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Correlation of Microstructure with Electrical Behavior of Ti/GaN Schottky Contacts

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We correlate structural and electrical characteristics of as-deposited and low-temperature annealed Ti contacts on GaN. Temperature dependent current-voltage measurements are used to determine the effective barrier heights of the respective contacts, while high-resolution transmission electron microscopy is utilized for structural characterization. As-deposited Ti contacts are slightly rectifying with an effective barrier height of ~200 meV. After annealing at 230°C, the barrier height increases to values of ~450 meV. A similar behavior of Schottky contacts with more strongly rectifying diodes upon low-temperature annealing is observed for Zr metal contacts on GaN. As-deposited Ti already forms a thin TiN layer at the GaN interface. After annealing at 230°C, the average thickness and the distribution of TiN grains remain practically unchanged, but the interface with GaN roughens. We correlate the observed barrier height changes with interface roughness and phase formation and we discuss the results in terms of interface damage and the Schottky-Mott theory.

Key words: GaN, metal contacts, Schottky barrier height, structural characterization

INTRODUCTION

The rapid progress in the growth of high quality GaN epilayers has led to the successful development of a variety of nitride-based electronic and optical devices.[1–5] Metal contacts are an essential component of every semiconductor device. However, the electrical characteristics and thermal stability of commonly used contacts have not yet been optimized and clearly still limit GaN device performance. Further improvements require a better understanding of stable and reliable ohmic and Schottky contacts.

Several publications have reported recently on ohmic contacts formed on n-type GaN with very low contact resistivities.[6–8] These contacts display a number of similarities. All of them are formed with Ti in contact with the GaN surface, and all are reactive ion etched (RIE) prior to metal deposition, rapid thermally annealed (RTA) after metal deposition, or subjected to both a predeposition RIE and post-deposition RTA. On the other hand, the Schottky barrier height of Ti, deposited on GaN without RIE etching or RTA, has been reported to be 0.59 eV.[9] Many groups have reported initially rectifying behavior for evaporated Ti/metal (metal = Au or Al) contacts on GaN which have not been exposed to RIE. High temperature annealing renders such contacts ohmic.[10,11]

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The favorable low contact resistances might be associated with the formation of TiN and adjacent nonstoichiometric GaN regions at the Ti/GaN interface. Nonstoichiometric GaN is expected to be rich in N-vacancies and therefore strongly n-type (n^+), leading to efficient tunneling. Another explanation considers the formation of a new phase with a low Schottky barrier.[7,12] Equilibrium thermodynamics predicts TiN to be stable in contact with GaN at room temperature.[13] Our previous study showed the formation of a thin TiN layer at the GaN interface after metal deposition of a metal multilayer structure.[12] It was found that RTA increases the amount of TiN and the thickness of the damaged GaN region near the interface. However, it was not clear whether TiN itself or the nonstoichiometry of the interface is responsible for the low resistivity contact behavior.

Luther et al. found that ohmic contacts were not formed from Ti/Al multilayers until Al had diffused to the Ti/GaN interface.[14] In this case, no TiN formation was observed by x-ray photoelectron spectroscopy (XPS) after annealing at 600°C for 15 s.

RESULTS AND DISCUSSION

In order to clarify the role of metal-nitride formation for ohmic contacts, we have investigated the structural and electrical behavior of thin films of Ti on GaN. We utilized x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) to characterize the interactions that are occurring at the interface. The electrical characteristics were investigated for Ti and Zr by current-voltage (I-V) measurements.

The GaN films used in this study were grown by metalorganic chemical vapor deposition (MOCVD) on sapphire substrates. The layer thickness was approximately 2 μm with n-type doping levels in the mid-10^{17} cm^{-3} range and room-temperature mobilities of 240 cm^2/Vs. Prior to metallization, the samples were degreased in hot xylene, acetone, and methanol. They were then etched for 5 min in buffered oxide etch (BOE:H_2O, 1:10) and rinsed in DI water. A layer of 1500Å Ti or Zr was deposited by electron beam evaporation at room temperature in a vacuum better than 5×10^{-6} Torr. Some contacts were capped with an additional layer of 500Å Au to prevent oxygen incorporation. Samples were annealed in a vacuum of 60 mTorr for 60 min between 60 and 350°C; this annealing allowed for an in-situ current-voltage (I-V) characterization of the contacts. Cross-sectional high-resolution electron microscopy (HREM) was performed, employing Topcon 002B and ARM microscopes operated at 200 and 800 kV, respectively. Samples were mechanically ground, followed by ion milling on a liquid-nitrogen cooled stage.

