Journal of Electronic Materials, Vol. 28, No. 3, 1999

Electrical Characteristics and Thermal Stability of W, WSiN, and Nb Contacts to p- and n-Type GaN

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A comprehensive annealing study of W, WSiN, and Nb refractory contacts to both p- and n-GaN was performed. Samples were examined by current-voltage (I-V) measurements. Both W and Nb contacts to n-GaN showed rectifying characteristics with Schottky barrier heights ($q\phi_B$) of 0.63 eV. For p-GaN, the I-V curves showed very leaky behavior. In contrast, I-V curves of WSiN/n-GaN were very leaky while those of WSiN/p-GaN were rectifying with $q\phi_B$ of 0.8 eV. The degradation temperature of both W and WSiN contacts was 700°C and that of Nb contacts was 300°C.

Key words: GaN, metal contacts, Schottky barrier, work function

INTRODUCTION

Recently, GaN-based materials have been intensively studied for optoelectronic devices and high-temperature/high-power electronic devices, and visible light-emitting diodes,[1] ultraviolet (UV) detectors,[2] microwave-operation AlN/GaN field-effect transistors (MESFETs),[3,4] and high-electron-mobility transistors (HEMTs)[5] have been demonstrated.

As device performance improves, studies of both ohmic and Schottky contacts to GaN are of interest. The Schottky barrier height ($q\phi_B$) is expected to be dependent on the metal work function due to the ionic nature of GaN,[6] but available data are still contradictory. For n-GaN, it has been reported that the slope (S) parameters of the barrier ($S = \partial q\phi_B / / \partial \chi_s$, where χ_s is the metal electronegativity) are 0.7[7] and almost unity,[8] while the S parameters of Ni, Pd, and Pt/n-GaN do not obey this rule.[9–11] For p-GaN, because the contacts tend to exhibit very leaky Schottky characteristics, i.e., a low barrier, but high series resistance, the mechanism of current flow through the interface has not been established and the exact value of $q\phi_B$ has not yet been estimated.[12,13]

Because GaN is used for high-temperature/high-power electronic devices, the thermal stability of the contacts is an important issue, and there have been reports on the thermal stability of contacts such as Ni, Ti, Ti/Al, Pt, Pd, W, Re, NiSi, PtSi, WSi on n-GaN.[9,14–25] In most of these studies, the results of x-ray diffraction, Rutherford backscattering spectroscopy, and Auger electron spectroscopy are correlated with the contact resistance of ohmic contacts and the barrier height of Schottky contacts formed on n-GaN as a function of high-temperature annealing. As examples of thermally stable Schottky contacts to n-GaN, there are Pt and Pd, which do not form a nitride and have a high $q\phi_B$ of around 1 eV.[10,11] However, these metal films form islands when annealed above 700°C.[18] NiSi and PtSi contacts, on the other hand, are thermally stable up to 600°C without the island problem.[23,24] For ohmic contacts, M.W. Cole et al. have found that the W_2N interfacial phase is formed after annealing in the temperature range of 600 to 1000°C for 1 min and the contact resistance of W/n$^+$-GaN ($n = 1.5 \times 10^{19}$ cm^{-3}) is 8.0×10^{-5} Ωcm^2.[19] This W_2N phase is also found at the interface of WSi/GaN after annealing at 700°C.[25] For the GaN-based HEMTs reported to date, since device performance has been the focus rather than the thermal stability of contacts, Ag, Au, Ti/Pd/Au, and Pt/Au were used as gate contacts.[3,4,26–28]

This paper comprehensively examines the basic electrical characteristics and thermal stability of refractory metal contacts to both p- and n-type GaN. Contacts formed from refractory metals W, WSiN, and Nb were prepared. Tungsten was chosen because it is commonly used as a gate metal in MESFETs. Niobium reacts with N, forming the stable compound

(Received July 20, 1998; accepted December 4, 1998)

