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E. A. Preble, K. M. Tracy, S. Kiesel, et al.

Electrical, structural and microstructural characteristics of as-deposited and annealed Pt and Au contacts on chemical-vapor-cleaned GaN thin films

E. A. Preble, K. M. Tracy, S. Kiesel, H. McLean, P. Q. Miraglia, R. J. Nemanich, and R. F. Davis[a)]
Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-7907

M. Albrecht
Institut für Werkstoffwissenschaften, Lerhstuhl VII, Universität Erlangen-Nürnberg, Martensstrasse 7, D-91058 Erlangen, Germany

David J. Smith
Center for Solid State Science and Deptartment of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287-1704

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Schottky contacts of Pt(111) and Au(111) were deposited on chemical-vapor-cleaned, *n*-type GaN(0001) thin films. The growth mode of the deposition, as determined by x-ray photoelectron spectroscopy analysis, followed the two-dimensional Frank–van der Merwe growth model. The resulting as-deposited metal films were monocrystalline and epitaxial with a (111)//(0002) relationship with the GaN. Selected samples were annealed for three minutes at 400 °C, 600 °C or 800 °C. The rectifying behavior of both contacts degraded at 400 °C; they became ohmic after annealing at 600 °C (Au) or 800 °C (Pt). High-resolution transmission electron micrographs revealed reactions at the metal/GaN interfaces for the higher temperature samples. X-ray diffraction results revealed an unidentified phase in the Pt sample annealed at 800 °C. A decrease in the room temperature in-plane (111) lattice constant for both metals, ranging from −0.1% to −0.5%, was observed as the annealing temperature was increased from 400 to 800 °C. This plastic deformation was caused by tensile stresses along the [111] direction that exceeded the yield strength as a result of the large differences in the coefficients of thermal expansion between the metal contacts and the GaN film. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1432127]

I. INTRODUCTION

Physical and chemical degradation of the metal contacts employed in devices based on the (Al, Ga, In)N system are likely to occur under their anticipated operating conditions.[1] Pt and Au are promising candidates for Schottky contacts on *n*-type GaN because of their high work function and chemically inert nature. Variability in the electrical behavior of metal contacts can be attributed to differences in surface preparation which leave varying levels of contamination or insulating material on the surface of the GaN prior to contact deposition.[2] A primary goal of these studies was to achieve a significant reduction in the variability of surface preparation by using *in situ* cleaning and contact deposition. A chemical-vapor-cleaning (CVC) procedure was developed that removed all detectable hydrocarbon and oxygen contamination from the GaN surface. Subsequent deposition of either Pt or Au was conducted prior to removal from the ultra high vacuum system.

The following sections focus on the electrical and microstructural characteristics of thin Pt and Au films deposited on Si-doped, *n*-type, monocrystalline GaN(0001). Particular consideration is given to the metal/GaN interface in the as-deposited state and after annealing under ultra high vacuum. The experimental approaches used in this research are discussed and correlated with the results of both the electrical measurements and the physical and chemical changes observed within the contacts and at the metal/GaN interfaces as a function of heat treatment.

II. EXPERIMENTAL DETAILS

The 1.1 μm thick GaN(0001) films used in this research were grown by metalorganic vapor-phase epitaxy at 1020 °C and 40 Torr on 50 mm diameter 6H-SiC(0001) wafers on which an ~0.1 μm thick buffer layer of AlN or $Al_{0.2}Ga_{0.8}N$ had been previously deposited. The films were doped with Si; capacitance–voltage measurements revealed an effective ionized donor concentration (N_D-N_A) of 1×10^{17} cm^{-3}. They were subsequently diced into 15mm square samples. Surface cleaning prior to vacuum insertion consisted of sequential immersion in trichloroethylene, acetone, and methanol, followed by a 10-min dip in 49% hydrochloric acid. A chemical vapor cleaning (CVC) process was developed for *in situ* surface preparation and involved annealing the GaN samples in an ammonia atmosphere at a surface temperature of 860 °C for 15 min. X-ray photoelectron spectroscopy results showed the surfaces to be free of carbon and oxygen. Atomic force microscopy revealed the rms surface roughness

a)Electronic mail: Robert_Davis@ncsu.edu

before and after CVC processing to be 5–10 Å. Auger results showed the stoichiometry of the Ga-terminated (0001) surface to be the same before and after the cleaning procedures. Thus, the CVC cleaning process neither roughened the surface nor changed its chemistry. Details of this process have been published separately.[3,4] The samples were subsequently transferred under ultra high vacuum to the metal deposition chamber and coated with either 1200 Å of Au or 600 Å of Pt.

