Effects of fluorine-based plasma treatment and thermal annealing on high-Al content AlGaN Schottky contact

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Fluorine plasma treatment was used prior to the Schottky metal deposition on the undoped $Al_{0.45}Ga_{0.55}N$, which aimed at the solar-blind wavelength. After fluorine plasma treatment and before depositing the Ni/Au Schottky, the samples were thermal annealed in the N_2 gas at 400 °C. The reverse leakage current density of $Al_{0.45}Ga_{0.55}N$ Schottky diode was reduced by 2 orders of magnitude at −10 V. The reverse leakage current density was reduced by 3 orders of magnitude after thermal annealing. Further capacitance–frequency analysis revealed that the fluorine-based plasma treatment reduces the surface states of AlGaN by one order of magnitude at different surface state energies. The capacitance–frequency analysis also proved that the concentration of carriers in AlGaN top is reduced through fluorine plasma treatment.

Keywords: plasma treatment, reverse leakage current, surface states

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1. Introduction

Wide band gap material AlGaN has attracted a great deal of attention for its application in devices such as ultraviolet light emitting diodes (UVLEDs) and ultraviolet photo detectors (UVPDs).[1–3] With the Al content increase from 0 to 1, the band gap of $Al_xGa_{1-x}N$ changes from 3.4 eV to 6.2 eV (corresponding to the wavelength from 365 nm to 200 nm). The solar-blind AlGaN UVPDs, with a cut-off wavelength $\lambda_c \leq 280$ nm, have many applications in missile threat detection, flame monitoring, and biological detection. Schottky AlGaN solar-blind PD is popular for its simple fabrication, fast response, and the use in array photodetectors. However, it suffers from the high dark current due to the high density of dislocations of AlGaN thin film with Al content $\geq 40\%$ and surface defects, which as a result increases the device noise and influences the performance of Schottky photodetectors.[4]

Recently, it has been reported that the fluorine-based plasma treatment fabricated E-mode AlGaN/GaN high-electron-mobility transistors (HEMTs) form a conventional D-mode HEMT structure. The impacts about fluorine treatment on GaN Schottky contact have been reported.[5] However, the effects of Fluorine plasma treatment on high Al content AlGaN and especially the change of surface states after treatment are still unknown.

In this paper, the CHF_3 fluorine plasma treatment was used prior to the Schottky metal deposition. We performed the thermal anneal after fluorine plasma treatment before depositing the Ni/Au Schottky.

2. Experiments

All samples used in this work were grown by a plasma-assisted molecular beam epitaxy system (SVTA) with conventional Knudsen cells for metal sources and radio frequency plasma sources for active nitrogen species. The AlGaN thin films were grown on a thick AlN template prepared by metalorganic chemical vapour deposition (MOCVD) on the sapphire substrate. The structure consisted of a 1000-nm-thick Si-doped $Al_{0.45}Ga_{0.55}N$ layer on top of a 400-nm-thick unintentionally doped n-type $Al_{0.45}Ga_{0.55}N$. The structure of the samples is shown in Fig. 1.

n-AlGaN 50 min 1 μm (4×10^{17} cm^{-3})
i-AlGaN 20 min 40 nm
AlN/AlGaN PALE 6 periods
PALE AlN
LT-AlN
sapphire

Fig. 1. The structure of the sample.

Firstly, wafer was cleaned by the conventional organic cleaning process, then Ohmic contacts were formed by standard photolithography on AlGaN surface, using a Ti/Al/Ni/Au (30 nm/175 nm/35 nm/100 nm) metal layer annealed at 850 °C in N_2 for 35 s in a rapid thermal annealing system. The linearity of Ohmic contact was checked by *I*–*V* measurement before the next processing. The samples were divided into four groups (A, B, C, D). Prior to the deposition of the Ni/Au (10/10 nm) Schottky contact metals on the AlGaN, samples B and C were treated by CHF_3 using inductive coupled plasma (RIE-ICP) while samples A and D were taken as control. Samples C and D were annealed in the N_2 atmosphere at

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400 °C. The process of the four samples is summarized in Table 1. The Ni/Au metals were deposited with a diameter of 1000. The current–voltage (I–V) characteristic was measured using the Keithley 4200 semiconductor characterization system. The capacitance–voltage (C–V) and capacitance–frequency (C–F) characteristics were measured using the Agilent 4294A impedance analyzer.

