Epitaxial and polycrystalline HfN$_x$ ($0.8 \leq x \leq 1.5$) layers on MgO(001): Film growth and physical properties

H.-S. Seo, T.-Y. Lee, I. Petrov, a) and J. E. Greene
Frederick Seitz Materials Research Laboratory and Materials Science Department, University of Illinois, 104 South Goodwin, Urbana, Illinois 61801

D. Gall
Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York 12180

(Received 1 December 2004; accepted 14 January 2005; published online 6 April 2005)

While many transition metal (TM) nitrides—including TiN, ZrN, and TaN—have been widely studied and are currently used as hard wear-resistant coatings, diffusion barriers, and optical coatings, little is known about a related TM nitride, HfN. Here, we report the results of a systematic investigation of the growth and physical properties of HfN$_x$ layers, with $0.8 \leq x \leq 1.50$, deposited on MgO(001) by ultrahigh vacuum reactive magnetron sputtering at 650 °C in mixed N$_2$/Ar discharges. HfN$_x$ layers with $0.80 \leq x \leq 1.20$ crystallize in the B1–NaCl structure with a cube-on-cube epitaxial relationship to the MgO(001) substrate, while films with $1.24 \leq x \leq 1.50$ contain a N-rich second phase. The relaxed bulk lattice parameter of HfN$_x$(001) decreases only slightly with increasing N/Hf ratio, ranging from 0.4543 nm with $x=0.80$ to 0.4517 nm with $x=1.20$. The room-temperature resistivity $\rho$ of stoichiometric HfN(001) is 14.2 $\mu\Omega$ cm and $\rho(x)$ increases with both increasing and decreasing $x$ to 140 $\mu\Omega$ cm with $x=0.80$ and 26.4 $\mu\Omega$ cm with $x=1.20$. The hardness $H$ and elastic modulus $E$ of HfN(001) are 25.2 and 450 GPa, respectively. $H(x)$ initially increases for both over- and understoichiometric layers due to defect-induced hardening, while $E(x)$ remains essentially constant. Single-phase HfN$_x$(001) is metallic with a positive temperature coefficient of resistivity (TCR) between 50 and 300 K and a temperature-independent carrier density. It is also superconducting with the highest critical temperature, 9.18 K, obtained for layers with $x=1.00$. In the two phase regime, $\rho$ ranges from 59.8 $\mu\Omega$ cm with $x=1.24$ to 2710 $\mu\Omega$ cm with $x=1.50$. TCR becomes positive with $x \approx 1.38$, no superconducting transition is observed, and both $H$ and $E$ decrease. © 2005 American Institute of Physics. [DOI: 10.1063/1.1870097]

I. INTRODUCTION

Transition metal (TM) nitrides are well known for their remarkable physical properties including high hardness and mechanical strength, chemical inertness, and electrical resistivities which vary from metallic to semiconducting. As a result, they are widely studied and have become technologically important for applications such as hard wear-resistant coatings, diffusion barriers, decorative coatings, and optical thin films. Among the large family of TM nitrides, the group IVB nitrides TiN and ZrN have elicited particular interest because of their low resistivity ($\rho < 25 \mu\Omega$ cm) due to partially filled TM $d$ orbitals, their excellent mechanical properties resulting primarily from the covalent component of the bonding between TM and N, and their distinctive gold color as a result of interband transitions combined with a high reflectance in the red and infrared. Reactive magnetron sputtering, due to its inherent capability for low-temperature deposition at relatively high growth rates, is currently the primary technique used for growing TM nitride layers.

TiN$_x$ has a wide single-phase field extending from $x = 0.6$ to 1.2. Deviation from stoichiometry has been attributed to anion vacancies for $x < 1$ and interstitial N atoms for $x > 1$. Greene et al. have demonstrated the growth of stoichiometric single-crystal TiN layers with all three low-index orientations and measured their physical properties. TiN(001), for example, is metallic with a room-temperature resistivity $\rho = 13 \mu\Omega$ cm, and a hardness $H$ of 21 GPa. ZrN, although less well studied, has also been grown as single crystals and their properties reported [e.g., $\rho = 25 \mu\Omega$ cm for ZrN(001)].

However, little is known about the fundamental properties of a related group IVB nitride, HfN, due to the lack of high-quality single crystals. The Hf–N phase diagram for N concentrations up to 50 at. % shows that the equilibrium phases are NaCl-structure HfN and two stacking variants, Hf$_3$N$_2$ and Hf$_5$N$_3$, consisting of hcp α-Hf and HfN. In the Hf–N system, unlike Ti–N where TiN is the terminal phase, several conflicting claims concerning the existence of uncharacterized N-rich phases have appeared in the literature.

Johansson et al. deposited polycrystalline HfN$_x$ layers, with $x$ ranging from 0 to 1.44, on steel and glass substrates at 400 °C by reactive dc magnetron sputtering in mixed N$_2$/Ar discharges for which the N$_2$ fraction $f_{N_2}$ was...
varied from 0 to 1. With increasing $f_{N_2}$, they obtained: $\alpha$-Hf, multiphase mixtures consisting of $\alpha$-Hf, HfN, Hf$_3$N$_2$ and/or Hf$_2$N$_3$, HfN, and higher nitrides. Their lowest reported resistivity was 225 $\mu\Omega$ cm and this was for HfN$_x$ with $x \approx 1$. Layers with $x > 1$ had very high resistivities ranging from 800 $\mu\Omega$ cm to 2.0 $\Omega$ cm, presumably due to lattice defects and the formation of higher nitrides. Shinkei and Sasaki\textsuperscript{17,18} obtained a resistivity of 27 $\mu\Omega$ cm for stoichiometric HfN layers grown at 450 °C on Si(001) and Si(111) substrates by ultrahigh vacuum (UHV) sputtering with $f_{\text{N}_2} = 0.04$. HfN$_x$ is superconducting and the highest reported critical temperature, $T_c = 8.7$ K, was obtained with understoichiometric layers ($x \approx 0.85$) synthesized by reacting Hf powder in NH$_3$ at 1000 °C.\textsuperscript{19} Overstoichiometric layers with $x > 1.12$ were not superconducting above 2 K.