The growth mode of the Pt and Au films was determined using the method of Sitar *et al.*[5] and King *et al.*[6] for growth of AlN and GaN films. A special set of Pt and Au films was initially and individually deposited in a stepwise manner of increasing thickness over two entire GaN surfaces. The accumulated thickness values for the Pt were 2, 3, 5, 10, 15, 20, and 700 Å; the analogous values for the Au were 2, 3, 5, 10, 12, 17, 20, 25 and 770 Å. X-ray photoelectron spectroscopy (XPS) data were collected using a Fisons-VG Scientific system after each deposition. Specifically, the intensities (area) of the XPS core levels of the uncoated GaN sample (I_o) were compared with the intensities after each layer of metal was deposited (I_s). The resulting trends for Pt and Au were obtained by plotting the ratios as a function of thickness. The mode of growth was then determined by comparing these plots with theoretical plots of the thermodynamically controlled modes of growth.

The 700 Å thick Pt samples and the 770 Å thick Au samples from these studies were removed from vacuum, diced to produce 7.5 mm square samples that were patterned using a two-step photolithography process. The first step involved formation of the Schottky contact pads; the second step involved formation of the ohmic contact rings of either Al or Ti(700 Å)/Au(300 Å) deposited via thermal and electron beam evaporation, respectively, and surrounding the Schottky pads. The respective ohmic contacts were used for the as-deposited and annealed samples. The photoresist was subsequently removed. The resulting pattern was a series of exposed ring-shaped regions. The contacts were then rapidly thermally annealed in a N_2 ambient for three minutes at the individual temperatures of 400 °C, or 600 °C, or 800 °C.

Transmission electron microscopy (TEM) studies of the interfacial characteristics of the metal/GaN assemblies used a JEM-4000EX operated at 400 keV and a Philips CM300UT operated at 300 keV. Scanning electron microscopy (SEM) images of the surface characteristics were obtained using a JEOL 6400 field-emission instrument. Determination of the lattice spacings of the metal and the GaN were achieved via high-resolution x-ray diffraction (XRD) using a Philips X'Pert Materials Research Diffractometer. The incident x-ray beam for the Philips system passed through a four-bounce Ge (220) crystal monochromator; the detector optics consisted of a three-bounce Ge (220) crystal. The current–voltage measurements were performed using a Keithley 236 source measure unit.

III. RESULTS

A. As-deposited contacts

The plot of the ratios of the intensities of the core levels of the sequentially metal coated and the uncoated GaN samples as a function of metal thickness is shown in Fig. 1. This figure also shows theoretical curves for the thermodynamically controlled two-dimensional (Frank–van der Merwe), three-dimensional (Volmer–Weber) and mixed two- and three-dimensional (Stranski–Krastanov) modes of film growth. The data for both Pt and Au agree well with the two-dimensional model.

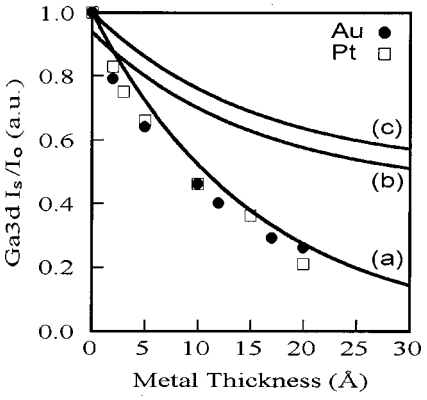

FIG. 1. Plot of the ratios of intensity (area) of the XPS Ga core levels of the sequentially deposited Pt and Au films (Is) divided by the intensity of the uncoated sample (Io) as a function of film thickness. Models shown are (a) Frank–van der Merwe (2D), (b) Stranski–Krastanov (mixed), (c) Volmer–Weber (3D).

