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Rapid thermal annealing induced changes on the contact of Ni/Au to N-doped ZnO

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ABSTRACT

N-doped p-type ZnO ($p \sim 10^{18} cm^{-3}$) was grown on sapphire(0 0 0 1) substrate by metal-organic chemical vapor deposition method. Ni/Au metal was evaporated on the ZnO film to form contacts. As-deposited contacts were rectifying while ohmic behavior was achieved after thermally annealing the contacts in nitrogen environment. Specific contact resistance was determined by circular transmission line method and a minimum specific contact resistance of $8 \times 10^{-4}\ \Omega\ cm^2$ was obtained for the sample annealed at 650 °C for 30 s. However, Hall effect measurements indicate that, as the rapid thermal annealing temperature increased up to 550 °C or higher the samples' conductive type have changed from p-type to n-type, which may be due to the instability nature of the present-day p-type N-doped ZnO or the dissociation of ZnO caused by annealing process in N_2 ambient. Evolution of the sample's electric characteristics and the increment of metal/semiconductor interface states induced by rapid thermal annealing process are supposed to be responsible for the improvement of electrical properties of Au/Ni/ZnO.

1. Introduction

ZnO has drawn much interest as a promising material for the fabrication of optoelectronic devices due to its large band gap of 3.37 eV and a high binding energy of 60 meV at room temperature. Recent reports have demonstrated light-emitting diodes (LEDs) based on ZnO p–n homojunctions and transparent ZnO thin film transistors on glass and sapphire substrates [1–3]. While n-type conductivity is easily realized by substituting a trivalent cation (Al, Ga, In) on the Zn site or by via oxygen vacancies, Zn interstitials, or hydrogen doping [4–9]. The reliable and reproducible realization of p-type ZnO is still a great challenge and is attracting much attention at the theoretical and experimental levels. *Ab initio* electronic band structure calculations indicate that nitrogen is a good candidate for p-type doping of ZnO [10], and p-type doping has been reported for films grown by N_2O plasma pulsed laser deposition (PLD) or N_2 plasma-assisted molecular beam epitaxy [11,12]. Our group also has reported N-doped p-type ZnO film grown on ZnO substrate by metal-organic chemical vapor deposition (MOCVD) method and p–n homojunction LED [13]. Of course, there is still substantial improvement needed to establish robust p-type doping, which often exhibits very low mobility and poor optical properties [14,15]. Reports also showed it may revert to n-type conductivity over a few days at room temperature [16]. Whether or no, in addition to achieving stable and high hole concentrations p-type ZnO, work is also needed to develop high-quality ohmic and schottky contacts, which is essential for the realization of high performance ZnO-based optoelectronic devices as well [17–19].

So far, in literatures, the metal schemes for ohmic contact to n-type ZnO mainly focus on Al base and Ti base, such as Al, Al/Pt, Ti/Au, Ti/Al/Pt/Au, and non-alloyed In, Pt-Ga, low specific contact resistance scope from 10^{-4} to $10^{-8}\ \Omega\ cm^2$ has been obtained [20]. The reasons for the improved ohmic contacts to n-type ZnO were attributed to the increment of O vacancy in the metal/semiconductor interface via alloying by rapid annealing process, which increased the local carrier concentration, and then facilitated ohmic contact behavior forming [21–23]. For p-type ZnO, due to the difficulty in doping, contact to it has not been extensively studied. Up to now, there is only a little report on Ni/Au, Au, Au/Ni/Au and Ni/ITO contact to Sb doped, P doped and ZnMgO p-type ZnO respectively [24–27]. N replace O site is considered as a effective route to realize p-type ZnO [28–30] and rapid thermal annealing process is a critical step in realizing low specific contact resistance for metal contacts to semiconductor. In this paper, we studied rapid annealing effect on Ni/Au contacts to the N-doped ZnO film and effect on the character of the N-doped ZnO film. Evolution of the sample's electric characteristics and the increment of metal/semiconductor interface states induced by rapid thermal annealing

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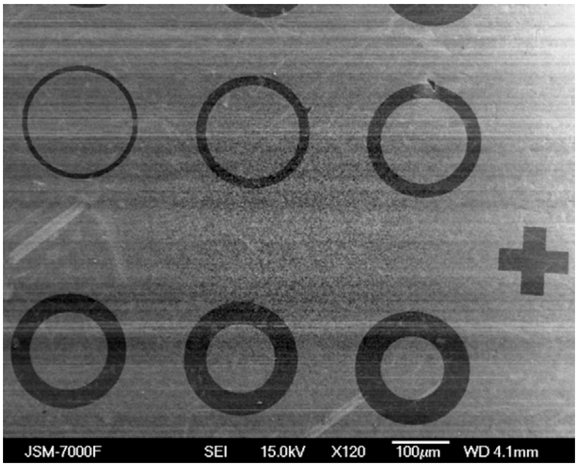

Fig. 1. Scanning electron micrograph of the CTLM pattern.

process are supposed to be responsible for the improvement of electrical properties of Au/Ni/ZnO.

2. Experimental details

The N-doped p-type ZnO epitaxial films in this study was grown by home-made metal-organic chemical vapor deposition (MOCVD) system which has been used to fabricate high-quality ZnO epilayers and homojunction LEDs in our group [13]. A undoped ZnO buffer layer was initially deposited on the Al_2O_3 (0 0 0 1) substrate using diethylzinc (DEZn) and O_2 as the reaction precursors, followed by nitrogen-doped ZnO layer growth using N_2O as both oxidizing and doping sources, finally, the sample was annealed in O_2 ambient at 900 °C for 15 min to activate the nitrogen dopants. The thickness of the resultant ZnO layer is around 2 μm. X-ray diffraction (XRD) shows that the sample exhibits single-phase hexagonal wurtzite structure with highly preferred orientation along *c*-axis. From Hall effect measurements under the van der Pauw configuration, we found that the N-doped ZnO layer exhibits p-type conduct behavior, with a hole concentration, mobility, and resistivity of $3.265 \times 10^{18}\ \mathrm{cm}^{-3}$, $1.526\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$, $0.60\ \Omega\ \mathrm{cm}$ respectively at room temperature.

