ZnO has recently been the subject of great attention to replace GaN-based optical devices because of its characteristic features that include a large band gap energy of 3.37 eV, a large exciton binding energy of 60 meV, the possibility of high doping, and bandgap engineering. In addition, the availability of the large area ZnO thin films, which is an important material in the realization of ZnO light-emitting diodes, including an ultraviolet light emitters. A few key technologies for ZnO device fabrication including ohmic contacts and etching processes have been reported, but they were related only to n-type ZnO.2,3 Ohmic contacts to n-type ZnO produced the specific contact resistances of $10^{-2}$ to $10^{-1}$ $\Omega$ cm$^2$, which are low enough to be used in a ZnO-based device. The ohmic contact to p-type ZnO, however, has not been reported to date, mostly due to the lack of p-type ZnO film, even though the ohmic contacts to p-type ZnO is a critical issue for device fabrications. Several groups have reported on the new p-type doping methods for the growth of p-type ZnO thin films, which is an important material in the realization of ZnO light-emitting diodes.4-6 Recently ZnO-based homojunction devices using excimer laser doping11 and hybrid beam deposition12 have been reported with poor performance on the p-type ohmic contact. Therefore, it is necessary to investigate the electrical behaviors and ohmic contact mechanisms for p-ZnO to realize the ZnO-based light-emitting diodes.

In this study we report on the development of a Ni/Au ohmic contact to p-type ZnO. It is shown that the Ni/Au metallization scheme on p-type ZnO yields a low specific contact resistance of $7.67 \times 10^{-3}$ $\Omega$ cm$^2$ without an annealing process and $1.72 \times 10^{-4}$ $\Omega$ cm$^2$ with an annealing process at 600°C in an air ambient. Glancing angle X-ray diffraction (GXRD) and Auger electron spectroscopy (AES) analysis were adopted to study the mechanism of ohmic contact by examining the structural and chemical evolution of Ni/Au films on p-type ZnO.

**Experimental**

A phosphorus-doped p-type ZnO layer with a thickness of 300 nm was prepared on a (0001) sapphire substrate by a radio frequency (rf) magnetron sputtering method using a ZnO target containing 1 wt % $P_2O_5$ and a subsequent thermal annealing process. Details of the growth process and annealing process dependence of the properties of p-type ZnO films in this study were published elsewhere.8 The p-type ZnO films used in this study had a hole concentration of $1.0 \pm 0.2 \times 10^{18}$ cm$^{-3}$ and a Hall mobility of 2.0 cm$^2$/Vs. The ZnO thin film was degreased prior to metal deposition using trichloroethylene, acetone, methanol, and deionized water, successively. To characterize the extent of interdiffusion between the metal layers and the p-type ZnO film, AES analysis was performed using a PHI 670 Auger microscope with an electron-beam energy of 10 keV and current of 0.029 nA. The interfacial reaction products formed during annealing treatments were identified by GXRD using Cu Kα radiation in a Rigaku diffractometer (D/Max-R). To characterize the extent of interdiffusion between the metal layers and the p-type ZnO film, AES analysis was performed using a PHI 670 Auger microscope with an electron-beam energy of 10 keV and current of 0.029 nA. The interfacial reaction products formed during annealing treatments were identified by GXRD using Cu Kα radiation in a Rigaku diffractometer (D/Max-R).

**Results and Discussion**

Figure 1 shows current-voltage characteristics of the Ni/Au contacts on p-type ZnO. The as-deposited and annealed contacts exhibit a linear ohmic behavior. When the sample was annealed at 400°C,
the contact resistance was slightly improved compared to that of the as-deposited one. The contact annealed at 600°C under an air ambient, however, showed drastically improved I-V characteristics. We performed the Hall effect measurement in order to confirm that the hole concentration in p-type ZnO was not changed by the RTA process because the contact resistance may be decreased by the increase in the hole concentration in the p-type ZnO due to the RTA process. The hole concentration of p-type ZnO, however, was not changed after the RTA process up to 600°C under an air ambient. Specific contact resistances were calculated from plots of the measured resistances vs. the spacings between the c-TLM pads. The specific contact resistance was determined to be $7.67 \pm 10^{-3}$ V cm$^2$ for the as-deposited contact, $6.06 \pm 10^{-3}$ V cm$^2$ for the contacts annealed at 400°C, and $1.72 \pm 10^{-4}$ V cm$^2$ for contact annealed at 600°C under an air ambient. It is noteworthy that the thermal annealing process at 600°C reduces the specific contact resistance by more than one order of magnitude compared to that of the as-deposited contact. The low specific contact resistance for the as-deposited and annealed Ni/Au contacts to p-type ZnO illustrates the potential use of nonalloyed ohmic contacts to p-type ZnO for the realization of ZnO LEDs.

