Low-resistance and highly transparent Ni/indium-tin oxide ohmic contacts to phosphorous-doped p-type ZnO

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The use of a Ni (50 Å)/indium tin oxide (ITO) (500 Å) bilayer scheme for low-resistance and transparent ohmic contacts to phosphorous doped p-type ZnO was investigated. Ni/indium tin oxide (ITO) (50/500 Å) layers were prepared by electron-beam evaporation. Although the as-deposited Ni/ITO contact was highly resistant and opaque, contact resistance and transparency were greatly improved by a thermal annealing process. A specific contact resistance as low as $6.2 \times 10^{-5}$ $\Omega$ cm$^2$ was obtained after thermal annealing at 400 °C for 1 min under an N$_2$ ambient. The measured light transmittance of the Ni/ITO (50/500 Å) bilayer on p-type ZnO was determined to be above 80% at a wavelength of 400–600 nm. These results strongly indicate that the use of a Ni/ITO has considerable promise for ZnO-based optical devices. © 2005 American Institute of Physics.

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Zinc oxide (ZnO) is an attractive material that competes with III-V nitrides in applications for optoelectronic devices, such as ultraviolet (UV) and blue light-emitting diodes (LEDs) and laser diodes in the spectral region and solar cells.1–4 ZnO has a wide direct band gap ($E_g = 3.37$ eV), a large exciton binding energy (60 meV). The band gap may be tuned in the range from 2.8 to 3.3 eV and 3.3 to 4 eV when alloyed with CdO and MgO, respectively. One of the key issues in the fabrication of ZnO-based devices is the high-quality ohmic contacts for n- and p-type ZnO. Although ohmic contacts to n-type ZnO have been reported to be as low as $\sim 10^{-6}$ $\Omega$ cm$^2$ in specific contact resistance using Ti/Au, Al/Pt, Ru metal scheme,8,9,12 the ohmic contact for p-type ZnO film has not yet been reported. Ryu et al.13 reported on the ohmic contact to a p-type ZnO film using Ni/Au (30/100 nm) metal layers but did not discuss the specific contact resistance and ohmic mechanism. In this study, we report on an investigation of a Ni/indium tin oxide (ITO) (50/500 Å) scheme for achieving high-quality ohmic contacts to p-ZnO with low resistance, high conductivity, and high transparency.

ZnO films 0.3 μm thick and p type were deposited by radio-frequency sputtering on a 1.0 μm thick undoped ZnO layer on a sapphire c-plane substrate using a ZnO target containing 1 wt% P$_2$O$_5$. These epilayers were then annealed at 800 °C in a N$_2$ ambient for 1 min to produce p-type ZnO. A detailed description of the growth procedures can be found elsewhere.14 To confirm the p-type properties, Hall effect measurements with the van der Pauw geometry were conducted, giving hole concentration and mobility values of $3 \times 10^{19}$ cm$^{-3}$ and 3.2 cm$^2$/V s, respectively. The annealed ZnO films were ultrasonically degreased in trichloroethylene, acetone, and then methanol for 3 min for each step, and then rinsed with deionized water. Standard photolithography and lift-off techniques were used to define the circular transmission line method (c-TLM) patterns with an inner radius of 200 μm. The spacings between the inner and the outer radii were varied from 5 to 50 μm. Ni/ITO (50/500 Å) films were then deposited on the p-type ZnO by electron-beam evaporation. The deposited samples were subsequently annealed at temperatures ranging from 300 °C to 600 °C under various ambients (N$_2$ and air) in a rapid thermal annealing (RTA) system (AST™). The contact resistances of the samples were measured at room temperature using a parameter analyzer (HP 4155A). To investigate the extent of interdiffusion between the metal layers and the p-type ZnO film, an Auger electron spectroscopy (AES) analysis was carried with Auger depth profiling of the ohmic layers using a PHI 670 Auger microscopy system. X-ray photoemission spectroscopy (XPS) was also performed to investigate the chemical bonding states at the interfaces using a PHI 5200 XPS system. UV-visible transmission spectroscopy was used to measure the transparency of the ohmic layers in the ultraviolet-visible region.

Figure 1 shows the effect of RTA temperature on the specific contact resistance of ohmic contacts annealed under different gas ambients. It is noteworthy that both the annealing atmosphere and temperature have an influence on the formation of the ohmic contact. An electrical current was not detectable in the as-deposited and vacuum-annealed samples. The results show that optimum contact resistivity can be formed on the p-ZnO annealed at 400 °C for 1 min under...
both N₂ and air ambients and that the specific contact resistance of the N₂-annealed contact is much lower than that of the air-annealed contact. The contact resistance was determined from plots of the measured total resistance versus the spacing between the c-TLM pads, giving values of 6.2 × 10⁻² Ω cm² and 1.9 × 10⁻² Ω cm² for contacts annealed at 400 °C in a N₂ or air ambient, respectively.