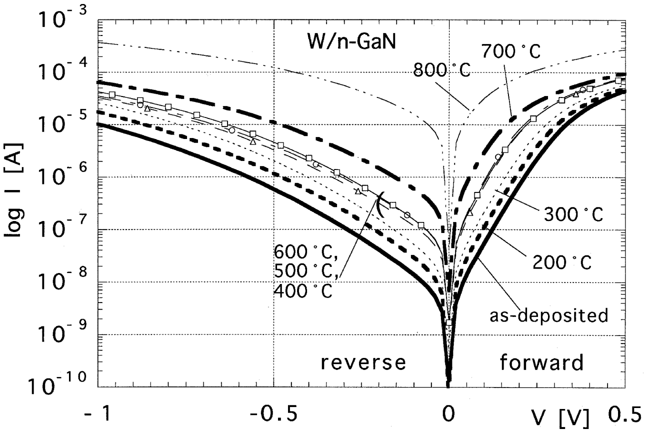


Fig. 1. Typical I-V characteristics of W/n-GaN contacts in a semi-log plot.

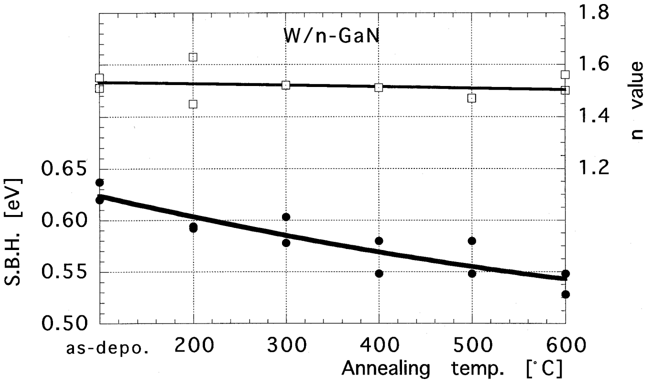


Fig. 2. Annealing temperature dependencies of the Schottky barrier heights and n-value for W/n-GaN.

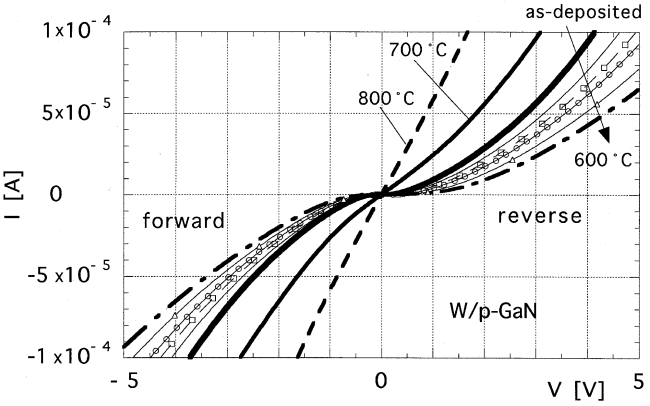


Fig. 3. I-V characteristics of W/p-GaN contacts in a linear plot.

NbN, which might be a more stable contact at high temperature. WSiN with saturated N content shows higher thermal stability than W and WSi to GaAs[29,30] and is thus, in contrast to Nb, expected to be nonreactive. The current-voltage (I-V) measurements were carried out for these contacts after isochronal annealing for 10 min at temperatures up to 800°C. Low-carrier concentration (p, n = 10^{17} cm^{-3}) GaN substrates were used in order to evaluate the interfacial reactions and the sensitivity of Schottky barriers to anneal.

EXPERIMENTS

The 1 μm thick GaN films for this study were grown on sapphire using metalorganic chemical vapor deposition (MOCVD). The carrier concentration of both the p- and n-GaN was 1×10^{17} cm^{-3}. The GaN surface was degreased in acetone and methanol, and then the surface oxide was removed in buffered hydrofluoric acid solution (BHF) before loading the samples into a sputtering metal deposition chamber. The W (160 nm thick) or Nb (45 nm thick) was deposited by magnetron sputtering in Ar plasma with a sputtering power of 350 W. The deposition of WSiN (100 nm thick) was carried out by reactive sputtering in a mixture of Ar and N_2 with a sputtering power of 300 W. The deposited WSiN films contain a saturated N content of 37%. The experimental details are described in Ref. 31. The metal films were patterned into circular dots (100–200 μm diameter) for I-V measurements. A circular transmission line model (TLM) pattern[32] was also prepared to estimate the contact resistance (see Fig. 7) when the I-V curve was linear. Ten minute isochronal annealing was conducted up to 800°C in a furnace with a nitrogen ambient.