Table 1. Process of samples.

No.	No surface treatment	Fluorine-based plasma treatment	Annealing in the N_2 atmosphere at 400 °C for 10 min
Sample A	yes		
Sample B		yes	
Sample C		yes	yes
Sample D	yes		yes

3. Results and discussion

The I–V characteristics of AlGaN Schottky diode with and without fluorine plasma treatment and annealed are shown in Fig. 2. The current density at −10 V of the AlGaN Schottky diode with CHF_3 plasma treatment is significantly reduced by nearly 2 orders of magnitude compared with that of the AlGaN Schottky diode as control. The reverse leakage current density after being annealed in the N_2 atmosphere at 400 °C was lower than Ni/Au annealed in the same condition.

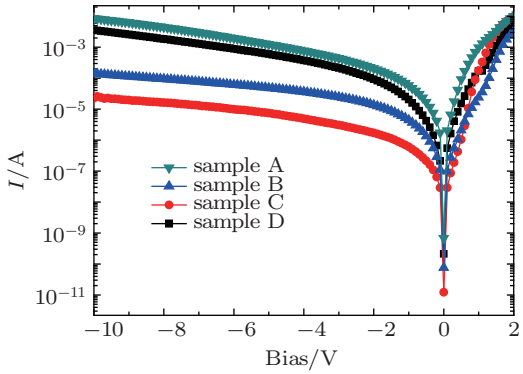


Fig. 2. (color online) The I–V characteristic of AlGaN Schottky diode.

For thermionic emission ($V > 3kT/q$), the general diode equation is[6]

$$I = I_s\left[e^{q(V-IR)/nkT} - 1\right], \tag{1}$$

where $I_s = AA^*T^2 e^{-q\Phi_b/kT}$ is the saturation current, R is the series resistance, A and n are the contact area and the ideality factor, respectively, Φ_b is the effective barrier height, and A^* is the effective Richardson constant. For $Al_{0.45}Ga_{0.55}N$, the electron effective mass $m_e^* = 0.337m_e$. Many methods have been suggested to calculate the barrier heights and ideality factors of a metal–semiconductor Schottky contact from I–V data. Here, a nonlinear fitting method is used to fit the obtained data. Equation (1) can be expressed as

$$V = \frac{nkT}{q}\ln\left(\frac{I}{I_s} + 1\right) + IR_s. \tag{2}$$

Assume that $a = nkT/q$, $b = 1/I_s$, and $c = R_s$. The parameters n, I_s, and R_s can be deduced from the nonlinear fitting method.

Table 2. Parameters of AlGaN Schottky diode.

	n	Φ_b/V	R_s/Ω
Sample A	2.7	1.18	943
Sample B	5.7	1.12	2.7×10^5
Sample C	3.84	1.28	5.7×10^5
Sample D	2.5	1.22	901

As shown in Table 2, fluorine plasma treatment induces the ideality factors increasing and the series resistance increasing largely.

