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Elastic constants, Poisson ratios, and the elastic anisotropy of VN(001), (011), and (111) epitaxial layers grown by reactive magnetron sputter deposition

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Elastic constants are determined for single-crystal stoichiometric NaCl-structure VN(001), VN(011), and VN(111) epitaxial layers grown by magnetically unbalanced reactive magnetron sputter deposition on 001-, 011-, and 111-oriented MgO substrates at 430 °C. The relaxed lattice parameter $a_0 = 0.4134 \pm 0.0004$ nm, obtained from high-resolution reciprocal space maps, and the mass density $\rho = 6.1$ g/cm$^3$, determined from the combination of Rutherford backscattering spectroscopy and film thickness measurements, of the VN layers are both in good agreement with reported values for bulk crystals. Sub-picosecond ultrasonic optical pump/probe techniques are used to generate and detect VN longitudinal sound waves with measured velocities $v_{001} = 9.8 \pm 0.3$, $v_{011} = 9.1 \pm 0.3$, and $v_{111} = 9.1 \pm 0.3$ km/s. The VN $c_{11}$ elastic constant is determined from the sound wave velocity measurements as $585 \pm 30$ GPa; the $c_{44}$ elastic constant, $126 \pm 3$ GPa, is obtained from surface acoustic wave measurements. From the combination of $c_{11}$, $c_{44}$, $\rho$, and $\nu$ we obtain the VN $c_{12}$ elastic constant $178 \pm 33$ GPa, the VN elastic anisotropy $A = 0.62$, the isotropic Poisson ratio $\nu = 0.29$, and the anisotropic Poisson ratios $\nu_{001} = 0.23$, $\nu_{011} = 0.30$, and $\nu_{111} = 0.29$. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4881817]

I. INTRODUCTION

NaCl-structure $\delta$-VN$_x$ has an extended single-phase field with $x$ ranging from 0.8 to 1.0 at $T_m = 500$ °C. Polycrystalline VN$_x$ thin films are employed in a variety of applications, including diffusion barriers in microelectronic devices, anodes in rechargeable lithium-ion batteries, and hard wear-, abrasion-, and scratch-resistant coatings. The wide range of VN$_x$ applications stems not only from high hardness and mechanical strength but also from the enhanced physical properties achieved with VN-based nanostructures and alloys. Epitaxial TiN/VN(001) superlattices were the first man-made superhard (defined as $H > 40$ GPa (Refs. 9 and 10)) materials with a hardness, depending on bilayer thickness, of up to $H = 54$ GPa, which exceeds the hardnesses of the two parent compounds by more than a factor of two ($H_{\text{TiN}} = 22$ GPa and $H_{\text{VN}} = 15.9$ GPa). $\delta$-VN$_x$ thin films are employed in a variety of applications, including diffusion barriers in microelectronic devices, anodes in rechargeable lithium-ion batteries, and hard wear-, abrasion-, and scratch-resistant coatings. The wide range of VN$_x$ applications stems not only from high hardness and mechanical strength but also from the enhanced physical properties achieved with VN-based nanostructures and alloys. Epitaxial TiN/VN(001) superlattices were the first man-made superhard (defined as $H > 40$ GPa (Refs. 9 and 10)) materials with a hardness, depending on bilayer thickness, of up to $H = 54$ GPa, which exceeds the hardnesses of the two parent compounds by more than a factor of two ($H_{\text{TiN}} = 22$ GPa and $H_{\text{VN}} = 15.9$ GPa). VN-based solid solutions TiAlVN and CrAlVN, as well as TiAlN/VN superlattices, exhibit enhanced high-temperature ($T > 600$ °C) wear-resistance due to the formation of a lubricious oxide, $V_2O_5$, which, as a result of a low melting point ($T_m = 690$ °C), liquefies during wear applications, thus decreasing the friction coefficient. Recently, alloys of VN with cubic MoN or WN were predicted to provide higher hardness and ductility (i.e., higher toughness) than VN, a result which has been confirmed experimentally for V/MoN alloys by Kindlund et al.

