Epitaxy of Al films on GaN studied by reflection high-energy electron diffraction and atomic force microscopy

Q. Z. Liu, L. Shen, K. V. Smith, C. W. Tu, E. T. Yu, and S. S. Lau
Department of Electrical and Computer Engineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093-0407

N. R. Perkins and T. F. Kuech
Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706-1691

(Received 6 September 1996; accepted for publication 17 December 1996)

Epitaxy of Al films deposited on GaN has been studied using reflection high-energy electron diffraction (RHEED), atomic force microscopy (AFM), x-ray diffraction, and ion channeling techniques. Al (111) films have been found to grow epitaxially on GaN (0001) surfaces with Al ⟨211⟩‖GaN⟨2110⟩. For growth at 15 and 150 °C with a deposition rate of 0.26 Å/s, the epitaxial quality of the film was poor initially, as evidenced by the observation of diffuse RHEED patterns. After a few monolayers, a sharp and streaky RHEED pattern develops and is maintained during subsequent deposition, indicating an improvement in epitaxial quality with a two-dimensional growth mode. AFM studies indicate that the initial GaN surface quality is a significant factor in achieving epitaxial growth, and that the size of Al epitaxial islands increases substantially for higher growth temperatures. X-ray diffraction and ion channeling results confirm the epitaxial nature of the Al films in spite of a significant lattice mismatch of 10.2%.
[S0003-6951(97)04208-3]

GaN-based materials have been the subject of intensive research recently for blue and ultraviolet light emission[1,2] and high-temperature/high-power electronic devices.[3–5] For device applications, control of metal/semiconductor interface quality is important; ideally, metal/semiconductor interfaces should be inert, epitaxial, oxide- and defect-free, and atomically smooth. While the epitaxy of metal films on GaAs and other III–V semiconductors has been studied extensively,[6] studies of metal epitaxy on GaN have been rare. For GaAs and other common III–V semiconductors, a thin oxide layer (several to tens of Å) grows rapidly on the surface when exposed to air,[7] necessitating *in situ* cleaning of GaAs surfaces under ultrahigh-vacuum (UHV) conditions for the epitaxial growth of metal films.[6] For GaN, an *in situ* cleaning method under UHV has been developed[8] and used in the growth of thin Al and Ni films on GaN (0001).[9,10] Epitaxy of Sc films on GaN with a thin ScN intermediate layer formed at high temperatures (645 °C and above) has been reported.[11] Recently, we have found that Pd, Ni, and Pt can be grown epitaxially on GaN in a conventional e-beam evaporation system without *in situ* cleaning in UHV.[12] Other metals, such as Au, Al, Ti, and Hf, have also been found to grow epitaxially on GaN under conventional vacuum conditions.[13] These findings suggest that after the GaN surface has been cleaned by acid etching, the presence of oxides on GaN surfaces is minimal and, furthermore, that native oxides do not grow rapidly on the GaN surface during the time (<30 min) required to load the samples in the vacuum deposition chamber.

In this letter we report the investigation of epitaxial growth of Al films on GaN primarily by reflection high-energy electron diffraction (RHEED) and atomic force microscopy (AFM). Al deposition on GaN is of interest because Al is one of the metal layers used in ohmic contacts in nitride devices.[2] In addition, controlled deposition of Al in a molecular-beam-epitaxy (MBE) system allows real time, *in situ* monitoring of surface quality by RHEED. Subsequent characterization by AFM, x-ray diffraction, and ion channeling techniques can then provide detailed information about the structure of the epitaxially grown films.

GaN/AlN/sapphire structures for these studies were produced in a horizontal metal-organic vapor-phase-epitaxy (MOVPE) system. The layer structures and growth system have been described in detail elsewhere.[14] The thickness of the GaN layers was about 3 μm, and full width at half-maximum of the double-crystal x-ray rocking curve was about 330 arcsec. For deposition of Al films, GaN samples were first cleaned with organic solvents, then etched in boiling aqua regia ($3HCl:HNO_3$) for 15 min, and finally loaded into a MBE system, in which the base pressure was $\sim 1 \times 10^{-10}$ Torr. The total exposure time to air following cleaning was about 30 min. Al films were deposited at a rate of either $\sim$0.26 or 0.89 Å/s on the GaN samples at a substrate temperature T_s of 15 or 150 °C. These studies allowed the influence of both growth temperature and deposition rate on epitaxial film structure to be investigated.

