Validity/invalidity of Schottky-Mott rules for Schottky contacts to III-V nitride semiconductor heterostructures

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Carrier transport through the metal/semiconductor and metal/semiconductor/semiconductor ($M/S/S$) Schottky contact interfaces has been studied. Metal/n-GaN, metal/n-$Al_xGa_{1-x}N$, and metal/n-$Al_xGa_{1-x}N$/n-GaN diodes have been chosen for the study. It has been observed that, owing to the presence of the piezoelectric polarization field and a quantum well at the $Al_xGa_{1-x}N$/GaN interface, the $Al_xGa_{1-x}N$/GaN contacts exhibit properties distinctly different from those of the $Al_xGa_{1-x}N$ contacts. The superiority of the $Al_xGa_{1-x}N$/GaN contacts to that of the $Al_xGa_{1-x}N$ contacts largely disappears at high temperatures. While the GaN and $Al_xGa_{1-x}N$ contacts appear to obey the Schottky-Mott rule, the $Al_xGa_{1-x}N$/GaN contacts tend to disobey it. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2358956]

In this investigation we attempt to study high temperature Schottky-Mott characteristics of metal/GaN (S1), metal/$Al_xGa_{1-x}N$ (S2), and metal/$Al_xGa_{1-x}N$/GaN (S3) diodes and to shed light on the validity/invalidity of Schottky-Mott rule for them. To our knowledge, no efforts have so far been made to address this rule for the $M/S/S$ diodes. The dependence of room-temperature electron affinity χ_S on the Al mole fraction x of $Al_xGa1_{1-x}N$ may be given by[1] $\chi_S(Al_xGa_{1-x}N)=\chi_S(GaN)-m_S x$, where $\chi_S(GaN)=4.31$ eV and $m_S=0.9$ eV. Thus $\chi_S(Al_{0.2}Ga_{0.8}N)=4.13$ eV, as determined from the room-temperature plot presented earlier.[2] The famous Schottky-Mott rule[3] predicts that barrier height ϕ_B is equal to the difference between the electron affinity χ_S of the semiconductor and the work function ϕ_M of the metal. More specifically, if E_G is the semiconductor energy band gap, then $q\phi_B=q\phi_M-\chi_S$ for contacts to n semiconductor and $q\phi_B=(\chi_S+E_G)-q\phi_M$ for contacts to p semiconductor.

Semiconductor layers were grown on 400 μm thick (0001) sapphire substrate by metal-organic chemical vapor deposition method. For the S3 diodes, 60 nm thick GaN buffer layer was first grown on sapphire substrate. It was followed successively by the growth of a 2 μm thick undoped GaN, a 5 nm thick undoped $Al_xGa_{1-x}N$, a 10 nm thick (5.0×10^{18} cm^{-3}) Si-doped $Al_xGa_{1-x}N$, and finally a 5 nm thick (1.0×10^{19} cm^{-3}) Si-doped GaN. For the S2 diodes, 60 nm thick GaN buffer layer was first grown on 400 μm thick sapphire substrate. It was followed successively by the growth of a 1 μm thick lowly Si-doped ($\sim1.0\times10^{17}$ cm^{-3}) $Al_xGa_{1-x}N$ and a 5 nm thick (5.0×10^{18} cm^{-3}) Si-doped GaN. For the S1 diode, a 1 μm thick lowly Si-doped ($\sim1.0\times10^{17}$ cm^{-3}) GaN was grown on the substrate. The growth temperatures were 1010 °C for GaN and 1070 °C for $Al_xGa_{1-x}N$ ($x=0.2$). The flows of trimethyl aluminum and trimethyl gallium were adjusted over time to achieve $Al_xGa_{1-x}N$ ($x=0.20$). The flow of silane was adjusted to achieve n doping of semiconductors.

Several samples were cut from each wafer and cleaned by degreasing in a soap solution followed by 3 min ultrasonic baths ($T=27$ °C) successively in trichloroethylene, acetone, and methanol. The samples were then dipped in a heated bath ($T=70$ °C) of $NH_4OH:H_2O_2:H_2O$ (1:1:5) mixture for 3 min, followed by a 3 min dip in a heated $HCl:H_2O_2:H_2O$ (1:1:5) mixture ($T=70$ °C). They were rinsed in de-ionized water after the acid treatment.

