Properties of epitaxial GaN on refractory metal substrates

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The authors demonstrate here that GaN films with good surface morphology and structural, optical, and electronic properties can be grown on metallic titanium carbide substrates. X-ray rocking curve and Raman scattering measurements confirmed the high crystalline quality of the wurtzite structure film. Variable temperature photoluminescence measurements of sharp and intense emission lines provided insights into the nature of the recombination processes, the carrier background type, and the carrier concentration. The high quality of the interface and substrate Ohmic contacts was verified. The ability to grow high-quality films on metallic substrates provides the means for advanced vertical and high-power and/or high-temperature device fabrication. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2709512]

The III-nitride semiconductor system possesses a unique combination of physical and chemical properties that allows the formation of alloys and heterostructures necessary for the fabrication of optical devices and electronic devices capable of operating at high power and high temperature and/or under extreme environmental conditions. Ternary or quaternary alloys of GaN, AlN, and InN have been grown to produce optical devices that emit light spanning from red to deep UV. Green, blue, near/deep-UV, and white light emitting devices, UV detectors, and near-UV lasers are presently commercially available. These remarkable successes resulted from the better understanding of the nitride nucleation process and control of the properties of the intermediate nucleation layers, which allowed the reproducible growth of heteroepitaxial GaN films on sapphire and SiC substrates. Despite the large concentration of n-type carriers and dislocations commonly incorporated in these heteroepitaxial films, they have been adequately tailored for optical and electronic device fabrication. These achievements also open up the possibility for the growth of III-nitride films on a number of different metallic, ferroelectric, or ferromagnetic substrates, which could result in the development of a variety of advanced electronic devices.[1,2] Here we are particularly interested in metallic substrates, which allow the fabrication of vertical devices capable of operating at high temperature and high power. The vertical geometry minimizes the deleterious effects of dislocations on device performance, while the metallic substrate avoids current crowding at the interface, minimizes substrate and contact resistance, and improves thermal management. We have investigated the deposition of GaN films on both hafnium and titanium carbide (TiC) and report here on the properties of GaN deposited on TiC substrates.

TiC is a cubic material with a rocksalt structure and a lattice parameter of 0.4331 nm,[3] which gives GaN a 4% lattice mismatch to TiC as a substrate. It is a metal which offers specific advantages, namely, electrical conduction losses from the substrate are minimized; the substrate is essentially an Ohmic contact to the semiconductor. The improved thermal management using metallic substrates also enables the device to withstand higher currents. Very high fields can also be placed on metals. In the case of an array of field emitters of GaN or its alloys on a metallic substrate, this may allow much more efficient field emission than possible on semiconducting substrates such as SiC. Note that, in the case of sapphire substrates, electrical contacts must be placed on the front side of the device, cutting down on absorption in the case of detectors and emission in the case of emitters.

Substrates of (100) and (111) TiC, 5 mm square and ~1.0 mm thick, were loaded into an organometallic vapor phase epitaxy reactor for the GaN epitaxial growth. TiC substrates were heated in hydrogen at 1350 °C for 3 min, then cooled down to 450 °C for growth of a nucleation layer. Aluminum nitride was utilized for the nucleation layer as its atomic spacing is intermediate between GaN and TiC. A GaN or alloyed AlInGaN nucleation layer can also be used with the same result. Triethylaluminum (1.5×10^{-4} mol/min) and 2.5 SLM (standard liters per minute) ammonia were used as reactants in 3.5 SLM hydrogen carrier gas. Following formation of the nucleation layer, which took approximately 13 min, the temperature was raised to 1000 °C over a period of 5 min. Once 1000 °C was reached, GaN growth commenced. Trimethylgallium (4.1×10^{-5} mol/min) and 2.5 SLM ammonia were used as reactants in 3.5 SLM hydrogen carrier gas. Growth of the GaN took place for 85 min. All growth was carried out at a total pressure of 57 torr. Samples were cooled in 2.5 SLM ammonia and 3.5 SLM of hydrogen. Growth on substrates of (100) TiC resulted in polycrystalline GaN with rough morphology and will not be discussed further. All results discussed here after involve GaN on (111) TiC. The center of the unintentionally doped (UID) film grown on (111) TiC is about 3.3 μm thick, measured by

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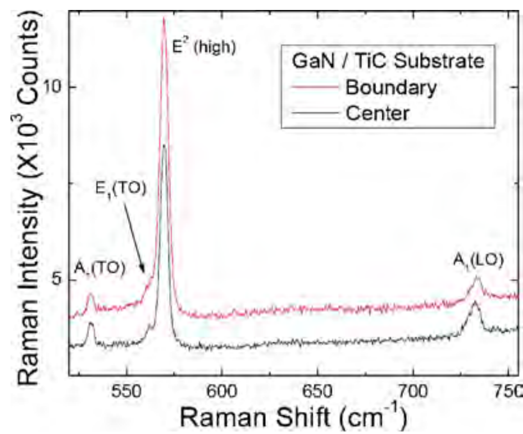

FIG. 1. (Color online) First-order Raman scattering spectra of the GaN/TiC. Note the small increase in the phonon linewidths in the region away from the central part of the film.

