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Electrical and structural properties of rapidly annealed Pd/Mo Schottky contacts on n-type GaN

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Abstract

Electrical and structural properties of palladium/molybdenum (Pd/Mo) Schottky contacts on n-type GaN have been investigated as a function of annealing temperature by current–voltage (*I–V*), capacitance–voltage (*C–V*), x-ray diffraction (XRD) and Auger electron spectroscopy (AES) techniques. An as-deposited Pd/Mo/n-GaN Schottky diode exhibits a barrier height of 0.68 eV (*I–V*) and 0.82 eV (*C–V*), which increased to 0.75 eV (*I–V*) and 0.89 eV (*C–V*) after annealing at 400 °C. However, it is noted that the barrier height slightly decreased to 0.73 eV (*I–V*) and 0.87 eV (*C–V*) when the contact was annealed at 500 °C. A maximum barrier height of 0.78 (*I–V*) and 1.09 eV (*C–V*) was achieved on the Pd/Mo contacts annealed at 600 °C. The Norde method was also employed to extract the barrier height of Pd/Mo contacts, and the values are 0.70 eV for the as-deposited and 0.82 eV for the contact annealed at 600 °C which are in good agreement with those obtained by the *I–V* technique. Based on the Auger electron spectroscopy and x-ray diffraction studies, the formation of gallide phases at the Pd/Mo/n-GaN interface could be the reason for the increase of Schottky barrier heights upon annealing at elevated temperatures. The AFM results showed that there was no significant degradation in the surface morphology (rms roughness of 4.61 nm) of the contact even after annealing at 600 °C. These results make Pd/Mo Schottky contacts attractive for high-temperature device applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Gallium nitride (GaN) is a chemically stable compound semiconductor with a wide direct band gap (3.4 eV), which has superior characteristics such as high thermal conductivity, excellent thermal stability and large avalanche breakdown field, which are beneficial for the fabrication of devices operating in a hostile environment [1]. They have attracted a high degree of interest due to their wide applications for high-temperature, high-frequency and high-power electronic devices such as blue/ultraviolet light emitting devices (LEDs) [1, 2], sun blind solar detectors [3], metal semiconductor field effect transistors (MESFETs) and high electron mobility transistors (HEMTs) [4, 5]. The excess reverse bias leakage current is still a major impediment in GaN-based Schottky contacts even though continuous improvement in the synthesis of III–nitride materials by different growth techniques leads to increased device quality. The performance of GaN-based devices can often be limited by the quality of the ohmic and Schottky contacts, hence the characterization and understanding of the properties of metal/GaN contacts are essential [6]. Therefore, the development of high-quality ohmic and Schottky contacts with good thermal stability is still a challenge.

Various metals have been used for the formation of Schottky contacts on n-type GaN by many research groups, [7–17]. Wang *et al* [14] investigated the electrical characteristics of Au/n-GaN Schottky contacts with different film thickness, and reported the barrier height of 0.79 eV (*I–V*) and 1.05 eV (*C–V*) for a thickness of 28 nm. Miura *et al* [11] studied thermal annealing effects on Ni/Au-based Schottky contacts on n-GaN and AlGaN/GaN after inserting high work function metals such as Pt, Ir, Pd or Mo. Mehandru *et al* [12] investigated W contacts on n-GaN, and reported that the barrier height of an as-deposited sample was 0.80 eV and the Schottky barrier height reduces to ∼0.4 eV when samples were annealed at 500–600 °C. Khanna *et al* [8] investigated W_2B-based rectifying contacts to n-GaN, and showed that the contacts are stable against annealing up to ∼500 °C. Ramesh *et al* [13] investigated the electrical properties of a Mo/n-GaN Schottky diode as a function of annealing temperature by *I–V* and *C–V* techniques and reported a barrier height of 0.81 eV (*I–V*) and 1.02 eV (*C–V*), and showed that the Mo Schottky contact was fairly stable during annealing at 400 °C. Recently, Reddy *et al* [15] investigated the electrical and structural properties of a Ru/Au/n-GaN Schottky diode as a function of annealing temperature. They showed that the formation of gallide phases at the interface could be the reason for the improvement of electrical properties after annealing at elevated temperatures. The strength of the interfacial reactions between the metal and semiconductor plays an important role in determining the quality of the resultant Schottky barriers in GaN as in other compound semiconductor systems. High Schottky barrier height (SBH), low leakage current and good thermal stability in Schottky contacts play key roles in many electronic and optoelectronic devices. In this work, Pd was selected because it has a high work function of 5.12 eV, and high reactivity with GaN. Schottky contacts with Pd/Mo metal alloy can operate stably in the high-temperature and high-power system because the melting point of Mo is very high. In the present work, we have investigated the thermal annealing effects on the electrical and structural properties of Pd/Mo Schottky contacts on moderately doped n-type GaN (∼4.07×10^{17} cm^{-3}).