RHEED patterns were obtained from the GaN substrate prior to deposition and periodically during Al deposition. For Al (111) layers deposited on GaN (0001), high-symmetry directions are along $\langle 211\rangle_{Al}$ $(\|\langle 2110\rangle_{GaN})$ and $\langle 011\rangle_{Al}$ $(\|\langle 1100\rangle_{GaN})$ respectively; these directions alternate cyclically and are separated by $\phi = 30°$. Figure 1 shows the RHEED patterns obtained from the GaN (0001) surface at $T_s = 15$ °C along the $\langle 2110\rangle_{GaN}$ and $\langle 1100\rangle_{GaN}$ directions. The RHEED patterns were streaky and sharp with Kikuchi lines clearly visible, indicating that the GaN surface is smooth and relatively free of oxides or other contaminants. It should be noted that this pattern was obtained from a GaN surface cleaned *ex situ*, as described above, without any *in situ* cleaning. This is consistent with the studies of Khan *et al.*,[8] and provides strong evidence of the inertness of the GaN (0001) surface compared to other III–V semiconductors

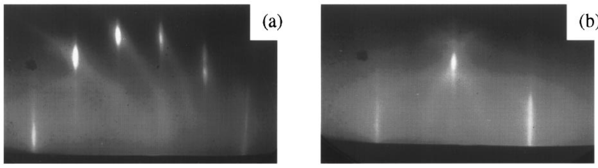

FIG. 1. Reflection high-energy electron diffraction patterns of GaN (0001) surface at 15 °C, (a) $\langle 2\bar{1}\bar{1}0\rangle_{GaN}$ azimuth ($\phi=0°$), (b) $\langle 1\bar{1}00\rangle_{GaN}$ azimuth ($\phi=90°$). The GaN substrate was cleaned in boiling aqua regia for 15 min before loading. No *in situ* cleaning was performed before RHEED patterns were recorded.

such as GaAs. This inertness makes the epitaxy of metals on GaN possible under conventional vacuum conditions.[12,13]

Figure 2 shows a series of RHEED patterns for the $\langle 2\bar{1}\bar{1}\rangle_{Al}$ direction obtained during deposition of the Al overlayers. Figure 2(a), 2(b), and 2(c) show the RHEED patterns after deposition of ~5, ~9, and ~380 Å of Al, respectively, for $T_s=15$ °C; Figs. 2(d), 2(e), and 2(f) show the corresponding diffraction patterns for $T_s=150$ °C. In both cases the Al deposition rate was 0.26 Å/s. Comparison of RHEED patterns from the GaN (0001) and Al (111) surfaces indicates that epitaxial growth of Al occurs with $\langle 2\bar{1}\bar{1}0\rangle_{GaN}\|\langle 2\bar{1}\bar{1}\rangle_{Al}$ and $\langle 1\bar{1}00\rangle_{GaN}\|\langle 01\bar{1}\rangle_{Al}$. As shown in Fig. 2, the streaky and sharp RHEED pattern characteristic of the GaN surface becomes weaker and more diffuse upon commencement of Al deposition. This suggests a roughening of the surface, possibly due to the 10.2% lattice mismatch between Al and GaN. However, after deposition of a few monolayers (ML) of Al [1 ML is defined as the spacing between Al (111) planes, 2.338 Å], the RHEED patterns become streaky and sharp again, and remain so even after deposition of more than 380 Å of Al, suggesting an improvement in the crystalline quality of the Al surface after a few ML of deposition. The persistent streakiness of the RHEED patterns seems to suggest a two-dimensional growth mode for the Al films, even though RHEED oscillations were not observed. This observation is consistent with the "Poissonian" or statistical growth mode,[15] in which little surface migration of atoms occurs during deposition, leading to a two-dimensional growth front and consequently a streaky RHEED pattern, but also an atomically rough surface. The growth mode is not three dimensional as in islandlike growth. The absence of spotty RHEED patterns throughout the entire growth indicates that the Al growth surface remains relatively flat without any prominent cluster formation, as confirmed by the AFM characterization of the Al film surface. For Al growth at a higher rate of 0.89 Å/s at 15 °C, the RHEED patterns are not as streaky and sharp throughout the entire growth to ~470 Å; however, upon *in situ* annealing at 300 °C, the RHEED patterns can improve from diffraction-ringlike to streaky and sharp.

