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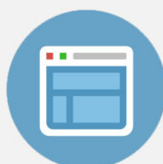

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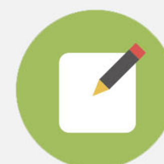

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Effect of (O, As) dual implantation on p-type doping of ZnO films

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Optical and electrical characteristics of ZnO films co-implanted with O and As ions have been investigated by photoluminescence (PL), Hall-effect, and current-voltage (I-V) measurements. 100-nm-thick ZnO films grown on n-type Si (100) wafers by RF sputtering have been implanted with various fluences of 30 keV O and 100 keV As ions at room temperature, and subsequently annealed at 800 °C for 20 min in a N_2 ambient. The dually-implanted ZnO films show stable p-type characteristics for particular implant combinations, consistent with the observation of dominant PL peaks at 3.328 and 3.357 eV that are associated with the acceptor levels. For these dually-implanted p-type ZnO films/n-type Si diodes, the I-V curves show rectifying p-n junction behavior. Other singly (As)- or dually-implanted samples show n-type or indeterminable doping characteristics. These results suggest that O implantation plays a key role in forming p-type ZnO films by reducing the oxygen vacancy concentration and facilitating the formation of As-related acceptors in ZnO. © *2011 American Institute of Physics*. [doi:10.1063/1.3662908]

I. INTRODUCTION

ZnO has attracted attention as a promising material for ultraviolet optoelectronic devices such as light-emitting diodes and laser diodes because of its direct-gap band structure, large bandgap (3.479 eV), and high exciton binding energy (60 meV).[1,2] This has led to a broad range of studies on the structural, electrical, optical, and magnetic properties of ZnO thin-films.[3–7] Undoped ZnO films are n-type semiconductor with native defects such as oxygen vacancies, Zn vacancies, oxygen interstitials, Zn interstitials, and oxygen antisites.[8] Currently, it is very difficult to obtain stable and reproducible *p*-type ZnO due to the high self-compensating intrinsic donor defects, the high ionization energy of acceptor impurities, and the low solubility of p-type dopants in ZnO.[9,10] The choice of acceptor dopant and doping method is therefore crucial for the preparation of high-quality p-type ZnO and significant effort has been devoted to this aim in the recent years.[11–13] Despite this effort, no well-accepted and controllable method has emerged for realizing p-type ZnO and the issue remains unsolved.

One feasible method to overcome the inherent obstacles to p-type doping is the donor-acceptor co-doping method proposed by several research groups.[3,4,14] However, this approach is limited by low mobility at high hole concentrations. Ion-implantation and subsequent heat treatment is a well-established doping technique, especially for selective-area doping and most p-type ZnO films produced by ion implantation exhibit higher mobility than those obtained by the co-doping method.[15,16] In this paper, we employ the dual ion implantation of O and As for p-type doping of ZnO films, in which O ions are expected to reduce intrinsic donor defects, thereby facilitating p-type doping, and study the resulting optical and electrical properties of these dually-implanted films.

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II. EXPERIMENTAL DETAILS

The ZnO targets (99.99%) were mounted in a RF magnetron sputtering system and used to deposit ZnO films on n-type Si (100) wafers. Prior to use, the substrates were ultrasonically cleaned in acetone and alcohol, and then rinsed in de-ionized (DI) water. After the system was evacuated to a base pressure of 3×10^{-6} Torr, the substrates were pre-sputtered at a power of 50 W for 10 min. The ZnO sputtering was then performed at room temperature (RT) for 50 min at a working pressure of 10^{-3} Torr. Other deposition conditions are as follows: RF power, 70 W; deposition rate, 2 nm/min; and gas mixing ratio of O_2/Ar, 1:8. The resulting ZnO films were subsequently implanted at RT, firstly with 30 keV O^- ions to fluences of 1×10^{14} and 1×10^{15} cm^{-2}, and secondly with 100 keV As ions to fluences of 1×10^{14}, 5×10^{14}, and 1×10^{15} cm^{-2}. They were then annealed at 800 °C for 20 min in a N_2 ambient. The peak excess-As and O concentrations for these implants were calculated from SRIM simulation to be in the range from 2.4×10^{19} to 2.4×10^{20} $As.cm^{-3}$, and 1.6×10^{19} to 1.6×10^{20} $O.cm^{-3}$.[17]