Nitrogen vacancy has been researched for a long time. It not only forms in the growth natively (especially in metal-rich growth conditions) but also could be produced by the processing steps of fabricating devices, such as high-temperature thermal annealing of Ohmic contact, activation of implanted dopants, and plasma induced damage. It is commonly thought that N vacancy is a shallow donor in GaN and AlGaN, which could lower the barrier height and cause excess leakage current in GaN and AlGaN Schottky diodes.[7,8]

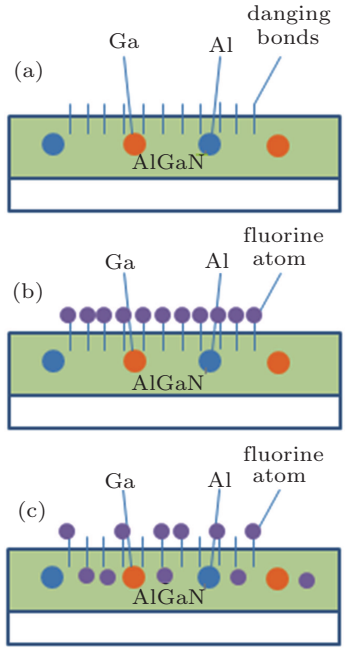


Fig. 3. (color online) Schematic diagram of (a) nitrogen vacancy, (b) fluorine-based plasma treatment, and (c) fluorine-based plasma treatment and annealed.

In this work, the fluorine-based treatment by RIE-ICP in our experiments has a slight etching effect on AlGaN. We think that the fluorine-based plasma treatment effectively reduces the leakage current by reducing the nitrogen vacancy rather than forming the insulating layer. We give the following model to explain the I–V results. Surface states which are due to the nitrogen vacancy existing on the AlGaN surface are shown in Fig. 3(a). As shown in Fig. 3(b), when fluorine-based

plasma treatment is done, the surface state is passivated by fluorine. We believe that the Ga–F and Al–F bonds form, but no evidence indicates the formation of GaF_3 and AlF_3 insulating layers. The reduced number of surface states reduces the reverse leakage. After annealing, some of the fluorine ions are effectively incorporated into AlGaN as shown in Fig. 3(c). A fluorine atom possesses strong electronegativatity, so the incorporating of the fluorine reduces the carrier concentration, and the reverse leakage is reduced.[9,10]

To further verify our postulation, we researched the capacitance–frequency characteristic and the result is shown in Fig. 4. The platform of capacitance is not observed because of the limit of the device, where the measure range is 100 Hz–1 MHz.

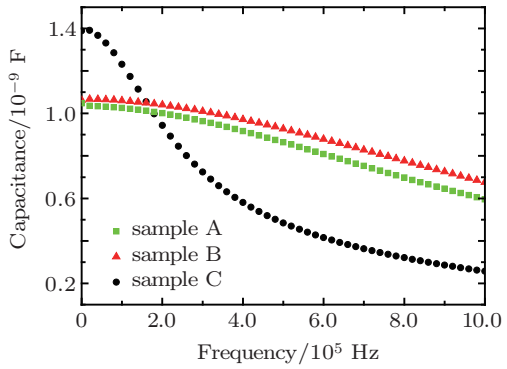


Fig. 4. (color online) The C–F characteristic of the diode.

We analyzed the surface states of the AlGaN Schottky diode with and without fluorine-based plasma treatment. As the surface states contribute to the capacitance of the diode only at the low frequency, the capacitance depending on the frequency is as follows:

$$C = C_{ss} + C_{sc}, \quad \text{at low frequency}, \tag{3}$$

$$C \cong C_{sc}, \quad \text{at high frequency}, \tag{4}$$

where C_{ss} is the surface state capacitance and C_{sc} is the space–charge capacitance.

The surface state density of the diode can be obtained by

$$N_{ss} = \frac{C_{ss}}{q^2 A}, \tag{5}$$

where q is the electron charge and A is the effective area of Schottky contact. The energy of surface state E_{ss} with respect to the bottom of the conduction band (E_c) at the surface of the semiconductor is given by