2. Experimental details

The samples used in this investigation are 2 μm thick Si-doped GaN grown by metal organic chemical vapor deposition (MOCVD) on a c-plane Al_2O_3 substrate. The electron concentration obtained by means of Hall measurement was ∼4.07×10^{17} cm^{-3}. The n-GaN layer is first ultrasonically degreased with warm trichloroethylene followed by acetone and methanol for 5 min each. This degreased layer was then dipped into boiling aqua regia (HNO_3: HCl = 1:3) for 10 min to remove the surface oxides, and then rinsed in deionized water. Ti (20 nm)/Al (30 nm) ohmic contacts were deposited on a portion of the sample using a electron beam evaporation system under a pressure of 5×10^{-6} Torr. The samples were annealed at 850 °C in nitrogen ambient for 30 s. Then the metals under investigation, Pd (30 nm)/Mo (30 nm) Schottky contacts with a diameter of 1 mm, were deposited through a stainless steel mask under a vacuum pressure of 1×10^{-5} Torr. The Pd/Mo Schottky diodes were sequentially annealed at various temperatures from 300 to 600 °C for 1 min under nitrogen ambient in a rapid thermal annealing (RTA) system. Current–voltage (*I–V*) and capacitance–voltage (*C–V*) characteristics of the Schottky diode were measured by a Keithley source measure unit (Model No 230) and a Hewlett-Packard LCR meter (Model No 4274 A), respectively. Auger electron microscopy (AES: VG: Microlab 350) depth profiling was performed to examine the intermixing of the metal and GaN before and after annealing. X-ray diffraction (Siefert XRD PW 3710) (using Cu Kα radiation) was employed to characterize the interfacial reactions between the metal and GaN layers. Atomic force microscopy (AFM) was also carried out to characterize the surface morphology of the samples.

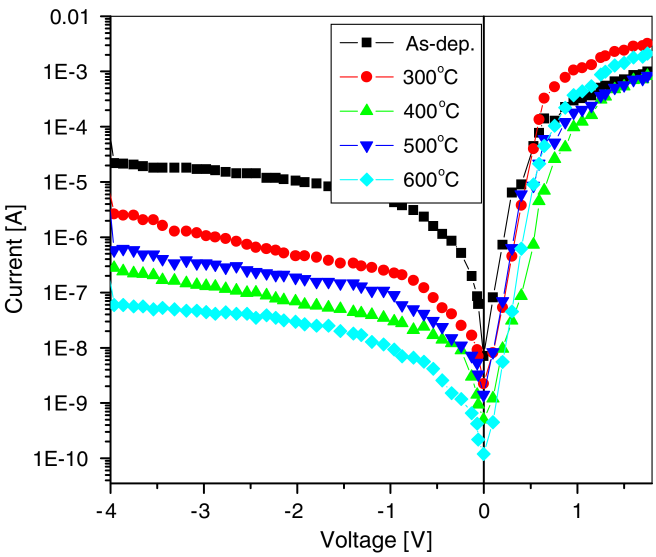

Figure 1. The typical *I–V* characteristics for the Pd/Mo Schottky contact on n-type GaN as a function of annealing temperature.