The crystal structure of the ZnO films was investigated by using an X-ray diffractometer, and their thickness was estimated to be 100 nm by using a surface profiler (alpha step IQ). Photoluminescence (PL) spectra were measured using the 325 nm line of a He-Cd laser as the excitation source. Emitted light was collected by a lens and analyzed using a grating monochromator and a GaAs photomultiplier tube. Standard lock-in detection techniques were used to maximize the signal-to-noise ratio. The laser beam diameter was about 0.3 mm and the power density was about 2.12 W/cm^2.

Hall-effect measurements were performed in an apparatus (Ecopia model HEM-2000) by using the Van der Pauw method. For Ohmic contacts, an In film of 500 μm in diameter

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was deposited on the ZnO film by using a shadow mask in a thermal evaporator and was subsequently annealed at 300 °C for 10 min. The intensity of the B field was 0.37 T, and the current was varied from 0.1 μA to 10 mA. All Hall measurements were done in a dark room to exclude ambient light.

III. RESULTS AND DISCUSSION

Figure 1 shows PL spectra of unimplanted and singly-/dually-implanted ZnO films measured at 22 K. The unimplanted ZnO shows two PL peaks at 3.320 and 3.357 eV, which are known to originate from two-electron satellite (TES) recombination of neutral-donor-bound exciton[18] and neutral-acceptor-bound exciton (A^0X) transition,[19,20] respectively. After As implantation to a fluence of 5×10^{14} cm^{-2} the TES peak is lowered relative to the A^0X peak. When the As fluence is increased to 1×10^{15} cm^{-2} a new PL peak, identified as free electron to acceptor level (FA) transition,[19,20] appears at 3.328 eV, while the TES peak is further reduced. The FA peak increases further after the additional implantation of O to a fluence of 1×10^{14} cm^{-2}, suggesting that the O implantation facilitates the formation of acceptors by reducing the native defects. The two major emissions FA and A^0X, which are believed to be closely related to As dopant-related acceptors, are essentially unaffected by the further increase of O fluence to 1×10^{15} cm^{-2} at a fixed As fluence of 1×10^{15} cm^{-2}.

From an Arrhenius plot of the A^0X PL intensity for the sample dually (O, As) implanted to fluences of 1×10^{14} cm^{-2} and 1×10^{15} cm^{-2}, respectively, we extracted the binding energy of the A^0X emission to be $\sim$18.5 meV. Subsequently, the As-acceptor binding energy was estimated to be $\sim$185 meV using the Haynes rule,[21] in good agreement with previously-reported values,[21,22] meaning that the acceptor level was well formed in the bandgap of ZnO.

Hall measurements were performed on all implanted samples, and their results are summarized in Table I. It was not possible to measure the Hall effect for the samples singly implanted to a fluence of 1×10^{14} As cm^{-2} and dually implanted to fluences $\leq 5 \times 10^{14}$ As cm^{-2}. The singly-implanted ZnO films are n-type at a fluence of 5×10^{14} As cm^{-2}, but n- or p-type (indeterminable) at a fluence of 1×10^{15} As cm^{-2}. The dually-implanted ZnO films show stable p-type characteristics at a As fluence of 1×10^{15} cm^{-2} for both O fluences. The ZnO films dually implanted to fluences of 1×10^{15} As cm^{-2} and 1×10^{14} O cm^{-2} exhibit the highest mobility, 32.9 cm^2/Vs, together with the lowest resistivity, 0.0486 Ω cm, the latter being much lower than the values previously reported for As-doped ZnO.[19,23]

TABLE I. Hall-effect results of implanted ZnO films.