The $NH_4OH:H_2O_2:H_2O$ (1:1:5) mixture does not generally remove the oxide/hydroxide layers completely from throughout the surface. So, to overcome this problem, samples were cleaned using aqua regia ($H_2O:HNO_3:HCl=1:2:6$) and then de-ionized water. They were kept immersed in methanol during the idle time of processing after aqua regia treatment to avert subsequent oxide/hydroxide formation. Schottky diodes were fabricated using two-step photolithography.[2] The Ohmic contact was the Ti/Al/Pd/Au (200 Å/600 Å/400 Å/500 Å) multilayer contact, and the Schottky contact was the bilayer Ni/Au (1000 Å/300 Å) contact. For both S2 and S3 diodes, Schottky barrier heights and ideality factors were measured[4] by current-voltage (I-V) and capacitance-voltage (C-V) methods as functions of temperature T.

Figure 1(a) compares the I-V based Schottky barrier height ϕ_B of the S2 and S3 diodes. As evident from Fig. 1(a), the measured variation of ϕ_B with T for the S3 diodes is opposite to that for the S2 Schottky diodes. For the S2 diodes, ϕ_B, as determined for 26, 100, 150, 200, 250, and 300 °C, are 1.03, 0.95, 0.83, 0.72, 0.59, and 0.49 V, respectively. For the S3 diodes, ϕ_B, as determined for 26, 100, 150, 200, 250, and 300 °C, are 0.762, 0.835, 0.973, 1.104, 1.233, and 1.321 V, respectively. The S3 diodes have quantum well and two-dimensional electron gas (2DEG) at the $Al_xGa_{1-x}N$/GaN interface. As a result, some of the thermally activated metal electrons, while trying to tunnel into the

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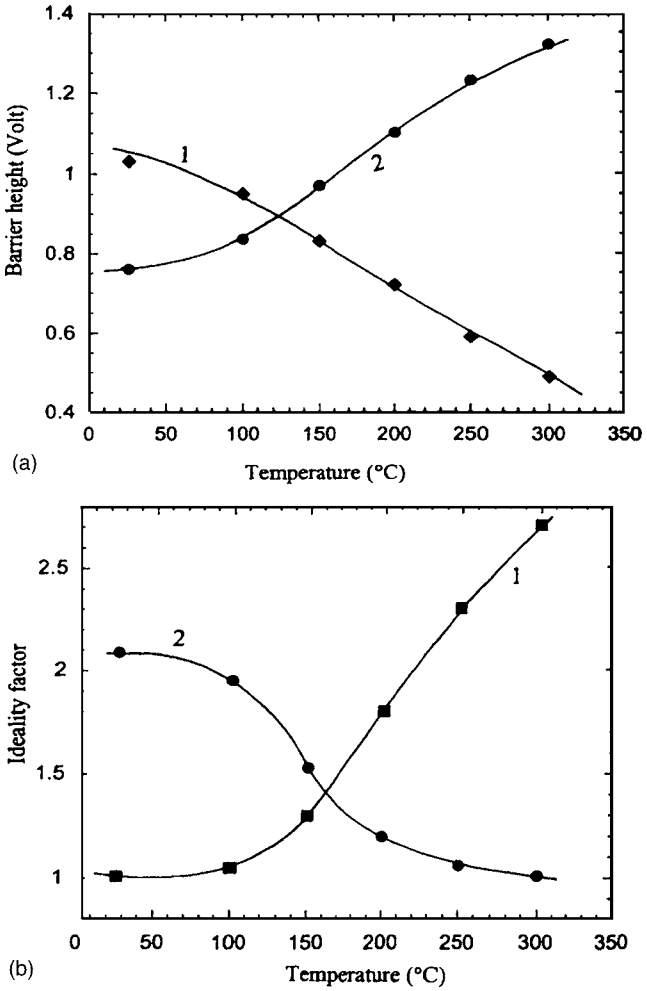