We have previously shown that single-crystal B1–NaCl structure HfN layers can be grown on MgO(001) by UHV reactive magnetron sputter deposition in mixed N$_2$/Ar discharges.\textsuperscript{20} Based upon this, together with the results for the low-temperature epitaxial growth ($T_d/T_m = 0.35$, where $T_d$ is the deposition temperature and $T_m$ is the melting point in K) of TiN,\textsuperscript{9,21,22} TaN,\textsuperscript{23,24} CrN\textsuperscript{23,24} and ScN\textsuperscript{25,26} using low energy ($E_i < 50$ eV) and high flux ($J_i/J_{\text{Me}} > 5$) ion irradiation, the present HfN$_x$/MgO(001) growth experiments were carried out at $T_s = 650$ °C ($T_d/T_m = 0.25$) with $E_i = 25$ eV and $J_i/J_{\text{Me}} = 5 - 69$.

In this article, we present the results of an investigation of fundamental physical properties of HfN$_x$ as a function of the N/Hf ratio $x$. All layers are grown on MgO(001). The combination of Rutherford backscattering spectroscopy (RBS) and x-ray diffraction (XRD) demonstrate that HfN$_x$ layers with $0.8 < x < 1.20$ have the B1–NaCl structure and grow epitaxially with a cube-on-cube relationship to the substrate: (001)$_{\text{HfN}}$∥(001)$_{\text{MgO}}$ and [100]$_{\text{HfN}}$∥[100]$_{\text{MgO}}$. Glancing-angle XRD (GA-XRD) analyses show that HfN$_x$ layers with $x > 1.24$ contain a N-rich second phase. Based upon analyses of high-resolution reciprocal lattice maps (HR-RLMs), the relaxed bulk lattice constant of HfN$_x$(001) decreases only slightly with increasing N/Hf ratio, ranging from 0.4543 nm with $x = 0.80$ to 0.4517 nm with $x = 1.20$. The epitaxial layers are of high crystalline quality with relatively large x-ray coherence lengths and low mosaicity. Stoichiometric HfN(001) has a room-temperature resistivity $\rho$ of 14.2 $\mu\Omega$ cm, a hardness $H$ of 25.2±0.7 GPa, and an elastic modulus $E$ of 450±9 GPa. $\rho(x)$ and $H(x)$ increase for both over- and understoichiometric layers, while $E(x)$ remains essentially constant at 438±20 GPa with 0.90 $\leq x \leq 1.32$. The combination of positive temperature coefficients of resistivity (TCR) between 50 and 300 K and temperature-independent carrier concentrations indicates HfN$_x$(001) layers with $0.8 < x \leq 1.20$ are metallic. They are also superconducting with the highest critical temperature, 9.18 K, obtained for layers with $x = 1.0$. Layers with $x > 1.24$ exhibit significant changes in electronic structure leading to a dramatic increase in $\rho(x)$ up to 2710 $\mu\Omega$ cm for $x = 1.50$. Negative TCR, no superconducting transition above 2 K, and a decrease in $H$ and $E$ are observed for HfN$_x$ with $x > 1.38$.

II. EXPERIMENTAL PROCEDURE

HfN$_x$(001) layers, 0.5 $\mu$m thick, are grown in a loadlocked multi-chamber UHV stainless-steel magnetically unbalanced magnetron sputter deposition system described in detail in Ref. 27. The pressure in the sample introduction chamber is reduced to less than $5 \times 10^{-8}$ Torr ($7 \times 10^{-8}$ Pa), using a 50 l s$^{-1}$ turbo-molecular pump (TMP), prior to initiating substrate exchange into the deposition chamber which has a base pressure of $5 \times 10^{-10}$ Torr ($7 \times 10^{-8}$ Pa), achieved using a 500 l s$^{-1}$ TMP. The target is a 7.62-cm-diam water-cooled Hf disk, 99.9% pure (the only detectable contaminant is Zr, the usual impurity in Hf). Sputter deposition is carried out at a constant power of 150 W and a total pressure of 20 mTorr (2.67 Pa) in mixed atmospheres consisting of Ar (99.9999% pure) and N$_2$ (99.999%) with a target-to-substrate separation of 5 cm. The gases are introduced through high precision solenoid valves while the pressure is measured by a capacitance manometer and maintained constant with an automatic mass-flow controller.

The substrates are polished 10×10×0.5 mm$^3$ MgO(001) wafers cleaned with successive rinses in ultrasonic baths of trichloroethane, acetone, ethanol, and deionized water and blown dry with dry N$_2$. They are then mounted on resistively heated Ta platens using Mo clips and inserted into the sample introduction chamber for transport to the growth chamber where the wafers are thermally degassed at 800 °C for 1 h, a procedure shown to result in sharp MgO(001)1×1 reflection high-energy electron diffraction patterns.\textsuperscript{28} Just prior to initiating deposition, the target is sputter etched for 5 min with a shutter shielding the substrate. The HfN$_x$(001) layers are grown at $T_s = 650$ °C, including the contribution due to plasma heating. $T_s$ is measured with a pyrometer calibrated by a thermocouple bonded to a HfN-coated MgO substrate. Following deposition, the samples are allowed to cool below 100 °C before transferring them to the load-lock chamber which is then backfilled with dry N$_2$.