Despite extensive engineering applications, studies of the VN elastic constants are scarce, with reported experimental elastic constants, obtained using acoustic microscopy, and theoretical results based on density functional theory, differing by up to ~150 GPa (~30%).

Here, we determine VN elastic constants using sub-picosecond ultrasonic optical pump/probe measurements, carried out on single-crystal stoichiometric VN(001), VN(011), and VN(111) thin films. The VN layers are grown by magnetically unbalanced reactive magnetron sputter deposition on 001-, 011-, and 111-oriented single-crystal MgO substrates at $T_s = 430$ °C ($T_s/T_m = 0.30$, in which the VN melting point $T_m$ is $2350$ K (Ref. 21)). X-ray diffraction (XRD) $\omega$-20 and $\phi$ scans, with selected area electron diffraction (SAED) and high-resolution cross-section transmission electron microscopy (HR-XTEM) analyses, establish that VN films grow fully relaxed with film/substrate epitaxial relationships: (001) VN|$||$(001)MgO and [100]VN|$||$(100)MgO and [011]VN|$||$(111)MgO, and [111]VN|$||$(111)MgO. The VN relaxed lattice parameter $a_0 = 0.4134 \pm 0.0004$ nm, obtained from high-resolution reciprocal lattice maps (HR-RLM), is in good agreement with reported values for bulk crystals, $a_0 = 0.4134$ nm.

Sub-picosecond acoustics is a well established method for generating and detecting longitudinal sound waves in thin films and nanostructures. The approach, discussed by Vardney and Tauc and Lee et al., employs a focused ~20-μm-diameter laser pulse to locally heat the sample surface by several degrees. The resulting thermal stress relaxes by launching an acoustic strain pulse that reflects from buried interfaces back to the surface where it changes the optical...
reflectivity $R$ by an amount $\Delta R$. Reflectivity changes, due to echoes at constant time intervals $\Delta t$, are measured by means of time-delayed laser probe pulses. VN longitudinal sound velocities $v_{\text{hl}}$ are determined from $\Delta t$ and film thickness measurements. The VN elastic constant $c_{11}$ is then obtained from $v_{\text{hl}}$.28,29

Several surface acoustic wave (SAW) methods have been proposed for obtaining the shear elastic constant $c_{44}$. The techniques utilize a laser-generated SAW, the wavelength $\Lambda$, which is determined by passing the incident beam through a diffraction mask30 or an absorption grating etched into, or deposited onto, the sample.31 Time-delayed laser probe pulses are then used to measure the SAW frequency. In the present experiments, we employ a phase-shift mask with a pump/probe laser system32 to measure SAW velocities from which we determine $c_{44}$ using a Green’s function method.33 The $c_{12}$ elastic constant is then obtained from the combination of $c_{11}$ and $c_{44}$ with $v_{\text{hl}}$, thus yielding the complete set of VN elastic constants. We also determine the VN isotropic and anisotropic Poisson ratios and the elastic anisotropy factor.

II. EXPERIMENTAL PROCEDURE

VN films, approximately 300 nm thick, are grown in a load-locked ultra-high-vacuum (UHV) magnetically unbalanced magnetron sputter deposition system described in detail by Petrov et al.34 The pressure in the sample introduction chamber is reduced below $5 \times 10^{-8}$ Torr ($7 \times 10^{-6}$ Pa), using a 50 l/s 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 TMP.

The target is a 7.62-cm-diameter, water-cooled, 99.95% pure, V disc from Princeton Scientific Corporation. Film deposition is carried out at a constant target power of 100 W in 20 mTorr $N_2$ atmospheres with a target-to-substrate separation of 6 cm. Ultra-high purity $N_2$ (99.9999%) is introduced from high-precision solenoid valves; the pressure is measured by a capacitance manometer and maintained constant through high-precision solenoid valves. The relatively high deposition pressure is chosen to thermalize sputtered atoms using an automatic mass-flow controller. The relatively high deposition pressure is chosen to thermalize sputtered atoms and the majority of ions which are neutralized and reflected from the target.35 As a result, the primary energetic species are ions incident at the growing film with energy $E_i = e[V_f - V_p]$, in which $V_f$ is the negative floating potential and $V_p$ the plasma potential, as discussed below.