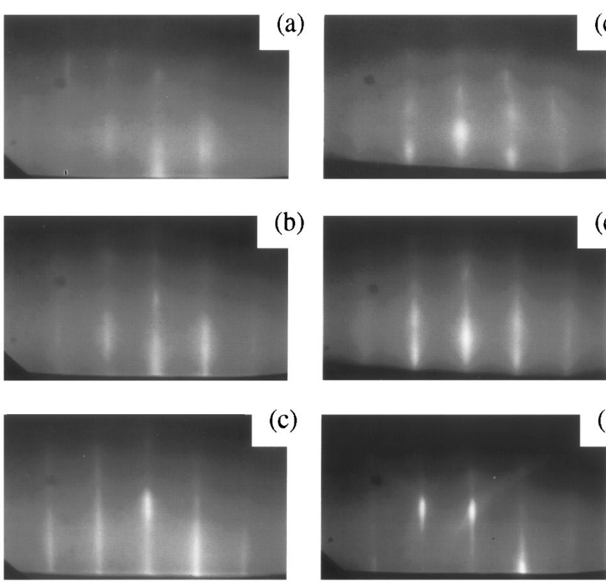

FIG. 2. RHEED patterns from Al films grown on (0001) GaN with a deposition rate of 0.26 Å/s ($\langle 2\bar{1}\bar{1}\rangle_{Al}$ azimuth, $\phi=0°$) at $T_S=15$ °C, (a) after depositing ~5 Å of Al, (b) after ~9 Å, (c) after ~380 Å; and at $T_S=150$ °C (d) after depositing ~5 Å of Al, (e) after ~9 Å, (f) after ~380 Å.

The epitaxial nature of the Al layer on GaN has been verified by x-ray diffraction and by 2.3 MeV He^{++} ion channeling analysis. Ion channeling analysis performed on an ~380 Å Al film grown on GaN at 15 °C and an ~380 Å Al film grown on GaN at 150 °C produced channeling yields of 70% and 50%, respectively, suggesting an improvement in crystalline quality at higher growth temperature. These channeling yields are high, even for a lattice mismatch of 10.2%, suggesting good but not outstanding crystalline quality. In epitaxial growth of Al on GaAs (lattice mismatch <2%), a channeling yield of ~10% has been observed.[16] For other metal films, such as Pd, on GaN (0001), however, a channeling yield as low 16% has been observed.[12] Since RHEED patterns and x-ray thin-film camera results indicated that Al overgrowth was of good crystalline quality and the RHEED patterns showed that $\langle 110\rangle_{GaN}\|\langle 2\bar{1}\bar{1}\rangle_{Al}$ and $\langle 1\bar{1}00\rangle_{GaN}\|\langle 01\bar{1}\rangle_{Al}$, we may conclude that a definite crystallographic relationship between the Al overlayer and the GaN substrates exists, i.e., Al is "epitaxial" on GaN and not merely highly textured.