Scanning electron microscopy investigation revealed a smooth, featureless surface for both metals. Cross-sectional high-resolution TEM micrographs of the interface of the samples are shown in Fig. 2. These micrographs and the analyses of associated diffraction patterns showed that both metals were single crystal and epitaxial, with a $(111)_{\text{metal}}//(0002)_{\text{GaN}}$ orientation relationship with the GaN. The interfaces were abrupt and smooth, with no visible reac-

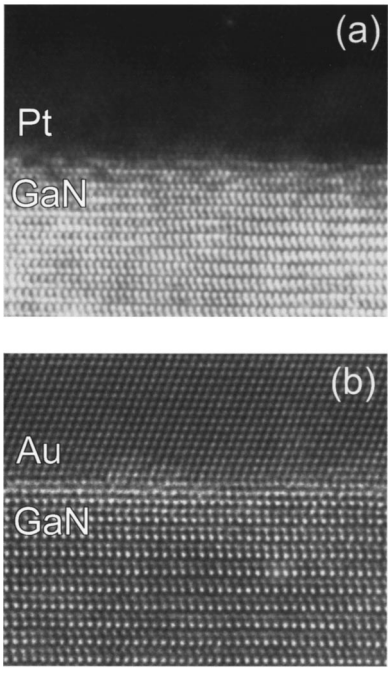

FIG. 2. Cross-sectional, high-resolution electron micrographs of the interfaces of as-deposited Pt/GaN (a) and Au/GaN (b).

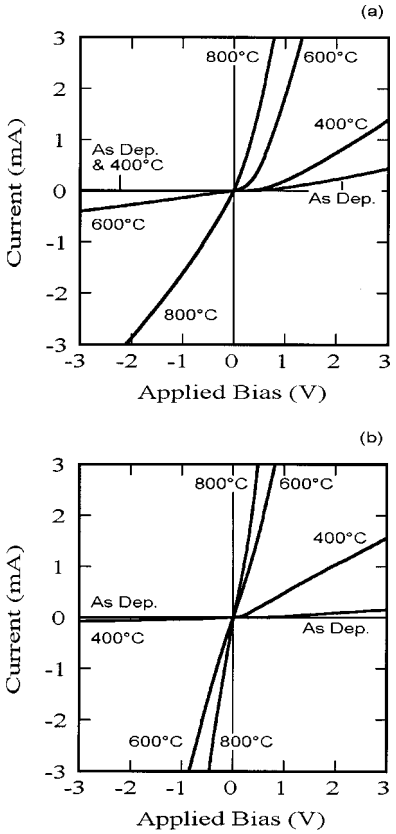

FIG. 3. Current–voltage curves for the as-deposited and the annealed Pt (a), and Au (b) contacts.

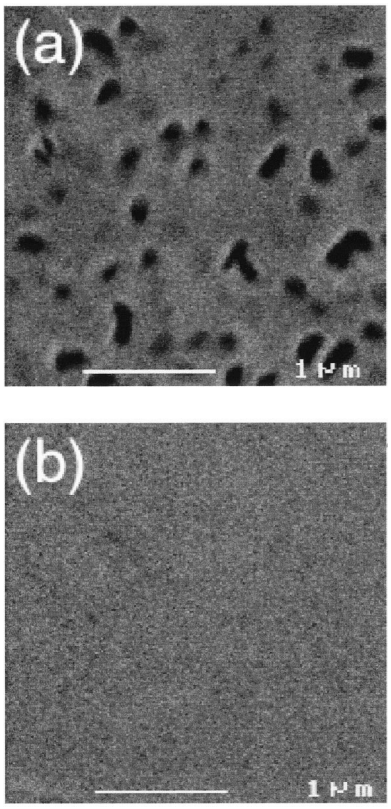

FIG. 4. Scanning electron micrographs of the surfaces of the Pt (a) and Au (b) contacts after annealing for 3 min at 800 °C.

tions or mixing in either the Pt or the Au contacts. Numerous twinning defects were observed in both metals; however, no other significant structural defects were observed that would alleviate the mismatch strain between the metal layers and the GaN films. X-ray diffraction analysis discussed below also corroborated the single crystal nature of the films, as well as the (111) growth orientation.

B. Annealed contacts

The as-deposited Pt and Au contacts behaved in a quasi-rectifying manner, as shown in Fig 3. The reverse bias leakage currents at −3 V were 0.007 nA and 20 nA for the Pt and the Au contacts, respectively. Annealing of the contacts gave the principal result that the rectifying behavior of the contacts was degraded, eventually becoming ohmic after annealing at 600 °C or 800 °C, as shown in Fig. 3.

