Growth of Hf and HfN on GaN by Molecular Beam Epitaxy

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Hf and HfN thin films were grown on n-type GaN(000$\bar{1}$) by MBE using a custom built Hf electron beam source and an ammonia leak. The films were characterized by reflection high-energy electron diffraction (RHEED) and atomic force microscopy (AFM). It was found that epitaxial growth of Hf is possible even at room temperature. GaN films varying in thickness of 0.6-1.8 microns were grown on c-plane sapphire using ammonia as a precursor, to serve as a substrate. Then the film was annealed in ammonia as the temperature was lowered in order to produce an N termination. Hf was then deposited on top of GaN at temperatures between 20°C and 700°C, both with and without ammonia incident on the sample. Deposition of pure Hf at room temperature revealed an epitaxial 2D (though with some 3D character) RHEED pattern with six fold symmetry. The surface is reconstructed with a $(\sqrt{2}\times\sqrt{2})$R30° structure. We propose that the pattern is 30 degrees rotated with respect to that of the substrate GaN because of a HfN interlayer between the GaN and Hf layers. When the films were annealed in vacuum up to 730°C, the 2D pattern became more transmission like. If Hf was deposited at substrate temperatures above 350°C, a diffraction pattern corresponding to that of a polycrystalline material was observed.

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I. INTRODUCTION

GaN has been shown to be a technologically important material for applications in optoelectronics [1] and high temperature/high power electronic devices [2,3]. With the progress in device fabrication the need for stable high quality ohmic and Schottky barrier contacts to this material becomes especially important. Recently there have been a few reports on success in fabrication of contacts to both n- and p-type material [4–8]. However, the problem of thermal and mechanical stability of the contact materials has not been fully resolved [8,9]. Transition metals have been widely used in recent years in contacts to III-Nitrides. These include Ti/Al layers used as ohmic contacts to n-type GaN and Ni/Au layers for p-type GaN. Most of these metals have very different structures and lattice parameters than GaN. Hf and HfN are noteworthy in that they are closely lattice matched to GaN. Like GaN (Wurtzite), Hf is hcp. Their compatibility has been demonstrated by Beresford et al. who have recently reported on growth of GaN on bulk Hf substrates [10]. They have suggested that Hf has the possibility of being a compliant substrate. Further, HfN have been studied as a diffusion barrier for Al ohmic contacts on Si [11]. Because of their thermal and crystallographic compatibility, Hf and HfN epitaxial layers on GaN would offer the possibility of studying nearly ideal contacts. In this paper we report the first studies on preparing such films. Hf and HfN films were grown on GaN by molecular beam epitaxy (MBE) using NH_3. The films were studied with reflection high energy electron diffraction (RHEED) and atomic force microscopy (AFM). Based on the RHEED results, a model is proposed in which Hf grows on GaN through the formation of a HfN interface layer.

II. EXPERIMENTAL

GaN(000$\bar{1}$) films were grown on c-plane sapphire by molecular beam epitaxy (MBE) using a Ga K-cell and an ammonia leak. The growth was conducted in a custom built system with a background pressure of 1x10^{-9} Torr.

Commercial, Union Carbide sapphire samples of approximately 10 × 11 mm in size with one side polished were cleaned in 1:1 mixture of $H_2SO_4 : H_3PO_4$ at 65 °C for 5 min. Then, the samples were rinsed in DI water dried by nitrogen gas followed by cleaning them in acetone and methanol subsequently as described in detail by R. Held et.al. [12]. To increase radiation absorption from the heater behind the sample, 500 Å of Ti followed by 2000 Å of Mo were deposited on back, unpolished side of the samples in an e-beam evaporator. The samples prepared this way were then used as substrates for GaN growth.

The c-plane sapphire substrate was nitrided by annealing it in an ammonia flux with a beam equivalent pressure BEP=1×10^{-5} Torr at 850°C for 15 min. Then a low temperature GaN buffer layer was grown under conditions of excess ammonia. This procedure would produce an N polar film. GaN was then grown at 750°C, using a Ga flux of 0.3 ML/s and an NH_3 BEP of 5×10^{-6} Torr. GaN(000$\bar{1}$) films with thicknesses between 0.6-1.8 micron were grown. RHEED was used to determine the Ga condensation temperature and further GaN growth monitoring [12]. The surface was then annealed in ammonia as the temperature lowered to room temperature. The films had relatively streaky, 2D RHEED patterns and possessed an rms roughness of less than 1 nm as determined by AFM. These films were used as substrates for subsequent Hf and HfN growth, without exposure to the

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atmosphere.

