Donor-acceptor pair luminescence of nitrogen-implanted ZnO single crystal

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Donor-acceptor-pair (DAP) luminescence is a direct probe of the acceptors in ZnO. We report the near-surface doping of a ZnO single crystal by ion implantation with nitrogen and titanium. Secondary-ion-mass spectroscopy shows that the doping depth is approximately 80 nm (N) and 50 nm (Ti). The DAP photoluminescence centered at 3.232 eV is observed from both the undoped and doped ZnO single-crystal samples. The luminescence spectrum of the nitrogen-doped sample shows enhancement of the DAP transition compared to the “pure” ZnO sample. The acceptor energy is calculated to be 177 meV, consistent with nitrogen as the acceptor in DAP luminescence. The DAP recombination lifetime is found to be ~5.5 ns. The temperature evolution of spectra shows the gradual transition from DAP luminescence to electron+ acceptor recombination luminescence at temperatures above 37 K. Our experimental results suggest that ion implantation is an effective way of doping nitrogen into ZnO. © 2005 American Institute of Physics. [DOI: 10.1063/1.1854208]

INTRODUCTION

ZnO has received a lot of attention in the past decade for its potential as an ultraviolet diode laser material. The 59-meV exciton binding energy and the availability of large high-quality single-crystal substrates make ZnO interesting as a possible alternative to GaN. Despite the fact that some technical problems have been solved, a particular challenge remains: how to produce reliable p-type ZnO. Various groups1–10 (also as reviewed by Look and Claf tin11) have reported results on fabricating p-type ZnO. However, many of these samples suffer generally from reproducibility12,13 and stability14,17 issues. The prevalence of donors in naturally grown ZnO materials and their compensation effect on attempted p doping14 pose a challenge to achieving high-quality p-type ZnO. In addition, the verification of p-type conduction by Hall effect measurement is difficult in highly compensated material.16

As in other II-VI and III-V semiconductors,17,18 the donor-acceptor-pair (DAP) transition in ZnO is an important light-emission mechanism. The observations of DAP luminescence in ZnO and other acceptor-related luminescence, such as acceptor bound excitons8 and free electron + acceptor recombination,19 have been reported. These luminescence signatures are direct probes of the acceptors in ZnO. For example, the donor-acceptor-pair luminescence is observed in ZnO (Ref. 19) with acceptor concentrations as low as 2 × 1015 cm−3. Thonke et al.19 and Zeuner et al.20 assigned their observed 3.232-eV peak in ZnO luminescence spectra to a DAP transition. In both cases it was believed that the acceptor participating in the DAP transition is N0 (nitrogen substituting on an oxygen site). However, more experimental evidence is necessary to further confirm the assignment of the 3.232-eV photoluminescence (PL) line to N0-related DAP transition.

Nitrogen is regarded as the most promising dopant to achieve p-type ZnO.21 Among many methods of attempting nitrogen doping, there were recently several reports on doping of ZnO with nitrogen by ion implantation.22–24 Georgobiani et al. reported p-type ZnO by nitrogen-ion implantation followed by annealing in oxygen radicals.24 However, we have not yet seen reports on the DAP luminescence of nitrogen-ion-implanted ZnO.

In this paper, we report the observation of the 3.232-eV DAP luminescence in ZnO single-crystal codoped with nitrogen and titanium by ion implantation. The lifetime of DAP recombination and the temperature evolution of the spectra were studied in order to further understand the nature of the 3.232-eV PL line. Our results support the assignment of this line to a DAP transition. The corresponding acceptor energy is calculated to be 177 meV, in agreement with N0 as the acceptor.

EXPERIMENT

The ZnO single-crystal wafer used for ion implantation was grown by Eagle–Picher Inc. using a seeded chemical-vapor transport technique. The (0001) wafer surfaces were chemomechanically polished to epitaxy substrate standards
The incorporation of N and Ti into ZnO is verified by SIMS measurement.

by Eagle–Picher. The ion implantation was carried out by using a metal vapor vacuum arc (MEVVA) ion source, a high current device which can readily produce an ion-beam current of several hundreds of microamperes on target.\textsuperscript{25} A TiN (>99.5% purity) rod was chosen as the target. The base pressure was $2 \times 10^{-6}$ mbar. After 2000 conditioning shots, TiN was implanted into the (0001) surface of ZnO at room temperature. The extraction potential was 40 kV. The ion-beam current was 40 mA.

The measured TiN dose was $2.1 \times 10^{15}$ cm$^{-2}$, characterized by Rutherford backscattering. The effectiveness of incorporating nitrogen and titanium into ZnO by ion implantation is verified by secondary-ion-mass spectroscopy (SIMS), as shown in Fig. 1. According to SIMS, the implant doping depths of Ti and N are approximately 50 and 80 nm, respectively, with Gaussian profiles. Energy dispersive x-ray spectroscopy (EDX) mapping shows a uniform distribution of Ti and N along the crystal surface of ZnO.