A pair of external Helmholtz coils with Fe pole pieces is utilized to controllably unbalance the magnetic circuit in the magnetron sputtering system through the addition of a uniform axial magnetic field $B_{\text{ext}}$ in the region between the target and the substrate. This provides the ability to shape the discharge near the substrate and allows independent control of the energy and flux of ions incident at the growing film with negligible effect on the target sputtering rate.\textsuperscript{27}

Electrostatic probes are used to measure plasma characteristics in the vicinity of the substrate during film growth following the procedure described in Ref. 27. The ion flux $J_i$, plasma potential $V_p$, and floating potential $V_f$ are obtained from the current-voltage characteristics of a 6-mm-diam stainless-steel disk probe mounted in a through hole drilled in the center of a special substrate plate. The surface of the probe is coincident with the substrate surface and is electrically isolated from the platen by a 0.25 mm vacuum gap. In this geometry, the actual current densities at the substrates are measured irrespective of the value of $B_{\text{ext}}$. To minimize edge effects, the probe and substrate platen are maintained at the same potential with respect to the grounded chamber.
The film growth experiments are carried out with $B_{\text{ext}} = 180$ G while varying $f_{\text{N}_2}$ from 0.04 to 1. Stoichiometric HfN(001) layers are obtained with $f_{\text{N}_2} = 0.07$. The ion-to-Hf flux ratio $J_i/J_{\text{Hf}}$, incident at the growing film ranges from 5 with $f_{\text{N}_2} = 0.04$ to 69 with $f_{\text{N}_2} = 1$, while an applied bias $V_e$ is used to maintain the ion energy, $E_i = e(V_e - V_p)$, constant at 25 eV. The vast majority of the ions incident at the substrate and growing film during deposition experience the full substrate sheath potential since the mean free paths for Ar$^+$ and N$^+$ charge exchange collisions, $\lambda = 6$ and $\approx 8$ mm, respectively, are much larger than the sheath width, estimated from the Child–Langmuir equation to be $0.3–0.5$ mm.

HfN$_x$(001) layer compositions are determined by RBS. The probe beam consists of 2 MeV He$^+$ ions incident at $22.5^\circ$ relative to the sample surface normal with the detector set at a $150^\circ$ scattering angle. The total accumulated ion dose is $22.5^\circ$ relative to the sample surface normal with the detector provides an angular beam divergence of $\pm 1$ arcsec with a wavelength spread $\lambda = 0.154$ nm.

A Rigaku D-Max diffractometer operated with Cu Ka radiation ($\lambda = 0.154$ nm and $\lambda = 0.154$ nm) is utilized for $\omega-2\theta$, $\omega$-rocking, and glancing angle (GA) XRD measurements. The $\omega-2\theta$ scans are carried out in the powder diffraction mode with an incident slit divergence of 0.05$^\circ$ resulting in a resolution of 0.01$^\circ$ $2\theta$. GA-XRD $2\theta$ scans, which are sensitive to the presence of small volume fractions of randomly oriented grains, are obtained using an x-ray incidence angle $\omega$ of $4^\circ$ and a slit divergence of $1^\circ$.

A high-resolution Philips X-pert MRD diffractometer with a Cu Ka$_1$ source ($\lambda = 0.154$ nm) and a four-crystal Ge(220) monochromator is used for the $\phi$-scan and HR-RLM analyses. A two-crystal Ge(220) analyzer in front of the detector provides an angular beam divergence of $\pm 0.05^\circ$. HR-XRD $\phi$ scans from HfN$_x$ and MgO are obtained in the parallel-beam mode with $\omega$ and $2\theta$ angles set to detect the 220 peaks at a tilt angle of $45^\circ$ with respect to the surface normal. Lattice parameters $a$, along the growth direction, in-plane lattice parameters $a_t$, and residual strains $e$ are obtained from HR-RLMs around 113 asymmetric reflections. The reciprocal lattice maps consist of a series of $\omega-2\theta$ scans acquired at different $\omega$ offsets.

Four-point probe measurements are used to determine room-temperature resistivities $\rho_{\text{room}}$ of HfN$_x$(001) as a function of $x$. Temperature dependent resistivities between 2 and 300 K, as well as carrier type and density, are obtained using a Quantum Design physical property measurement system with a magnetic field of 7 T. In order to eliminate the effect of the HfN$_x$ native oxide layer in these experiments, electrical contacts are fabricated in an FEI Strata DB-235 dual-beam focused ion beam system by Ga$^+$-ion etching four 2-$\mu$m-diam holes, in the van der Pauw geometry, and then filling the holes with Pt without breaking vacuum.

The hardness $H$ and elastic modulus $E$ of HfN$_x$ layers are determined from nanoindentation responses measured with a Hysitron TriboScope instrument attached to an atomic force microscope. The area function of the triangular Berkovich diamond tip is calibrated following the procedure described in Ref. 33 and the calibration checked using epitaxial

![Fig. 1. XRD $\omega$-2$\theta$ scans from 0.5-um-thick HfN$_x$ layers grown on MgO(001) at 650 $^\circ$C: (a) $x = 0.80$, (b) $x = 0.85$, (c) $x = 0.90$, (d) $x = 1.00$, (e) $x = 1.20$, (f) $x = 1.38$, and (g) $x = 1.50$.](image)

TiN/MgO(001) layers of known hardness and the same thickness as the HfN$_x$ samples. The maximum load is varied from 0.05 to 9 mN with a minimum of ten indent sequences for each load.

### III. RESULTS AND DISCUSSION

Initial HfN$_x$ deposition experiments were carried out as a function of the N$_2$/Ar fraction $f_{\text{N}_2}$ from 0.04 to 1 and the resulting layers analyzed by RBS and XRD. RBS results show that the N/Hf ratio of HfN$_x$ layers grown on MgO(001) at $T_s = 650$ $^\circ$C varies continuously from $x = 0.80$ with $f_{\text{N}_2} = 0.04$ to $x = 1.50$ with $f_{\text{N}_2} = 1$. Stoichiometric HfN$_x$ layers with $x = 1.00\pm0.03$ are obtained using $f_{\text{N}_2} = 0.07$. Figure 1 shows typical $\omega-2\theta$ XRD scans from HfN$_x$ layers with $x = 0.80, 0.85, 0.90, 1.00, 1.20, 1.38$, and 1.50. All scans are offset vertically and the peak intensities of the $x = 0.80$ and 1.50 layers are increased by $10^\times$ and $100^\times$, respectively. The 002 $\langle 100 \rangle$ and $\langle 101 \rangle$ reflections from HfN$_x$ and MgO are observed with the HfN$_x$ peak positions continuously shifting to higher $2\theta$ values at increasing $x$ due to corresponding changes in film composition and residual strain. Stoichiometric HfN$_x$ layers ($x = 1$) have the highest 002 peak intensity, with $I_{002} = 8.8 \times 10^4$ cps, and the narrowest full width at half maximum (FWHM) intensity, $\Gamma_{002} = 0.05^\circ$. $I_{002}$ decreases and $\Gamma_{002}$ increases with both $x < 1$ and $x > 1$; e.g., $I_{002} = 2.6 \times 10^4$ cps and $\Gamma_{002} = 0.26^\circ$ for $x = 0.85$ while $I_{002} = 1.4 \times 10^4$ cps and $\Gamma_{002} = 0.22^\circ$ for $x = 1.38$.