Hf was deposited in the MBE chamber using a custom built, Jonker-style electron beam source [13] that was surrounded by a liquid nitrogen cryoshroud. A cylindrical Hf rod (3N purity) was used as a source material. Biased at +7 kV the Hf piece is selectively heated by the electrons emitted from a circular tungsten filament. The Hf source was operated at about 150 W to achieve a deposition rate of up to 300 Å per hour. Hf was deposited on top of GaN at the temperatures between 20°C and 730°C both with and without ammonia in the system.

RHEED studies of GaN and Hf films have been conducted using a Physical Electronics Industries 10 kV electron gun, and custom built octupole electrostatic deflectors.

III. RESULTS

Hf was deposited on the GaN films as described in Sec. II. Initially transmission features in the diffraction pattern were observed; after about 100 nm of deposition the pattern showed more of a 2D, streak character, as shown in Fig. 1. The film was epitaxial with the underlying GaN surface, and the measured separation between the streaks repeated every 60°, as expected for the hexagonal lattice. Also, the Hf RHEED pattern was found to be rotated by 30° with respect to that of the underlying GaN. The lattice parameter of Hf is very close to GaN. But the separations of the diffracted beams parallel to the surface in the 30° pattern from GaN is 1.43 times the separation of the Hf 0° pattern. This suggests a $(\sqrt{2} \times \sqrt{2})$R30° surface reconstruction.

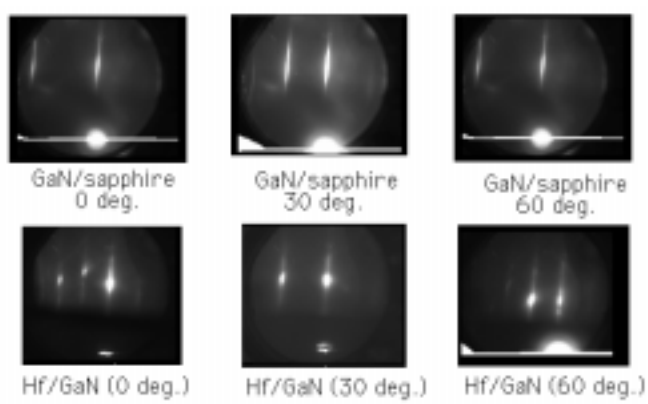

FIG. 1. RHEED patterns of GaN substrate and 100 nm thick Hf film grown on this substrate.

Atomic force microscopy was used to examine the surface morphology of the Hf films. A 5 μm area scan presented in Fig. 2 indicates a rough film surface consisting of hills with a step and terrace structure. A 1 μm scan of the plateau area is presented in Fig. 3. It shows that the growth of the Hf film occurs by a hillock mechanism, though the nucleation process of Hf on GaN is yet to be studied. The surface of the film contains macrosteps with the average height of 10 nm. An rms roughness of the plateau areas is found to be of the order of 3.2 nm. The step edges show some pinning; no clearly defined screws can be resolved.

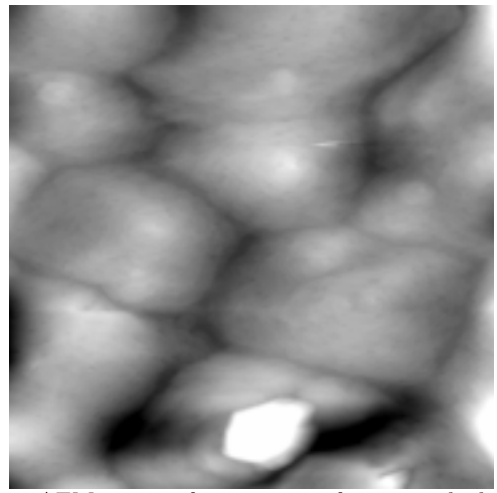

FIG. 2. AFM image of 5 μm area of 100 nm thick Hf film grown on GaN at room temperature

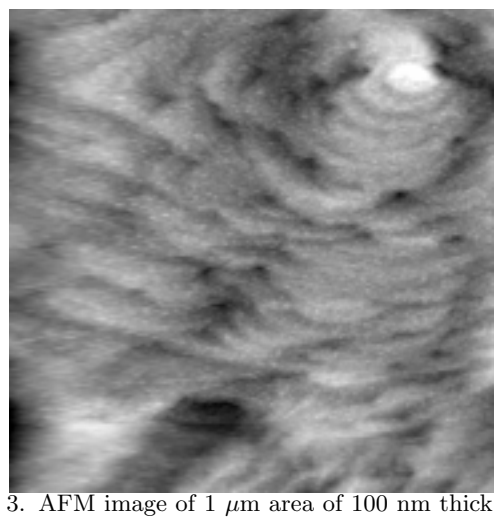

FIG. 3. AFM image of 1 μm area of 100 nm thick Hf film grown on GaN at room temperature. The macrosteps in the figure have a mean height of 10 nm.

