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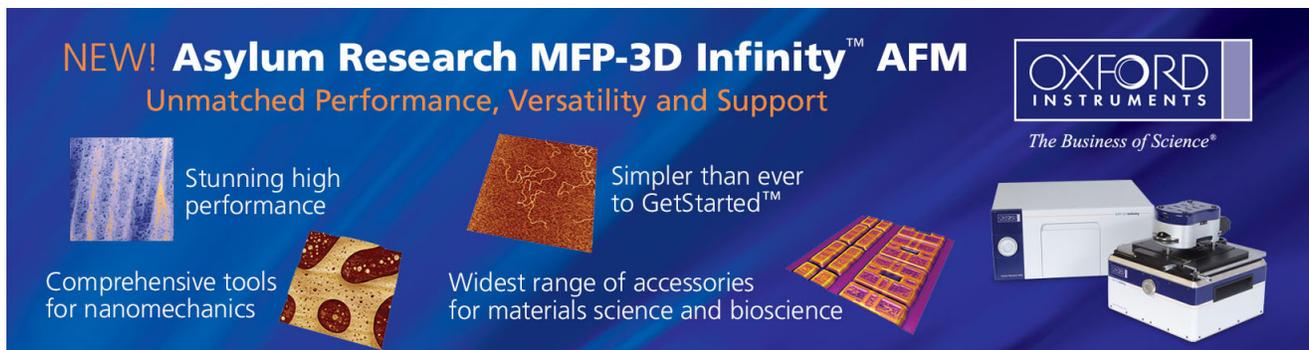
Properties of nitrogen-implanted p-type ZnO films grown on Si_3N_4/Si by radio-frequency magnetron sputtering

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An nitrogen-implanted p-type ZnO film has been grown on a Si substrate buffered with Si_3N_4 using radio-frequency magnetron sputtering. The Si_3N_4 buffer layer can effectively improve film stoichiometry and reduce the formation of oxygen vacancies compared to ZnO on Si. The electrical properties of the p-type ZnO films implanted with 5×10^{12}–1×10^{14} cm^{-2} N^+ dose show a hole concentration of 5.0×10^{16}–7.3×10^{17} cm^{-3}, hole mobility of 2.51–6.02 cm^2/V s, and resistivity of 10.11–15.3 Ω cm. The p-type ZnO films also showed an excellent crystallinity and a strong ultraviolet emission peak near 3.30 eV at room temperature. Moreover, as evidenced by extended x-ray absorption fine structure analysis, the local structure of the p-type ZnO films was changed due to the substitution of nitrogen ions for oxygen ions in p-type ZnO films. Our finding of p-type ZnO films grown on a Si_3N_4/Si substrate could provide a simple method to fabricate reproducible p-type ZnO films on silicon substrate for the development of large-scale optoelectronic integration device. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1763640]

Wide-band-gap optoelectronics, especially for zinc oxide (ZnO), are attracting more attention due to their potential applications in various fields, such as ultraviolet (UV) resistive coating, gas sensors, solar cells, and optical devices.[1,2] For the development of ZnO-based optoelectronic devices, it is necessary to grow high-quality both p- and n-type ZnO thin films. The n-type ZnO is easily available even without any doping, while it has been recognized that it is very difficult to obtain p-type ZnO because ZnO is a natural n-type semiconductor and the acceptors may have a natural tendency to pair with native defects or background impurities to form electrically inactive complexes although high densities of holes could be achieved with nitrogen as the dopant along with other techniques. Furthermore, the presence of native defects, such as zinc interstitials and oxygen vacancies, causes a deviation from stoichiometry.[3] In order to overcome this problem, recently, several research groups proposed many methods to obtain p-type ZnO films.[4–10] These thin-film growers have demonstrated that nitrogen will enter the ZnO films as shallower acceptor if N_2, N_2O, or NH_3, depending on the growing technique, is used as a source.[11]

It was well known that that as the ZnO films were deposited on substrates, such as sapphire and silicon, a thin oxide layer (probably amorphous SiO_2) is easily grown on its surfaces, and thus, more "extra defects" are easily induced to affect the defect equilibrium in ZnO films due to the formation of the thin oxide layer. On the other hand, in our previous study,[12] it was found that as Si_3N_4 buffer layer was

deposited on Si prior to growing ZnO films, the defect concentration of ZnO film on Si_3N_4/Si was much reduced that is very close to characteristics of intrinsic semiconductor (e^-: -1.40×10^{14} cm^{-3}).