Figure 2 shows 002 $\omega$-rocking curves, offset vertically, for the same seven films corresponding to the $\omega-2\theta$ scans in Fig. 1. The FWHM is a minimum, $\Gamma_{002} = 0.58^\circ$, with $x = 1.00$ and increases continuously for both increasing $x$ ($\Gamma_{002} = 5.3^\circ$ with $x = 1.50$) and decreasing $x$ ($\Gamma_{002} = 1.8^\circ$ with $x = 0.80$). XRD $\phi$ scans from HfN$_x$ layers with $0.80 \leq x \leq 1.38$ exhibit four 90°-rotated 220 peaks at angles which are identical for both MgO and HfN$_x$ (see, for example, Fig. 3). The combination of these results show that HfN$_x$(001) layers with $x$
and parallel, respectively, to the reciprocal diffraction length \(l\) lateral film mosaicity, and the perpendicular x-ray coherence \(x\) between 0.80 and 1.38 are plotted in Fig. 4.

The relaxed lattice constants and residual strains of epitaxial HfN(001) layers with \(x = 0.80, 1.00, 1.20, 1.24, 1.38,\) and 1.50. Scans obtained from all layers grown with \(x \approx 1.20\) are completely featureless [see, for example, Figs. 5(a)–5(c)], showing that they are single phase. However, layers grown with \(1.24 \leq x \leq 1.38\) exhibit a broad GA-XRD peak at \(2\theta = 28^\circ\) [Figs. 5(d) and 5(e)] arising from the presence of a randomly oriented second phase. The position of these new peaks ranges from \(27.49^\circ\) with \(x = 1.24\) to \(28.58^\circ\) with \(x = 1.38\). Thus, HfN layers with \(1.24 \leq x \leq 1.38\) are two-phase mixtures consisting of NaCl-structure HfN(001) together with N-rich inclusions. For layers with \(x = 1.50\), there are no observable diffraction peaks in either \(\omega-2\theta\) [Fig. 1(g)] or \(\phi\) scans. However, GA-XRD results [see Fig. 5(f)] contain (111), (200), (220), and (311) diffraction peaks from polycrystalline NaCl-structure HfN, as well as a second phase peak at \(2\theta = 31.68^\circ\).

The highest crystalline quality, corresponding to the largest values of \(\xi_1\) and \(\xi_\perp\), is obtained for stoichiometric HfN(001) layers. \(\xi_1\) and \(\xi_\perp\) for these layers are 22 and 185 nm, respectively. Measured x-ray coherence lengths decrease with both higher and lower N/Hf values to \(\xi_1 = 7\) nm and \(\xi_\perp = 14\) nm for HfN_{0.30}(001) and \(\xi_1 = 15\) nm and \(\xi_\perp = 44\) nm for HfN_{1.38}(001). Previously reported results for 345-nm-thick ScN(001) layers\(^{25}\) are \(\xi_1 = 15\) nm with \(\xi_\perp = 57\) nm, while \(\xi_1 = 21\) nm with \(\xi_\perp = 112\) nm for 500-nm-thick TaN(001) layers\(^{21}\) and \(\xi_1 = 86\) nm with \(\xi_\perp = 142\) nm for 300-nm-thick TiN(001) layers.\(^{34}\) A comparison of these results shows that both in-plane and out-of-plane x-ray coherence lengths for stoichiometric HfN(001) are higher than those of ScN(001) and TaN(001), while \(\xi_\perp\) for HfN(001) is even higher than that of TiN(001). Considering the larger film/substrate mismatch between HfN and MgO, 7.46%, compared to 6.90% for ScN, 2.85% for TaN, and only 0.72% for TiN on MgO(001), stoichiometric HfN(001) layers are clearly of high crystalline quality with relatively low mosaicity.\(^{35}\)

Figure 5 is a series of GA-XRD scans from HfN\(_x\) layers with \(x = 0.80, 1.00, 1.20, 1.24, 1.38,\) and 1.50. Scans obtained from all layers grown with \(x \approx 1.20\) are completely featureless [see, for example, Figs. 5(a)–5(c)], showing that they are single phase. However, layers grown with \(1.24 \leq x \leq 1.38\) exhibit a broad GA-XRD peak at \(2\theta = 28^\circ\) [Figs. 5(d) and 5(e)] arising from the presence of a randomly oriented second phase. The position of these new peaks ranges from \(27.49^\circ\) with \(x = 1.24\) to \(28.58^\circ\) with \(x = 1.38\). Thus, HfN layers with \(1.24 \leq x \leq 1.38\) are two-phase mixtures consisting of NaCl-structure HfN(001) together with N-rich inclusions. For layers with \(x = 1.50\), there are no observable diffraction peaks in either \(\omega-2\theta\) [Fig. 1(g)] or \(\phi\) scans. However, GA-XRD results [see Fig. 5(f)] contain (111), (200), (220), and (311) diffraction peaks from polycrystalline NaCl-structure HfN, as well as a second phase peak at \(2\theta = 31.68^\circ\).