In previous investigations of metal growth on GaN, room-temperature deposition of metal films on atomically clean surfaces under UHV conditions did not lead to epitaxial growth of the metal films. For example, when Ni is deposited on atomically clean GaN, the as-deposited Ni is disordered and chemical reactions at the interface may also occur.[9] Upon annealing at high temperatures, i.e., 700–800 °C, the thin Ni layer agglomerates into epitaxial islands, which induces epitaxial growth during subsequent deposition of thicker Ni layers at room temperature. Interfacial reactions between Al (Ref. 10) or Sc (Ref. 11) with atomically clean GaN have also been observed before any epitaxial growth can follow. In our case, the GaN surface was cleaned by an acid solution before loading into a vacuum chamber. Oxygen and carbon have been shown to be present on acid-etched GaN surfaces, and therefore the surfaces are not atomically clean.[17] Interfacial reactions between the deposited metal and GaN are not expected to occur at 15 °C in our experiments. It is interesting to note that epitaxial growth of Al and other fcc metals occurs near room temperature[12,13] in spite of the presence of O and C on the GaN surface and the large lattice mismatch between the metal film and GaN.

Atomic force microscopy studies provide insight into the

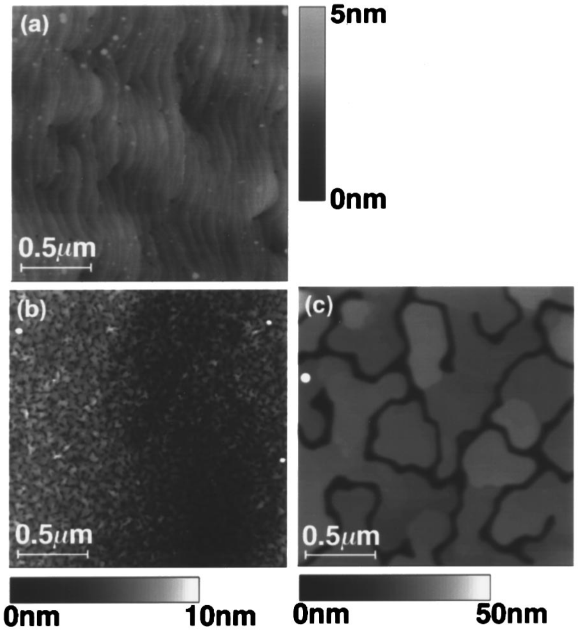

FIG. 3. Atomic force microscopy (AFM) images of (a) the GaN (0001) surface, Al films grown on GaN (0001) at (b) $T_S = 15$ °C, (c) $T_S = 150$ °C. The deposition rate was 0.26 Å/s.

role of initial GaN surface quality on film growth and the structure of Al epitaxial film surfaces. Figure 3(a) shows an AFM image of the GaN (0001) surface after *ex situ* cleaning. The rms roughness of such surfaces is typically ~ 7 Å, and atomic steps are clearly visible in the image. Studies of metal deposition on a variety of GaN surfaces in our laboratory indicate that epitaxial metal growth occurs only on flat GaN surfaces exhibiting the clear terrace structure shown in Fig. 3(a). Figures 3(b) and 3(c) show AFM images of 380 Å Al films deposited at $T_S = 15$ and 150 °C, respectively, at a growth rate of 0.26 Å/s. In both cases, epitaxial islands with a characteristic hexagonal geometry are apparent; however, the average island diameter is approximately ten times greater for growth at 150 °C. For growth at 15 °C, islandlike structures separately by shallow (~ 40 Å) trenches are present, with an overall rms surface roughness of ~ 12 Å. For growth at 150 °C, much larger island structures with extremely flat tops (rms roughness $\sim 6-9$ Å) are observed. In many cases the crevices separating the islands are sufficiently wide that an average depth of ~ 200 Å, i.e., roughly half of the film thickness, may be deduced, suggesting that the Al film is continuous rather than consisting of discrete islands; in some instances, however, the crevices appear to be too narrow to be completely profiled by the AFM.