FIG. 1. Temperature dependence of the Schottky diode (a) barrier height and (b) ideality factor for the $Al_xGa_{1-x}N$ and $Al_xGa_{1-x}N/GaN$ diodes. Curve 1 is for the $Al_xGa_{1-x}N$ diode and curve 2 is for the $Al_xGa_{1-x}N/GaN$ diode.

semiconductor, are nullified by the polarized induced positive charges; others are transported into the quantum well(s). More $Al_xGa_{1-x}N$ donor atoms are thus ionized at higher T, and the free electrons, thus created, are drifted into the quantum well. The M/S depletion region is consequently widened, and ϕ_B enlarged. The ϕ_B thus becomes higher than what it should otherwise be under normal circumstances. This effect is absent in the S2 and S1 diodes.

Figure 1(b) depicts the temperature dependent ideality factor n_{idl} obtained from I-V plots. For the S3 Schottky diodes, n_{idl} decreases with increasing T. But, for the S2 Schottky diodes, it increases with increasing T. Such an increase in n_{idl} with T was found also for the Pt/n-GaN Schottky contacts.[5] Transport mechanisms such as trap-assisted tunneling, field emission, and thermionic field emission are very highly sensitive to ϕ_B. They decrease almost exponentially with increasing ϕ_B. So, for the S2 Schottky diodes, for which ϕ_B decreases with increasing T, the forward current I_F is dominated by these transport mechanisms more at $T>300$ K than at $T=300$ K. Consequently n_{idl} is larger at higher T. In contrast, for the S3 Schottky diodes, for which ϕ_B increases with increasing T, I_F is hardly affected by these transport mechanisms at higher T. The ideality factor n_{idl} is, therefore, far smaller at $T>300$ K than at $T=300$ K.

The electron affinity χ_S of a semiconductor is the energy difference between the vacuum level and its conduction band edge E_C. Chen and Lue[6] found that χ_S is essentially independent of T for $0\ \text{K} \leqslant T \leqslant 300$ K. The temperature dependence of this χ_S may be estimated also from temperature dependent conduction band edge of the semiconductor. For this, the temperature dependent energy band gap of GaN and AlN may be assumed to have the form[7]

$$E_G(T) = E_G(0) - \alpha_G T^2/(T + T_G), \tag{1}$$

where $E_G(0)$ is the energy band gap at 0 K, and α_G and T_G are fitting parameters. $E_G(0)=3.48$ eV, $\alpha_G=1.08$ meV/K, and $T_G=745$ K for GaN; $E_G(0)=6.29$ eV, $\alpha_G=1.80$ meV/K, and $T_0=1462$ K for AlN. If $E_{GA} \equiv E_G(Al_xGa_{1-x}N)$, $E_{GB} \equiv E_G(AlN)$, and $E_{GC} \equiv E_G(GaN)$, then the energy band gap of $Al_xGa_{1-x}N$, as a function of Al mole fraction x and the temperature T, may be given by[8]

$$E_{GA}(x,T) = xE_{GB}(T) + (1-x)E_{GC}(T) - bx(1-x), \tag{2}$$

where $E_{GB}(300\ \text{K})=6.20$ eV, $E_{GC}(300\ \text{K})=3.39$ eV, and $b=1.0\pm0.3$ eV. Equation (2), together with Eq. (1), gives $E_G(Al_xGa_{1-x}N)$ as a function of T. This E_G shrinks at higher T. If it is assumed that the conduction band edge E_C shifts downward, the valence band edge E_V shifts upward during this shrinkage, and that these two shifts are equal and opposite, then $\chi_S(T)$ of $Al_xGa_{1-x}N$, with respect to that at $T=300$ K, may be

$$\chi_S(T) = \chi_S(300\ \text{K}) + [E_G(T) - E_G(300\ \text{K})]/2\ (\text{eV}). \tag{3}$$

The variation of $\chi_S(T)$ with T is shown in Fig. 2. It indicates that, following the same trend, as suggested by Chen and Lue,[6] $\chi_S(T)$ for $Al_xGa_{1-x}N$ is quite insensitive to T. For $26\ ^\circ\text{C} \leqslant T \leqslant 300\ ^\circ\text{C}$, the change in $\chi_S(T)$ is only 0.09 eV.