The substrates are polished 10 $\times$ 10 $\times$ 0.5 mm$^3$ MgO(001), (011), and (111) wafers which are cleaned and degreased by successive rinses in ultrasonic baths of trichloroethylene, acetone, methanol, and deionized water, and then blown dry in dry $N_2$. The wafers are mounted on resistively heated Ta platens using Mo clips and inserted into the sample introduction chamber for transport to the growth chamber where they are thermally degassed at 800 °C for 1 h, a procedure shown to result in sharp MgO(001)1$\times$1 reflection high-energy electron diffraction patterns.36 Immediately prior to initiating deposition, the target is sputter etched for five min with a shutter shielding the substrate. The film growth temperature is monitored using a 0.25-mm-diameter chromel-alumel thermocouple clamped to the surface of a sacrificial substrate. Stoichiometric VN films are obtained at $T_s = 430$ °C ($T_f/T_m = 0.30$). The film growth rate is 0.10 nm/s, as determined from deposition times and cross-sectional transmission electron microscopy (XTEM) film thickness measurements, calibrated with SiO$_2$/Si(001) layers of known oxide thicknesses. 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 $N_2$.

The magnetic circuit of the magnetron is unbalanced by the addition of a tunable external axial magnetic field which provides the ability to shape the plasma near the substrate.34 This, in turn, allows low-energy (less than the bulk lattice-atom displacement threshold), high-current ion irradiation of the growth surface to enhance adatom mean free paths during deposition which has been shown to increase crystalline quality.37-39 Electroprobe statics are used to measure plasma characteristics, and hence ion-irradiation energies and fluxes, in the vicinity of the substrate during film growth.40 A detailed account of the procedure is given in Ref. 34. The plasma potential ($V_p = -31$ V) and floating potential ($V_f = -43$ V) are determined from current-voltage (I–V) responses of a 1-mm-long W Langmuir probe with a diameter of 0.1 mm. The ion flux ($J_i = 15.8 \times 10^{15}$ ions/cm$^2$s) is obtained from the I–V characteristics of a 6-mm-diam stainless-steel disc mounted in a through-hole drilled in the center of a special substrate platen. 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. To minimize edge effects, the probe and substrate platen are maintained at the same potential with respect to the grounded chamber. The substrate sheath width is estimated from the Child–Langmuir equation as 0.4 mm, much smaller than the mean-free-path for $N_2^+$ charge-exchange collisions.8 $\sim$8 mm. As a result, the vast majority of ions incident at the growth surface experience the full substrate sheath potential and ion irradiation is essentially monoenergetic with $E_i = e[V_f - V_p] = 12$ eV. The ion-to-V flux ratio, $J_i/J_V$, is 28.

As-deposited VN$_x$ film compositions $x$ and mass densities $\rho$ are determined by Rutherford backscattering spectroscopy (RBS). The probe beam consists of 2 MeV He$^+$ ions incident at 22.5° relative to the sample surface normal with a total accumulated ion dose of 100 $\mu$C; the detector is set at a 150° scattering angle. Backscattered spectra are analyzed using the SIMNRA simulation program43 yielding N/V ratios of 1.00 $\pm$ 0.05.