The relaxed lattice constants and residual strains of epitaxial HfN(001) layers are determined as a function of \(x\) from analyses of HR-RLM results. A typical HR-RLM about an asymmetric 113 reflection is shown in Fig. 6 for a layer with \(x = 1.00\). Diffracted intensity distributions are plotted as iso-intensity contours as a function of the reciprocal lattice

---

**FIG. 2.** XRD 002 \(\omega\)-rocking curves from 0.5-\(\mu\)m-thick HfN\(_x\) layers grown on MgO(001) at 650 °C: (a) \(x = 0.80\), (b) \(x = 0.85\), (c) \(x = 0.90\), (d) \(x = 1.00\), (e) \(x = 1.20\), (f) \(x = 1.38\), and (g) \(x = 1.50\).

**FIG. 3.** XRD 220 \(\phi\) scans from an epitaxial stoichiometric HfN layer grown on MgO(001) at 650 °C.

**FIG. 4.** In-plane \(\xi_1\) and perpendicular \(\xi_\perp\) x-ray coherence lengths for HfN\(_x\) layers grown at 650 °C on MgO(001) as a function of \(x\).

The in-plane x-ray coherence length \(\xi_1\), a measure of the lateral film mosaicity, and the perpendicular x-ray coherence length \(\xi_\perp\), limited by both the film thickness and vertical mosaicity, are determined using the relationships\(^{28}\)

\[
\xi_1 = \frac{2\pi}{\Delta g_\perp} = \frac{\lambda}{2\Gamma_x \sin \theta} \quad (1)
\]

and

\[
\xi_\perp = \frac{2\pi}{\Delta g_\parallel} = \frac{\lambda}{\Gamma_x \cos \theta} \quad (2)
\]

\(\Delta g_\perp\) and \(\Delta g_\parallel\) are the widths of the Bragg reflections perpendicular and parallel, respectively, to the reciprocal diffraction vector \(g\) and \(\lambda\) is the x-ray wavelength. Results for HfN\(_x\) layers with \(x\) between 0.80 and 1.38 are plotted in Fig. 4.
k vectors parallel and \( k_{\perp} \) perpendicular to the surface. \( k_i \) and \( k_{\perp} \) are related to peak positions in \( \omega-2\theta \) space through the relationships:\(^{36}\)

\[
k_i = 2r_E \sin(\theta)\cos(\omega-\theta)
\]

and

\[
k_{\perp} = 2r_E \sin(\theta)\sin(\omega-\theta),
\]

where \( r_E \) is the Ewald sphere radius given by \( r_E = 1/\lambda \). For a 113 reflection from an 001 oriented NaCl-structure sample, the in-plane \( a_{\parallel} \) and out-of-plane \( a_{\perp} \) lattice parameters are given by \( a_{\parallel} = \sqrt{2}/k_i \) and \( a_{\perp} = 3/k_{\perp} \). Relaxed bulk HfN\(_{1.00}\) lattice constants \( a_o \) are determined from \( a_{\parallel} \) and \( a_{\perp} \) values through the relationship

\[
a_o = a_{\parallel} \left( 1 - \frac{2\nu(a_{\perp} - a_{\parallel})}{a_{\parallel}(1 + \nu)} \right),
\]

where \( \nu \) is the film Poisson ratio. The residual in-plane strain \( \varepsilon_{\parallel} \) is defined as

\[
\varepsilon_{\parallel} = \frac{a_{\parallel} - a_{o}}{a_{o}}.
\]

The fact that the substrate and layer peaks in Fig. 6 are misaligned along \( k_{\parallel} \) indicates the presence of in-plane-strain relaxation due to misfit dislocations. All layers are found to be nearly fully relaxed at the growth temperature and contain a small amount of residual compressive strain \( \varepsilon_{\parallel} \), which ranges from \(-0.05\% \) for HfN\(_{0.80}\) to \(-0.86\% \) for HfN\(_{1.38}\), due to differential thermal contraction during sample cooling following deposition. Although the N-rich samples tend to have slightly larger compressive strains, there is no obvious trend in \( \varepsilon_{\parallel} \) as a function of \( x \).

The vertical separation between the film and substrate diffracted intensity distributions in Fig. 6 corresponds to a lattice mismatch in the growth direction of 7.43\% yielding an out-of-plane HfN\(_{1.00}(001)\) lattice constant \( a_{\perp} = 0.4536 \) nm. The in-plane lattice constant \( a_{\parallel} \) is 0.4506 nm. Substituting these values together with an estimated Poisson ratio of 0.25 into Eq. (5), we calculate a relaxed lattice constant \( a_o \) of 0.4524 nm for HfN. This is very close to the published value for bulk powder samples, 0.4525 nm.\(^{37}\)

While the Poisson ratio \( \nu \) for HfN is unknown, \( \nu \) values for related cubic TM nitrides vary only from 0.21 for TiN\(^{38}\) to 0.29 for CrN.\(^{39}\) We chose an average value of 0.25 for determining the relaxed lattice constant \( a_o \) of HfN. The uncertainty in \( a_o \) introduced by \( \nu_{\text{HfN}} \) is \( \pm 0.0002 \) nm (\( \pm 0.004\% \)).

Figure 7 shows that \( a_o(x) \) for HfN\(_{1.00}\) decreases linearly from 0.4543 nm with \( x = 0.80 \) to 0.4517 nm with \( x = 1.20 \) to 0.4504 nm with \( x = 1.38 \). From the results in Fig. 7, it is clear that the rate of change in the normalized HfN\(_{x}\) lattice constant as a function of \( x \), \( \zeta = d(a_o(x)/a_o(\text{HfN})) / dx \), where \( a_o(\text{HfN}) \) is the relaxed lattice constant of stoichiometric HfN, is quite small: \( \zeta \approx -0.012 \). Previous reports for bulk HfN\(_{x}\) samples synthesized by nitriding Hf powder in NH\(_3\) at 1000 °C give \( a_o(x) \) between 0.4524 nm for \( x = 0.85 \) and 0.4507 nm for \( x = 1.12 \),\(^{19}\) corresponding to \( \zeta = -0.016 \). These values are within the range of our results. A linear decrease in \( a_o \) vs. \( x \) has also been reported for the group IVB-VA compound TiN\(_{x}\) (1.0 \( \leq \) \( x \) \( \leq \) 1.16)\(^{5}\) and the VB-VA nitride TaN\(_{x}\) (0.94 \( \leq \) \( x \) \( \leq \) 1.37),\(^{21}\) with \( \zeta \) values of \(-0.038 \) and \(-0.015 \), respectively.