3. Results and discussion

Figure 1 shows the forward and reverse *I–V* characteristics of Pd/Mo Schottky contacts measured as a function of annealing temperature. It was observed that the properties of all Pd/Mo Schottky diodes are uniform over different diodes. For the as-deposited and annealed at 300 °C Pd/Mo Schottky contacts, the observed leakage currents are 4.6×10^{-6} A and 2.4×10^{-7}A at −1 V, respectively. However, the leakage current slightly decreases to 3.2×10^{-8} A for the sample annealed at 400 °C, and then slightly increases to 1.0×10^{-7} A at −1 V after annealing at 500 °C. For the sample annealed at 600 °C, it is observed that the leakage current further decreased to 1.0×10^{-8} A at −1 V which indicates that the Schottky barrier height is improved upon annealing. The forward *I–V* characteristics were analyzed by using a standard thermionic emission relation for electron transport from a metal–semiconductor with low doping concentration, and the equation is given by [18]

$$I_d = I_s \exp\left(\frac{qV_d}{nkT}\right)\left[1 - \exp\left(\frac{-qV_d)}{kT}\right)\right], \tag{1}$$

Table 1. The saturation currents (I_s), Schottky barrier heights (ϕ_b) and ideality factor (n) of Pd/Mo Schottky diodes on n-GaN as a function of annealing temperature.

Sample	Saturation current (I_s) in A	Schottky barrier height (SBH) ϕ_b (eV)			Ideality factor 'n'
		I–V	Norde	*C–V*	
As-deposited	5.6×10^{-8}	0.68	0.70	0.82	1.75
300 °C	1.3×10^{-8}	0.72	0.74	0.84	1.77
400 °C	7.4×10^{-9}	0.75	0.78	0.89	1.90
500 °C	4.5×10^{-9}	0.73	0.75	0.87	1.75
600 °C	1.1×10^{-9}	0.78	0.82	1.09	1.40

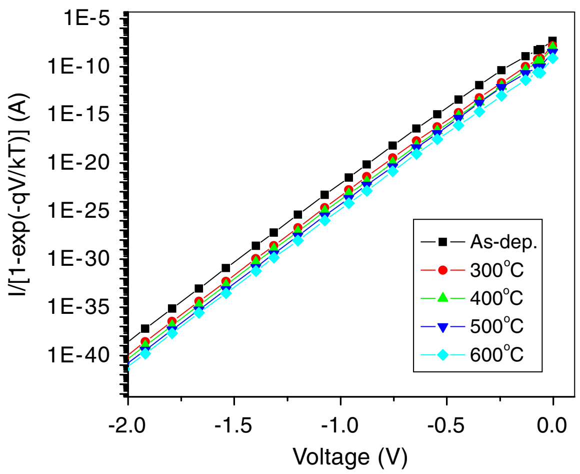

Figure 2. Plot of $I/[1 - \exp(-qV/kT)]$ versus V for the Pd/Mo Schottky contacts annealed at different temperatures.

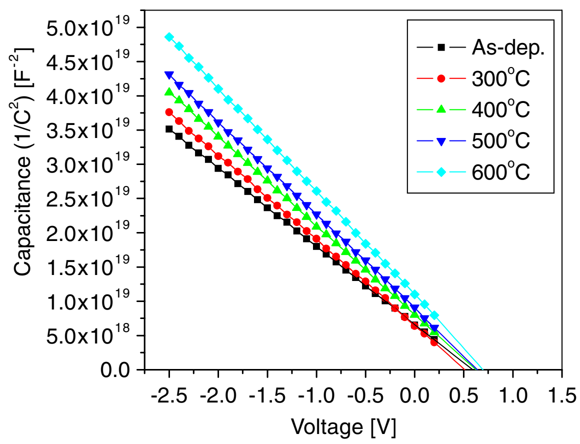

Figure 3. Plot of $1/C^2$ versus V for the Pd/Mo Schottky contacts annealed at different temperatures.

