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Characteristics of Schottky contacts to ZnO:N layers grown by molecular-beam epitaxy

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We have investigated the characteristics of Au Schottky contacts to ZnO:N layers grown on (0001) GaN/Al₂O₃ substrates by plasma-assisted molecular-beam epitaxy. It is found that the Schottky characteristics are dependent on the growth temperature and polar direction of ZnO:N layers. The Schottky barrier height for the Au contact to a ZnO:N layer (300 °C, Zn-polar) is estimated to be 0.66 and 0.69 eV by current–voltage measurements and capacitance–voltage measurements, respectively. It is found that the Schottky barrier height is proportional to the resistivity and incorporated N concentration of ZnO:N layers. Consequently, we believe that the low growth temperature and Zn-polar direction are favored for N incorporation in the growth of ZnO:N layers, which contributes to the increased resistivity in ZnO:N layers and results in good Schottky characteristics. © 2005 American Institute of Physics. [DOI: 10.1063/1.1854191]

ZnO has emerged to gain increasing attention for blue and ultraviolet optoelectronic applications. An important issue in ZnO is establishing technology for the fabrication of high-quality Schottky contact, which has a crucial role in MESFETs and UV detectors. The Schottky contact to ZnO was first reported by Mead *et al.*^{1,2} However, their results did not include its detailed properties. Recently, there have been several reports on Schottky contacts to ZnO.^{3–7} Auret *et al.* have reported the Schottky barrier diode with an ideality factor of 1.1 in a Au contact onto ZnO, grown by vapor-phase epitaxy.³ Coppa *et al.* and Polyakov *et al.* have reported on the surface treatments in the formation of Schottky contact to ZnO, grown by chemical-vapor transport, whose characteristics are improved by surface cleaning such as physical cleaning by O₂/He plasma and chemical cleaning by chemical solutions, respectively.^{4,5} On the other hand, Ip *et al.* have reported on the annealing effect for a Pt Schottky contact to thin film ZnO, grown by pulsed-laser deposition, whose characteristics are degraded by the annealing process.⁶

As indicated in previous studies, the presence of conducting layers at ZnO surface could cause leakage current and hamper Schottky contact formation. Moreover, the crystal-polar direction of ZnO surface could give an important role in the formation of Schottky contact. However, the systematic study on Schottky contacts for various resistivities and crystal-polar directions is still lacking, especially for thin film ZnO. In this letter, we report on Au Schottky contacts onto ZnO layers doped with N, grown on GaN templates by plasma-assisted molecular-beam epitaxy (P-MBE). The resistivities of ZnO layers are systematically varied by controlling the growth temperature and crystal-polar direction of ZnO layers.

ZnO:N layers were grown by P-MBE, equipped with a Zn solid source, an O rf-plasma source, and a N rf-plasma

source, on Ga-polar GaN templates predeposited by metalorganic-chemical-vapor deposition on (0001) Al₂O₃ substrates. The material properties of ZnO is influenced by the crystal-polar direction.^{8,9} The polar direction of ZnO is easily engineered by controlling preexposure condition, when ZnO is grown on Ga-polar GaN; a Zn-polar ZnO layer is formed by Zn-exposure prior to ZnO growth, while an O-polar ZnO layer is formed by O-plasma exposure.⁹ The Ga-polar GaN templates used in this work were 4000 nm-thick and *n*-type with an electron concentration of $6 \times 10^{16} \text{ cm}^{-3}$. Before growing ZnO:N layers, high temperature annealing was preceded at 800 °C, followed by the growth of low temperature ZnO buffer layers at 300 °C. Subsequently, ZnO:N layers were grown at 300–600 °C after O-exposure and Zn-exposure, respectively. Then, N rf-plasma power and flow rate for doping was 200 W and 0.25

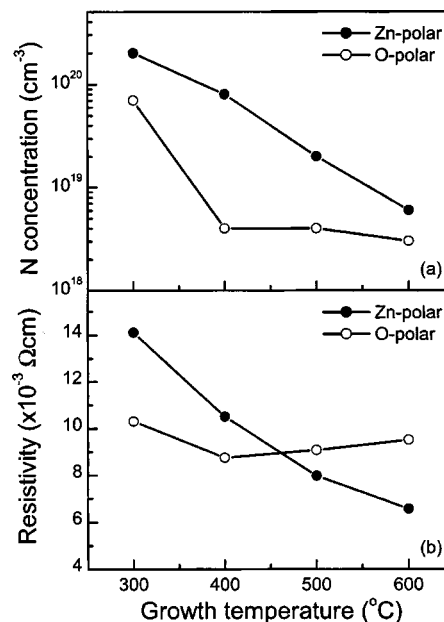


FIG. 1. Resistivities and incorporated N concentrations for Zn-polar ZnO:N layers and O-polar ZnO:N layers grown at 300–600 °C.