The electrical properties, $q_{\phi}B$, and ideality factor (n-value) were determined by the I-V method in terms of the thermionic emission model[33] using

$$J = A^{**}T^2\exp(-q\phi_B/kT)[\exp(qV/nkT)-1], \qquad (1)$$

where A^{**} is the effective Richardson constant (24 A/cm^{2}K^2 for n-GaN-based on $A^{**} = 4\pi m^* qk^2/h^3$ and $m^* = 0.20m_0$,[34] and 72 A/cm^{2}K^2 tor p-GaN with $m^* = 0.60\ m_0$[33]). T is the temperature, q is the electron charge, k is the Boltzman constant, and V is the applied voltage.

RESULTS

Typical I-V characteristics of W/n-GaN contacts are shown in Fig. 1. In the as-deposited condition, the contacts show Schottky behavior. The currents gradually increase as the annealing temperature increases to 400°C, and then the current increment is suppressed at 600°C. Upon annealing at 700°C, the current increases again, and finally the I-V curves do not show rectifying behavior after 800°C annealing. Figure 2 shows the annealing temperature dependencies of $q\phi_B$ and the n-value for W/n-GaN. As the annealing temperature is increased to 600°C, $q\phi_B$ decreases from 0.63 to 0.54 eV, while the n-value is a constant 1.5.

For W/p-GaN, I-V curves exhibit very leaky behavior as shown in Fig. 3. The current decreases as the annealing temperature increases, and the current after 600°C annealing is almost half that in the as-deposited condition. Upon annealing at 700°C, the current increases significantly and becomes larger than that formed in the as-deposited condition. Finally, some dots show linear I-V curves after 800°C annealing.

Typical I-V characteristics of Nb/n-GaN contacts after annealing up to 300°C in a semi-log plot and from 400 to 800°C in a linear plot are shown in Figs.

4a and 4b, respectively. The I-V curve in the as-deposited state shows Schottky behavior. The Schottky barrier and the n-value are 0.63 eV and 1.28. The I-V curve after annealing at 200°C is the same as that in the as-deposited condition, but upon annealing above 200°C, I-V characteristics become ohmic and almost the same current level is kept up to 800°C. The typical contact resistance is 0.5 Ωcm^2, as measured by the TLM method.

As shown in Fig. 5, the Nb/p-GaN contacts exhibit similar I-V characteristics to W/p-GaN. However, the current decreases monotonically up to 800°C.

The WSiN contacts show different I-V characteristics from W and Nb. Figure 6 shows I-V curves of WSiN/n-GaN. All the curves are almost linear, and keep the same shape up to 700°C. As with the W contacts, some dots show linear I-V curves after 800°C annealing.

On the other hand, the WSiN/p-GaN contacts exhibit very leaky rectifying behavior up to 600°C annealing, as shown in Fig. 7. Upon 700°C annealing, the current significantly increases. Figure 8 shows the $q\phi_B$ and n-value as a function of annealing temperature. The Schottky barrier height in as-deposited contacts is 0.79 eV. The $q\phi_B$ is virtually constant at 0.81 eV in the temperature range between 200 and 500°C, and drops to 0.72 eV upon 600°C annealing. The n-value of as-deposited sample is as high as 3.5. As the annealing temperature increases to 400°C, the n-value decreases to 2.4. Above 500°C, the n-value increases again.

In order to estimate the interfacial reaction macroscopically, the resistance of the metal films themselves was measured. The results are shown in Fig. 9. The resistance of the W and WSiN films stays constant over the entire annealing temperature range, while the resistance of the Nb film increases slightly at 400°C and then greatly at 600°C. Figures 10a and 10b, respectively, show optical microscope images of the W and Nb/n-GaN samples after annealing at 600°C. The surfaces of the W and WSiN dots are smooth even after 800°C annealing. On the other hand, a spotty interfacial reaction is observed on the