where V_d is the voltage across the diode ($V_d = V - IR$), R is the series resistance, n is the ideality factor and I_s is the saturation current, given by

$$I_s = AA^{**}T^2 \exp\left(\frac{-q\phi_b}{kT}\right), \tag{2}$$

where A^{**} is the effective Richardson constant, A is the area of the diode, and ϕ_b is the Schottky barrier height. The value of ϕ_b can be deduced directly from the *I–V* curves if the effective Richardson constant A^{**} is known. The theoretical value of A^{**} is 26.4 A cm^{-2} K^{-2} based on the effective mass ($m^* = 0.22\ m_o$) of n-GaN [19], and is used here to deduce ϕ_b. From equation (1), a plot of $\ln\{I_d/[1 - \exp(-qV/kT)]\}$ versus V_d (figure 2) yields I_s as the intercept. The I_s values are given in table 1. Once I_s is determined, the barrier height (ϕ_b) is estimated from it. Calculations yield that the SBH of the Pd/Mo/n-GaN Schottky diode is 0.68 eV for the as-deposited, 0.72 eV for the annealed at 300 °C, 0.75 eV at 400 °C, 0.73 eV at 500 °C and 0.78 eV at 600 °C. The forward *I–V* characteristics in each case showed that the ideality factor was greater than one. The higher values of ideality factor are probably due to potential drop in the interface layer and the presence of excess current and the recombination current through the interfacial states between the semiconductor/insulator layers [20]. The series resistance R_s of the diode was calculated from *I–V* measurements using a method developed by Cheung and Cheung [21]. Calculations showed that the series resistance is in the range $R_s = 205$–704 Ω for the as-deposited and annealed Pd/Mo Schottky contacts. The Norde method was also employed [22] to compare the Schottky barrier height of contacts because high series resistance can hinder accurate evaluation of barrier height from the standard ln(*I*)–*V* plot. In this method, a function $F(V)$ is plotted against the V. $F(V)$ is given by $F(V) = V/2 - kT/2\ \ln[I\,(V)/AA^{**}\,T^2]$. The effective SBH is given by $\phi_b = F(V_{\min}) + V_{\min}/2 - kT/q$, where $F(V_{\min})$ is the minimum value of $F(V)$, and $V_{\min}$ is the corresponding voltage. A plot of $F(V)$ versus V will give $F(V_{\min})$ and $V_{\min}$ values (plot not shown here). The extracted Schottky barrier heights are 0.70 eV for the as-deposited, 0.74 eV at 300 °C, 0.78 eV at 400 °C, 0.75 eV at 500 °C and 0.82 at 600 °C, respectively. It is observed that these values are in good agreement with those obtained by the *I–V* method.

Capacitance–voltage (*C–V*) characteristics of Pd/Mo Schottky diodes were measured as a function of annealing temperature. Figure 3 shows a plot of $1/C^2$ as a function of bias voltage for the as-deposited and annealed samples of Pd/Mo. The *C–V* relationship for the Schottky diode is given by [18]

$$\frac{1}{C^2} = \frac{2\left(V_{\mathrm{bi}} - \frac{kT}{q} - V\right)}{A^2 q N_d \varepsilon_s}, \tag{3}$$

where V_{bi} is the flat band voltage, N_d is the donor concentration, A is the area of the Schottky contact and ε_s is the permittivity of the semiconductor ($\varepsilon_s = 9.5\ \varepsilon_{\mathrm{o}}$). The x-intercept of the plot of $(1/C^2)$ versus V, V_{o} is related to the built in potential V_{bi} by the equation $V_{\mathrm{bi}} = V_o + kT/q$, where T is the absolute temperature.

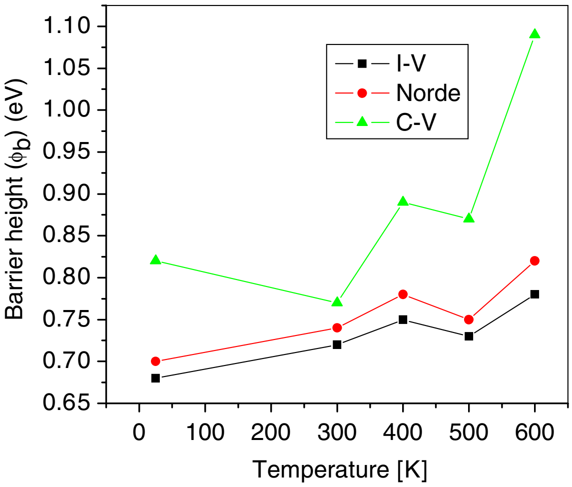

Figure 4. Plot of barrier heights versus annealing temperatures for Pd/Mo Schottky contacts on n-type GaN.