The in-depth Auger profiles of the as-deposited and annealed Ni/Au contact layers on p-type ZnO were examined and illustrated in Fig. 2. Figure 2a shows that there is no interdiffusion between the metal layers and p-type ZnO of the as-deposited sample. The hole concentration of p-type ZnO, however, was not changed after the RTA process up to 600°C under an air ambient. Specific contact resistances were calculated from plots of the measured resistances vs. the spacings between the c-TLM pads. The specific contact resistance was determined to be $7.67 \times 10^{-3}$ Ω cm$^2$ for the as-deposited contact, $6.06 \times 10^{-3}$ Ω cm$^2$ for the contacts annealed at 400°C, and $1.72 \times 10^{-4}$ Ω cm$^2$ for contact annealed at 600°C under an air ambient. It is noteworthy that the thermal annealing process at 600°C reduces the specific contact resistance by more than one order of magnitude compared to that of the as-deposited contact. The low specific contact resistance for the as-deposited and annealed Ni/Au contacts to p-type ZnO illustrates the potential use of nonalloyed ohmic contacts to p-type ZnO for the realization of ZnO LEDs.
annealed sample (Fig. 3b), the GXRD plot shows additional peaks identified as NiO (012) and Au₃Zn (202). These results indicate that the outdiffusion of Zn near the surface of ZnO films to metal layers is enhanced by thermal annealing to form Ni-Zn and Au-Zn phases and further decreases the specific contact resistance due to the increased hole concentration in the annealed sample.

The source of oxygen used in the formation of NiO in the annealed sample is interesting to note. If the oxygen is released from the ZnO layer, the specific contact resistance could be increased by the annealing process because the oxygen vacancies are known as donors, resulting in a decrease in the hole concentration. However, our sample shows the decrease in the specific contact resistance by the thermal annealing process. Therefore, we believe that the oxygen in NiO is originated from the air atmosphere during the thermal annealing process. This is also consistent with the fact that the ZnO formation is more favorable than the NiO formation because the formation enthalpy of NiO ($\Delta H_f = -239.9 \text{kJ/mol}$) is larger than that of ZnO ($\Delta H_f = -350.9 \text{kJ/mol}$). In the previous studies of Ti/Au and Pt/Al contact schemes on n-type ZnO which showed low specific contact resistance by the formation of Ti-O and Al-O phase in the as-deposited sample, the source of oxygen was believed to come from ZnO because the formation enthalpies of TiO and AlO are smaller than that of ZnO. The oxygen vacancies in the ZnO film act as donors, showing an improved ohmic behavior in the as-deposited Ti/Au and Pt/Al contact schemes on the n-type ZnO.

These results indicate that during the RTA process Ni atoms were diffused out through the grain boundaries of Au layers to react with oxygen in air and in turn, Au atoms diffuse into the Ni layer in an early stage of oxidation reaction. Similar diffusion behavior was also observed in Ni/Au contacts to p-GaN. The Ni-Zn phases were then formed and Au reacted also with ZnO, resulting in Au₃Zn phases in the annealed sample. The observation of Au₃Zn phase indicates that more Zn was outdiffused from the ZnO layer by a thermal annealing process. The outdiffusion of Zn results in the accumulation of Zn vacancies at the surface region of the ZnO layer, which can act as acceptors in ZnO. Thus, it is believed that the increase in the hole concentration at the surface region of ZnO could be responsible for the improved ohmic property of the annealed Ni/Au contacts on the p-type ZnO.

**Conclusion**

As-deposited and annealed Ni/Au contacts to p-type ZnO with a hole concentration of $1.0 \times 10^{19} \text{cm}^{-3}$ were investigated using AES and GXRD. The Ni/Au contact annealed by RTA at 600°C for 30 s under an air ambient showed a low specific contact resistance of $1.72 \times 10^{-4} \Omega \text{cm}^2$. The thermal annealing process was found to decrease the specific contact resistance by forming Au phase under the NiO layer and the interfacial reaction products of the Ni-Zn and Au-Zn phases due to the outdiffusion of Zn from the ZnO layer. The outdiffusion of Zn is believed to increase the concentration of Zn vacancies, which act as acceptors, resulting in the decrease of a specific contact resistance in the annealed sample.

**Acknowledgments**

This work was partially supported by National Research Laboratory Program for Nanophotonic Semiconductors in Korea.

**References**