X-ray diffraction (XRD) ω-rocking curves and 022 scans are obtained using a Philips Xpert MRD diffractometer operated with CuK$\alpha$ radiation of wavelength $\lambda = 0.15418$ nm, a Ni filter to remove CuK$\beta$ reflections, and thin-film parallel plate collimator secondary optics. X-ray ω-2θ scans and high-resolution reciprocal lattice maps (HR-RLM) are acquired in a second Philips Xpert MRD diffractometer using CuK$\alpha$ radiation in line focus. The primary optics on the second diffractometer consist of a parabolic mirror and a two-reflection Ge monochromator, providing an angular beam divergence of <12 arc-sec with a wavelength spread of $\Delta \lambda/\lambda = 7 \times 10^{-5}$; a high-speed linear detector serves as the secondary optics.
High-resolution cross-sectional Z-contrast scanning transmission electron microscopy (STEM) analyses are carried out in a CEOS spherical-aberration-corrected JEOL 2200 microscope. An ~0.1-nm-diameter electron probe, generated with a field-emission source operated at 200 keV, is rastered across the specimen while incoherently scattered electrons are collected using a high-resolution high-angle annular dark-field detector. Bright-field XTEM images and corresponding SAED patterns are acquired in a separate JEOL 2100 instrument equipped with a LaB6 crystal field-emission source operated at 200 keV.

Cross-sectional specimens are prepared by gluing films to glass slides and cutting vertical sections. The samples are mechanically ground to thicknesses of ~30 μm and then thinned to electron transparency using a Gatan PIPS ion miller with two 3.5 keV Ar+ beams incident simultaneously from below and above the substrate at shallow angles of 8°. Samples are rotated during ion etching. Final thinning is carried out using 100 eV Ar+ ions.

VN longitudinal sound velocities along the 001, 011, and 111 directions are obtained by optical pump-probe techniques and used, together with the VN mass density ρ, to determine the c_{11} elastic constant. The technique employs sub-picosecond light pulses, generated with a mode-locked Ti:sapphire laser operating at wavelength λ = 785 nm, to locally heat the specimen surface and detect corresponding surface reflectance changes ΔR(t) as a function of time t. Temporal resolution is achieved by splitting the laser pulses into probe and pump beams and offsetting the beams with a time delay. In order to enhance surface reflectance changes, 80-nm-thick Al blanket layers, which serve as optical transducers, are deposited on VN(001), (011), and (111) samples by magnetron sputtering.

To determine SAW velocities v_{SAW} in VN(001), we fabricate polydimethylsiloxane (PDMS) phase-shift mask gratings, (CH3)3Si(O(CH3)2)Si(OSi(CH3)3, with bars along the [100] direction using a Si mold as described in Ref. 32. The gratings have a period of 700 nm with square-wave grooves 350 nm wide and 350 nm in depth. Upon illumination by pump-laser pulses, the phase-shift mask spatially modulates incident light intensity, thereby creating a periodic temperature profile, with corresponding thermal strain, in the VN(001) surface. Relaxation occurs by launching SAW waves, with the same spatial period as the grating, in a direction orthogonal to the grating grooves. SAW velocities, determined from time-shifted probe beams, are used to obtain the VN c_{44} elastic constant. The c_{12} elastic constant is acquired from the combination of 011- and 111-longitudinal sound velocities and c_{11} and c_{44} elastic constants.

III. RESULTS AND DISCUSSION

A. Film nanostructure

Initial film growth experiments, with deposition temperatures T_s between 160 and 460 °C, were carried out to determine the T_s range which yields stoichiometric epitaxial VN layers. XRD ω-2θ, glancing-angle, and azimuthal ϕ-scans reveal that all films are single-phase B1 NaCl-structure VN_{x}, for which RBS results show that the N/V ratio decreases monotonically from 1.36 with T_s = 160°C to 0.88 at 460 °C due to an increasing rate of associative N2 desorption at elevated temperatures.44 Stoichiometric VN films with N/V = 1.00 ± 0.05 are obtained with T_s = 430 °C (T_s/T_m = 0.3). The VN mass density determined from the combination of RBS areal density and XTEM thickness measurements, ρ = 6.1 g/cm³, is in good agreement with reported values for bulk VN.45 All VN films discussed below are grown at 430 °C.