The barrier height (ϕ_{cv}) is given by the equation $\phi_{cv} = V_{bi} + V_n$, where $V_n = (kT/q)\ \ln(N_c/N_d)$. The density of states in the conduction band edge is given by $N_c = 2\ (2\pi m^* kT/h^2)^{3/2}$, where $m^* = 0.22\ m_o$, and its value was 2.6×10^{18} cm^{-3} for GaN at room temperature [23]. The estimated carrier concentration of Pd/Mo Schottky contacts is in the range of $(3\text{–}8) \times 10^{16}$ cm^{-3} for the as-deposited and annealed samples. It is observed that the calculated carrier concentration values from *C–V* measurements are lower than the values determined using Hall measurements. This may be due to the leaky nature of the Schottky contact, where the leakage current disturbs the *C–V* measurements, resulting in an error involved in the estimation of net doping concentration. The extracted barrier heights of the Pd/Mo Schottky contact are 0.82 eV (as-deposited), 0.77 eV after annealing (at 300 °C), 0.89 eV (400 °C), 0.87 eV (500 °C) and 1.09 eV (600 °C), respectively. The observed values of saturation currents, Schottky barrier heights and ideality factors of Pd/Mo Schottky diodes as a function of annealing temperature are given in table 1. It can be seen from the table that the barrier heights ϕ_b estimated from *I–V* measurements are lower than those obtained from *C–V* measurement, which suggests the presence of native oxides at the metal junction to the semiconductor, [24] and is also ascribed to the lowering of barrier height by the image force due to the current flow across the barrier [25]. It could also be that the transport mechanism in these diodes is not purely thermionic emission in nature. For these diodes the ϕ_b obtained from the *I–V* method is voltage or electric field sensitive, unlike the ϕ_b obtained from the *C–V*.

Figure 4 shows a plot of barrier heights of Pd/Mo/n-GaN as a function of annealing temperature. It can be seen clearly from figure 4 that the barrier height of the Pd/Mo Schottky diode decreases upon annealing at 300 °C. However, there is a slight increase of Schottky barrier height of Pd/Mo/n-GaN contacts after annealing at 400 °C. Further annealing at 500 °C the barrier height decreased and then slightly increased upon annealing at 600 °C. Based on the *I–V*, Norde and *C–V* measurements, the variation in the barrier heights of Pd/Mo Schottky contact annealing suggests that Pd/Mo films may react with the GaN, as will be confirmed by AES and XRD examinations.

