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Properties of nitrogen-implanted \( p \)-type ZnO films grown on Si\(_3\)N\(_4\)/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\(_3\)N\(_4\) using radio-frequency magnetron sputtering. The Si\(_3\)N\(_4\) 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 \( 5 \times 10^{12} - 1 \times 10^{14} \) \( \text{cm}^{-2} \) \( \text{N}^+ \) dose show a hole concentration of \( 5.0 \times 10^{16} - 7.3 \times 10^{17} \) \( \text{cm}^{-3} \), hole mobility of \( 2.51 - 6.02 \text{cm}^2/\text{V} \cdot \text{s} \), and resistivity of \( 10.11 - 15.3 \Omega \cdot \text{cm} \). 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\(_3\)N\(_4\)/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.

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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\(_3\)N\(_4\)/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\(^+\) concentration, the (002) peak in ZnO films grown on Si substrate shows a strong negative affect on crystalline characteristics of the ZnO films. In contrast, when the ZnO films were grown on Si\(_3\)N\(_4\)/Si substrates, it was found that (002) diffraction peak becomes stronger with the increase of the implanted N\(^+\) from 5 \(\times\) 10\(^{12}\) to 5 \(\times\) 10\(^{15}\) cm\(^{-2}\). This reveals that the occupation of the implanted N\(^+\) on oxygen vacancies can improve the crystallinity of ZnO films on Si\(_3\)N\(_4\)/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\(_3\)N\(_4\)/Si substrate exhibit p-type conduction and the carrier concentration increases up to 7.3 \(\times\) 10\(^{17}\) cm\(^{-3}\) with an increase of N\(^+\)-implanted concentration from 5 \(\times\) 10\(^{12}\) to 1 \(\times\) 10\(^{15}\) cm\(^{-2}\). According to our previous study, as the ZnO films were deposited on the Si\(_3\)N\(_4\)/Si structure, x-ray photoelectron spectroscopy analysis demonstrates that a lower oxygen vacancies concentration and thinner interface layer was detected for ZnO on Si\(_3\)N\(_4\)/Si structure compared to that on Si. Furthermore, the film stoichiometry was improved because of the reduction in oxygen vacancies, indicating the ratio of Zn:O was decreased. 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 hololelike carriers to transform original conduction (compensate the native carriers). However, a further increase in the implanted dose of the N\(^+\) up to 5 \(\times\) 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 \(\times\) 10\(^{12}\) to 1 \(\times\) 10\(^{14}\) cm\(^{-2}\), both hole concentration and Hall mobility increase, but the resistivity decreases. The p-type ZnO films grown on Si\(_3\)N\(_4\)/Si show a hole concentration of 7.3 \(\times\) 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 \(\times\) 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\(^+\) dose 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. 1](image1.png) FIG. 1. XRD patterns of ZnO films sputtered at Si, and Si\(_3\)N\(_4\)/Si substrates with or without N\(^+\)-implanted various doses.

![Fig. 2](image2.png) FIG. 2. Electrical conduction type of N\(^+\)-implanted ZnO films as a function of various doses.

![Fig. 3](image3.png) FIG. 3. Variation of resistivity and Hall mobility as a function of different N\(^+\)-implanted doses.
for the N$^+$-implanted ZnO film with the dose of 5 \times 10^{15} \text{ 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$_3$N$_4$/Si substrate 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 Zn 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. The ZnO film implanted with \(1 \times 10^{14} \text{ cm}^{-2} \) N$^+$ dose, the Zn—O bond length in ZnO/Si$_3$N$_4$/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 \(1 \times 10^{14} \text{ cm}^{-2} \) 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$_3$N$_4$/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, \(5 \times 10^{12} \), \(1 \times 10^{14} \), and \(5 \times 10^{15} \text{ cm}^{-2} \) 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 \(1 \times 10^{14} \text{ cm}^{-2} \) 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 \(5 \times 10^{12} – 1 \times 10^{14} \text{ cm}^{-2} \) 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 \(5 \times 10^{15} \text{ cm}^{-2} \) 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$_3$N$_4$/Si by rf magnetron sputtering, implanted with \(5 \times 10^{12} – 1 \times 10^{14} \text{ cm}^{-2} \) 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 \(5.0 \times 10^{16} – 7.3 \times 10^{17} \text{ cm}^{-3} \), 2.51–6.02 cm$^2$/Vs, and 10.11–15.3 Ω cm, respectively. PL spectra of the N$^+$-implanted ZnO/Si$_3$N$_4$/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$_3$N$_4$ 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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