When the Hf films were annealed in vacuum at temperatures up to 700°C, a change to a transmission diffraction pattern was observed. If Hf was deposited at NH_3 BEP= 10^{-7} Torr and substrate temperatures above 350°C, a diffraction pattern consisting of arcs and corresponding to that of a polycrystalline material was observed. AFM

Material	Structure	Lattice Parameter Å, R.T.	Melting Point
GaN	Wurtzite	a=3.19 c=5.19	$\geq 800°$C decomp
Hf	HCP	a=3.19 c=5.04	2231°C
HfN	NaCl	a=4.52	3305°C

TABLE I. Selected properties of GaN, Hf, and HfN from Refs. 15 and 16.

found these to have an rms roughness of up to 40 nm for a 100 nm film. Auger Electron Spectroscopy (AES) indicated the Hf:N ratio in these films is roughly stoichiometric HfN.

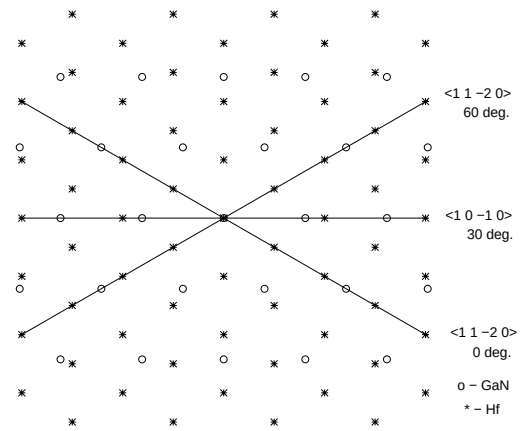

FIG. 4. Model of $(\sqrt{2} \times \sqrt{2})$R30° reconstruction

IV. DISCUSSION

Both Hf and HfN are well lattice matched to GaN, as can be seen in the data listed for reference in Table 1. As a group IVB element, Hf is predicted to be thermodynamically unstable on GaN [14]. Theoretical studies of the Hf-Ga-N ternary system indicated that HfN phase forms a tie-line with GaN while pure Hf does not [14]. Hence we expected that for pure Hf deposition onto GaN it would have been more difficult to obtain a smooth, unreacted interface than with HfN. However, at the temperatures required for HfN deposition this was not the case. Smoother films could ultimately be grown with Hf alone.

The RHEED data of Fig. 1 indicate a 30° rotation within the c-plane of Hf grown on GaN at room temperature. To see this examine the Ewald construction of Fig. 4. In this RHEED geometry the Ewald sphere is nearly tangent to the reciprocal lattice rods and so it is easiest to imagine a plane rather than a sphere as the locus of the allowed diffracted beams. Viewing the surface reciprocal lattice rods from above, the construction consists of a line perpendicular to the incident beam superimposed on the reciprocal lattice. The points of intersection are the allowed beams. In Fig. 4, three lines are drawn, corresponding to the planes perpendicular to the three incident directions in Fig. 1. In the construction, the circles correspond to the reciprocal lattice rods of GaN and the crosses correspond to that of Hf, taken from Fig. 1. Because the electron beam cannot penetrate the Hf overlayer, both patterns are not seen together. The rotation, by itself, is apparent because, for example, the 0° pattern of GaN shows the beams with their largest separation, while for Hf, the beams are at their closest separation. The ratio of the streak separations in the 30° pattern and the 0° pattern is 1.43. Together we conclude that, with perhaps a 2% expansion, the Hf surface has a $(\sqrt{2} \times \sqrt{2})$R30° reconstruction. Previously, Beresford [10] observed bulk crystalline Hf(0001) surfaces that were prepared by a sputter and anneal cycle that did not show this reconstruction. In their procedure, however, hydrogen was not used and so, as for other metal surfaces, H adsorption might induce the reconstruction we observe.

We suggest that the 30° rotation is due to reaction at the GaN/Hf interface. To explain this model consider certain structural properties of Hf, HfN, and GaN as presented in Table 1. GaN has a Wurtzite structure with an atomic layer stacking sequence along the c-axis corresponding to that of the hexagonal close-packed (hcp) structure with two atoms per basis. Such a periodicity can be represented as ABAB... where atoms of each sublattice in GaN move from position A to position B as depicted in Fig. 5b. If there were no interfacial reaction, Hf, which also has an hcp structure and which is lattice matched to GaN, would grow with the original substrate stacking sequence resulting in an unchanged RHEED pattern. Instead, Hf reacts with GaN at the interface forming HfN that has a sodium chloride structure with the atomic layer sequence along the close-packed direction of ABCABC... as shown in Fig. 5a. The formation of the HfN(111) at the interface changes the GaN stacking sequence to that of a cubic HfN that further changes again to that of the hcp Hf as more material is grown. Such changes in the atomic layer stacking sequence that can be represented as ABAB... C...ACAC...(Fig. 5c) cause a 30° rotation in the c-plane, as seen with RHEED. This type of rotation could occur in the middle of a flat terrace on a GaN surface; it could also happen at a step edge. The latter would limit the formation of domain boundaries in the Hf overlayer.