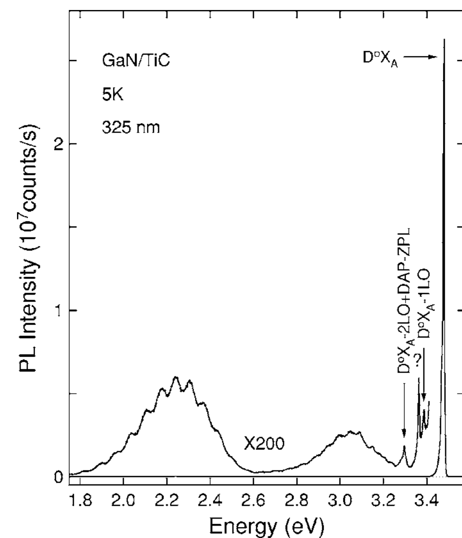

FIG. 2. Low-temperature and low-resolution photoluminescence spectra of the GaN film grown on TiC.

fitting reflectance interference fringes in the spectral range between 1.45 and 3.3 eV. A surface roughness of 0.55 nm was measured by atomic force microscopy. We observe a film thickness reduction at positions away from the center of the sample. Scanning electron micrography probing, also performed in the central region of the sample, confirms the good surface morphology. However, we also observed the presence of nanopipes.[4] These nanopipes are just a reproduction of the nanopipes present at the substrate surface. Close to the edge of the sample we observed three-dimensional GaN growth, which may be introduced by temperature variation and/or flow turbulence.

The (0002) x-ray diffraction reflection yielded a symmetric line with full width at half maximum (FWHM) of 420 arc sec, obtained by fitting the spectrum with a single Gaussian. This value is only 25% larger than the average FWHM value of optimized GaN films deposited on vicinal-cut, *a*-plane sapphire substrates, for which FWHM values span from 258 to 425 arc sec for vicinal-cut orientation between 0° and 1°, respectively.[5] However, large differences have been reported for small vicinal-cut *a*-plane and on-axis *c*-plane sapphire substrates, for which a FWHM of $\leqslant$269 arc sec is observed for vicinal-cut orientation between 0.25° and 0.4°.[6] The first-order room temperature Raman scattering spectra, measured at the center and at a point 2.5 mm away, are shown in Fig. 1. The peak position and relatively small linewidth of the allowed phonons indicate the good crystalline quality and low residual stress of the film. Comparison of the E_2(high) phonon frequency with that of a high-quality freestanding hydride vapor phase epitaxial GaN substrate indicates that the film is under smaller tensile stress, only 0.3 GPa, as compared with films on sapphire substrates.[7] A_1(LO) phonon line shape analyses yield carrier concentrations of $1.9\times10^{17}/\text{cm}^3$ and $2.5\times10^{17}/\text{cm}^3$ at the center and 2.5 mm away from the center, respectively. These values are in excellent agreement with capacitance-voltage (C-V) measurements carried out on this film, considering that the Raman scattering measurements probe the total thickness of the films.[8]

Figure 2 depicts the low-resolution 5 K photoluminescence (PL) spectrum of the UID GaN film deposited on TiC. The intensity of the near band edge emission at 3.482 eV, represented by $D^\circ X_A$ and previously assigned to a recombination process associated with the annihilation of excitons involving holes from valence band A (X_A) bound to a shallow neutral donor (D°) or donors, is dominant.[9] However, the ~3.0 and 2.25 eV (yellow band) emissions are observed in the 200× magnified spectrum, confirming the presence of other competing recombination channels and indicating partial compensation of the shallow donor(s). Higher resolution PL measurements, as represented in Fig. 3, clearly show the presence of recombination processes due to free excitons, which involve holes from valence band A, commonly represented by "FEA" or X_A. Thermal quenching studies of the PL band edge spectra, highlighted in Fig. 3, show increasing contribution of FEA recombination processes with increasing sample temperature. Line shape fitting analyses indicate that the integrated intensity of the $D^\circ X_A$ line decreases more than twofold in the temperature range between 5 and 25 K, while the integrated intensity of the FEA line increases by a similar ratio. Therefore, the increase of the population of free excitons is directly related to the thermal release of the excitons from the shallow neutral donor(s). This observation is consistent with a high crystalline quality heteroepitaxial film

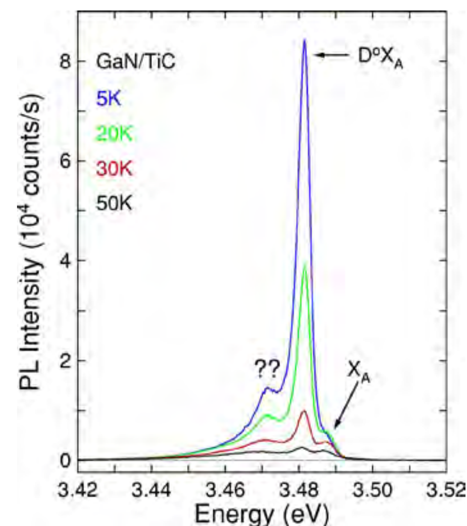

FIG. 3. (Color online) High-resolution photoluminescence spectrum of the GaN/TiC film in the near band edge spectral region. Note that the FEA (X_A) emission line becomes dominant with increasing sample temperature.

