Transparent RuO\textsubscript{x} Contacts on n-ZnO

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100 nm thick Ru films were deposited onto n-ZnO epitaxial layers by radio frequency sputtering. It was found that highly transparent RuO\textsubscript{x} was formed after O\textsubscript{2} annealing. With an incident wavelength of 460 nm, it was found that transmittances of as-grown, 500\degree C-annealed, 600\degree C-annealed, and 700\degree C-annealed Ru films were 56.8, 73.5, 79.6, and 81.8\%, respectively. It was also found that as-deposited Ru formed Schottky contact on n-ZnO. However, good ohmic contacts were formed between the annealed Ru films and the underneath ZnO. With 650\degree C annealing, we achieved a specific contact resistance of only 2.72 × 10\textsuperscript{-11} \Omega cm\textsuperscript{2}. Such a low specific contact resistance should be attributed to the formation of RuO\textsubscript{x} and the dissociation of oxygen atoms in ZnO during annealing.

ZnO has attracted much attention because it is an n-type semiconductor with large exciton binding energy of 60 meV and wide bandgap energy of 3.37 eV at room temperature. These properties have made ZnO as a promising photonic material which is potentially useful in the blue and ultraviolet (UV) regions. It is also possible to use the unique properties of ZnO to fabricate various optoelectronic devices, such as light emitting diodes (LEDs) and laser diodes (LDs), and UV photodetectors.\textsuperscript{1-4} In recent years, much progress has been achieved in ZnO-based materials, such as improvement of crystal quality, understanding of residual donor, and control of p-type doping.\textsuperscript{5,6} However, it is also necessary to achieve high-quality ohmic contacts on ZnO for practical device applications. These contacts should be highly reliable, with low resistance, chemically stable, and thermally stable. Previously, it has been shown that ohmic contacts on ZnO could be achieved by oxygen desorption and diffusion of zinc. Using this technique, one can reduce the thickness of the Schottky barrier at the metal/ZnO interface. Thus, carriers will be injected into ZnO through tunneling.\textsuperscript{7-9} To investigate the contact properties, we deposited Ru metal onto the as-grown ZnO epitaxial layers by rf sputtering. During Ru deposition, the base pressure, sputtering power, and Ar flow rate were kept constant. Finally, we evaluated the contact properties by the circular transmission line method (CTLM) patterns. We then rapid thermal annealed (RTA) the samples in situ at 700\degree C in O\textsubscript{2} atmosphere. The as-grown samples were characterized by X-ray diffraction (XRD) and Hall measurements.

\begin{itemize}
  \item To investigate the contact properties, we deposited Ru metal onto the as-grown ZnO epitaxial layers by rf sputtering. During Ru deposition, the base pressure, sputtering power, and Ar flow rate were kept at 10 mTorr, 100 W, and 10 sccm, respectively. The deposition rate was 12.5 nm/min and we kept the thickness of Ru films at 100 nm.
  \item Photolithography was used to define circular structures for measuring specific contact resistance by the circular transmission line model (CTLM) method. We kept the diameter of outer contact at 500 \mu m while the gaps between the inner and outer contacts were 10, 20, 30, 40, 50, and 60 \mu m. A standard lift-off process was used to define the CTLM patterns. We then rapid thermal annealed (RTA) the samples in O\textsubscript{2} ambient at various temperatures. We also deposited Ru onto glass substrates followed by the same RTA process. Then we loaded the Ru/glass samples onto a Hitachi model U-3310 spectrophotometer to measure the transmittances of as-deposited and annealed Ru films. The measured transmission spectra of Ru/glass were then normalized by the transmission spectrum of the glass substrate. Resistivities and crystal qualities of the as-deposited and annealed Ru films were also measured by a four-point probe system and XRD, respectively. We also used Auger electron spectroscopy (AES) to evaluate the surface properties of the as-deposited and annealed Ru films. Finally, we evaluated the contact properties between the deposited Ru and the underneath n-ZnO by a Keithley 4200 semiconductor parameter analyzer.
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Experimental