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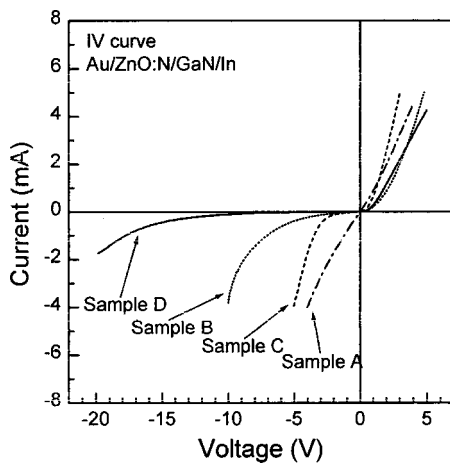


FIG. 2. I - V curves at room temperature for ZnO:N layers. Sample A— $T_g=400$ °C, O-polar; sample B— $T_g=400$ °C, Zn-polar; sample C— $T_g=300$ °C, O-polar; sample D— $T_g=300$ °C, Zn-polar.

sccm. The thickness of ZnO:N layers was 450–600 nm.

For the ZnO:N layers, incorporated N concentrations and resistivities were investigated by secondary-ion-mass spectroscopy (SIMS) and the van der Pauw method, respectively. In SIMS measurements, Cs^+ accelerated at 5 kV and 50 nA was used as primary ion and NO^+ as secondary ion. Figure 1(a) shows that the incorporated N concentration increases with the decrease of growth temperature, and Zn-polar ZnO layers exhibit larger N incorporation than O-polar ZnO layers. Figure 1(b) shows that the resistivity increases with the increase of incorporated N concentration. Based on the two results, it can be expected that the degree of N incorporation is closely related to the resistivity of a ZnO:N layer. Here, we note the crossover point in Fig. 1(b). In undoped ZnO, it is reported that the electron mobility of Zn-polar ZnO is larger than that of O-polar ZnO.¹⁰ As the growth temperature decreases, it is expected that larger N incorporation in Zn-polar ZnO layers reduces the electron mobilities of Zn-polar layers (due to enhanced ionized-impurity scattering) faster than those of O-polar ZnO layers, which induces the crossover of resistivity curves.

For the N incorporation in ZnO layers, we should consider two aspects. First, N incorporation is strongly influenced by growth temperature. N is well known as a very efficient p -type dopant in ZnSe.¹¹ Qiu *et al.* have reported that N incorporation in ZnSe increases at lower growth temperature, which is ascribed to the increased sticking coefficient.¹¹ It well explains the phenomenon that N incorporation in ZnO layers increases at lower growth temperature. Second, a crystal-polar direction influences N incorporation. The polar-direction dependence for impurity incorporation has also been reported for GaN:Mg.¹² However, the origin is not yet fully understood. In this letter, we propose a simple model of N incorporation mechanism. For the case of a Zn-polar ZnO layer, the surface is composed of Zn atoms with one dangling bond and three occupied Zn–O bonds. Zn atoms, forming electropositive centers, tend to bond with electronegative N atoms. These Zn–N bonds compete with Zn–O bonds during ZnO:N growth and affect N incorporation. For the case of an O-polar ZnO layer, the surface is composed of O atoms with one dangling bond and three occupied O–Zn bonds. It is relatively difficult for N atoms to bond with O atoms, because the difference of electronegativity between N and O is small. Consequently, it is suggested that the Zn-polar direction is favorable for N incorporation in the growth

of ZnO:N layers. Recently, Kato *et al.* have reported that the growth rate of Zn-polar ZnO is faster than that of O-polar ZnO, which is ascribed to the larger sticking coefficient in Zn-polar ZnO.¹³