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characterized by a lower carrier concentration than the typical level of $\geqslant 1\times 10^{17}$ cm^{-3} in UID films deposited on sapphire or SiC. GaN films with this carrier concentration or greater require higher temperatures to thermally release excitons due to the high excess of shallow neutral donors with large recapture cross section.[9] This thermal quenching behavior is also consistent with a relatively small contribution from competing nonradiative recombination processes. Note that the penetration depth of the 325 nm HeCd laser line used in the PL experiment is only about 0.1 μm, which indicates that the lower carrier concentration region is located near the film surface. This observation is in agreement with the *C-V* study of this film, which yields a carrier concentration of about 1×10^{16} electrons/cm^3 at the film's surface.[8] The *C-V* measurements also show that the doping concentration increases with increasing depth, as suggested by the micro-Raman studies, which probe the total film thickness.

The observation of multiple optical phonon replicas of the $D^\circ X_A$ (1LO and 2LO), in Fig. 1, confirms the high quality of the film. Also observed is a weak shallow-donor-shallow-acceptor zero phonon line and a line represented by "?" (3.364 eV), which may be associated with a structural defect. The line represented by "??" (3.4715 eV), in the spectra of Fig. 2, previously observed in GaN films deposited on sapphire and SiC, has not yet been identified. The FWHM of $D^\circ X_A$ of this thin film is 3.3 meV, which is close to the ~3 meV observed on ~3 μm thick films deposited on sapphire.[9] The 5 meV redshift of the $D^\circ X_A$ is consistent with smaller biaxial strain in films deposited on TiC than those deposited on sapphire substrates.[9] The peak position and FWHM of the exciton-related emission at room temperature are 3.42 and 36 meV, respectively. All the listed values and spectral features are similar to those reported for high-quality GaN films deposited on sapphire and SiC substrates.

Investigation of vertical and lateral electronic transport properties of GaN on sapphire has indicated that dislocations are responsible for the sixfold reduction of the carrier mobility on planar Schottky diodes.[10] Recent study of vertical Schottky diodes fabricated on thick freestanding GaN substrates confirms this observation.[11] In addition, the latter work confirmed the potential of GaN for the fabrication of rectifiers and switching devices based on the observed high breakdown fields and ultrafast reverse recovery device characteristics.[11]

To obtain insights into the transport properties of the GaN films on TiC substrates and their potential application for vertical electronic devices, we measured the *I-V* characteristics of the film deposited on (111)TiC substrate. The TiC substrate was bonded to a device carrier, which provides good Ohmic contact and thermal stability. The *I-V* curve represented in Fig. 4 was acquired with an HP4145B semiconductor parameter analyzer at room temperature, using a point probe at the GaN surface. This curve is typical for the combination of Schottky (point probe) and Ohmic (GaN film and TiC substrate interface) contacts. This preliminary result suggests that this structure may be adequate for vertical device fabrication. The lower contact resistance, lack of current crowding, and high-temperature stability, combined with the simplicity of the device structure and fabrication, should make GaN/TiC reliable and convenient for high-power and/or high-temperature device applications. However, more elaborate experiments using metal contacts must be performed to obtain a quantitative analysis.

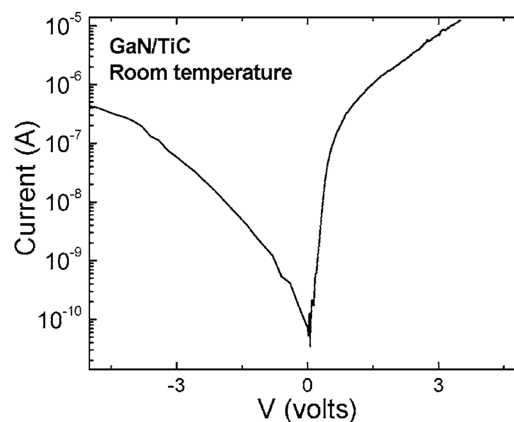

FIG. 4. *I-V* characteristic of the GaN film on (111) TiC mounted on a device carrier, measured with a point probe at the GaN surface.

In summary, we have demonstrated that films characterized by good surface morphology, high crystalline quality, and relatively low-background donor concentration can be deposited on refractory metals such as TiC. The properties of these films are similar to high-quality films deposited on sapphire and SiC substrates and far superior to films previously deposited on metals. The low compensation and low concentration of background carriers indicate that *p*-type doping can be achieved at least as easily as on sapphire substrates, which will allow the fabrication of *p-n* and *p-i-n* device structures. Point probe testing showed good rectifying behavior with relatively low leakage current for the GaN/TiC structure. Our sample has been thermally cycled many times in the temperature range between 5 and ~500 K and no delamination has been observed, indicating excellent film adhesion to the substrate. These findings clearly confirm the feasibility of fabricating device structures on metal substrates and the potential use of these heterostructures for advanced design and high-power and/or high-temperature device fabrication.

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