The unintentionally doped n-type ZnO samples used in this study were all epitaxially grown on (1120) sapphire substrates by MBE with an oxygen source supplied from a radio frequency (rf) activated plasma cell. Elemental Zn (6N) source was evaporated using a conventional effusion cell. After cleaning and annealing sapphire substrates, a 50 nm thick low-temperature ZnO buffer layer was first grown at 350\degree C. During the growth of this buffer layer, we kept the growth rate, Zn beam equivalent pressure (BEP), and O\textsubscript{2} flow rate at 0.2 \mu m/h, 1 × 10\textsuperscript{-6} Torr, and 0.9 sccm, respectively. We subsequently increased the substrate temperature to 430\degree C to grow a 500 nm thick unintentionally doped ZnO epitaxial layer. During the growth, oxygen flow rate and BEP were fixed at 1.5 sccm and 3.2 × 10\textsuperscript{-6} Torr, respectively. We then annealed the samples in situ at 700\degree C in O\textsubscript{2} atmosphere. The as-grown samples were characterized by X-ray diffraction (XRD) and Hall measurements.

From room temperature Hall measurements, it was found that carrier concentration and mobility of the as-grown unintentionally doped ZnO films were 4.16 × 10\textsuperscript{17} cm\textsuperscript{-3} and 42.3 cm\textsuperscript{2}/V s, respectively. The relatively low mobility observed from our ZnO epitaxial layers should be attributed to threading dislocations generated at the lattice-mismatched ZnO/sapphire interface.\textsuperscript{10,11} Figure 1 shows the
measured XRD spectrum of the 500 nm thick ZnO epitaxial layer prepared on sapphire substrate. We observed a ZnO (002) XRD peak at 2θ = 34.43° with a full width at half maximum (fwhm) of 452 arcsec. The peak occurring at 2θ = 41.65° in the spectrum originated from the (006) plane of the sapphire substrate. Such a result indicates that the ZnO epitaxial layers were preferentially oriented in the c-axis direction. Although our ZnO films were grown on lattice-mismatched sapphire substrates, the small XRD fwhm indicates that crystal quality of our ZnO epitaxial layers was reasonably good.

Figure 2 shows normalized transmission spectra of the 100 nm thick Ru films fabricated in this study. With an incident wavelength of 460 nm, it was found that transmittances of as-grown, 500°C-annealed, 600°C-annealed, and 700°C-annealed Ru films were 56.8, 73.5, 79.6, and 86.8%, respectively. In other words, we could significantly enhance optical transmittance of the deposited Ru by postdeposition O2 annealing, probably through the formation of RuO2. The 86.8% transmittance observed from the 700°C-annealed Ru film was much larger than that observed from conventional metal contacts such as Ni/Au. The highly transparent nature of annealed Ru suggests such a material is potentially useful for applications in various optoelectronic devices.

Figure 3 shows the XRD spectra of as-deposited and 650°C-annealed Ru films. For the as-deposited Ru film, we observed a strong Ru(100) XRD peak at 2θ = 37.9° with a fwhm of 0.47°, a weak Ru(110) XRD peak, and a weak RuO2(101) XRD peak. The weak RuO2(101) XRD peak observed in as-deposited Ru film is probably due to the native Ru oxide and/or oxidation of Ru during sputtering. In contrast, RuO2-related peaks dominate the XRD spectrum for the 650°C-annealed Ru film. The XRD peaks located at 2θ = 27.86, 34.3, and 43.93° correspond to RuO2(110), (101), and (200), respectively. In contrast, Ru-related peaks became much smaller after annealing. The observation of strong RuO2-related peaks confirmed the formation of RuO2 after O2 annealing. Such a result also agrees well with that observed in Fig. 2, showing the annealed Ru films became much more transparent. Figure 4 shows current–voltage (I–V) characteristics of Ru deposited on the epitaxial ZnO layers with and without annealing. We used the CTLM pattern and kept the spacing between inner and outer contacts at 20 μm when we measured these current–voltage (I–V) curves. It can be seen that the as-deposited Ru film formed Schottky
contact on ZnO. However, good ohmic contacts were formed between the annealed Ru films and the underneath ZnO. From the slopes of the I–V curves, it was found that we achieved the lowest specific contact resistance from the 650°C-annealed Ru film. Because standard CTLM patterns were used in our study, the relationship between voltage drop $\Delta V$ and the spacing, $d$, between inner and outer contacts could be expressed as:\textsuperscript{16,18}