The decision to choose TiN as the target follows the concept of codoping. Recent reports have suggested that ZnO codoped with Ga and N is a promising approach to achieve $p$-type ZnO.\textsuperscript{26,27} The chemical valence (3+) of titanium is the same as that of gallium. The role of Ti in our doped ZnO is still under investigation.

After implantation, the crystal turned slightly brown in color. The coloration is believed to be due to a near-edge absorption band due to N doping, as suggested by Garces et al.\textsuperscript{28} No significant luminescence signal was observed before annealing, indicating that the ion-implantation-induced defects act as nonradiative recombination centers.\textsuperscript{22} The sample was then annealed in vacuum ($1 \times 10^{-6}$ Torr) at 850 °C for 15 min. Annealing removes the structural defects introduced by ion implantation\textsuperscript{22,23} and provides a way to activate the nitrogen acceptors passivated by, for example, N–H pairs.\textsuperscript{26–30} After annealing, the crystal was still brown in color, but less so.

For purpose of comparison, another piece of Eagle–Picher ZnO single crystal from the same wafer as the implanted piece was used as a reference. Both samples were characterized at the same experimental condition. A Hamamatsu C2830 streak camera (with slow speed streak unit M2548) was used to capture the time-resolved photoluminescence spectra.

**RESULTS**

The spectrum of the undoped sample is shown in Fig. 2(a). The dominant peak at 3.360 eV is the luminescence of a neutral-donor-bound exciton ($D^0X$) complex. The phonon-assisted transitions of $D^0X$ are located at 3.282 eV ($D^0X$ +LO) and 3.203 eV ($D^0X$+2LO), respectively. The two-electron-satellite (TES) peak of $D^0X$ is centered at 3.314 eV. According to the peak positions of the TES and $D^0X$, we can calculate the electron binding energy of the donor ($E_D$) to be 46 meV. Our result of $E_D$ is close to the literature reports of 52–54 meV (Ref. 29) and 40 meV.\textsuperscript{19}

The DAP peak from the undoped sample located at 3.232 eV is several times weaker than its $D^0X$+2LO neighbor at 3.203 eV. The native DAP peak from the undoped ZnO crystal produced by Eagle–Picher has been previously observed by Thonke et al.,\textsuperscript{19} who suggested that nitrogen may be responsible.

The DAP luminescence intensity of the nitrogen-implanted sample prepared on the identical ZnO single-crystal substrate demonstrates an enhancement of peak intensity, as seen in Fig. 2(b). Its intensity is stronger than the $D^0X$+2LO peak, and the one-phonon replica of DAP is
clearly visible at 3.153 eV. Given the fact that for both samples the DAP peak positions are the same, it is believed that the same type of acceptor, most likely related to nitrogen, is responsible for the DAP transition at 3.232 eV. In addition, the 3.232-eV peak position closely matches the reported DAP photoluminescence of ZnO films doped with N by chemical-vapor deposition. Furthermore, we have found no evidence from the literature that the Ti-related defects luminesce in this wavelength region.

The enhancement of the DAP peak intensity indicates the increase of acceptor concentration after N- and Ti-ion implantation. However, the doped sample is believed to be still n type since the D^0X luminescence remains dominant in the luminescence spectrum.

By calculating the acceptor energy, we obtain further indication that the DAP luminescence results from nitrogen acceptors. The acceptor energy, E_a, is given by the following equation:

\[
E_a = E_{gap}(T) - E_d - E_{DAP} + \alpha N_d^{1/3},
\]

where \(E_{gap}(T)\) is the band gap of ZnO at temperature \(T\), \(E_d\) is the donor energy, and \(E_{DAP}\) is the energy of DAP. The last term \(\alpha N_d^{1/3}\) approximates the average inherent Coulomb potential energy of each DAP. The coefficient \(\alpha\) is 2.7 \(\times 10^{-8}\) eV cm for ZnO.\(^{19}\) \(N_d\) is the donor concentration, which is 1.7 \(\times 10^{17}\) cm\(^{-3}\) in the undoped Eagle–Picher ZnO single crystal.\(^{19,5}\) The band gap \(g_{gap}(T)\) (Ref. 32) is 3.440 eV at 16 K.

By plugging these parameters into the Eq. (1) above, we obtain the acceptor energy \(E_a = 177\) meV above the valence band maximum. Thonke et al.\(^{19}\) found a similar result of 195 meV. Zeuner et al\(^{29}\) fit the DAP luminescence decay time to the Thomas–Hopfield model\(^{31}\) and calculated the nitrogen acceptor energy to be 165 meV.