For the ZnO:N layers, the characteristics of Au/ZnO:N Schottky contacts was investigated by current–voltage (I - V) measurements using a HP 34401A multimeter and an Yokogawa 7651 dc power source and capacitance–voltage (C - V) measurements using a YHP 4275A LCR meter, respectively. In order to fabricate a Schottky diode, a Au electrode with a diameter of 1 mm was deposited on the surface of a ZnO:N layer, and an In electrode was deposited on a GaN template after partially removing the ZnO layer by chemical etching. Then, the electrodes were evaporated in a vacuum chamber immediately after organic cleaning in order to remove contaminants from the sample surface. In this work, other special surface treatments were not followed, in order to see the only effect on resistivity change.

Figure 2 shows I - V curves for four sets of ZnO:N layers among the samples revealed in Fig. 1 ($T_g=400$ °C, O-polar—sample A; $T_g=400$ °C, Zn-polar—sample B; $T_g=300$ °C, O-polar—sample C; $T_g=300$ °C, Zn-polar—sample D). In the cases with the same polar direction, ZnO:N layers grown at 300 °C exhibit larger breakdown voltages and less leakage currents in the reverse bias region than samples grown at 400 °C. In the cases of ZnO:N layers grown at the same growth temperature, Zn-polar samples exhibit larger breakdown voltages and less leakage currents than O-polar samples. As a result, a Zn-polar ZnO:N layer grown at 300 °C (sample D) exhibits the largest breakdown voltage.

Figure 3(a) shows the I - V curve for sample D in detail. For thermionic emission and $V \gg 3kT/q$, the general diode equation in forward bias is¹⁴

$$I = I_0 \exp\left(\frac{q(V - IR)}{nkT}\right) \quad (1)$$

where I is the current, I_0 is the reverse saturation current, q is the unit charge of an electron, V is the applied voltage, R is the series resistance, n is the ideality factor, k is the Boltzmann constant, and T is the temperature (≈ 295 K). In terms of the theoretical fitting using Eq. (1), the ideality factor in the Au/ZnO:N Schottky contact is obtained to be 1.8. Here, the relatively high ideality factor could be due to the existence of interfacial layers or surface states.⁴ The reverse saturation current I_0 is given by $I_0 = A^*AT^2 \exp(-\Phi_{\text{SB}}/kT)$, where A^* is the Richardson constant (≈ 32 A/cm² K²), A is the contact area, and Φ_{SB} is the Schottky barrier height.⁷ Using the reverse saturation current ($I_0 = 1 \times 10^{-7}$ A) experimentally obtained, the Schottky barrier height is calculated to be 0.66 eV. In the I - V curve analysis, the Schottky barrier in the ZnO/GaN interface could be neglected, because Ohmic characteristics was confirmed in I - V curves for the structures of In/ZnO/GaN/In.

Figure 3(b) shows the C - V curves for sample D measured at 100–1000 kHz. It was found that the measured built-in potential decreases as the measurement frequency increases. It may be induced by series resistance due to trap centers.^{15–17} Consequently, the built-in potential is determined by^{7,15}

$$\left(\frac{1}{C^2}\right) = \frac{2}{q\epsilon A^2 N_d} (V - V_{bi}^{meas}), \quad (2a)$$

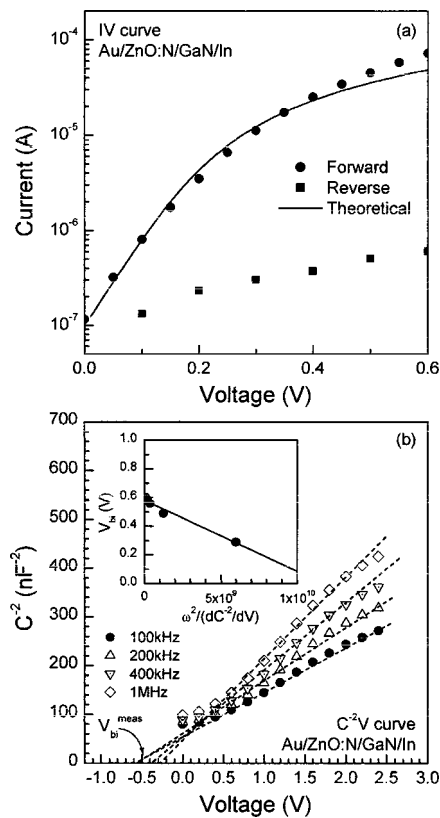


FIG. 3. Detailed characteristics for sample D ($T_g=300^\circ\text{C}$, Zn-polar). (a) I - V curves at room temperature. The solid line is the theoretical fitting result in a forward bias region. (b) C - V curves measured at 100, 200, 400, and 1000 kHz. Inset—built-in potential as a function of measurement frequency.

