ZnO is a wide bandgap semiconductor material that has a variety of applications, e.g., transparent conducting electrodes, window materials in displays and solar cells, varistors, piezoelectric transducers, and surface-acoustic-wave devices. In addition, ZnO has a low-power threshold for optical pumping at room temperature and a large exciton binding energy of 60 meV at room temperature.1–5 Recently, owing to the growth of p-type ZnO, great attention has been paid to ZnO for its potential for replacing GaN,6,7 and this is of utmost importance for the fabrication of optoelectronic devices. To realize high-performance ZnO-based optoelectronic devices, the formation of high-quality ohmic and Schottky contacts are essential. Studies have been limited mostly to n-type contacts. This is mainly because the growth of p-type ZnO layers is extremely difficult to achieve. Thus, various types of n-type contacts to ZnO, such as Al-, Ti-, Ta-, and Re-based contacts,8–11 have been extensively investigated so far. It was shown that these contacts produced specific contact resistance in the range of \(10^{-4}\) to \(10^{-3}\) \(\Omega\) cm\(^2\) upon annealing. Such a postdeposition annealing at high temperatures during a device process has been widely used to improve ohmic contact characteristics. However, thermal annealing at high temperatures may cause surface roughening, surface decomposition, and spiky interfaces, resulting in the deterioration of device performance and hence device reliability.12 To improve thermal degradation, Kim et al.11 introduced a refractory Re layer between Ti/Au and ZnO layers. In addition, other groups made efforts to obtain nonalloyed ohmic contacts using various surface treatment techniques prior to metal deposition. For example, Lee et al.13 showed that plasma-treatment was effective in forming nonalloyed Ti/Au ohmic contacts on n-ZnO with contact resistivity of 4.3 \(\times\) \(10^{-3}\) \(\Omega\) cm\(^2\). Akane et al.14 used KrF excimer laser treatment to form nonalloyed In ohmic contacts to n-ZnO. However, their samples produced relatively high specific contact resistance of 7 \(\times\) \(10^{-4}\) \(\Omega\) cm\(^2\). In this work, we have investigated KrF laser irradiation effects (in different gas atmospheres) on the electrical properties of nonalloyed Ti/Au ohmic contacts to n-ZnO. The results show that the electrical behaviors of the Ti/Au contacts are influenced by the gas atmospheres used. For example, the contacts give specific contact resistances of 3.22 \(\times\) \(10^{-4}\) and 1.82 \(\times\) \(10^{-4}\) \(\Omega\) cm\(^2\) when laser-irradiated in O\(_2\) and N\(_2\) ambient, respectively. The 0.7-\(\mu\)m thick Al-doped n-type ZnO layers were grown on (0001) sapphire substrates at 800°C by rf sputtering system using a ZnO target containing 0.01 wt% Al\(_2\)O\(_3\). The rf power was 100 W with a frequency of 13.65 MHz, and the working pressure was 10 mTorr with Ar/O\(_2\) gas ratio of 1:3. The carrier concentration and mobility of the samples were measured to be \(3 \times 10^{17}\) \(\text{cm}^{-3}\) and \(-7.9\) \(\text{cm}^{2}/\text{V}\) s, respectively. Prior to laser irradiation, the ZnO layers were ultrasonically degreased using trichloroethylene, acetone, methanol, and deionized (DI) water for 5 min for each step, followed by N\(_2\) blowing. After that, the samples were laser-irradiated ten times using a homogenized KrF excimer laser. The 248 nm excimer laser has pulse durations of 25 ns as a repetition rate of 1 Hz with energy of 300 mJ/cm\(^2\) as measured by an energy power meter. Four different samples were investigated, the ZnO surfaces were laser-irradiated in O\(_2\) (400 Torr) and N\(_2\) ambient (400 and 760 Torr), and under vacuum; these samples are referred to here as O\(_2\)-, N\(_2\)-, and vacuum-irradiated samples, respectively. For comparison, an as-grown ZnO sample (not irradiated) was also investigated. After the laser irradiation, circular transfer length method (CTLM) patterns were defined by the standard photolithographic technique for measuring specific contact resistance. The inner dot radius was 120 \(\mu\)m, and the spacing between the inner and outer radii varied from 4 to 24 \(\mu\)m. Ti (30 nm)/Au (50 nm) layers were then deposited on the ZnO layers by electron beam evaporation. The electrical properties of the films were characterized by Hall effect measurement with the Van der Pauw geometry using a commercial system (BIO-RAD HL 5500PC). Current-voltage (I-V) measurements were carried out using a parameter analyzer (HP 4155A), and the chemical bonding states of the laser-irradiated ZnO were characterized by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250 XPS spectrometer). XPS was carried out using an Al K\(_\alpha\) X-ray source in an ultrahigh vacuum system with chamber base pressure of \(10^{-10}\) Torr.