For S2 diodes, an increase in T accompanies an increase in energy of the metal electrons and hence a decrease in ϕ_M. Although, at higher T, there occurs some increase in χ_S, this increase is small. As a result, in line with the Schottky-Mott rule, ϕ_B, at higher T, decreases with decreasing ϕ_M. For the same reason, ϕ_M for the S3 diodes is also lower at higher T. Metal electrons, at these temperatures, have additionally higher energy and higher coupling with the $Al_xGa_{1-x}N$ surface electrons, which affect the polarization charges σ_p of the $Al_xGa_{1-x}N$ surface. Band structure diagram for the S3 diodes is shown in Fig. 3. The diagram indicates that polarization charges $-\sigma_p$ of the quantum well is consequently affected, and the sheet carrier concentration of the 2DEG is reduced. A reduction of the sheet carrier concentration of the 2DEG promotes drift of electrons from $Al_xGa_{1-x}N$ into the quantum well, creating larger number of ionized donor atoms and wider depletion region. The ϕ_B value is consequently increased. So, at higher T, both ϕ_B and χ_S increase, but ϕ_M decreases. Consequently the Schottky-Mott rule $q\phi_B = q\phi_M - \chi_S$ is hardly obeyed. To our knowledge, this is a very important observation made for the S3 diodes for the first time. It strongly suggests that any modification of a M/S structure interfering the charge alignment at its M and S faces tends to undo the validation of the rule: $q\phi_B = q\phi_M - \chi_S$.

In order to determine whether the temperature dependent changes in ϕ_B and n_{idl} resulted from structural changes at the interface, an investigation of the reversibility of these measurements was conducted. For this, I_F vs V plot for the A_0

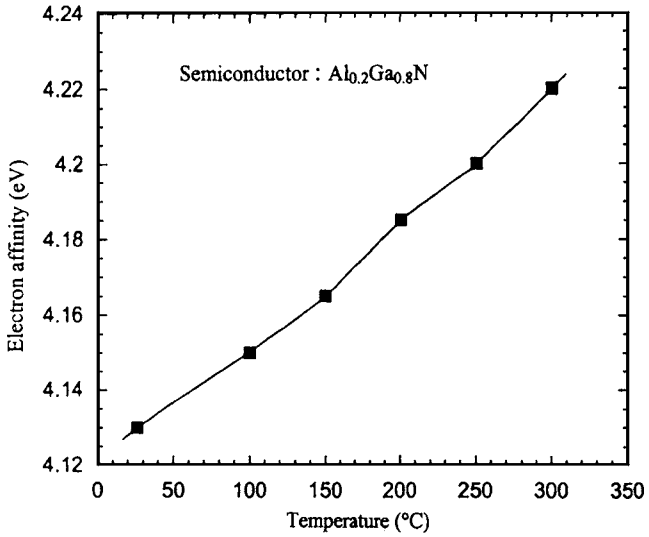

FIG. 2. Calculated variation of metal electron affinity modified by high temperature chemistry.

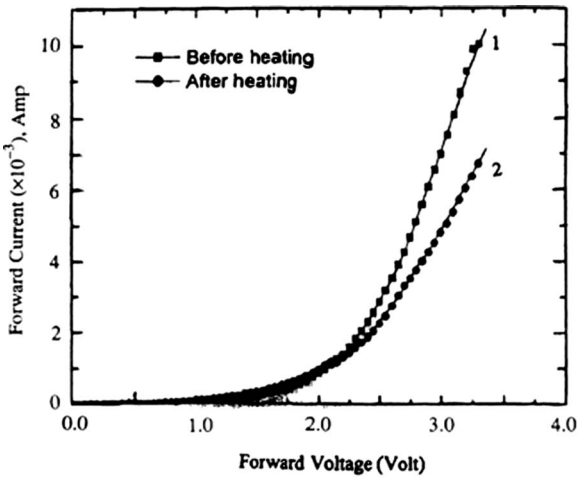

FIG. 4. Forward current-voltage characteristics of $Al_xGa_{1-x}N/GaN$ Schottky diodes before and after heating; curve 1 was obtained for the diodes before heating, and curve 2 was obtained for the diodes after heating, both at room temperature.