In conclusion, epitaxy of Al films on MOVPE-grown GaN (0001) surfaces cleaned *ex situ* by acid etching has been studied by RHEED, channeling, x-ray diffraction, and AFM. Epitaxial growth occurs only on GaN surfaces exhibiting a relatively flat topography with atomic terraces visible in AFM. For two substrate temperatures and two deposition rates, (111) Al grows epitaxially on the basal plane of GaN with $\langle \bar{2}\bar{1}10\rangle_{GaN} \| \langle 2\bar{1}\bar{1}\rangle_{Al}$ and $\langle 1\bar{1}00\rangle_{GaN} \| \langle 01\bar{1}\rangle_{Al}$. At a low deposition rate (0.26 Å/s), the Al films are of poor quality for the first few ML, but improve substantially with further deposition as indicated by a significant improvement in the RHEED patterns observed. The growth mode appears to be two dimensional rather than three dimensional, resulting in a flat growth surface. Higher substrate temperature improves the epitaxy of Al as determined by channeling measurements and increases the epitaxial island size within the films, although the islands formed at the higher temperature are separated by deep crevices. A higher growth rate leads to poorer film quality and 3D growth, although the film quality can be improved substantially be thermal annealing. The understanding of the epitaxy of Al films should be helpful in understanding the epitaxy of metals on GaN in general, with considerable impact on nitride device technology and potentially on the development of new devices based on epitaxial metal-nitride structures.

The authors would like to acknowledge valuable technical assistance from W. G. Bi, and encouragement from Professor H. H. Wieder and Professor W. S. C. Chang at UCSD. The work at UCSD is supported by BMDO (Dr. Kepi Wu) monitored by the U.S. Army Space and Strategic Defense Command. The University of Wisconsin acknowledges financial support from the Naval Research Laboratory and the ARPA URI on Visible Light Emitters.

[1] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, Jpn. J. Phys. **35**, L74 (1996).
[2] S. Nakamura, M. Senoh, N. Iwasa, and S. Nagahama, Appl. Phys. Lett. **67**, 1868 (1995).
[3] S. C. Binari, L. B. Rowland, W. Kruppa, G. Kelner, K. Doverspike, and D. K. Gaskill, Electron. Lett. **30**, 1248 (1994).
[4] M. A. Khan, M. S. Shur, J. N. Kuznia, Q. Chen, J. Burm, and W. J. Schaff, Appl. Phys. Lett. **66**, 1083 (1995).
[5] T. P. Chow and R. Tyagi, IEEE Trans. Electron Devices **41**, 1481 (1994).
[6] T. Sands, C. J. Palmstrom, J. P. Harbison, V. G. Keramidas, N. Tabatabaie, T. L. Cheeks, R. Ramesh, and Y. Siberberg, Mater. Sci. Rep. **5**, 99 (1990), and references therein.
[7] C. W. Wilmsen, in *Physics and Chemistry of III–V Compound Semiconductor Interfaces*, edited by C. W. Wilmsen (Plenum, New York, 1985), Chap. 7.
[8] M. A. Khan, J. N. Kuznia, D. T. Olson, and R. Kaplan, J. Appl. Phys. **73**, 3108 (1993).
[9] V. M. Bermudez, R. Kaplan, M. A. Khan, and J. N. Kuznia, Phys. Rev. B **48**, 2458 (1993).
[10] V. M. Bermudez, T. M. Jung, K. Doverspike, and A. E. Wickenden, J. Appl. Phys. **79**, 110 (1996).
[11] R. Kaplan, S. M. Prokes, S. C. Binari, and G. Kelner, Appl. Phys. Lett. **68**, 3248 (1996).
[12] Q. Z. Liu, S. S. Lau, N. R. Perkins, and T. F. Kuech, Appl. Phys. Lett. **69**, 1722 (1996).
[13] Q. Z. Liu, K. V. Smith, E. T. Yu, S. S. Lau, N. R. Perkins, and T. F. Kuech, presented at Fall Meeting of the MRS, Boston, Massachusetts, December 1996.
[14] N. R. Perkins, M. N. Horton, D. Zhi, Z. Z. Bandic, T. C. McGill, and T. F. Kuech, presented at Spring Meeting of the MRS, San Francisco, CA, April, 1996.
[15] J. Y. Tsao, *Materials Fundamentals of Molecular Beam Epitaxy* (Academic, New York, 1993), p. 254.
[16] R. S. Williams, L. C. Feldman, and A. Y. Cho, Radiat. Eff. **54**, 217 (1981).
[17] L. L. Smith, S. W. King, R. J. Nemanich, and R. F. Davis, J. Electron. Mater. **25**, 805 (1996).