Figure 2 shows the current-voltage (I-V) characteristics for Ni/ITO contacts to p-type ZnO films obtained after annealing at 400 °C for 1 min in N₂ and air ambients. The results show that the contacts annealed at 400 °C in an N₂ ambient have superior contact resistivities, compared to the contacts annealed in an air ambient. To characterize the chemical composition and chemical bonding state of the interface region between the ITO/Ni layers and the ZnO, AES, and XPS analyses were done. Figure 3 shows Auger profiles of as-deposited and annealed Ni/ITO films on p-type ZnO film. For the as-deposited sample, there is no clear evidence for interdiffusion between the Ni/ITO metal layers and p-type ZnO film was found, as shown in Fig. 3(a). For the N₂-annealed sample, however, a significant amount of Ni outdiffused into the top ITO layer and a small amount of In or Sn also diffused from the ITO layer to Ni metal layer and the ZnO, as shown in Fig. 3(b). In addition, Zn is also diffused from the ZnO to the upper layers. This suggests that Zn-related compounds (Zn–In–O, Zn–Sn–O, and Zn–Ni–O) might be formed at the interface. The AES depth profile of an air-annealed sample [Fig. 3(c)] shows that a small amount of Ni had diffused into the top ITO layer and In and Sn are also diffused from the ITO electrode toward the Ni metal layer and the p-type ZnO film. This suggests that a small amount of Ni reacts with oxygen released from the ITO electrode, resulting in the formation of oxidized nickel (NiO).

In order to further confirm the formation of NiO at the interface, an XPS analysis was conducted. Figure 4 shows the Ni 2p core-level peaks of the ITO/Ni/p-ZnO interfaces before and after thermal treatment. For the as-deposited sample, the XPS spectrum in Fig. 4(a) shows that the shape of the Ni 2p core-level peak is slightly asymmetrical with a weak shoulder on the binding energy side of the main peak, implying the formation of a small amount of NiO. The binding energy of the 2p core level of pure Ni is reported to be 852.7 eV. The Ni 2p peak of the as-deposited sample indicates that most of the Ni is in a metallic state prior to the thermal treatment. For the annealed sample, however, the XPS spectrum in Fig. 4(b) shows that the Ni 2p core-level peak is shifted in the direction of the high binding energy side, indicating the formation of NiO. It is known that the binding energy of the Ni 2p peak of NiO is in the range of 853.3–835.8 eV and the binding energy of the Ni 2p peak of Ni-related compounds (Ni–In–O, Ni–Sn–O, and Ni–Zn–O) which may exist at the interface would be expected to be 853.1 eV as indicated by an oval in Fig. 4(b). It is noteworthy that Ni was not only oxidized, but also undergoes chemical bonding with In or Sn atoms in the ITO layer to form Ni–In–O or Ni–Sn–O compounds. These XPS results are in good agreement with the AES analysis data for the interdiffused layer at the interface. The formation of NiO at the interface between Ni and p-ZnO during the annealing process is also important, in that it appears to lower interface resistance. The NiO shows a p-type property with high conductivity which can decrease the specific contact resistance.

For good current uniformity on the LED, the sheet resistance of the contacted films on the p-type ZnO should also be 852.7 eV. The Ni 2p peak of the as-deposited sample indicates that most of the Ni is in a metallic state prior to the thermal treatment. For the annealed sample, however, the XPS spectrum in Fig. 4(b) shows that the Ni 2p core-level peak is shifted in the direction of the high binding energy side, indicating the formation of NiO. It is known that the binding energy of the Ni 2p peak of NiO is in the range of 853.3–835.8 eV and the binding energy of the Ni 2p peak of Ni-related compounds (Ni–In–O, Ni–Sn–O, and Ni–Zn–O) which may exist at the interface would be expected to be 853.1 eV as indicated by an oval in Fig. 4(b). It is noteworthy that Ni was not only oxidized, but also undergoes chemical bonding with In or Sn atoms in the ITO layer to form Ni–In–O or Ni–Sn–O compounds. These XPS results are in good agreement with the AES analysis data for the interdiffused layer at the interface. The formation of NiO at the interface between Ni and p-ZnO during the annealing process is also important, in that it appears to lower interface resistance. The NiO shows a p-type property with high conductivity which can decrease the specific contact resistance.

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be reduced. In this experiment, the sheet resistance of Ni/ITO contacts was not changed before and after thermal annealing under N\textsubscript{2}, while the sheet resistance of Ni/ITO annealed under an air ambient was increased from 170 to 1100 Ω/cm\textsuperscript{2}. This result suggests that the formation of oxygen vacancies occurs more readily in the N\textsubscript{2}-annealed ITO sample than in the air-annealed ITO sample.\textsuperscript{17} It is well known that the preferred formation of oxygen vacancies results in the increase of carrier concentration, improving the conductivity of contacted layers. Therefore, the N\textsubscript{2}-annealed contacts are preferable to the air-annealed ones in order to increase LED performance.

The optical transmittance of the Ni/ITO ohmic layers deposited on p-type ZnO was measured and these data are shown in Fig 5. The light transmittance of an as-deposited sample was determined to be 71 to 87% and 77 to 85% in the wavelength range of 400–600 nm for the samples annealed in air and N\textsubscript{2} ambients, respectively. The ITO films deposited using electron-beam evaporation were initially almost opaque, but their transparency was improved after thermal treatment under N\textsubscript{2} and air.\textsuperscript{18} The transformation of Ni to NiO and the compensation of oxygen vacancies of the ITO electrode by the thermal treatment under an air ambient further improves the transmittance of the Ni/ITO scheme. The optical transmittance of the air-annealed Ni/ITO contact is slightly higher than that of the N\textsubscript{2}-annealed Ni/ITO contact.

In summary, we report on a promising Ni/ITO(50/500 Å) ohmic contact scheme for a phosphorous-doped p-type ZnO film. The annealed Ni/ITO scheme showed good ohmic properties with a low resistance, high conductivity, and high transparency. In particular, the contact produced a very low specific contact resistance of $6.2 \times 10^{-5}$ Ω cm\textsuperscript{2}, when annealed at 400 °C for 1 min under a nitrogen ambient.

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