Typical XRD ω-2θ scans from VN films grown on 001-, 011-, and 111-oriented MgO substrates are plotted in Figures 1(a)–1(c) as a function of 2θ between 10 and 110°. ω-2θ scans from VN/MgO(001), Fig. 1(a), exhibit two sets of peaks. Those at 42.86 and 94.01° 2θ arise from 002 and 004 MgO reflections, whereas the peaks at 43.68 and 96.18° 2θ correspond to 002 and 004 VN reflections. ω-2θ scans from VN/MgO(011), Fig. 1(b), contain one set of reflections, with peaks at 62.29 and 63.59° 2θ assigned to MgO 022 and VN 022. Two pairs of peaks are present in ω-2θ scans from VN/MgO(111), Fig. 1(c): 111 and 222 reflections from the MgO substrate, at 36.95 and 78.64°, and 37.70 and 80.49° from VN. All VN reflections are symmetric about the 2θ axis.

HR-RLMs about symmetric 002, 022, and 222 film reflections are measured to assess the mosaicity of VN(001), VN(011), and VN(111) overlayers. Figure 2 shows a typical map for VN/MgO(001), in which the diffracted intensities are represented by logarithmically spaced isointensity contours as a function of reciprocal lattice vectors k_0 parallel and k_1 perpendicular to the surface. k_0 and k_1 are related to the peak positions in ω-2θ space by:46,47

\[ k_0 = 2\pi \sin(\theta) \cos(\omega - \theta) \] (1a)

and

\[ k_1 = 2\pi \cos(\theta) \sin(\omega - \theta), \] (1b)

FIG. 1. XRD ω-2θ scans from 300-nm-thick epitaxial VN layers grown on (a) MgO(001), (b) MgO(011), and (c) MgO(111) at T_s = 430 °C by magnetically unbalanced reactive magnetron sputter deposition in pure N2 discharges with an incident ion/V flux ratio I/I_V = 28 and an ion energy E_i = 12 eV.
MgO(111) surfaces develop triangular facets with exposed vicinal planes.

XRD [111] pole figures from VN overlayers grown on MgO(001), MgO(011), and MgO(111) are plotted in Figures 3(a)–3(c) as stereographic projections over azimuthal angles \( \psi = 0 - 85^\circ \) and rotational angles \( \varphi = 0 - 360^\circ \). Diffraacted intensities are represented by logarithmic isointensity contours. \{111\} maps from VN(001) [Fig. 3(a)] exhibit four peaks, separated by 90° in \( \varphi \) and tilted by \( \psi = 54.74^\circ \) from the surface normal, corresponding to the 111, 111, and 111 reflections. Pole figures from VN(011) [Fig. 3(b)] exhibit two peaks, 180°-apart in \( \varphi \) and tilted by \( \psi = 35.26^\circ \), arising from 111 and 111 lattice planes. VN(111) pole figures [Fig. 3(c)] contain four peaks: one at the surface normal (\( \psi = 0^\circ \)) and three, separated by \( \varphi = 120^\circ \), at \( \psi = 70.53^\circ \). The high-angle triplet stems from off-axis 111, 111, and 111 reflections.

Typical XRD \( \phi \)-scans from VN/MgO(001), collected with \( \omega \) and 2\( \theta \) angles set to detect 022 film and substrate peaks, are plotted in Figure 4. The scans show four 90°-rotated 220 peaks at identical angles for both VN and MgO. The combination of the XRD \( \omega \)-2\( \theta \), pole figures, and \( \varphi \) scans establish that VN(001) layers grow epitaxially with a cube-on-cube orientational relationship with respect to the MgO(001) substrate: (001)\(_{\text{VN}}\||\langle 001\rangle_{\text{MgO}}\) and [100]\(_{\text{VN}}\||[100]\(_{\text{MgO}}\). Similar analyses for VN/MgO(011) and VN/MgO(111) reveal the following orientational relationships: (011)\(_{\text{VN}}\||\langle 011\rangle_{\text{MgO}}\) with [100]\(_{\text{VN}}\||[100]\(_{\text{MgO}}\) and [111]\(_{\text{VN}}\||[111]\(_{\text{MgO}}\) with [110]\(_{\text{VN}}\||[110]\(_{\text{MgO}}\).