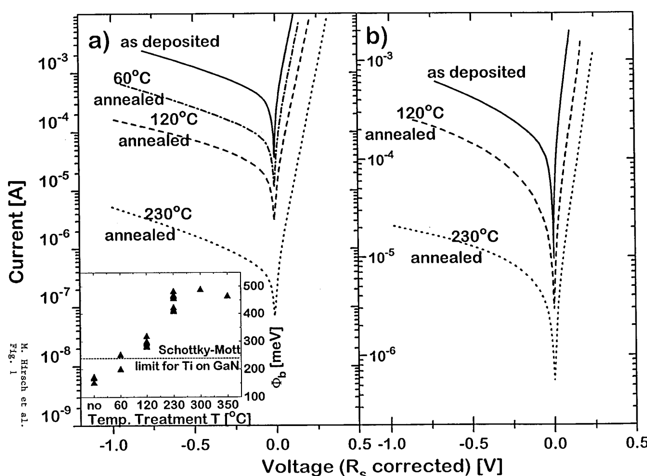

Fig. 1. (a) Room temperature I-V characteristics for Ti contacts (A = 2.45×10^{-3} cm^2) after different annealing treatments. The rectifying behavior improved significantly with successive annealing steps. The inset shows the evolution of barrier heights (derived from I-V-T measurements[15]) with annealing for several Ti contacts. (b) Zr contacts show an analogous development of more rectifying diode behavior with increasing annealing temperatures.

The electrical characteristics of the diodes were investigated by I-V measurements. The as-deposited Ti and Zr yielded leaky diodes with reverse bias currents in the range of mA for a reverse bias voltage of –2V. Figures 1a and 1b show the evolution of I-V characteristics (corrected for series resistance R_s) for annealing up to 230°C for the Ti and Zr contacts. In both cases, the rectifying behavior of the contacts improved significantly upon annealing. Temperature dependent I-V measurements (I-V-T) were used to determine the effective barrier height Φ_{bo} and the Richardson constant A** within a thermionic emission model for the Ti contacts.[15] The evolution of the effective barrier heights for several samples for subsequent annealing steps is depicted in the inset of Fig. 1a). The change in the I-V characteristics with annealing is mainly attributed to an increase of the barrier height from about 200 meV in the as-deposited case up to 450 meV after the 230°C annealing step, while the Richardson constant remained nearly constant at $A^{**} \approx 1 \times 10^{-2}$ Acm^{-2}K^{-2}. Details about the electrical measurements of the Ti contacts can be found in Ref. 15. Annealing at even higher temperatures (300 and 350°C) did not further change the barrier height. For Zr contacts, the large diode ideality factor $n \cong 1.5$ prohibited evaluation of an effective barrier height. However, the observed changes of the I-V behavior for both metals indicate that structural or compositional changes must occur at the interface.

Investigations of the structure of the metal/GaN interface were performed for the Ti contacts. After annealing, *no macroscopic* phase formation was observed by XRD or RBS. The surface remains planar as shown by SEM. Images obtained with HREM and the corresponding electron diffraction patterns for as-deposited and annealed Ti layers on GaN are shown in Fig. 2. In both cases, the Ti layers are polycrystal-

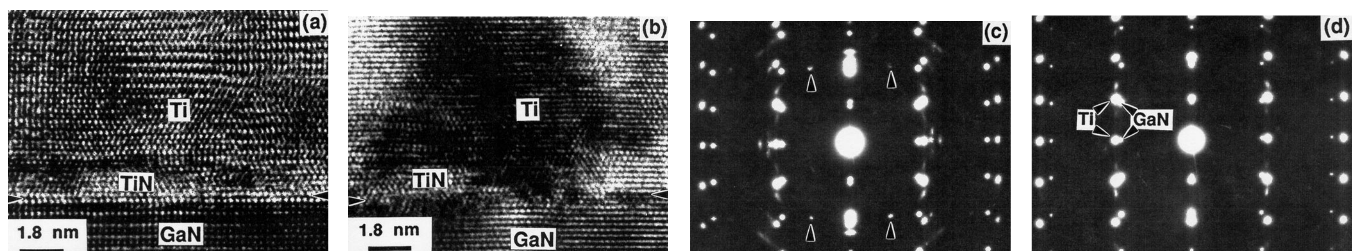

Fig. 2. (a)–(d): Cross-sectional HREM images of interfacial areas and corresponding diffraction patterns from as deposited (a), (c) and annealed (b),(d) Ti layer on GaN. Arrows in (c) show additional spots from grains within-plane c-axis.