For TiN\(_{x}\), \( a_o(x) \) is a maximum at the stoichiometric composition and decreases with both higher and lower N/Ti.

---

**FIG. 5.** GA-XRD 2θ scans obtained from 0.5-μm-thick HfN layers grown on MgO(001) at 650 °C: (a) \( x = 0.80 \), (b) \( x = 1.00 \), (c) \( x = 1.20 \), (d) \( x = 1.24 \), (e) \( x = 1.38 \), and (f) \( x = 1.50 \).

**FIG. 6.** HR-RLM around the 113 reflection from an epitaxial stoichiometric HfN layer grown at 650 °C on MgO(001).
values due, according to ab initio density functional calculations, to the presence of Ti and N vacancies. However, \( a_x(x) \) in HfN\(_x\)(001) continuously decreases with \( x \) over the entire phase field between 0.80 and 1.38 while \( \xi \) for HfN\(_x\) is much smaller than that of TiN\(_x\). We attribute this behavior of HfN\(_x\) to a combination of vacancies and antisite defects. Hf has, in comparison to Ti and Ta, a much higher atomic volume. Assuming the same atomic density for fcc and hcp Hf lattices, metallic fcc Hf would have a lattice constant of 0.4479 nm, which is very close to that of HfN\(_x\) (0.4525 nm). This difference, only 1.02%, is much smaller than those between Ti and TiN (2.36%), and Ta and TaN (3.70%). Therefore, N vacancies in HfN\(_x\) have little effect on \( a_x(x) \). We obtain a \( \xi \) value of 0.01 by assuming a perfectly linear \( a_x(x) \) dependence (Vegard’s rule) from fcc Hf with \( a_0 = 0.4479 \) nm to stoichiometric HfN with \( a_s = 0.4525 \) nm. This is a crude estimate, but indicates that the small \( \xi \) value for \( x < 1 \) can be explained primarily by N vacancies.

In the case of overstoichiometric samples, however, \( a_x(x) \) cannot be explained by vacancies alone, since Hf vacancies in HfN\(_x\)(001) layers with \( x > 1 \) would result in a much larger \( \xi \) value. We therefore propose that antisite defects are also present. Antisite substitutions have previously been reported for TaN\(_x\)(001)\(^{21} \) with 0.94 \( \leq x \leq 1.22 \). We expect antisite defects to be present, to some degree, over the entire HfN\(_x\) composition range 0.80 \( \leq x \leq 1.38 \), and to be particularly important for samples with \( x > 1 \). These conclusions are consistent with carrier density measurements as a function of \( x \) presented below. We note that attempting to explain the composition of overstoichiometric HfN\(_x\) having \( x > 1.3 \) with Hf vacancies alone requires more than one vacancy per four Hf lattice sites. In the NaCl structure, this would result in nearest-neighbor vacancy sites which is a very high energy configuration.

HfN\(_x\)(001) room-temperature resistivities \( \rho_{300K} \) are plotted as a function of \( x \) in Fig. 8(a). The minimum resistivity for HfN\(_x\), \( \rho_{300K} = 14.2 \) \( \mu \Omega \) cm, is obtained at the stoichiometric composition. This is the lowest reported value for HfN and is comparable with that of TiN, the most common metallic TM nitride, for which \( \rho_{30N} = 13 \) \( \mu \Omega \) cm.\(^{6,9} \) For understoichiometric HfN\(_x\) layers, \( \rho_{300K} \) decreases from 140 \( \mu \Omega \) cm with \( x = 0.80 \) to 14.9 \( \mu \Omega \) cm with \( x = 0.95 \). For \( x > 1 \), \( \rho_{300K} \) increases from 20.9 \( \mu \Omega \) cm with \( x = 1.12 \) to 2710 \( \mu \Omega \) cm with \( x = 1.50 \).

The overall composition dependence of the resistivity of HfN\(_x\)(001), with the lowest value at \( x = 1 \), is typical for TM nitrides, including the other members of the IVB-VA group, TiN\(_x\)\(^{4,15} \) and ZrN\(_x\).\(^{15} \) The increase in \( \rho \) as the composition deviates from stoichiometry is primarily due to scattering from point defects, including N and Hf vacancies and antisite defects. An additional contribution to the resistivity increase for \( x > 1 \) is a decreasing carrier density as discussed below. From the XRD results, HfN\(_x\) layers with \( x \geq 1.24 \) contain N-rich inclusions. This is reflected in the dramatic increase in \( \rho(x) \) for \( x > 1.24 \) [see inset in Fig. 8(a)].

\( \rho \) vs. \( T \) plots between 2 and 300 K are shown in Fig. 8(b) for HfN\(_x\) layers with \( x = 0.80, 0.90, 1.00, 1.20, 1.27, 1.38, \) and 1.50. The temperature coefficient of resistivity (TCR), defined as...
ever, TCR becomes negative for HfN, with $0.80 \leq x \leq 1.27$. Films in this composition range exhibit metallic behavior with a constant resistivity $\rho_o$ at low temperature followed by the onset of phonon scattering near 50 K. The lowest $\rho_o$ value, $3.5 \mu\Omega$ cm, occurs for stoichiometric HfN(001). $\rho(x)$ increases with both $x < 1$ and $x > 1$ due to the correspondingly higher point defect densities, resulting in smaller elastic scattering lengths, and thus lower carrier mobilities. However, TCR becomes negative for HfN layers with $x \geq 1.38$. We attribute this to weak localization of conduction electrons resulting from the large perturbation in the periodic crystal potential associated with the very high densities of randomly distributed point defects.\(^{31,42}\) Conduction electrons scattered from random defects experience destructive self-interference. At higher temperatures, this effect becomes less pronounced, as scattering from phonons begins to dominate, thus reducing the electron coherence length and, in turn, the effect of self-interference. Note that while the TCR for HfN\(_{1.38}\) is slightly negative ($-1.9 \times 10^{-8} \Omega$ cm K\(^{-1}\)), the resistivity changes by less than 2% between 10 and 300 K as the effects of phonon scattering and carrier localization approximately cancel each other. TCR becomes more negative with further increases in $x$ ($-4.9 \times 10^{-6} \Omega$ cm K\(^{-1}\) with $x = 1.50$) due to the higher defect densities.