The relaxed VN lattice constant \( a_{\text{VN}} \) and residual film strains are determined from asymmetric HR-RLMs. Figure 5 shows a typical HR-RLM about the 113 reflection from VN/MgO(001). The film and substrate peaks are misaligned along \( k_\perp \), indicating VN overlayer relaxation. For (001), (011), and (111)-oriented NaCl-structure samples with...
surface-normal unit vectors \( \mathbf{n} = [001] \), \([011]/\sqrt{2} \), and \([111]/\sqrt{3} \), the in-plane \( a_\parallel \) and out-of-plane \( a_\perp \) lattice parameters are related to the reciprocal lattice vectors by the relationships:

\[
\begin{align}
    a_\parallel &= \frac{|\mathbf{g} - (\mathbf{g} \cdot \mathbf{n})\mathbf{n}|}{|k_\parallel|}, \\
    a_\perp &= \frac{(\mathbf{g} \cdot \mathbf{n})}{|k_\perp|}.
\end{align}
\]

\( \cdot \) is the vector dot product and \(|\mathbf{v}|\) denotes the vector length. From Eqs. (3), the VN(001) in-plane lattice parameter \( a_\parallel = \sqrt{2}k_\parallel = 0.4122 \text{ nm} \) and the out-of-plane lattice parameter \( a_\perp = 3/k_\perp = 0.4136 \text{ nm} \). In-plane and out-of-plane lattice parameters of VN overlayers grown on MgO(011) are determined from the asymmetric 311 reflection as \( a_\parallel = 3/k_\parallel = 0.4124 \) and \( a_\perp = \sqrt{2}k_\perp = 0.4136 \text{ nm} \). For VN/MgO(111), the 311 reflection yields \( a_\parallel = 2\sqrt{2}/k_\parallel = 0.4123 \) and \( a_\perp = \sqrt{3}/k_\perp = 0.4136 \text{ nm} \).

The relaxed VN lattice parameter \( a_0 \) is determined for VN films grown on each of the three orientations from \( a_\parallel \) and \( a_\perp \) through the relationship

\[
a_0 = a_\perp \left(1 - \frac{2\nu(a_\perp - a_\parallel)}{a_\parallel (1 + \nu)}\right),
\]

in which \( \nu \) is the corresponding anisotropic VN Poisson ratio obtained in Section III B. Substituting \( \nu \) and appropriate \( a_\parallel \) and \( a_\perp \) values into Eq. (4) yields \( a_0 = 0.4134 \pm 0.0004 \text{ nm} \), which is in excellent agreement with published values for bulk VN, 0.4134 nm.\(^{22,53}\) All films are found to be fully relaxed at the growth temperature with small compressive strains \( \epsilon_\parallel = (a_\parallel/a_0 - 1) \) of \(-0.0026 \) due to differential thermal contraction upon cooling to room temperature. The thermal expansion coefficient for MgO and VN are \( \alpha_{\text{MgO}} = 13 \times 10^{-6} \) (Ref. 53) and VN \( \alpha_{\text{VN}} = 9.7 \times 10^{-6} \text{ K}^{-1}.\(^{54}\)

Figure 6(a) is a [100] zone-axis bright-field XTEM image from a VN/MgO(001) layer; a corresponding SAED pattern is shown in Figure 6(b). The only contrast in the XTEM image is due to bend contours arising from the thin TEM foil. The SAED pattern, acquired with the aperture sampling the entire 300-nm-thick film and \( \sim 200 \text{ nm} \) of the substrate, contains only single-crystal reflections from VN and MgO. Due to the small film/substrate lattice mismatch \((m < 0.02)\), VN and MgO reflections appear superimposed in agreement with the simulated diffraction pattern, Figure 6(c), obtained using the experimental camera length.\(^{55}\)