The scanning electron micrographs shown in Fig. 4 of the metal surfaces after annealing at 800 °C reveal a loss of structural integrity in the surface of the Pt contacts; whereas, the Au contacts remained intact, smooth, and without bulges. Liu *et al.*[7] and Gasser *et al.*[8] observed that holes formed in their Pt films on GaN due to the formation of nitrogen gas that accumulated under the Pt surface and eventually escaped through perforations of the platinum layer. Although GaN does not dissociate in vacuum until above 800 °C, formation of nitrogen is accelerated by the reaction of Pt and GaN to form Ga_2Pt and N_2.[9] Our data agree with that reported in the literature. However, the reactions visible in our Pt samples were less severe due to the shorter annealing time of three minutes, rather than the 30–120 min, used by other investigators. For example, Liu *et al.*[7] reported complete electrical degradation of the Pt contacts after annealing at 400 °C for 120 min, in contrast to our 400 °C sample that showed increased leakage currents, but was not yet ohmic after three minutes at 400 °C. Similar ruptures of the Au contacts were not observed due either to the fact that the extent of the interfacial reaction was very limited (see TEM discussion below) or that the reaction did not form nitrogen, or both.

Studies of the interfaces of the annealed samples by cross-sectional TEM revealed increasing interface roughness and reaction products for both the Pt and Au samples, as shown in Fig. 5. The Pt film remained epitaxial and single crystal in the 400–600 °C range, as also demonstrated by diffraction pattern analysis. However, the Pt sample annealed at 800 °C showed some splitting of the diffraction pattern spots indicating the appearance of different orientation(s) in the Pt film. Furthermore, the interface of the 800 °C Pt sample became so distorted that high-resolution micrographs could no longer be obtained. The TEM results from the Au samples showed less dramatic changes than were observed in the Pt films. Some interface roughening was apparent and minor reactions were visible in the 800 °C sample, though to a lesser degree than in the Pt.

X-ray diffraction measurements performed on the annealed samples are shown in Fig. 6. The sample with the Pt contact shows the appearance of two unidentified peaks in the spectrum after annealing at 800 °C. These new peaks are

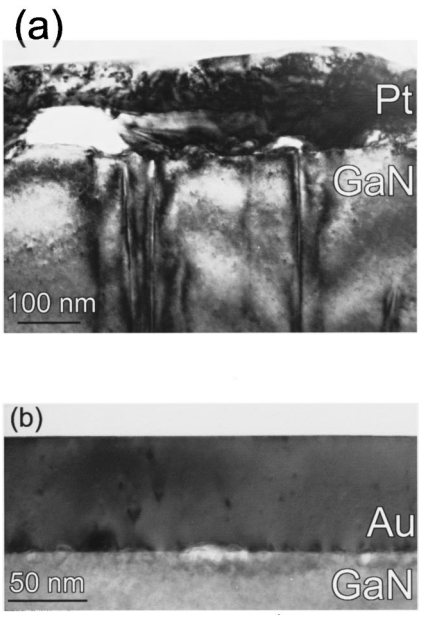

FIG. 5. Cross-sectional electron micrographs of the Pt/GaN (a) and the Au/GaN (b) interface after annealing for 3 min at 800 °C. Note the different scales.

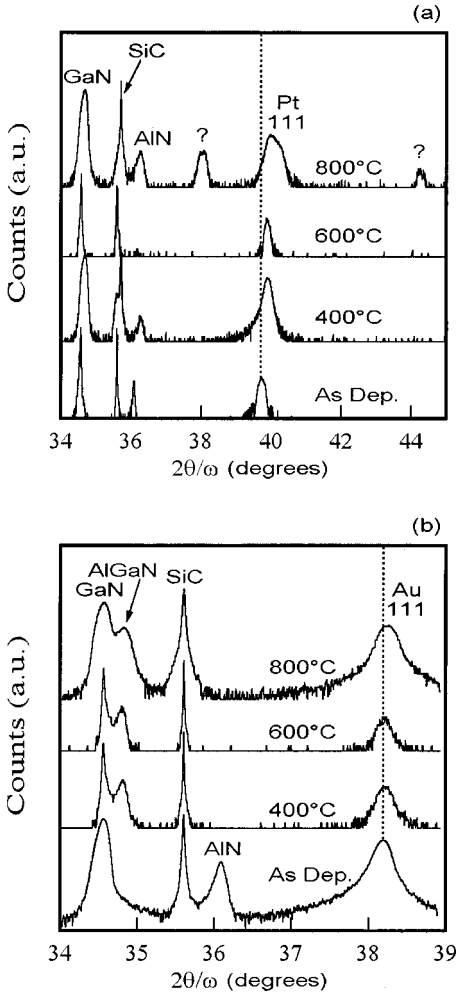

FIG. 6. X-ray diffraction spectra showing $2\theta/\omega$ profiles for the Pt (top) and Au contacts. Different temperatures are offset for ease of viewing. All data is normalized to the SiC (0006) peak.