HfN\(_x\)(001) superconducting transition temperatures $T_c(x)$ are plotted in Fig. 9. The highest critical temperature, $T_c = 9.18$ K, is obtained for stoichiometric HfN(001). $T_c$ values for other stoichiometric TM nitrides range from <1.4 K for ScN\(^6\) and YN\(^4\) to 5.35 K for TiN(001),\(^9\) 8.45 K for TaN(001),\(^21\) and 17.3 K for NbN.\(^{45}\) $T_c$ for HfN\(_x\)(001) continuously decreases with both over- and understoichiometry to values of 4.78 K with $x = 0.80$ and 7.65 K with $x = 1.20$. HfN\(_{1.38}\) and HfN\(_{1.50}\) layers are not found to be superconducting above 2 K. We interpret the decrease in $T_c(x)$ for HfN\(_x\)(001) as resulting from a decrease in the attractive electron-electron interaction strength since the increased density of point defects with both $x > 1$ and $x < 1$ leads to a corresponding localization of vibrational modes which in turn reduces the phonon-mediated long-range effective electron-electron coupling. The large difference in mass involved in the N (14 amu) on Hf (178.5 amu) antisite substitution (and, conversely, in the Hf on N antisite) and the lower lattice constants associated with overstoichiometric HfN$_x$ may also contribute to the observed trend. A similar composition dependence, with the highest $T_c$ obtained for near-stoichiometric layers, has been reported for other TM nitrides and carbides including TiN, TaN, VN, NbN, NbC, and TaC.\(^{21,43}\)

Hall-effect measurements are carried out at 10 and 300 K. The Hall coefficients $R_H$ of all HfN\(_x\) ($0.80 \leq x \leq 1.50$) samples are negative indicating that the charge carriers are electrons. The effective carrier density $n_{\text{eff}}$ is determined from $R_H$ through the relationship

$$n_{\text{eff}} = -\frac{1}{e} \frac{j_x \cdot B_z}{e \cdot E_y},$$

where $e$ is the elementary charge, $j_x$ is the applied current density, $B_z$ is the magnetic field in the $z$ direction, and $E_y$ is the measured Hall field. Figure 10 is a plot of $n_{\text{eff}}$ vs $x$ at 10 and 300 K. Room-temperature $n_{\text{eff}}$ values decrease with $x$ from $1.4 \times 10^{22}$ cm\(^{-3}\) for $x = 0.90$ to $2.6 \times 10^{20}$ cm\(^{-3}\) for $x = 1.50$. In defect-free stoichiometric HfN, each Hf atom provides three electrons to the conduction band, resulting in one charge carrier per formula unit and, in the absence of point defects, a carrier density of $4.32 \times 10^{22}$ cm\(^{-3}\). Each Hf vacancy in HfN\(_x\) results in a net loss of four conduction band electrons, giving rise to a dramatic reduction in carrier density for overstoichiometric samples. Only considering Hf vacancies within this simple charge-counting approximation, the carrier density of HfN\(_x\) should reach zero at $x = 1.33$. However, our results show that HfN\(_x\) layers with $x > 1.33$ still have high concentrations of conduction electrons ($n_{\text{eff}} = 4.6 \times 10^{20}$ cm\(^{-3}\) for HfN\(_{1.38}\) and $2.6 \times 10^{20}$ cm\(^{-3}\) for HfN\(_{1.50}\)). In contrast to the effect of Hf vacancies in overstoichiometric HfN\(_x\), every N\(_{\text{Hf}}\) antisite provides two electrons to the conduction band. Considering both Hf vacancies and N antisites, measured $n_{\text{eff}}$ and $x$ values yield Hf vacancy and N\(_{\text{Hf}}\) antisite densities of $8.9 \times 10^{21}$ cm\(^{-3}\) and $1.7 \times 10^{21}$ cm\(^{-3}\) for HfN\(_{1.38}\) and $8.8 \times 10^{21}$ cm\(^{-3}\) and $3.4 \times 10^{21}$ cm\(^{-3}\) for HfN\(_{1.50}\). Thus,
the coexistence of vacancies and antisites can, to first order, explain the \(n_{\text{eff}}(x)\) results for overstoichiometric HfN\(_x\) samples. Additionally, the second-phase inclusions in HfN\(_x\) layers with \(x \approx 1.24\) may also contribute to the observed \(n_{\text{eff}}(x)\) behavior.