$$V_{bi}^{meas} = V_{bi}^{real} + 2R^2\omega^2 \left(\frac{dC^{-2}}{dV} \right)^{-1}, \quad (2b)$$

where C is the capacitance, ε is the dielectric constant, N_d is the donor density, V_{bi}^{meas} is the measured built-in potential, V_{bi}^{real} is the real built-in potential, and ω is the measurement frequency. As shown in the inset of Fig. 3(b), the real built-in potential is obtained to be 0.58 V. Then, the Schottky barrier height is calculated to be 0.69 eV using $\Phi_{SB} = qV_{bi}^{real} + kT \ln(N_c/N_d)$, where N_c is the effective density of states in the conduction band ($=3.5 \times 10^{18} \text{ cm}^{-3}$).⁷ The Schottky barrier height deduced from C - V measurements is consistent with the result estimated by I - V measurements, which also agrees well with the result of 0.66 eV reported by Neville *et al.*²

Table I summarizes the Schottky characteristics and growth conditions for ZnO:N layers. The Schottky barrier heights and ideality factors in samples B and C are less than 0.6 eV and larger than 3, respectively. In the case of sample A, the leakage current was too large to be able to analyze its characteristics in detail. However, sample D with highest re-

TABLE I. Schottky barrier heights (Φ_{SB}) and ideality factors (n) for Au Schottky contacts on ZnO:N layers, and resistivities (ρ) and incorporated N concentrations (N) of ZnO:N layers.

Sample no.	T_g ($^\circ\text{C}$)	Polar dir.	Φ_{SB} (eV)	n (-)	ρ ($\Omega \text{ cm}$)	N (cm^{-3})
A	400	O-polar	8.75×10^{-3}	4×10^{18}
B	400	Zn-polar	0.55	3.2	1.05×10^{-2}	8×10^{19}
C	300	O-polar	0.37	3.5	1.03×10^{-2}	7×10^{19}
D	300	Zn-polar	0.66	1.8	1.41×10^{-2}	2×10^{20}

sistivity exhibits best Schottky characteristics. It indicates that the ideality factor and Schottky barrier height are dependent on the resistivity of a ZnO:N layer. On the other hand, in terms of C - V measurements, the electron concentration of sample D was estimated to be $5 \times 10^{16} \text{ cm}^{-3}$, which is one order lower than that of an undoped ZnO layer, $3 \times 10^{17} \text{ cm}^{-3}$. (Then, the depletion width was estimated to be 230 nm, smaller than the layer thickness of ZnO:N. It is expected that the electron concentration estimated by C - V measurements is not influenced by the GaN template.) Consequently, it is suggested that the increased resistivity is ascribed to the suppression of electron concentration due to N incorporation. However, the conduction type in ZnO:N layers was n -type, even if the concentration of incorporated N is $2 \times 10^{20} \text{ cm}^{-3}$. The origin of this phenomenon is still controversial. Oba *et al.* and Zhang *et al.* have suggested that self-compensation by donor-type defects such as V_o , Zn_i , and Zn_o should be significant in p -type doping, because their formation enthalpies are quite low.^{18,19} Yan *et al.* have proposed that incorporated substitutional N_2 makes ZnO n -type.²⁰

In conclusion, we investigated the characteristics of Au Schottky contacts to ZnO:N layers grown by P-MBE. In the growth of ZnO:N layers, lower growth temperature and a Zn-polar direction were favorable for N incorporation. We could obtain the Schottky contact with an ideality factor of 1.8 and a Schottky barrier height of -0.68 eV in a ZnO:N layer. We believe that the increased resistivity in ZnO layers due to large N concentration induces good Schottky characteristics.

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