A high-resolution cross-sectional Z-contrast STEM image showing the film/substrate interface is presented in Figure 6(d). The lighter contrast of the VN film compared to the MgO substrate results from the mass difference between V (50.94 amu) and Mg (24.30 amu). The interface is sharp with width \( w = 0.5 \text{ nm} \), corresponding to approximately one unit cell \((a_0 = 0.4134 \text{ nm})\). Well-defined VN lattice fringes spaced 0.413 nm apart extend parallel and perpendicular to the film-substrate interface in agreement with XRD

\[
\frac{\Delta k_\perp}{\Delta k_\parallel} = \frac{1}{\sqrt{\nu}}
\]

\( \Delta k_\parallel \) and \( \Delta k_\perp \) are the corresponding anisotropic VN Poisson ratio

\[
2k\parallel = a_0
\]

\( \text{VN} \)

\[
\text{MgO}
\]

\[
\text{VN(022)}
\]

\[
\text{MgO(022)}
\]

\[
\Phi [\text{deg}]
\]

\[
\text{Log intensity [a.u.}]
\]

\[
\text{Fig. 4. XRD (022) } \varphi \text{-scans from a 300-nm-thick epitaxial VN/MgO(001) layer grown at } T_s = 430 ^\circ \text{C} \text{ by magnetically unbalanced reactive magnetron sputter deposition in a pure N}_2 \text{ discharge with an incident ion/V flux ratio } J_\text{I}/J_\text{V} = 28 \text{ and an ion energy } E_\text{I} = 12 \text{ eV.}
\]

\[
\text{Fig. 5. HR-RLM about an asymmetric 113 reflection from a 300-nm-thick epitaxial VN layer grown on MgO(001) at } T_s = 430 ^\circ \text{C} \text{ by magnetically unbalanced reactive magnetron sputter deposition in a pure N}_2 \text{ discharge with an incident ion/V flux ratio } J_\text{I}/J_\text{V} = 28 \text{ and an ion energy } E_\text{I} = 12 \text{ eV.}
\]

\[
\text{Fig. 6. (a) Bright-field XTEM image acquired along the [100] zone axis from a 300-nm-thick epitaxial VN layer grown on MgO(001) at } T_s = 430 ^\circ \text{C} \text{ by magnetically unbalanced reactive magnetron sputter deposition in a pure N}_2 \text{ discharge with an incident ion-to-V flux ratio } J_\text{I}/J_\text{V} = 28 \text{ and an ion energy } E_\text{I} = 12 \text{ eV. (b) SAED pattern obtained with the aperture sampling the entire film and } \sim 200 \text{ nm} \text{ of the substrate; (c) simulated diffraction pattern corresponding to the SAED region outlined by the white square. (d) High-resolution cross-sectional STEM image from the same sample.}
\]
measurements. Across the interface, the lattice fringes are continuous, once again revealing the epitaxial nature of the overlayer.

B. Elastic constants

Longitudinal sound velocities along [001], [011], and [111] directions are determined using sub-picosecond ultrasonic optical pump/probe techniques. Figure 7 is a typical plot showing surface reflectivity changes ΔR as a function of the time delay t between pump and probe pulses for a blanket-Al coated VN(001) sample. ΔR exhibits an initial rapid rise, due to local heating by the 0.5 ps pump laser pulse, followed by a slow decay. Superimposed on the decay are small positive and negative peaks at times corresponding to the arrival at the surface of acoustic pulse echoes. Positive (negative) changes in ΔR occur for pulses which undergo phase shifts of π (zero) due to reflection from an interface with a region of lower (higher) acoustic impedance Z.56 This is illustrated schematically in the inset of Figure 7 for acoustic pulses reflected from both the Al/VN and VN/MgO interfaces. Since Z increases from air (Z_{air} = 410 N·s/m³) to Al (Z_{Al} = 1.73 × 10^{10} N·s/m³ (Ref. 57)) to MgO (Z_{MgO} = 3.31 × 10^{10} N·s/m³ (Ref. 58)) to VN (Z_{VN} = 6.0 × 10^{10} N·s/m³), pulses reflected from the Al/VN, VN/MgO, and air/Al interfaces have phase shifts of zero, π, and zero, respectively. Hence, the signs of successive acoustic pulse echoes are determined by the interfacial boundary conditions.