In this letter, we have shown that high reproducible p-type conduction ZnO films with high hole concentration can be grown on Si buffered with Si_3N_4 by radio-frequency (rf) magnetron sputtering along with nitrogen-implanted process. The role of nitrogen-implanted concentration in the electrical and photoluminescence, (PL) of ZnO films will be investigated. In addition, the exact origin of the UV emission and local structural behaviors of p-type ZnO films grown on Si_3N_4/Si is also discussed.

The ZnO thin films ($\sim$150 nm) were deposited on 4-in. Si substrates buffered with Si_3N_4 layers by rf magnetron sputtering using 99.99% ZnO as a target. The buffer layers were grown by electron evaporation and the thickness of the Si_3N_4 buffer layers was measured to be about 40 nm by transmission electron microscopy. The as-grown ZnO film was subsequently subjected to nitrogen ion implantation at room temperature. The nitrogen ion with energy of 80 keV was injected into the as-grown ZnO films. The dose range studied was from 5×10^{12}–5×10^{15} cm^{-2}. After ion implantation, the ZnO films were annealed at 850 °C for 20 min under pure nitrogen atmosphere.

The crystal structure was determined using Siemens D5000 x-ray diffraction (XRD) with Cu $K\alpha$ radiation and a Ni filter. PL measurement was performed by the excitation from 325 nm He–Cd laser at room temperature and 10 K. The electrical properties of the nitrogen-implanted ZnO films were investigated by van der Pauw method room-

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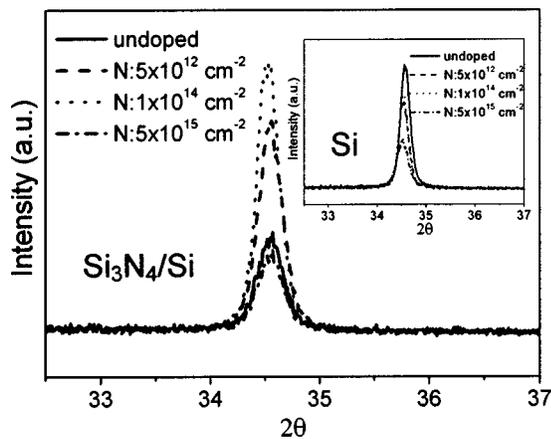
FIG. 1. XRD patterns of ZnO films sputtered at Si, and Si_3N_4/Si substrates with or without N^+-implanted various doses.
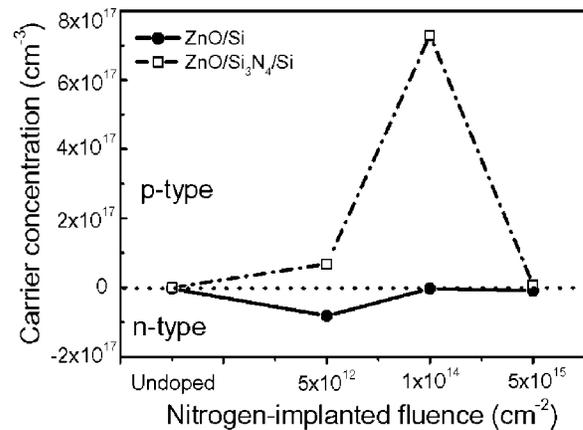

FIG. 2. Electrical conduction type of N^+-implanted ZnO films as a function of various doses.

temperature Hall measurements with nonsintered indium contacts and magnetic field of 0.315 T. The x-ray absorption spectra were recorded at the wiggler beamline SL-17B at National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan.

Figure 1 shows the XRD pattern of nitrogen ions (N^+)-implanted ZnO thin films on Si and Si_3N_4/Si, and then annealed at 850 °C in N_2 atmosphere. Only a sharp diffraction peak of (002) at $2\theta = 34.5°$ can be detected for all the ZnO films, indicating that these ZnO films were highly c-axis oriented. However, as increasing the N^+-implanted concentration form 5×10^{12} to 5×10^{15} cm^{-2}, the intensity of the (002) XRD peak in ZnO films grown on Si substrate decreases as shown in Fig. 1. This suggests that the implanted N^+ in ZnO film on Si presents a strong negative affect on crystalline characteristics of the ZnO films. In contrast, when the ZnO films were grown on Si_3N_4/Si substrates, it was found that (002) diffraction peak becomes stronger with the increase of the implanted N^+ from 5×10^{12} to 1×10^{14} cm^{-2} [Fig. 1]. This reveals that the occupation of the implanted N^+ on oxygen vacancies can improve the crystallinity of ZnO films on Si_3N_4/Si. However, above that, the peak intensity was rapidly decreased, implying that more implanted N^+ probably induces extra defects and this would lead to the lattice distortion.