$$E_c - E_{ss} = q\Phi_b - qV. \tag{6}$$

Figure 5 displays the relationship between the surface state density and the surface state energy E_{ss}, which is obtained from Eqs. (3)–(6). For sample A without fluorine-based plasma treatment, the surface state density increases from 1.62×10^{12} $eV^{-1}\cdot cm^{-2}$ in $(E_c - 1.18)$ eV to 1.89×10^{12} $eV^{-1}\cdot cm^{-2}$ in $(E_c - 0.78)$ eV. However, the surface state density does not increase as the surface state energy approaches the bottom of the conduction band in sample B with fluorine-based plasma treatment. It varies from 2.31×10^{11} $eV^{-1}\cdot cm^{-2}$ in $(E_c - 1.12)$ eV to 2.35×10^{11} $eV\cdot cm^{-2}$ in $(E_c - 0.72)$ eV. The surface state density in sample B is reduced by one order of magnitude compared with that in sample A. For the GaN sample, the surface states are mainly caused by N vacancies in the near surface area, which create many Ga dangling bonds. The fluorine-based plasma treatment could form GaF_3 and AlF_3, which would take the N vacancy position and reduce the Ga and Al dangling bonds. However, the reaction and incorporation of F ion in the near surface is not uniform, so the reduction of surface state density at different surface state energy is different, which is reflected in Fig. 5.

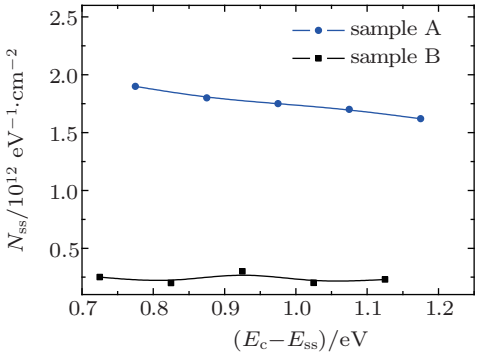


Fig. 5. (color online) Surface state densities at different surface state energy.

To prove the fluorine diffusion process in sample C, the capacitance–voltage characteristic in 1 MHz was researched and the results are shown in Fig. 6.

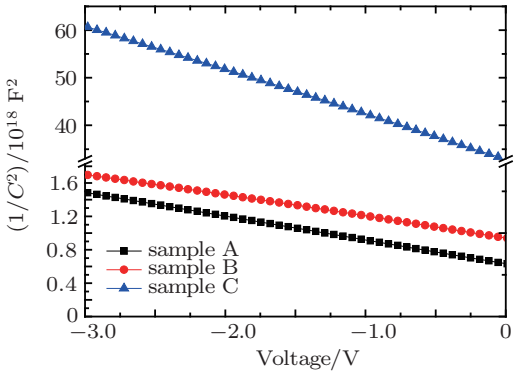


Fig. 6. (color online) The $1/C^2$–V characteristic of AlGaN Schottky diode.

The slope of $1/C^2$ reflects the concentration of carriers in the AlGaN top. From the C–V graph, the slopes of samples A and B are almost the same, but the slope of sample C changes apparently. The expression of $1/C^2$ is

$$\frac{1}{C^2} = \frac{2}{q\varepsilon_s\varepsilon_0 N A^2}(V_{bi} - V),$$

where ε_0 is the vacuum dielectric constant, N is the carrier concentration of material, and V_{bi} is the flat band voltage. The results show that the concentration of sample C changes largely, which proves that the fluorine ions are effectively incorporated into AlGaN. The concentrations of samples A, B, C are 2.6×10^{18} cm^{-3}, 1.8×10^{18} cm^{-3}, and 6×10^{16} cm^{-3}, respectively. Computing the results proved our theory.

4. Conclusion

In this work, the fluorine-based treatment by RIE-ICP in our experiments was done on the surface of AlGaN, and then the samples were annealed in the N_2 atmosphere at 400 °C for 10 mins. The leakage current was reduced by the treatment, and further deceased after annealing. By analyzing I–V and C–V characteristics, we obtained that the decrease of the leakage current was due to the decrease of the surface states after treatment, and the decrease of the leakage current was due to the reducing of the carrier concentration after annealing.

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