Figure 4 shows the result of cathodoluminescence measurements. For the as-grown ZnO, the ultraviolet (UV) emission is rather weak. This is due to the existence of defects, which act as nonradiative recombination centers. After 900 °C annealing, these defects are reduced, thus the UV emission is enhanced. After Al^+-implantation at a dose of 10^{14} Al^+/cm^2 and 800 °C annealing, it shows further enhancement, and after implantation at dose of 10^{15} Al^+/cm^2 and 900 °C annealing, the UV emission is enhanced by about 60 times as compared to the as-grown sample. This means that after recrystallization of the amorphous structure through annealing, the ZnO crystal quality is greatly improved. This is in good agreement with the increase of electron mobility as shown by the Hall measurements. Without amorphization, the UV emission shows no improvement, which is the case of the low dose (10^{13} Al^+/cm^2) implanted sample.

Summary

Vacancy clusters are produced by Al^+-implantation in ZnO. Amorphous layers are formed after implantation at doses higher than 10^{14} Al^+/cm^2. Upon annealing, large voids are formed through the rearrangement of the amorphous structure. After further annealing, these voids disappear due to recrystallization. The implanted Al^+ dopants are activated as donors after annealing. The Hall and cathodoluminescence measurements also show that the crystal quality of ZnO is improved after recrystallization.

References

[1] D. C. Look, Mater. Sci. Eng. B 80 (2001) 383.

[2] S. O. Kucheyev, J. S. Williams, C. Jagadish, J. Zhou, C. Evans, A. J. Nelson and A. V. Hamza, Phys. Rev. B 67 (2003) 094115.

[3] P. G. Coleman, *Positron Beams and their Applications* (World Scientific, Singapore, 2000).

[4] Z. Q. Chen, S. Yamamoto, M. Maekawa, A. Kawasuso, X. L. Yuan, T. Sekiguchi, J. Appl. Phys. to be appeared, scheduled issue October 15, 2003

[5] A. Van Veen, H. Schut and P. E. Mijnarends, in ref [3], p208.

[6] R. B. Gregory, Y. Zhu, Nucl. Instrum. Methods A 290 (1990) 172.

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10.4028/www.scientific.net/MSF.445-446

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[2] S. O. Kucheyev, J. S. Williams, C. Jagadish, J. Zhou, C. Evans, A. J. Nelson and A. V. Hamza, Phys. Rev. B 67 (2003) 094115.
10.1103/PhysRevB.67.094115