Samples (As cm^{-2}) (O cm^{-2})	Resistivity (Ωcm)	Mobility (cm^2/Vs)	Carrier concentration (cm^{-3})	Carrier type
5×10^{14} No oxygen	0.14	19.1	2.26×10^{18}	n
1×10^{15} No oxygen	0.08	5.7	1.17×10^{19}	n or p
1×10^{15} 1×10^{14}	0.0486	32.9	6.08×10^{18}	p
1×10^{15} 1×10^{15}	0.0548	19	1.98×10^{19}	p
Others	Failed to measure the Hall effects			

Figure 2 shows XRD spectra of unimplanted and implanted ZnO films. The peak at a 2θ of $\sim$34.2°, which is attributed to the ZnO (002) reflection,[24] is dominant for all samples. Despite a small increase in the bandwidth of the XRD peak after implantation, the peak intensity and position do not change, indicating little, if any, variation in the crystal quality of the ZnO films after implantation.

I–V characteristics were measured for the p-ZnO/n-Si wafer diode structures (the upper-left inset in Fig. 3) to confirm the p-type doping of the ZnO films dually implanted with two different O fluences. Figure 3 shows plots of the I–V characteristics clearly exhibiting rectifying $p-n$ junction behavior for both diodes. The diode with lower O fluence shows much better rectifying behavior, possibly resulting from better electrical matching with n-type Si wafer, even though its carrier concentration is smaller, as shown in Table I. The threshold voltage of this junction is in the range of 2–2.3 V, similar to previously-reported values.[21] The lower inset in Fig. 3 shows the I–V characteristics measured between two Al electrodes on the surfaces of both diodes, as

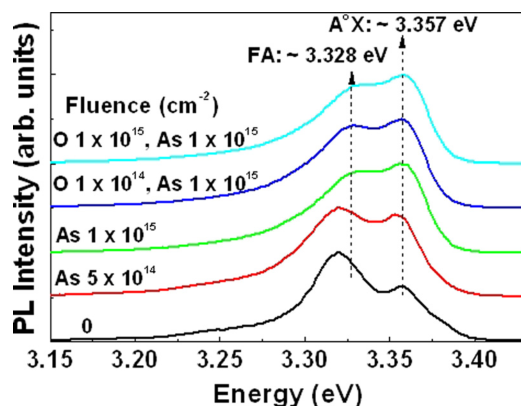

FIG. 1. (Color online) PL spectra of unimplanted and singly-/dually-implanted ZnO films measured at 22 K. The implantation was done with As ions alone or with O ions followed by As ions. The fluences are indicated.

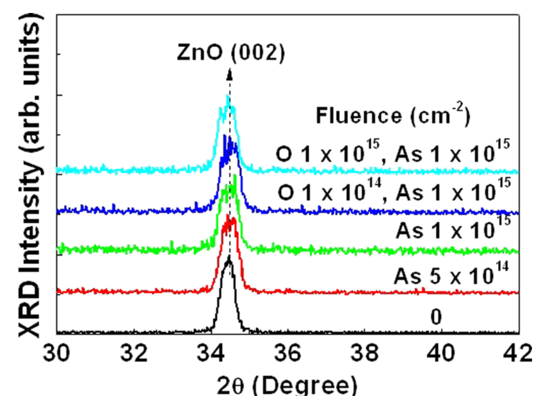

FIG. 2. (Color online) XRD spectra of same unimplanted and singly-/dually-implanted ZnO films used in Fig. 1.