Figure 1 shows 2-20 scan spectrum of the ZnO layers deposited on the (0001) sapphire substrates. There is a very symmetrical (0002) peak (near 34.4°) from the ZnO layer as well as the (0006) peak associated with the sapphire substrate. The XRD results show that the ZnO layer was epitaxially grown along the c axis normal to the sapphire substrate. The crystallinity of the ZnO layer was characterized by \(\omega\) rocking scanning. The inset in Fig. 1 shows the rocking curve for the ZnO layers, exhibiting a full width at half maximum (fwhm) of 0.12° (432 arccsec). These results show that the Al-doped ZnO layer grown on the sapphire substrate has a very high out-of-plane crystallinity.15

Figure 2 shows the I-V characteristics for Ti/Au contacts on ZnO layers before and after laser irradiation. The as-grown sample reveals nonlinear I-V behavior. It is, however, shown that the laser-irradiated samples give linear I-V behavior. The specific contact resistance was determined from plots of the measured resistance vs. the spacing between the CTLM pads.16 The linear least square method was used to fit a straight line to the experimental data. The specific contact resistances were measured to be 3.22 \(\times\) \(10^{-4}\) and 2.87 \(\times\) \(10^{-4}\) \(\Omega\) cm\(^2\) for the O\(_2\) (400 Torr) and N\(_2\) (760 Torr) irradiated samples, respectively, which are about two orders of magni-
tude lower than that (2.63 \times 10^{-2} \ \text{cm}^2) of the as-grown sample. It is noted that the electrical behaviors of the contacts are further improved when the ZnO layers were irradiated either under low pressure (400 Torr) of N\textsubscript{2} ambient or in vacuum. The specific contact resistance was 1.82 \times 10^{-4} and 1.13 \times 10^{-4} \ \text{cm}^2 for the N\textsubscript{2} (400 Torr) and vacuum-irradiated samples, respectively.

Figure 3 shows a variation of the sheet resistance and carrier concentration of the samples before and after laser irradiation. As compared to the as-grown sample, the laser-irradiated samples give much lower sheet resistance ($R_s$). For example, it was measured to be 2.24 \times 10^5, 1.41 \times 10^4, 1.21 \times 10^4, and 9.5 \times 10^3 \ \Omega/cm\textsuperscript{2} for the as-grown, O\textsubscript{2}-irradiated, N\textsubscript{2} (400 Torr)-irradiated, and vacuum-irradiated samples, respectively. On the other hand, the carrier concentrations are increased by about one order of magnitude when laser-irradiated. It is noted that the carrier concentration of the vacuum-irradiated sample is higher than those of the N\textsubscript{2} and O\textsubscript{2} irradiated samples.

Figure 4 shows the Zn 2p\textsubscript{3/2} XPS spectra obtained from the surface of the ZnO samples before and after laser irradiation. As compared with that of the as-grown sample, the Zn 2p\textsubscript{3/2} core levels of the irradiated samples shift by 0.15–0.35 eV toward the higher binding energy side. This implies that the laser irradiation causes a shift of the surface Fermi levels toward the conduction band minimum, resulting in a reduction of band banding in n-type material.\textsuperscript{19,20}

For low donor density, the current from metal to semiconductor flows due to thermionic emission (TE).\textsuperscript{21} In the intermediate doping range, the carriers are thermally excited to energy, where the barrier is sufficiently narrow for tunneling to occur, known as thermionic-field emission (TFE). For highly doped semiconductors, the current flow is dominated by field emission (FE).\textsuperscript{22,23} The three regimes can be determined by the tunnelling parameter ($E_{00}$) defined as:\textsuperscript{24}

\[
E_{00} = \frac{q \hbar}{4 \pi} \sqrt{\frac{N}{K_s m_0 n_{	ext{tun}}}} = 1.86 \times 10^{-11} \sqrt{\frac{N}{K_s (m_{	ext{tun}}/m)}}
\]

where $N$ is the doping concentration, $K_s$ is the dielectric constant of ZnO, $\epsilon_0$ is the vacuum permittivity, $m_{	ext{tun}}$ is the tunnelling effective mass, and $m$ is the free electron mass. Figure 5 shows the relations between $E_{00}$ and carrier concentration, which were calculated using the above equation and were also measured from the samples. The metal-semiconductor contact theory\textsuperscript{23,25} shows that for $kT \gg E_{00}$, the current flow is dominated by thermionic emission, for $kT = E_{00}$, thermionic-field emission dominates the current flow, and for $kT \ll E_{00}$, field emission is dominant. Measurements showed that $E_{00}/kT$ for the as-grown sample was 0.256. However, for the O\textsubscript{2}, N\textsubscript{2} (400 Torr), and vacuum-irradiated samples, it was 0.571.
To summarize, we have investigated the KrF excimer laser-irradiation effect on the electrical properties of nonalloyed Ti/Au contacts to ZnO under different irradiation atmospheres. Measurements showed that the specific contact resistances were about two orders of magnitude lower than that of the as-grown sample. The results show that the premetallization treatment of Al-doped ZnO by laser irradiation in a vacuum ambient may be potentially promising for achieving low resistance nonalloyed ohmic contacts to n-type ZnO for ZnO-based optical devices.

Acknowledgment

This work was in part supported by the U.S. Air force Office of Scientific Research (AFOSR)/Asian Office of Aerospace Research and Development (AOARD) and the Ministry of Commerce, Industry and Energy (MOCIE, Korea) grant (High-Brightness ZnO Light-Emitting Device Development Project).

Korea University assisted in meeting the publication costs of this article.

References