$$\Delta V = \frac{i_d R_S}{2\pi r_0} (d + 2LT), \quad L_T = \sqrt{\frac{R_C}{R_S}}$$ \hspace{1cm} [1]

where $R_s$, $R_C$, and $r_0$ were sheet resistance, specific contact resistance, and inner circular radius, respectively. Using this equation, we could determine sheet resistances of ZnO and specific contact resistances of Ru with and without annealing. Figure 5 shows calculated sheet resistances and specific contact resistances for the samples used in this study. It can be seen that we achieved the lowest sheet resistances of ZnO and the lowest specific contact resistance from the sample with 650°C-annealed Ru film. The $2.72 \times 10^{-4}$ $\Omega$ cm$^2$ specific contact resistance observed from the 650°C-annealed Ru film is smaller than those reported from Ti/Au and Ti/Al/Pt/Au ohmic contacts on n-ZnO with similar carrier concentrations.\textsuperscript{7,19} This low specific contact resistance achieved suggests O$_2$-annealed Ru is also electrically usable as the ohmic contact for ZnO-based optoelectronic devices.

Figure 6a and b shows AES depth profiles of the as-deposited and 650°C-annealed Ru contacts on ZnO, respectively. As shown from Fig. 6a, it was found that the as-grown ZnO epitaxial layers were not in stoichiometry. The reason that we achieved Zn-rich ZnO films was probably due to deviation of the Zn beam BEP during growth. No observable changes were found in the profiles of Ru and Zn, which indicated that neither in-diffusion of Ru nor out-diffusion of Zn occurred. As shown in Fig. 6a and b, it was found that O/Zn ratios were 0.96 and 2.06 when the sputtering time was 3500 s (i.e., near the interface) for the as-deposited and 650°C-annealed Ru contacts on ZnO, respectively. The O/Zn ratios of these two samples were both 0.56 when the sputtering time was 5500 s (i.e., in the ZnO epitaxial layer). These values seem to suggest that out-diffusion of oxygen had indeed occurred. It is also possible that oxygen incorporation occurred and reacted with Ru to form RuO$_2$ after O$_2$ annealing. Such a result again agrees well with those observed in Fig. 2 and 3. Previously, it has been shown that oxygen atoms in ZnO epitaxial layers dissociate and outdiffuse toward Al or Ti metal contacts, even without annealing, due to the strong reaction between Al or Ti and O.\textsuperscript{8,17} As shown in Fig. 6a, such autodissociation and out-diffusion did not occur in our samples. However, it was found that oxygen atoms in the ZnO epitaxial layer did dissociate and outdiffuse toward the Ru metal contact during annealing, as shown in Fig. 6b. It is possible that the out-diffused oxygen results in an increased carrier concentration near the ZnO surface. As a result, sheet resistances of the ZnO epitaxial layers become smaller, as shown in Fig. 5. The increased carrier concentration near the ZnO surface could also result in smaller contact resistance. Thus, we also achieved smaller specific contact resistances from the annealed samples. However, severe interface mixing might occur when the annealing temperature is too high. As also shown in Fig. 5, the measured sheet resistance of ZnO and the specific contact resistance both increased as we raised the annealing temperature to 700°C. Such a result indicates that we need to carefully control the annealing temperature for ZnO-based devices with Ru contact electrodes.

**Conclusion**

In summary, we deposited Ru films onto n-ZnO and annealed the samples in O$_2$ ambient. It was found that RuO$_2$ with a transmittance of 86.8% at 460 nm was formed after 600°C O$_2$ annealing. We also achieved an ohmic contact with specific contact resistance of $2.72 \times 10^{-4}$ $\Omega$ cm$^2$ from properly annealed samples.

**Acknowledgments**

This work was supported by the Center for Micro/Nano Technology Research, National Cheng Kung University, under projects from the Ministry of Education and the National Science Council of Taiwan (NSC 93-212-M-006-006).

**National Cheng Kung University assisted in meeting the publication costs of this article.**

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