The electrical conduction type of N^+-implanted ZnO films as a function of doping doses is shown in Fig. 2. The N^+-implanted ZnO films on Si substrate show n-type conduction independent of the implanted N^+ concentration. In sharp contrast, the N^+-implanted ZnO films on Si_3N_4/Si substrate exhibit p-type conduction and the carrier concentration increases up to 7.3×10^{17} cm^{-3} with an increase of N^+-implanted concentration from 5×10^{12} to 1×10^{14} cm^{-2}. According to our previous study, as the ZnO films were deposited on the Si_3N_4/Si structure, x-ray photoelectron spectroscopy analysis demonstrates that a lower oxygen vacancies concentration and thinner interface layer was detected for ZnO on Si_3N_4/Si structure compared to that on Si.[12] Furthermore, the film stoichiometry was improved because of the reduction in oxygen vacancies, indicating that the ratio of Zn:O was decreased.[13] In this condition, the concentration of active acceptors may exceed the donor concentration so that the conduction type was changed from n to p

type. The dependence of conduction type on the implanted N^+ concentration in ZnO films in Fig. 2 suggests the N^+-implanted process can product more holelike carries to transform original conduction (compensate the native carriers). However, a further increase in the implanted dose of the N^+ up to 5×10^{15} cm^{-2} leads to a decrease in hole concentration of p-ZnO and the conduction type of ZnO films would approach the intrinsic conductor.

Resistivity and Hall mobility as a function of implanted N^+ doses were measured and are shown in Fig. 3 for p-type conduction ZnO films. As increasing N^+ doses from 5×10^{12} to 1×10^{14} cm^{-2}, both hole concentration and Hall mobility increase, but the resistivity decreases. The p-type ZnO films grown on Si_3N_4/Si show a hole concentration of 7.3×10^{17} cm^{-3}, a mobility of 6.02 cm^2/V s, and a low resistivity of 10.3 Ω cm. Above that (1×10^{14} cm^{-2}), both hole concentration and Hall mobility decreases, but an increase in resistivity was observed. The initial increase in the hole concentration is due to a decrease in oxygen vacancy as the implanted N^+ doses increase. The decrease in hole concentration after the maximum value is caused by the formation of more defects due to excess N^+ that can compensate for a hole carrier which may correspond to the degradation of the crystal quality in p-type ZnO films as supported by the decrease in the peak intensity of (002) XRD peak in Fig. 1
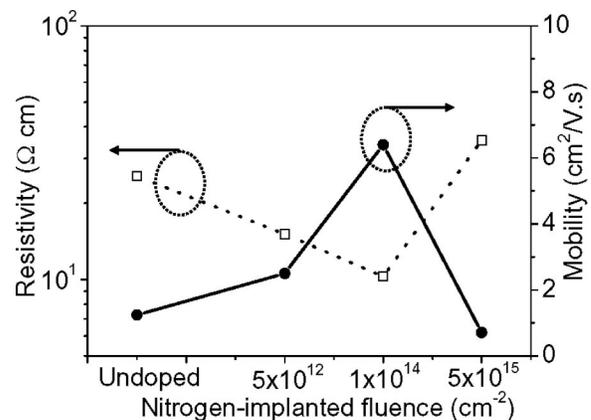

FIG. 3. Variation of resistivity and Hall mobility as a function of different N^+ implanted doses.
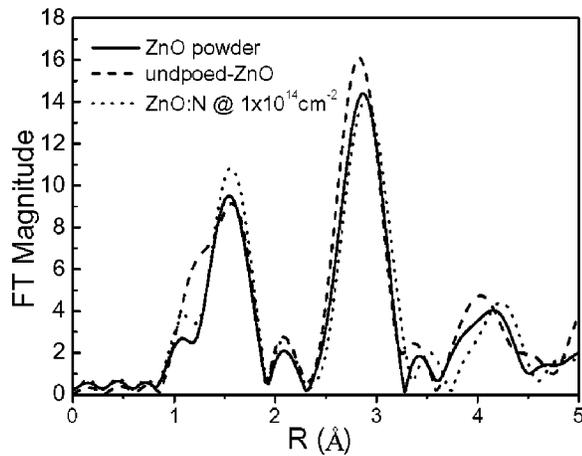
FIG. 4. Fourier transforms at Zn K edge for the ZnO powder standards, nonimplanted, and N^+-implanted $ZnO/Si_3N_4/Si$ samples.

FIG. 5. Room-temperature PL spectra of nonimplanted and N^+-implanted $ZnO/Si_3N_4/Si$ samples.

for the N^+-implanted ZnO film with the dose of 5×10^{15} cm^{-2}.