and B_0 diodes was performed. A_0 diodes are the S3 diodes kept at $T=26$ °C all the time. B_0 diodes are the S3 diodes, which underwent a stepwise heating process being kept at each temperature step for about 15 min. More specifically, the device temperature was increased stepwise from $T=26$ to 50 °C, from 50 to 150 °C; from 150 to 200 °C, and finally from 200 to 300 °C, respectively. The devices were then cooled down back to 26 °C. So, the B_0 diodes underwent some form of thermal annealing. The forward currents for the A_0 and B_0 diodes, shown in Fig. 4, were obtained at 26 °C. As may be noted from Fig. 4, these currents for the B_0 diodes are lower than those for the A_0 diodes. This might be due to the 2DEG sheet charge density for the B_0 diodes being lower than that for the A_0 diodes. The ϕ_B for the B_0 diodes was, however, higher than that for the A_0 diodes. The difference between the two might have resulted from different interfacial reactions and/or diffusion processes at high T,

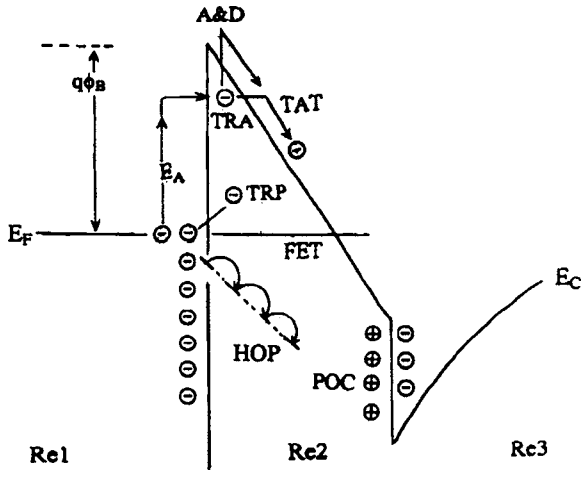

FIG. 3. Schematic diagram showing charge alignment due to polarization effect, two-step trap-assisted tunneling, field-emission tunneling, trapping, and hopping, in the interface regions of $Al_xGa_{1-x}N/GaN$ Schottky diodes. In the figure activation energy is denoted by E_A, deep level trapping by TRP, shallow-level trapping by TRA, two-step trap-assisted tunneling by TAT, activation and drift by A&D, field-emission tunneling by FET, hopping by HOP, polarization charge by POC, metal region 1 by RE1, $Al_xGa_{1-x}N$ region 2 by RE2, and GaN region 3 by RE3.

Ni/Au partial oxidation, and/or metal interdiffusion, which did not allow I_F, n_{idl}, and ϕ_B to revert back to the original value. The modification of interface states resulted also from the relaxation of strain of the $Al_xGa_{1-x}N/GaN$ heterostructure, formation of alloys, and change in ϕ_B due to annealing. There are ambiguities in x-ray diffraction patterns obtained for Au/Ni/GaN contacts alloyed at various temperatures.[9] Nevertheless, subject to further investigation, the primary products might have been Ni_3N and Ni_4N for an alloying temperature of 0 °C $< T_{RTA} <$ 200 °C. The primary products might have been Ga_4Ni_3, Ga_3Ni_2, Ni_3N, GaAu, and $GaAu_2$ for the alloying temperature of 500 °C $< T_{RTA} <$ 600 °C.

In conclusion, investigations have been made to highlight the Schottky characteristics of various diodes. While the highest ideality factor for the S2 diodes at 300 °C is about 2.7, the highest ideality factor for the S3 diodes at 300 K is about 2.1. This indicates that, at various T, the carrier transport in both the diodes is dominated by thermionic emission. Any deviation from thermionic characteristics is due to recombination and leakage. The most striking feature of our measurements is that they appear to successfully establish the validity of the Schottky-Mott rule for the S1 and S2 diodes and the invalidity of this rule for the S3 diodes.

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