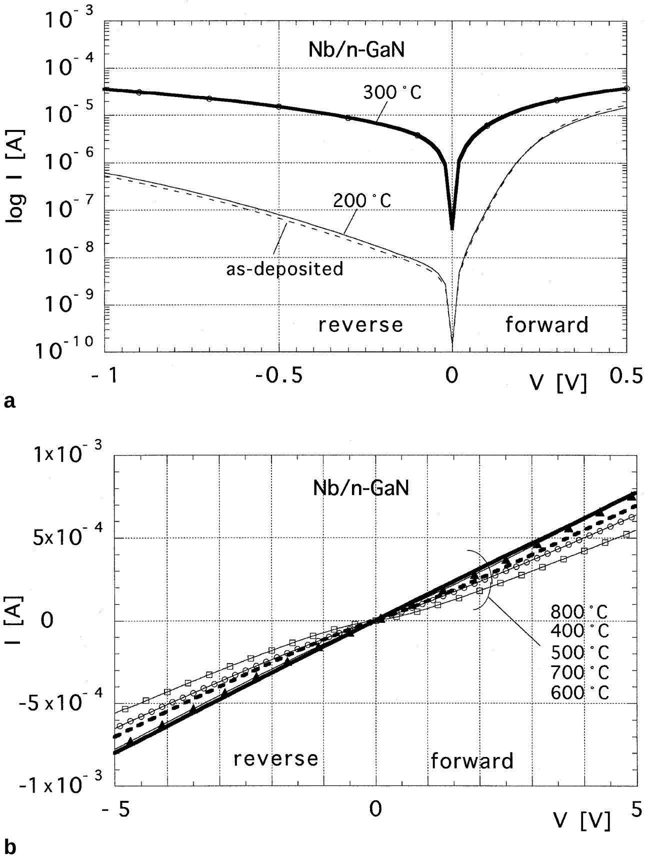


Fig. 4. Typical I-V characteristics of Nb/n-GaN contacts after annealing up to 300°C in a semi-log plot (a) and from 400 to 800°C in a linear plot (b).

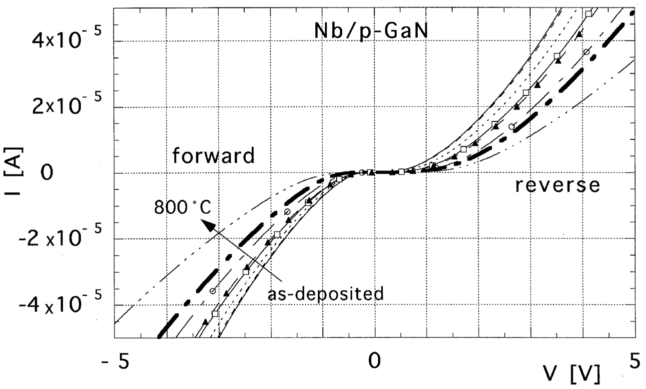


Fig. 5. I-V characteristics of Nb/p-GaN contacts in a linear plot.

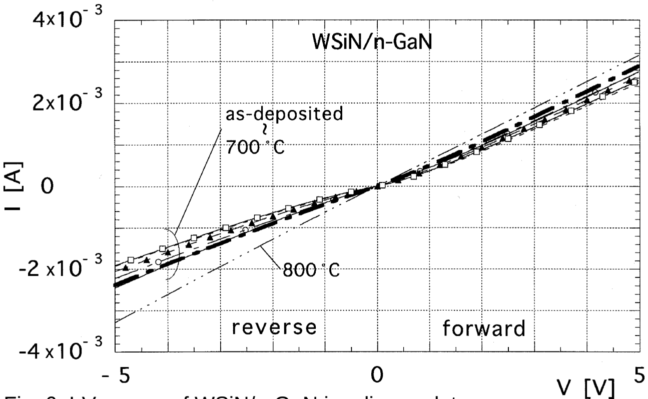


Fig. 6. I-V curves of WSiN/n-GaN in a linear plot.

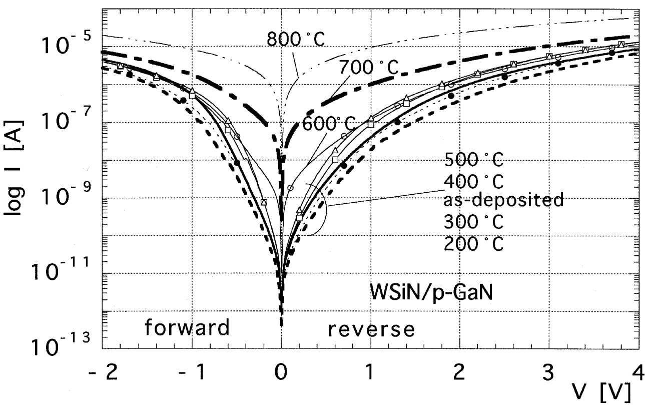


Fig. 7. I-V characteristics of WSiN/p-GaN contacts in a semi-log plot.