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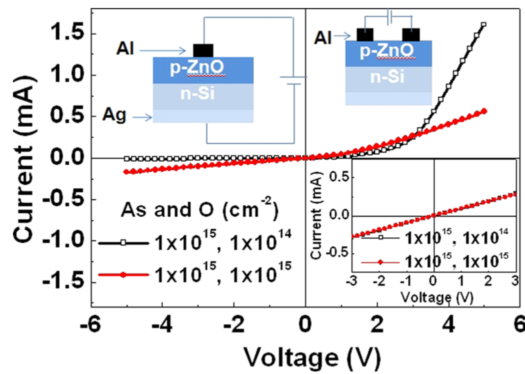

FIG. 3. (Color online) I–V characteristics of diode structures containing the dually-implanted ZnO films with two different O fluences on n-type Si wafers. The upper-left inset shows the diode structure. The lower inset shows the I–V characteristics measured between two Al electrodes on the surfaces of both diodes, as shown in the upper-right inset.

shown in the upper-right inset, demonstrating the Ohmic behavior.

The intrinsic properties of ZnO can be improved by controlling its preparation conditions,[25–27] for example, undoped p-type ZnO was produced by the density variation of the native oxygen defects due to the adjustment of oxygen partial pressure in the sputtering plasma. The ZnO films fabricated at higher oxygen partial pressure exhibited p-type conduction due to the increase in the density of zinc vacancies and the concomitant decrease in the density of oxygen vacancies.[26] In this previous study, the PL emissions from the n- and p-type ZnO films were dominated by neutral-donor- and neutral-acceptor-bound excitons, respectively. These results are consistent with the doping-type-dependent variations of PL spectra shown in Fig. 1.

A significant increase of the PL intensity in ZnO/ZnMgO multiple quantum wells has also been observed after implantation with low fluences of O, similar to those used in this work, and attributed to the suppression of the point defect complexes and transformation between defect structures by implantation and subsequent rapid thermal annealing.[28] However, high-fluence implantation led to lattice damage and agglomeration of defects to form large defect clusters resulting in an increase in nonradiative recombination.[28] It is also clear that p-type doping in ZnO is obtained by substituting group-V elements (N, P, and As) for O sites.[13] In the present case, it is similarly expected that the density of oxygen vacancies is reduced during annealing after O implantation, due to the occupation of vacant oxygen sites, resulting in the increase of stable Zn-O bonds[29] and thereby reducing the effect of self-compensation by intrinsic donor defects.

IV. CONCLUSION

100-nm-thick ZnO films grown on n-type Si (100) wafers by RF sputtering were implanted with As ions alone or with O ions followed by As ions for various fluences at RT, and subsequently annealed at 800 °C for 20 min in a N_2 ambient. The ZnO films dually implanted with particular fluences of O and As showed stable p-type behavior and rectifying p-n junction behavior, respectively, consistent with the observation of dominant acceptor-related PL peaks. These results suggest that the O implantation plays a key role in forming p-type ZnO films by reducing the density of oxygen vacancies and facilitating the formation of As-induced acceptors in ZnO.