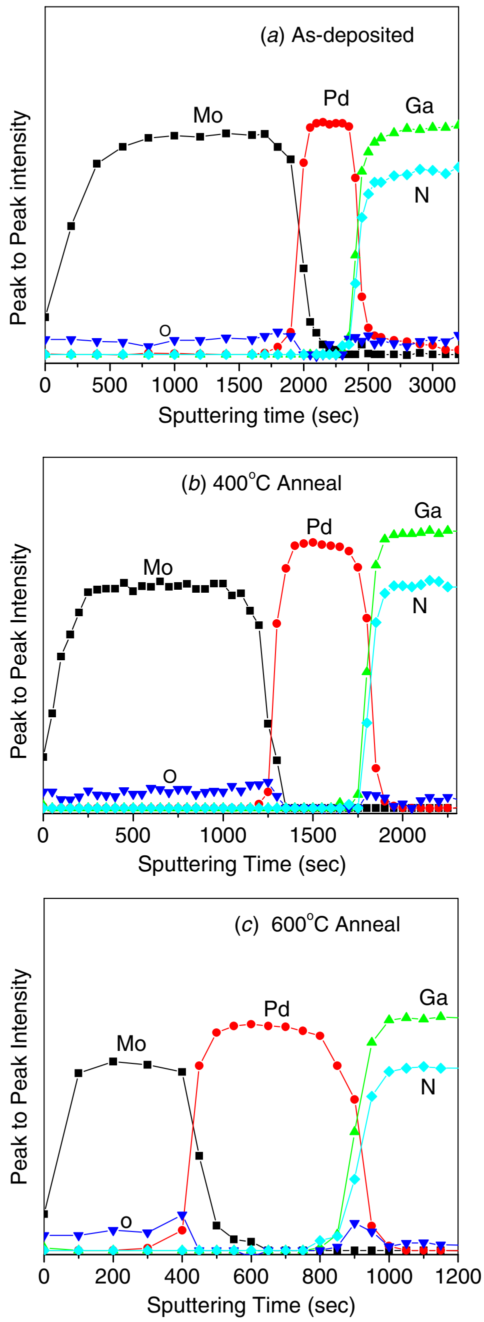

Figure 5. Auger depth profile of the Pd/Mo Schottky contact on n-type GaN: (*a*) as-deposited, (*b*) annealed at 400 °C and (*c*) annealed at 600 °C.

The AES depth profile of the Pd/Mo Schottky contacts to n-GaN before and after annealing at 600 °C for 1 min under nitrogen ambient are shown in figure 5. The as-deposited layers (Pd and Mo), figure 5(*a*), exhibit a relatively sharp interface, indicating the absence of significant interdiffusion into GaN. However, for the samples annealed at 400 °C, figure 5(*b*), a small amount of Ga out-diffused into the metal layer, indicating the possibility that Ga reacts with Pd to form gallide phases during annealing. There is no considerable change in the interface layers as compared to that of contacts

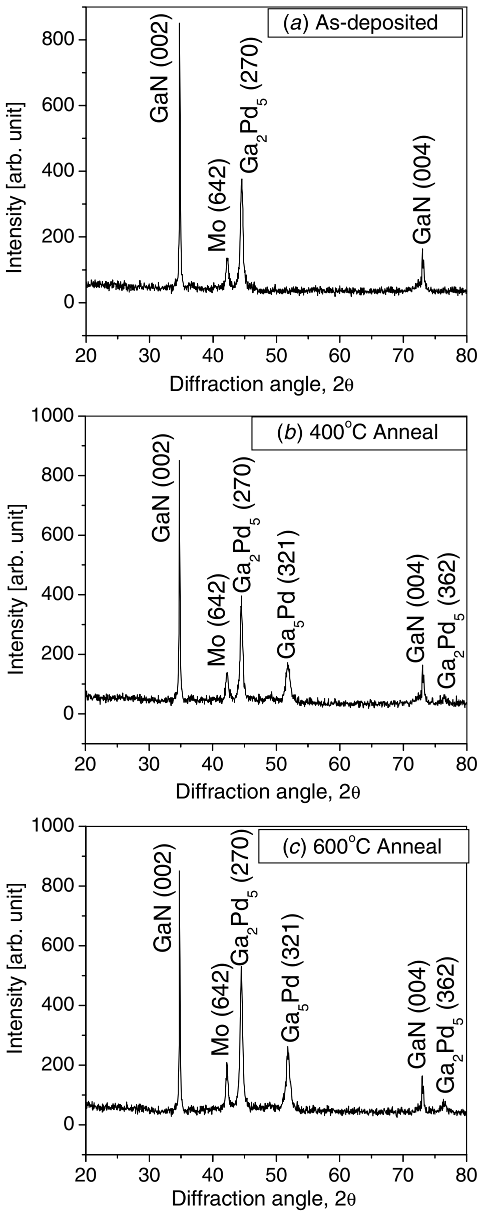

Figure 6. The XRD plot of the Pd/Mo Schottky contact on n-type GaN: (*a*) as-deposited, (*b*) annealed at 400 °C and (*c*) annealed at 600 °C.

annealed at 400 °C, which is shown in figure 5(*c*), when the sample is annealed at 600 °C. It indicates that there was no significant interdiffusion between the metal layers and GaN even after annealing at 600 °C. However, it is noted that the Mo thickness somewhat decreased after annealing at 600 °C, but at this moment there is insufficient experimental evidence to explain this. Further, it is noted that there is no clear evidence for out-diffusion of nitrogen into the metal layers. It is worth noting that the Mo layer remains very stable even after annealing at 600 °C.