The time-resolved photoluminescence spectrum in the form of a streak camera display is shown in Fig. 3. The upper streak at 3.232 eV is the DAP luminescence, whereas the bottom streak at 3.199 eV is the two-phonon replica of D^0X. Since the YAG pulse width is 3 ns, the observed lifetimes are the convolution of the actual lifetimes with the shape of the laser pulse. We have previously reported\(^{33}\) that the lifetime of D^0X in ZnO, and thus its corresponding phonon replicas, is about 50 ps at 16 K. So the bottom streak in Fig. 3 actually represents the shape of the YAG laser pulse. The observed duration of the DAP luminescence streak is 7.3 ns, which is considerably longer than the width of the laser pulse. After deconvolution, the DAP decay time to 50% of peak intensity is \(\tau_{1/2} = 5.5\) ns. (The Thomas–Hopfield model\(^{31}\) yields a non-exponential decay profile. However, the signal/noise ratio of the present data is not sufficient to try to fit the deconvoluted signal to the Thomas–Hopfield model.) Our 5.5-ns DAP lifetime is about 100 times longer than the result by Zeuner et al\(^{29}\). The difference may result from the sample dependence and/or excitation intensity. In either case, the DAP luminescence lifetime in ZnO is much shorter than in GaN (Ref. 34) and most other semiconductors. The reason is not apparent. The nanosecond recombination lifetime of DAP in our N-doped ZnO, distinguishing itself from the D^0X lifetime (50 ps), further supports the assignment of the 3.232 eV peak to DAP luminescence. It is also shown in Fig. 3 that the DAP peak rises up slightly later than that of the D^0X+2LO.

This extra delay might be attributed to the capture of electrons and holes at the donor and acceptor sites.

The temperature dependence of the spectra is plotted in Fig. 4. From 16 to 29 K, the DAP peak position has little shift. At 37 K and higher, the shape of the peak becomes asymmetric, and the position shifts to the blue side. Evidently, the spectra at 37 and 62 K have double-peak structures, as seen in Figs. 4(b) and 4(c). We fit the experimental spectra to a sum of two peaks, as shown in the dashed and dot curves in Figs. 4(b) and 4(c). The peak positions at 62 K are centered at 3.230 eV (DAP) and 3.238 eV, respectively. The 3.230-eV component is sufficiently close to the DAP peak already identified at 16 K (3.232 eV), that we have assigned it to DAP. Thonke et al\(^{19}\) observed a peak at 3.236 eV at 40 K, which they attributed to electron-acceptor recombination (\(e, A^0\)). We therefore attribute our 3.238-eV fitting component to \(e, A^0\). The spectral evolution from 16 to 62 K indicates that the donors become thermally ionized at higher temperature, which gives way to a new \(e, A^0\) peak at 2.338 eV, i.e., the free electron+acceptor...
transition. At even higher temperature, the \((e, A^0)\) peak starts to lose intensity, probably because the acceptor level becomes more populated. At the same time, since a broad free exciton (FE+LO) luminescence peak gains intensity as the temperature goes up, an inclined spectrum base line builds up at the acceptor luminescence peak position, originating from the free exciton luminescence shoulder. The broad free exciton luminescence eventually buries the \((e, A^0)\) peak when temperature goes up, as seen in Fig. 4(a).

CONCLUSION

In summary, we have shown that N and Ti can be codoped into ZnO crystals by ion implantation. Photoluminescence can only be observed after annealing the sample, suggesting that annealing is an effective way to achieve defect healing and activation of acceptors. The enhanced peak at ~3.232 eV is confirmed as a DAP transition by investigating the decay time of DAP luminescence, studying the temperature evolution of DAP and \((e, A^0)\) luminescence, and comparing with published results. We conclude that the nitrogen acceptor is responsible for the DAP luminescence with the acceptor energy of approximately 177 meV above the valence-band maximum. The temperature evolution of the spectra shows a gradual transition from DAP luminescence to electron-acceptor luminescence at temperatures above 37 K. The DAP recombination lifetime is measured as \(\tau_{1/2} = 5.5 \text{ ns}\), which is 100 times longer than the result by Zuener et al., while still short compared to the DAP lifetime in other materials.

A much weaker DAP peak can also be observed from the undoped Eagle–Picher ZnO sample, which has been reported before. Comparing the spectrum with our implanted sample led us to suggest that the DAP peak from the Eagle–Picher ZnO single crystal comes from unintentionally doped nitrogen introduced during the manufacturing process.

Our nitrogen-doped sample is still \(n\) type, characterized by the dominant \(D^0\)\(X\) luminescence peak. In the future, effort will be made to achieve near-surface net \(p\)-type doping. The role of Ti in the doped sample has not yet been completely studied.

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