line but well oriented in the growth direction. The layers have a hexagonal structure (a = 2.95Å, c = 4.68Å) which is pseudomorphically related to the GaN with an in-plane misfit of about 8%: (0001)Ti// (0001)GaN, $(1\bar{1}00)$Ti//$(1\bar{1}00)$GaN. In addition to the grains with the above orientation relationship, some grains with in-plane c-axis were found in the as-deposited layer. The weak spots from such grains are marked by arrows on the diffraction pattern of Fig. 2c). These grains cause Moiré fringes on electron micrographs at low magnification (not shown). After 230°C annealing, the grains disappear (note the lack of weak diffraction spots on Fig. 2d), and the structure of the Ti layer becomes more regular with pronounced columns. This stabilization of the α-Ti phase observed in our experiments was associated earlier with small amounts of oxygen dissolved in the Ti layer.[14]

In the as-deposited Ti layer, HREM indicates the formation of a cubic TiN (a = 4.24Å) layer at the Ti/GaN interface. Because of the difference in the lattice parameters of TiN and GaN, TiN grew as small grains which are a few monolayers in height and 1–1.5 nm in diameter. The orientation relationship between TiN and GaN substrate is: (111)TiN//(0001)GaN, $(\bar{1}10)$TiN//$(1\bar{2}10)$GaN.[12] The interface between TiN and GaN is abrupt as shown with HREM (Fig. 2a). Annealing at 230°C does not significantly change the average thickness and the distribution of TiN grains but leads to roughening of the TiN/GaN interface (Fig. 2b). This behavior may suggest interdiffusion of impurities from the surface of the Ti layer (e.g., oxygen) along grain boundaries between misoriented Ti columns.

The observed microstructural changes can explain the increasing barrier height determined by electrical measurements. In the as-deposited case the diode is very leaky, which we ascribe to defects forming at the interface during metal deposition. We have observed that I-V characteristics become almost linear (ohmic) when more energetic deposition methods, such as sputtering and pulsed laser deposition, are used. After annealing at 230°C, the barrier height increased to 0.45 eV. A similar effect of increasing barrier heights with surface roughening has been observed during annealing of Cr/GaAs Schottky contacts.[16] The presence of TiN in the as-deposited and the annealed contacts, indicates that the changes in barrier height with thermal annealing at moderate temperatures are not related to nitride formation. Moreover, the reported work function for TiN is 3.75 eV.[17] If the contact would obey the Schottky-Mott theory and the work function given above were correct, then the TiN/GaN contact should be ohmic. The work reporting this specific work function value, however, did not indicate which phase of TiN was studied, nor the stoichiometry. Either of these variables could affect the work function; in addition the TiN is highly oriented on the GaN. For comparison, the barrier height of $NiSi_2$ on Si changes by as much as 0.13 eV depending on the orientation of the silicide.[18] However, in terms of I-V measurements, the TiN interfacial layer of a few monolayers has probably to be considered just as part of the Ti/GaN interface.

The observed barrier heights of the Ti contacts increase monotonically to ~240 meV (at about 60°) with successive annealing steps up to 230°C. This barrier height is predicted by the Schottky-Mott theory based on the work function of Ti (4.3 eV)[19] and GaN (~4.06 eV).[20] Originally, it was expected that the barrier heights should agree well with theory because of the high ionicity of GaN.[21,22] Since our measurement on samples annealed at 230°C result in a barrier height of 450 meV, we conclude that neither Ti nor TiN are ohmic on our GaN samples and that the work functions of Ti or TiN do not seem to dominate the actual barrier heights.

We propose that low-temperature annealing removes defects induced by metal deposition at the metal-GaN interface and results in a slight roughening of the metal/semiconductor interface possibly due to the interdiffusion of impurities from the surface. These effects can lead to additional surface states which might dominate the observed barrier height. In contrast to the findings after mild annealing, nonstoichiometric GaN regions with an interfacial TiN layer of 5–10 nm at the interface[12] appear to dominate the contact resistivities of contacts annealed at high temperatures.

CONCLUSION

We correlate microstructure and electrical behavior of Ti/GaN Schottky contacts. We observe that TiN is always present at the GaN interface. The morphology of this interfacial TiN layer does not change significantly during annealing at 230°C for 60 min, but the interface becomes slightly rougher. We associate this roughening with the annealing of defects at the as-grown Ti/GaN interface. The structurally more perfect interface increases the barrier height to 0.45 eV. The structural transformations in the Ti layer and at the interface with GaN are most likely caused by impurity interdiffusion, e.g., oxygen. Neither Ti nor Zr led to ohmic contacts after low-temperature annealing treatments and we did not observe any formation of a strongly nonstoichiometric GaN layer at the interface. However, nonstoichiometric GaN layers might be responsible for the low contact resistances observed after high temperature annealing or RIE treatments. In contrast, after low-temperature annealing, it is the structure of the Ti/GaN interface that controls the electrical contact properties.

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