From the results in Fig. 10, \(n_{\text{eff}}\) for HfN\(_x\) with \(x\) between 0.80 and 1.38 is essentially independent of temperature between 10 and 300 K. In contrast, the effective carrier density of HfN\(_{1.50}\) at 10 K, \(1.4 \times 10^{20} \text{ cm}^{-3}\), is only approximately half of the room-temperature value, consistent with the temperature-dependent resistivity data indicating carrier localization for the \(x = 1.50\) sample. The ratio of the measured effective carrier density (\(n_{\text{eff}} = 4.8 \pm 0.2 \times 10^{21} \text{ cm}^{-3}\)) to the \(d\)-band electron density (\(n = 4.32 \times 10^{22} \text{ cm}^{-3}\)) for stoichiometric HfN(001), \(n_{\text{eff}}/n = 0.11\), is relatively small compared to ratios of 1.6 and 1.1 for the third-row TM nitrides TiN(001) and ScN(0001).\(^9\) We attribute this difference to HfN having a more complex Fermi surface containing pockets corresponding to both electrons and holes. Such behavior is related to the fact that the lowest 5d conduction band in HfN is relatively flat and likely exhibits some 4f-character.\(^1\,^3\)

The hardness \(H\) and elastic moduli \(E\) of HfN\(_x\) layers are determined from nanoindentation measurements following the procedure described in Ref. 7. Figure 11(a) shows a typical set of load-displacement curves from an epaxial HfN(001) layer. Multiple loading cycles are used with the sample unloaded to 10% of the peak load each time, and maximum peak loads ranging from 0.05 to 9 mN. A 10 s hold segment following the final unloading allowed a correction for thermal drift in the instrument. The total time required for the full set of indents is approximately 1 min.

\(H\) and \(E\) values for HfN\(_x\) layers grown on MgO(001) as a function of \(x\) are plotted in Fig. 11(b). \(H\) for stoichiometric HfN(001), 25.2±0.7 GPa, is higher than that of TiN(001), 20±0.8 GPa,\(^3\) and ScN(001), 21±1.1 GPa,\(^25\) but lower than that of CrN(001), 28.5±1.0 GPa,\(^23\) and TaN(001), 30.8±0.9 GPa.\(^44\) For HfN\(_x\) with \(x = 0.90\)\(< x \leq 1.32\), \(H\) increases for both over- and understoichiometry to values of 29.5 GPa with \(x = 0.90\) and 32.0 GPa with \(x = 1.32\). These results for \(H\) vs \(x\) are consistent with an increase in the defect density as discussed earlier. Hardness, a measure of a material’s resistance to the nucleation and glide of dislocations, is commonly observed in metals to increase with point-defect concentrations due to dislocation pinning at defect sites.\(^45\) However, \(H(x)\) begins to decrease again with both \(x = 0.85\) and \(x \approx 1.38\). We attribute the decrease in \(H\) with \(x = 0.85\) to reduced crystalline quality and the high N vacancy concentration lowering the average bond strength. Thus, at sufficiently large understoichiometry, these effects overcome the defect-induced hardening and \(H(x)\) decreases. The decrease in \(H\) for HfN\(_x\) layers with \(x \approx 1.38\) can be accounted for by the increasing volume fraction of the N-rich second phase.

For HfN\(_x\) with \(0.90 \leq x \leq 1.32\), \(E\) values remain essentially constant at 438±20 GPa. Similar to the results for \(H(x)\), however, \(E(x)\) decreases with both \(x = 0.85\) and \(x \approx 1.38\). \(E\) for stoichiometric HfN(001) is 450±9 GPa, nearly identical to values for other group IVB and VB TM nitrides (e.g., \(E\) for TiN(001) is 445±38 GPa\(^3\) while TaN(001) has a modulus of 457±16 GPa\(^44\)). This is expected based upon the similarity of the interatomic bonding in these compounds which is dominated by N 2p bands and CrN—TiN—TaN—have relatively high elastic moduli, \(E \approx 450\) GPa. In contrast, ScN (group IIIIB), with \(E = 356±18\) GPa,\(^3\) has empty \(d\) bands and CrN (group VIB), with \(E = 405±15\) GPa,\(^23\) has three electrons per formula unit which form localized magnetic moments and completely fill one subband (i.e., one spin direction) of the \(t_{2g}\,\text{Cr}\,3d\) bands,\(^24\) resulting in lower elastic moduli.

### IV. CONCLUSIONS

HfN\(_x\) layers with \(x\) ranging from 0.80 to 1.50 are grown on MgO(001) at \(T_i = 650\) °C by UHV magnetically unbalanced reactive magnetron sputter deposition in mixed N\(_2\)/Ar discharges. Layers with \(0.80 \leq x \leq 1.20\) crystallize in the B1 NaCl structure and exhibit an epitaxial cube-on-cube relationship with the substrate: \(\text{001}_{\text{HfN}}\parallel\text{[001]}_{\text{MgO}}\) and \([100]_{\text{HfN}}\parallel[100]_{\text{MgO}}\). The films are nearly fully relaxed and of high crystalline quality with a relaxed lattice constant which decreases linearly from 0.4543 nm with \(x = 0.80\) to 0.4517 nm with \(x = 1.20\). HfN\(_x\) layers with \(x\)
\( \rho \) of 14.2 \( \mu \Omega \) cm and \( \rho(x) \) increases continuously for layers with both \( x < 1 \) and \( x > 1 \). The highest resistivity, \( \rho = 2710 \mu \Omega \) cm, is obtained for HfN\(_{1.50}\) which consists of polycrystalline NaCl-structure HfN, and the N-rich second phase.

HfN\(_x\)(001) with 0.80 \( \leq x \leq 1.20 \) exhibits metallic behavior with positive temperature coefficients of resistivity and temperature-independent carrier densities. They are also superconducting with the highest critical temperature, 9.18 K, obtained for layers with \( x = 1.0 \). The hardness \( H \) and elastic modulus \( E \) of stoichiometric HfN(001) are 25.2 and 450 GPa, respectively. \( H \) initially increases for both over- and understoichiometric layers due to defect-induced hardening, while \( E \) remains approximately constant since the bond structure is not strongly affected by film composition within this range.

The resistivity of HfN\(_x\) increases dramatically with \( x \geq 1.24 \) as the high density of point defects results in the presence of a new N-rich phase which alters the character of the high point defect density.  

**ACKNOWLEDGMENTS**

This research was supported by the U.S. Department of Energy, Division of Materials Science, under Grant No. DEFG02-91ER45439 through the University of Illinois Frederick Seitz Materials Research Laboratory (FS-MRL). The authors also appreciate the use of the facilities of the FS-MRL Center for Microanalysis of Materials, which is partially supported by DOE, at the University of Illinois.