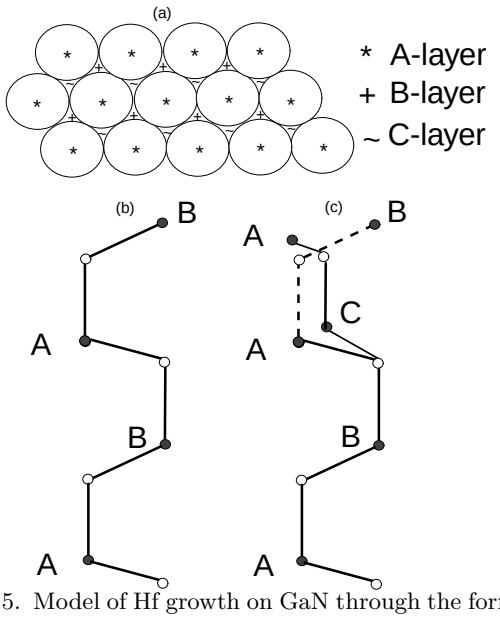

FIG. 5. Model of Hf growth on GaN through the formation of the HfN interface layer: (a) Atomic positions in the cubic close-packed structure; (b) stacking sequence along c-axis in Wurtzite GaN; (c) change in the stacking sequence along c-axis caused by the formation of the cubic close-packed phase

V. SUMMARY

Hf has been epitaxially grown on GaN at room temperature. RHEED indicated that Hf grows on GaN with a 30° rotation in the c-plane. This change in the RHEED pattern can occur due to the formation of a cubic HfN interface layer that introduces a rotation in the Hf structure with respect to the underlying GaN. Also, the RHEED data shows that the Hf surface is $(\sqrt{2} \times \sqrt{2})$R30° reconstructed, perhaps caused by the residual hydrogen in the system. Since smooth Hf films can be grown, they might serve as compliant substrates for subsequent GaN growth or for metal semiconductor superlattices.

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[1] S. Nakamura, T. Mukai, and M. Senoh, Jpn. J. Appl. Phys. 30, L1998 (1991)
[2] R. Gaska, A. Osinsky, J.W. Yang, M.S. Shur, IEEE Electron. Device Lett., 19, 89 (1998)
[3] Q. Chen, J.W. Yang, R. Gaska, M.A. Khan, M.S. Shur, G.J. Sullivan, A.L. Sailor, J.A. Higgings, A.T. Ping, I. Adesida, IEEE Electron. Device Lett., 19, 44 (1998)
[4] A.C. Schmitz, A.T. Ping, M. Asif Khan, Q. Chen, J.W. Yang, Journal of Electronic Materials, 27, 255 (1998)
[5] A.T. Ping, M. Asif Khan, and I. Adesida, Journal of Electronic Materials, 25, 819 (1996)
[6] M.E. Lin, Z. Ma, F.Y. Huang, Z.F. Fan, L.H. Allen, and H. Morkoç, Applied Physics Letters 64, 1003 (1994)
[7] J.K. Sheu and Y.K. Su, G.C. Chi, W.C. Chen, C.Y. Chen, C.N. Huang, and J.M. Hong, Y.C. Yu, C.W. Wang, and E.K. Lin,Journal of Applied Physics, 83, 3172 (1998)
[8] K.J. Duxstad and E.E. Haller, K.M. Yu, Journal of Applied Physics, 81, 3134 (1997)
[9] B.P. Luther, S.E. Mohney, J.M. Delucca, and R.F. Karlicek,Jr., Journal of Electronic Materials, 27, 196 (1998)
[10] R. Beresford, D.C. Paine, C.L. Briant, Jornal of Crystal Growth, 178, 189 (1997)
[11] R. Nowak, C.L. Li, Thin Solid Films, 305, 297 (1997)
[12] R. Held, D.E. Crawford, A.M. Johnston, A.M. Dabiran, and P.I. Cohen, Journal of Electronic Materials, 26, 272 (1997)
[13] B.T. Jonker, Journal of Vacuum Science Technology A, Vacuum Surface Films, 8, 3883, (1990)
[14] S.E. Mohney and X. Lin, Journal of Electronic Materials, 25, 811 (1996)
[15] CRC Handbook of Chemistry and Physics, edited by Davis R.Lide, CRC Press, Boca Raton (1990)
[16] L.E. Toth Transition Metal Carbides and Nitrides, Academic Press, New York and London (1971)