consistent with the TEM observations in that they indicate that an interface reaction has occurred. However, it is unclear whether the peaks can be attributed to the expected Ga_2Pt reaction product. The samples with Au contacts did not show new peaks after annealing. These results are in agreement with the electron microscopy observations, where the Pt samples showed a relatively larger material reaction volume. The Au samples showed only small volume fractions of reacted material that would probably be undetectable by x-ray analysis.

A second significant feature of the x-ray data, observed in both materials, was the shift in the (111) peaks of the films in the $2\theta/\omega$ scan toward smaller *d*-spacings (corresponding to compression) as a function of the increase in the annealing temperature. Since the as-deposited *d*-spacing (d_{a-d}) was equal to the theoretical value for both Pt ($d_{a-d}=d_{\mathrm{Pt}}=2.265$ Å) and Au ($d_{a-d}=d_{\mathrm{Au}}=2.355$ Å), this shift cannot be attributed to a relaxation in the contacts after annealing, as they were already fully relaxed. Therefore, the shift must be attributable to changes caused by alloying and/or stresses induced by the annealing process. Although reaction products were visible in both materials at high temperatures, the volume of material that had reacted was shown via TEM to be rather small. Moreover, there was no visible evidence of reactions in the samples annealed at 400 °C. Thus, the shift toward a compressed lattice constant was most likely due to annealing-induced stress resulting from differences in the coefficients of thermal expansion. Previous work by Duxstad *et al.*[10] the Pd/GaN system illustrated that differences in the coefficients of thermal expansion of Pd and GaN were sufficiently large that the compressive stress induced during annealing caused delamination of the film. The values of the in-plane, compressive stresses generated in the (111) plane while heating the samples from room temperature to the annealing temperatures in the Pt/GaN and Au/GaN systems calculated using the principles described by Peddada *et al.*[11] are shown in Table I. It is our hypothesis that these stresses were sufficiently large to deform the metals beyond their yield strengths along the [111] direction. The room temperature x-ray data for Pt show that a permanent decrease in the (111)

TABLE I. Calculated in-plane stress and strain values of Pt and Au contacts on GaN during annealing.

	Au ($\sigma_{\mathrm{UTS}}=120$ MPa at 298 °K)		Pt ($\sigma_{\mathrm{UTS}}=145$ MPa at 298 °K)	
Temp.	Strain	Calculated Stress (compressive)	Strain (compressive)	Calculated Stress (compressive)
400 °C	3.2×10^{-3}	246 Mpa	1.1×10^{-3}	183 MPa
600 °C	4.8×10^{-3}	377 Mpa	1.7×10^{-3}	280 MPa
800 °C	6.5×10^{-3}	508 Mpa	2.2×10^{-3}	378 MPa

lattice spacing occurred during heating to and cooling from 400 °C. An analogous change did not occur in the Au until heating within the range of 600–800 °C. This hypothesis is given further support by the fact that both metals would have experienced an in-plane tensile stress on cooling, however they did not return to the original in-plane lattice parameter observed prior to annealing.

IV. CONCLUSIONS

The epitaxial deposition of rectifying Pt(111) and Au(111) Schottky contacts on CVC-cleaned GaN(0001) has been accomplished. Stresses larger than the yield strengths of both Pt and Au were imparted parallel to the [111] direction during annealing, causing plastic flow of the metals and a permanent change in the room temperature x-ray lattice parameter of the (111) plane. Interfacial reaction between the Au and GaN was very limited. By contrast, the reactions were extensive in the case of the Pt contacts to the extent that the generation and escape of N_2 resulted in holes in the Pt metal. Annealing studies revealed mild degradation of the rectifying behavior at 400 °C for both systems. Ohmic behavior was evident at 600 °C and 800 °C for the Au and Pt contacts, respectively. Degradation of the interfaces caused by chemical reactions was the likely cause of the loss in electrical performance for both materials.

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