In order to further understand the local structure of p-type ZnO films, the extended x-ray absorption fine structure was investigated. Figure 4 shows the pseudoradial distribution functions obtained from the k^3-weighted Fourier transforms at Zn K edge for the nonimplanted and N^+-implanted ZnO films on a Si_3N_4/Si structure annealed at 850 °C in N_2 atmospheres, where pure ZnO powder was used as standards for comparison. The first peak in the Fourier transforms corresponds to the nearest-neighbor distance around zinc atoms. The peak position of zinc to oxygen for both bulk powder standards (ZnO: 99.999%) and nonimplanted ZnO thin films is equal to 1.945 Å. For the ZnO film implanted with 1×10^{14} cm^{-2} N^+ dose, the Zn—O bond length in $ZnO/Si_3N_4/Si$ is very similar to that of nonimplanted ZnO films and bulk powder standards. However, for the second nearest-neighbor distance around Zn^{2+}, it was found that the Zn—Zn bond length for nonimplanted ZnO films is shorter than that of N^+-implanted ZnO films. It could be due to the existence of oxygen vacancies in the ZnO lattice matrix that causes the secondary nearest-neighbor distance to become shorter. In comparison with bulk powder standards (3.27 Å), a little larger Zn—Zn bond length (3.28 Å) was also detected for N^+-implanted ZnO films. These observations suggest that the implantation of N^+ into ZnO films could affect the local structure of ZnO film, such as bond distance, but a limited range of 1×10^{14} cm^{-2} N^+ dose can effectively improve the crystal quality of ZnO films.

Figure 5 illustrates the room-temperature PL spectrum of ZnO films implanted with various N^+ doses on Si_3N_4/Si substrates. UV emission with peaks at 3.31, 3.28, 3.29, and 3.30 eV is dominantly observed for the ZnO films implanted with 0, 5×10^{12}, 1×10^{14}, and 5×10^{15} cm^{-2} N^+ dose, respectively. According to the spectrum, it is noticed that the peak intensity of the UV emission depends markedly on the N^+-implanted dose. The ZnO film implanted with a 1×10^{14} cm^{-2} N^+ dose not only shows a stronger peak intensity but also has a narrower full width at half maximum of 95
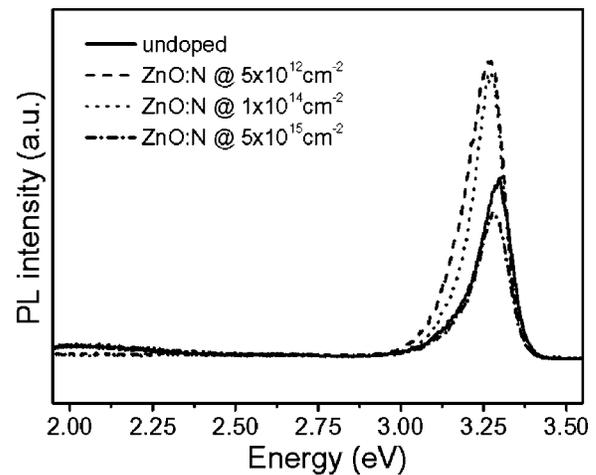
meV than that (110 meV) of nonimplanted ZnO films. In addition, the deep level emission in the ZnO-implanted with $5 \times 10^{12} - 1 \times 10^{14}$ cm^{-2} N^+ dose samples were almost covered by the background signal. In contrast, a weak deep-level emission at around 2.055 eV and 2.015 eV can be observed in nonimplanted and implanted with 5×10^{15} cm^{-2} N^+ dose sample, respectively. It means the point defects dominating the visible transition can be improved by suitable N^+ doping.

In summary, we report on the reproducible p-type ZnO films grown on Si_3N_4/Si by rf magnetron sputtering, implanted with $5 \times 10^{12} - 1 \times 10^{14}$ cm^{-2} N^+ dose and then annealed at 850 °C in N_2 ambient. The hole concentration, carrier mobility, and resistivity of p-type ZnO films were $5.0 \times 10^{16} - 7.3 \times 10^{17}$ cm^{-3}, 2.51–6.02 cm^{-2} V s, and 10.11–15.3 Ω cm, respectively. PL spectra of the N^+-implanted $ZnO/Si_3N_4/Si$ showed a sharp UV emission and invisible deep-level transition at room-temperature measurement. These results suggest that N^+-implanted ZnO films deposited on a Si buffer with Si_3N_4 show electrical and optical behaviors that make them excellent candidates for a good p-type layer for ZnO-based optoelectronic device on a Si-based substrate.

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