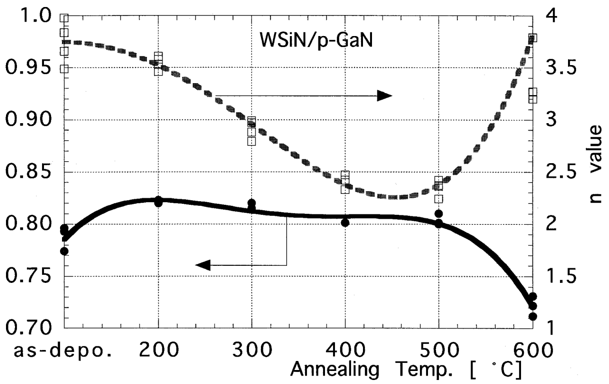


Fig. 8. Annealing temperature dependencies of the Schottky barrier height and n value for WSiN/p-GaN.

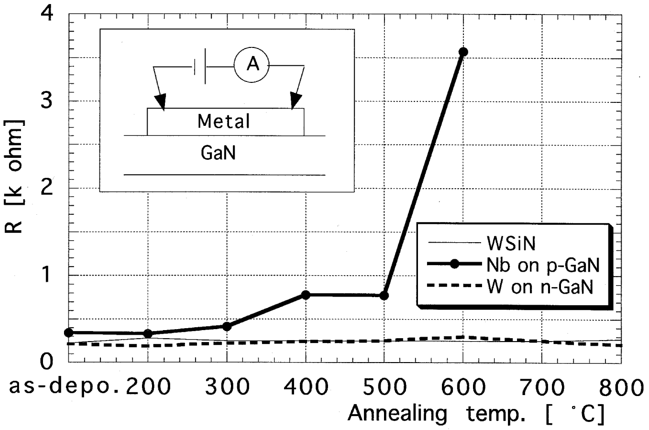


Fig. 9. Resistances of the metal films as a function of annealing temperature.

Nb dots upon annealing at 600°C, and the total thickness of Nb is consumed with the reaction in the spotty regions.

DISCUSSION

Electrical Characteristics

We extract two important observations to characterize the I-V curves. One is that the same $q\phi_B$ of 0.62 eV is obtained for W, Nb/n-GaN, while the work functions of W and Nb are 4.55 and 4.3 eV, respectively. The other is that, for all three metals, the I-V curves are very leaky with a large series resistance (almost linear) for one type of GaN, and are rectifying for the other type.

Band diagrams devised to explain the I-V characteristics are shown on Fig. 11. E.V. Kalinina and A.C. Schmitz have reported that the $q\phi_B$ of n-GaN contacts depends on the metal work function with S = 1 and 0.385, respectively.[8,35] The $q\phi_B$ of W and Nb/n-GaN can be estimated to be 0.5 and 0.3 eV from Kalinina's results, respectively, and Schmitz reported that both W and Nb/n-GaN contacts show slightly rectifying behavior. However, strong surface Fermi level (E_F) pinning at 0.63 eV can be seen in our results. All the metal films were deposited by sputtering in this work. It is known that sputtering deposition damages the semiconductor surface, and the damage pins the Fermi level.[30] The most widely accepted surface states are U-shaped.[36] Our band diagrams of the W and Nb contacts are shown in Fig. 11a, where it is assumed the bottom of the U-shaped interfacial states (Ns) are located above mid-gap. Because the interfacial state density is relatively small close to the conduction band (Ec), Ns does not affect the I-V characteristics for n-GaN very much. For p-GaN, because the Ns are large close to the valence band (Ev), the current can go through the barrier via the interfacial states.[37] This explains the very leaky I-V curves with large series resistance. When the U-shaped Ns are located below mid-gap, as shown in Fig. 11b, opposite I-V characteristics are expected, as the WSiN contacts demonstrated. Further detailed surface analysis is required in order to characterize the different location of the U-shaped Ns, but the major difference in the experimental condition is the sputtering ambient. The W and Nb films were sputtered in Ar, and the WSiN in a gas mixture of Ar and N_2 (15%). N_2 plasma may be effective in reducing the surface oxide and forming nitride.