Circular transmission line method (CTLM) was used to derive the specific contact resistance of Ni/Au contacts to N-doped ZnO film. No special surface treatment was done except degrease in acetone and ethanol prior to the metal deposition. A circular transmission line method (CTLM) pattern with nominal inner–outer ring spacings of 10–45 μm was created by lift off of e-beam deposited Ni(150 Å)/Au(350 Å) on the sample surface, the outer ring radius remain constant 100 μm, scanning electron micrograph of the pattern is shown in Fig. 1. Subsequently, some samples were annealed for 30 s in N_2 ambient at the temperature ranged from 250 to 950 °C. the current voltage (*I*–*V*) characteristics of the annealed samples were recorded with an Agilent 4156C parameter analyzer at room temperature, and the total resistance R_T between CTLM contact pads is given by the relation

$$R_T = \left(\frac{R_S}{2\pi}\right)\left[\ln\left(\frac{R}{r}\right) + L_t\left(\frac{1}{R} + \frac{1}{r}\right)\right]$$

where R_S is the sheet resistance of the semiconductor, R the radius of the outer circular contact, d the gap spacing ($d = R - r$), and L_t the transfer length. From a plot of R_T versus $\ln(R/r)$, the slope is $R_S/2\pi$, the intercept is $R_S L_T/\pi R$, and the specific contact resistance is then given by $L_T^2 R_S$.

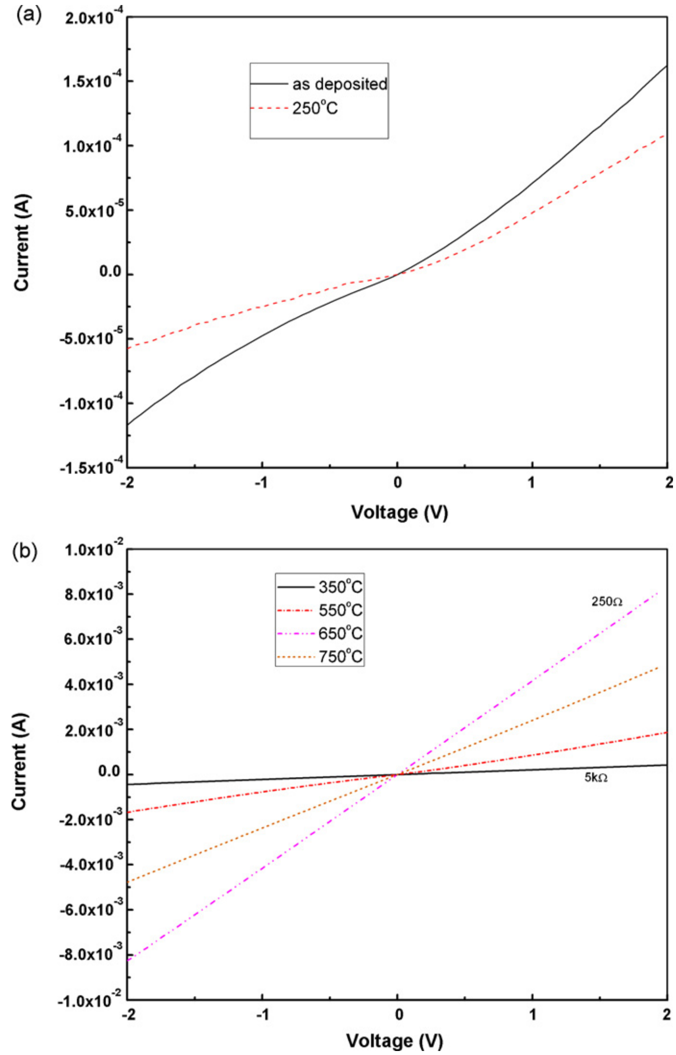

Fig. 2. *I*–*V* characteristics of Ni/Au contact on N-doped ZnO samples annealed at different temperatures.

To characterize the extent of interdiffusion between the Ni/Au and N-doped ZnO layers by the rapid annealing, Auger electron spectra (AES) was performed using a PHI 670 Auger microscope with electron beam of 10 kV and 0.0236 μA. The interfacial reaction products were identified by glancing angle XRD which was carried out with a Rigaku diffractometer (D/MAX-RC).

3. Results and discussions

Fig. 2 shows the *I*–*V* characteristics of Ni/Au metallization schemes on the annealed N-doped ZnO sample, measured between CTLM pads with a spacing of 37 μm. The as-deposited sample shows weak schottky behavior with high resistance, resulting in a current of only 0.1 mA at 2 V forward bias. As temperature increased up to 350 °C, linear ohmic behavior appeared and higher temperature annealing improved the ohmic contact behavior, as shown in Fig. 2(b), with the total resistance R_T decreased from 5 kΩ at 350 °C to 250 Ω at 650 °C. The specific contact resistance versus annealing temperature was plotted in Fig. 3(a), it shows that the specific contact resistance sustained $\sim 0.3\ \Omega\ \mathrm{cm}^2$ from 350 to 550 °C, however, after annealing at 650 °C, the specific contact resistance decreased almost three orders to a value of $8 \times 10^{-4}\ \Omega\ \mathrm{cm}^2$. Moreover, we found that the sheet resistance of