ACKNOWLEDGMENTS

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[1]X. Ma, P. Chen, D. Li, Y. Zhang, and D. Yang, Appl. Phys. Lett. **91**, 021105 (2007).
[2]J.-H. Lim, C.-K. Kang, K.-K. Kim, D.-K. Hwang, and S.-J. Park, Adv. Mater. **18**, 2720 (2006).
[3]H. L. Pan, B. Yao, T. Yang, Y. Xu, B. Y. Zhang, W. W. Liu, and D. Z. Shen, Appl. Phys. Lett. **97**, 142101 (2010).
[4]B. Y. Zhang, B. Yao, Y. F. Li, Z. Z. Zhang, B. H. Li, C. X. Shan, D. X. Zhao, and D. Z. Shen, Appl. Phys. Lett. **97**, 222101 (2010).
[5]D. K. Lee, S. Kim, M. C. Kim, S. H. Eom, H. T. Oh, and S.-H. Choi, J. Korean Phys. Soc. **51**, 1378 (2007).
[6]S. Kim, D. K. Lee, S. H. Hong, S. H. Eom, H. T. Oh, S.-H. Choi, H. N. Hwang, and C. C. Hwang, J. Appl. Phys. **103**, 023514 (2008).
[7]J. R. Neal, A. J. Behan, R. M. Ibrahim, H. J. Blythe, M. Ziese, A. M. Fox, and G. A. Gehring, Phys. Rev. Lett. **96**, 197208 (2006).
[8]B. Lin, Z. Fu, and Y. Jia, Appl. Phys. Lett. **79**, 943 (2001).
[9]S. B. Zhang, S. H. Wei, and A. Zunger, Phys. Rev. B **63**, 075205 (2001).
[10]D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002).
[11]Y. Yang, X. W. Sun, B. K. Tay, G. F. You, S. T. Tan, and K. L. Teo, Appl. Phys. Lett. **93**, 253107 (2008).
[12]Y. Nakano, T. Morikawa, T. Ohwaki, and Y. Taga, Appl. Phys. Lett. **88**, 172103 (2006).
[13]Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç, J. Appl. Phys. **98**, 041301 (2005).
[14]L. G. Wang and A. Zunger, Phys. Rev. Lett. **90**, 256401 (2003).
[15]K. Wang, Z. B. Ding, T. X. Chen, D. Chen, S. D. Yao, and Z. X. Fu, Nucl. Instrum. Methods Phys. Res. B **266**, 2962 (2008).
[16]C. C. Lin, S. Y. Chen, S. Y. Cheng, and H. Y. Lee, Appl. Phys. Lett. **84**, 5040 (2004).
[17]P. Biersack and L. G. Haggmark, Nucl. Instrum. Methods Phys. Res. B **174**, 257 (1980).
[18]B. K. Meyer, H. Alvesl, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straßburg, M. Dworzak, U. Haboeck, and A. V. Rodina, Phys. Status Solidi B **241**, 231 (2004).
[19]Y. R. Ryu, T. S. Lee, and H. W. White, Appl. Phys. Lett. **83**, 87 (2003).
[20]H. S. Kang, G. H. Kim, D. L. Kim, H. W. Chang, B. D. Ahn, and S. Y. Lee, Appl. Phys. Lett. **89**, 181103 (2006).
[21]T. S. Jeong, M. S. Han, C. J. Youna, and Y. S. Park, J. Appl. Phys. **96**, 175 (2004).
[22]C. Morhain, M. Teisseire, S. Ve'zian, F. Vigue', F. Raymond, P. Lorenzini, J. Guion, G. Neu, and J.-P. Faurie, Phys. Status Solidi B **229**, 881 (2002).
[23]Y.-J. Huang, M.-F. Shih, C.-C. Liu, S.-Y. Chu, and K.-Y. Lod, Electrochem. Solid-State Lett. **13**, H373 (2010).
[24]Z. Z. Zhi, Y. C. Liu, B. S. Li, X. T. Zhang, Y. M. Lu, D. Z. Shen, and X. W. Fan, J. Phys. D **36**, 719 (2003).
[25]G. Xiong, J. Wilkinson, B. Mischuck, S. Tuzemen, K. B. Ucer, and R. T. Williams, Appl. Phys. Lett. **80**, 1195 (2002).
[26]Y. Ma, G. T. Du, S. R. Yang, Z. T. Li, B. J. Zhao, X. T. Yang, T. P. Yang, Y. T. Zhang, and D. L. Liu, J. Appl. Phys. **95**, 6268 (2004).
[27]M.-S. Oh, S.-H. Kim, and T.-Y. Seong, Appl. Phys. Lett. **87**, 122103 (2005).
[28]X. Wen, J. A. Davis, L. V. Dao, P. Hannaford, V. A. Coleman, H. H. Tan, C. Jagadish, K. Koike, S. Sasa, M. Inoue, and M. Yano, Appl. Phys. Lett. **90**, 221914 (2007).
[29]A. Powell, W. E. Spicer, and J. C. McMenamin, Phys. Rev. Lett. **27**, 97 (1971).

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