The XRD measurement was made before and after annealing at 600 °C for 1 min under nitrogen ambient in order to investigate the interfacial reactions between metals and GaN. Figure 6(*a*) shows XRD plots of the as-deposited Pd/Mo Schottky contact. In addition to the characteristic peaks of GaN (002) (004), Mo (642), there is an additional peak observed, which is identified as Ga_2Pd_5 (270). Figures 6(*b*) and (*c*) show the XRD plots of the samples annealed at 400 °C and 600 °C. In addition to the peaks observed in the as-deposited sample, there are extra peaks which indicate the formation of new interfacial phases, as expected from the AES results (figures 5(*b*) and (*c*)). These phases are identified as Ga_2Pd (321) and Ga_2Pd_5 (362).

The condition of the surface of metal contacts to GaN is the key in determining electrical properties. Atomic force microscopy (AFM) was performed to characterize the surface morphology of the Pd/Mo Schottky contacts. The AFM images of the samples before and after annealing at 500 °C are shown in figure 7. The surface morphology of the as-deposited sample is fairly smooth with a root mean square (rms) roughness of 2.52 nm (figure 7(*a*)). For the sample annealed at 400 °C, the surface morphology is reasonably smooth with a rms roughness of 3.79 nm (figure 7(*b*)). The surface morphology of the Pd/Mo contact did not significantly degrade even after annealing at 600 °C. The rms roughness was 4.61 nm (figure 7(*c*)).

It is a well-known fact that the electrical properties of metal–semiconductor contacts could be varied due to the interface states and chemical reactions between metals and semiconductors. The variation in the barrier height of Pd/Mo Schottky contact with annealing temperature could be ascribed to the interfacial reaction occurring between metals and GaN, and their alloys which extend to GaN films. AES and XRD results showed that the diffusion of metals and their reactions with GaN to form interfacial phases at the interface, such as Ga_2Pd_5 (270) (362) and Ga_5Pd (362) at the Pd/Mo/n-GaN interface, results in accumulation of gallium vacancies at the GaN surface. The formation of gallide phases at the Pd/Mo/n-GaN interfaces is responsible for the increase of barrier heights upon annealing. The increase of the Schottky barrier height could be correlated with the reduction of nonstoichiometric defects in the metallurgical interface [26, 27]. The region involving the defects can be reduced due to the interdiffusion of metals into GaN. As a result, the consumption of the defect region is followed by an increase in the value of the Schottky barrier height extracted from the *I–V* characteristics when the sample is annealed at 600 °C. Similar findings were also observed by Wang *et al* [7] and Reddy *et al* [15]. Wang *et al* [7] investigated the thermal annealing behavior of Pt/n-GaN, and reported that the variation of barrier height upon annealing may be attributed to changes of surface morphology and variation of nonstoichiometric defects in the vicinity of the interface. Reddy *et al* [15] investigated the Schottky barrier heights as a function of annealing temperature and observed that the barrier height will be influenced by the interfacial product. Based on the results of Duboz *et al* [28], the higher value of barrier height on annealing at moderate temperatures can be attributed to a reduction in the density of interfacial defects. They also found that the Fermi level at metal/GaN interfaces is pinned by defects and a modification of the defect density on annealing could change the pinning, resulting in a change in the barrier height. For n-type GaN, the formation of gallide phases may create Ga vacancies in the GaN at the interface, and the Ga