Thermal Degradation

From the results in Fig. 9. and Fig. 10, it is clear that Nb is very reactive with GaN and the interfacial mixing proceeds readily. The onset temperature of the reaction was found to be 300°C from the I-V curves. Chemical analysis is required in order to determine the interfacial reacted phase; however, at such low temperature, outdiffusion of N into Nb and resulting accumulation of Ga are not expected. Because the enthalpy of formation (ΔH) for NbN is smaller than those for GaN and GaNb (ΔH_{NbN}, ΔH_{GaN}, AH_{Ga3Nb}, ΔH_{GaNb3} = –235.1, –109.6, –41.9, –40.5 KJ/mol), the most likely reacted phase can be expected to be NbN and a ternary compound.

No interfacial reaction was observed between W, WSiN, and GaN up to 800°C in Fig. 9 and Fig. 10, but the I-V characteristics degraded after annealing above 600°C. It has been reported that the sputtering damage can be recovered by annealing at around 600°C in WSiN/GaAs, InGaP.[30] In Fig. 2, the $q\phi_b$ of W/n-GaN approaches the value expected from Kalinina's results[8] (0.5 eV) as the annealing temperature is increased. On the other hand, the n value of as-deposited WSiN/p-GaN is as high as 3.5, but decreases as the annealing temperature is increased, as shown in Fig. 8. These could be considered symptoms of damage recovery. However, before significant recovery could be seen, the contacts degraded. The onset temperature of the degradation is consistent with the x-ray diffraction results reported by M.W. Cole.[19] They reported that only W_2N is formed at the interface upon high temperature annealing and attributed the resultant N vacancies, which are donors, to a low contact resistance for n^+-GaN. They also reported that W_2N is formed at the interface of WSi/GaN after annealing at 700°C.[25] This model is also available for the present degradation of W/n-GaN, but not for W/p-GaN. Another mechanism, such as segregation of Ga

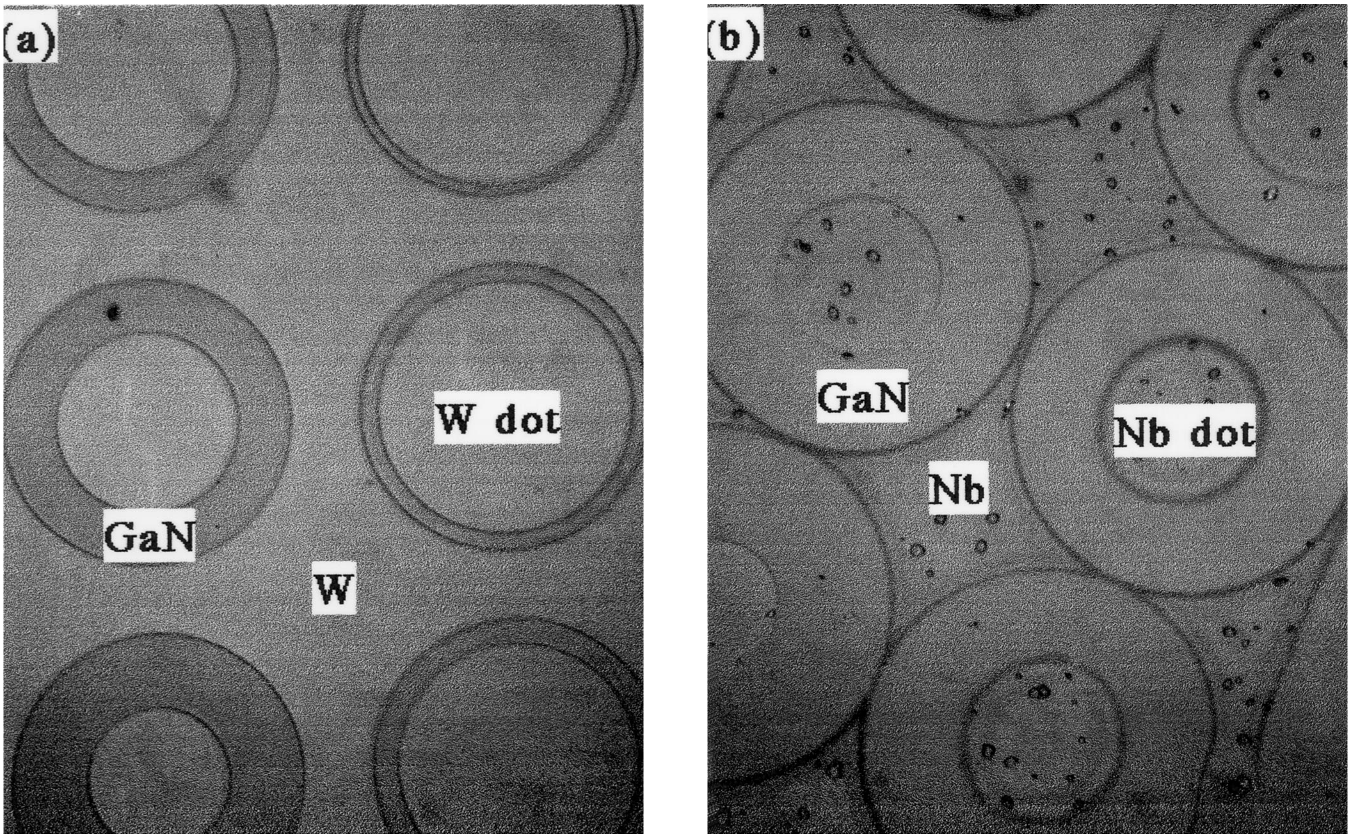
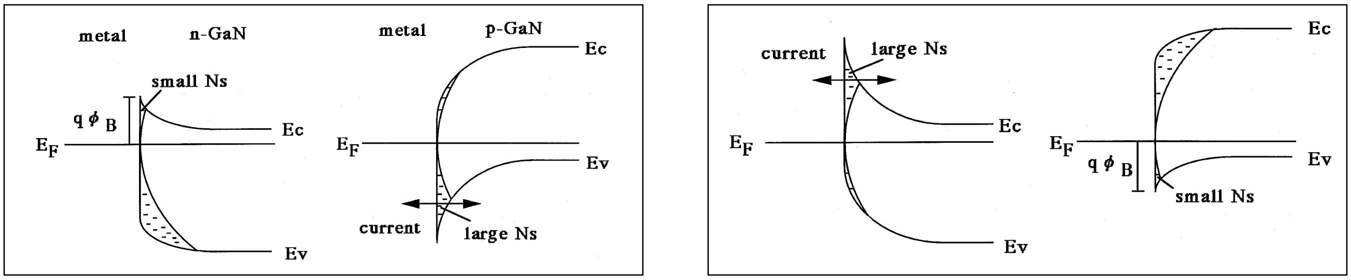


Fig. 10. Optical microscope images of W/n-GaN (a) and Nb/n-GaN (b) after annealing at 600°C.



a

b

Fig. 11. Band diagrams of metal/GaN contacts. It is assumed the bottom of the U-shaped interfacial states is located above mid-gap (a) and below mid-gap (b).

atoms behind W_2N,might be the cause.

The WSiN films remain amorphous and WSiN/GaAs contacts show excellent I-V characteristics even after 800°C annealing,[30] but WSiN/GaN degraded at lower temperature. During the WSiN deposition, N atoms are incorporated into WSi and the N content saturates at 37% when the sputtering power is 300 W.[31] Even though the WSiN film contains saturated N, N atoms could diffuse into the WSiN amorphous network because of the high vapor pressure of N on the GaN surface.

CONCLUSION

The comprehensive annealing study based on I-V measurements of W, WSiN, and Nb contacts to both p- and n-GaN was presented. The I-V curves for W and Nb contacts to n-GaN showed rectifying characteristics and their $q\phi_B$ were the same at 0.63 eV, while those for the W and Nb contacts to p-GaN showed very leaky behavior. In contrast, the I-V curves of WSiN/n-GaN showed very leaky behavior while those of WSiN/p-GaN were rectifying with $q\phi_B$ of 0.8 eV. We believe that U-shaped surface states induced during metal deposition could explain these reversible I-V characteristics.

The degradation temperature of both W and WSiN contacts was 700°C and that of Nb contacts was 300°C. The refractory metal contacts to GaN have lower thermal stability than those formed on GaAs.

ACKNOWLEDGMENT

The authors would like to thank Dr. Kazumi Nishimura of NTT System Electronics Labs. for the metal deposition.

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