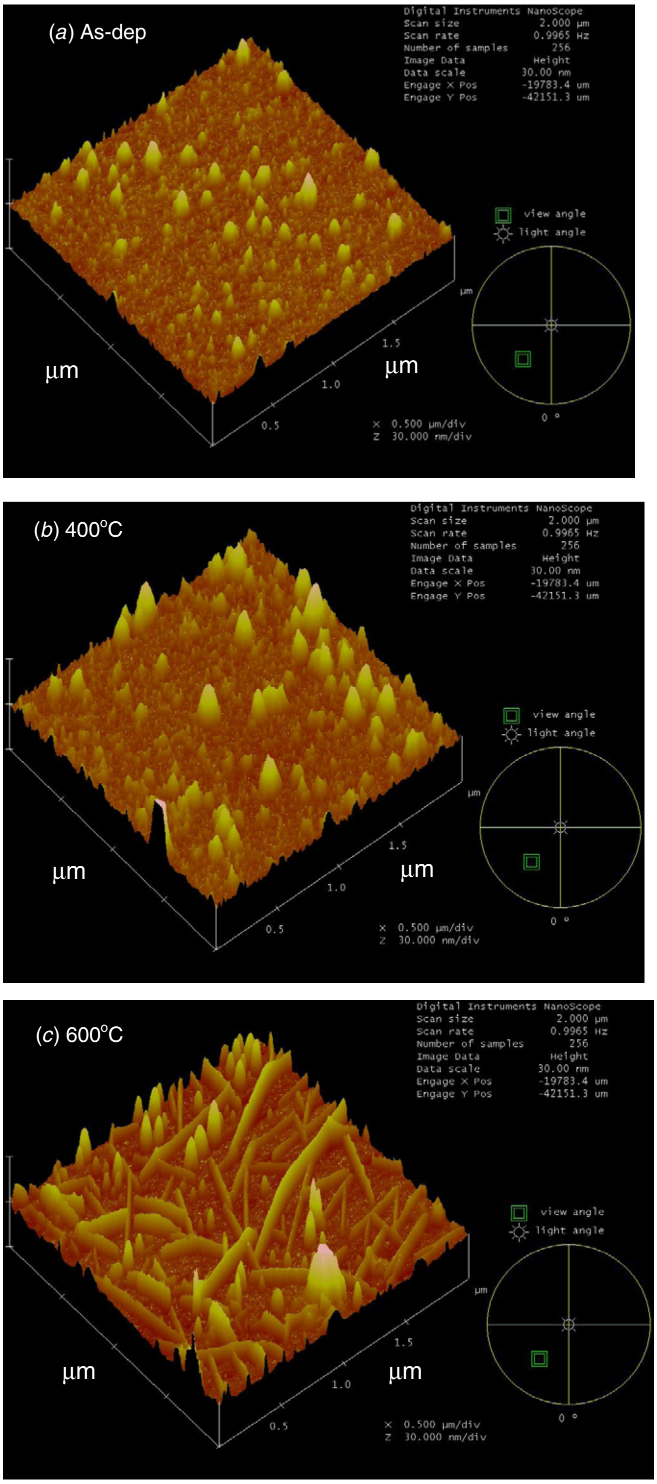

Figure 7. AFM micrographs of the Pd/Mo Schottky contacts to n-type GaN: (*a*) an as-deposited sample, (*b*) a 400 °C annealed sample, and (*c*) a 600 °C annealed sample.

vacancies in GaN [29] act as deep acceptors which cause the increase of barrier height at elevated annealing temperature.

4. Summary

The influence of thermal annealing effects on electrical and structural properties of Pd/Mo Schottky contacts on n-type GaN (4.07×10^{17} cm^{-3}) was investigated. The as-deposited Pd/Mo Schottky diode exhibits barrier heights of 0.68 eV (*I–V*) and 0.82 eV (*C–V*). It is observed that the Schottky barrier height increases to 0.75 eV (*I–V*) and 0.89 eV (*C–V*) after annealing at 400 °C for 1 min in N_2 ambient. However, when the sample is annealed at 500 °C, the barrier height slightly decreased to 0.73 eV (*I–V*) and 0.87 eV (*C–V*). Further, with an increase in annealing temperature up to 600 °C, the Schottky barrier height slightly increased to 0.78 eV (*I–V*) and 0.82 eV (*C–V*), respectively. The Norde method was also used to extract the Schottky barrier height of the Pd/Mo contact. The estimated values are 0.70 eV for the as-deposited and 0.82 eV for the contact annealed at 600 °C which are in good agreement with those obtained by the *I–V* method. The AES and XRD results showed that Ga_2Pd_5 and Ga_5Pd interfacial phases are formed at the Pd/Mo/n-GaN interface, which may be the reason for the increase in Schottky barrier height upon annealing at elevated temperatures. The AFM results showed that there was no significant degradation in the surface morphology (rms roughness of 4.61 nm) of the contact during annealing at 600 °C, compared to the as-deposited one (rms roughness of 2.52 nm). This result indicates that the Pd/Mo contact could be an attractive metallization scheme for high-temperature electronic device applications.

Acknowledgments

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