The time interval Δt between adjacent peaks represented by upward and downward facing solid triangles in Figure 7 is constant and corresponds to the time Δt_{Al} required for the acoustic pulse to traverse the Al layer twice. Correspondingly, the time Δt_{VN} between the peaks labeled with the first set of solid and open triangles is the time required for the pulse to travel twice through the VN(001) layer. The 001 VN longitudinal sound velocity v_{001} is obtained from the relationship v = 2h_{VN}/Δt_{VN}, in which h_{VN} = 300 nm, as v_{001} = 9.8 ± 0.3 km/s. VN longitudinal sound velocities along the [011] and [111] directions are found to be v_{011} = 9.1 ± 0.3 and v_{111} = 9.1 ± 0.3 km/s.

In cubic materials, sound velocities in the [001], [011], and [111] directions are a function of the c_{11} elastic constant and mass density ρ through the equations:28,59

\[ v_{001} = \sqrt{c_{11}/\rho}, \]  
\[ v_{011} = \sqrt{(c_{11} + c_{12} + 2c_{44})/2\rho}, \]  
\[ v_{111} = \sqrt{(c_{11} + 2c_{12} + 4c_{44})/3\rho}. \]

Here, we have measured the three sound velocities, the mass density of VN, and determined c_{44} independently (see below); thus, the set of homogenous equations are overdetermined. Solving Eq. (5a) yields c_{11} = 585 ± 30 GPa. Reported VN c_{11} values from line-focus acoustic microscopy and density functional theory calculations are 533 GPa (Ref. 60) and 680 GPa.20 The lower c_{11} values obtained in Ref. 60 are likely due to understoichiometry since the layers were grown by reactive magnetron sputtering at T_s = 700°C (vs. 430°C in the present experiments) for which increased N₂ desorption rates from the growth surface yield nitrogen deficient films as discussed in Sec. III A.

Figure 8 is a plot of ΔR as a function of the time delay t between laser pump and probe pulses, for a SAW propagating along the [010] direction on a VN(001) surface. The ΔR amplitudes are small (of the order of 10⁻⁵) compared to the initial increase in ΔR due to heating by the pump pulse. The SAW velocity is v_{SAW} = λ/τ_{SAW}, in which λ = 700 nm is the wavelength of the phase-shift mask and τ_{SAW} is the period of surface acoustic wave. For the results shown in Fig. 8, τ_{SAW} = 158.4 ps and v_{SAW} = 4420 ± 45 m/s. Kim et al.27 reported v_{SAW} values for VN(001) as a function of the effective film thickness h° = h/A. However, the films were rather thin, 0.01 < h < 0.12, and SAW velocities obtained from such thin layers vary with film thickness since the surface wave penetrates significantly into the substrate. In the present experiments, much shorter SAW wavelengths are used.
Thus, the effective thickness of our VN layer is $h^* = 0.43$, for which there is no significant substrate effect.

We obtain the VN $c_{44}$ elastic constant using a numerical Green’s function method for describing SAW velocities in layered structures. To simulate $v_{\text{SAW}}$, eight parameters are required: the elastic constants of MgO ($c_{11} = 299.8$, $c_{12} = 99.1$, and $c_{44} = 157.5$ GPa (Ref. 17)), the VN $c_{11}$ elastic constant (585 GPa), and the mass density $\rho$ of VN ($\rho_{\text{VN}} = 6.1$ g/cm$^3$) and MgO ($\rho_{\text{MgO}} = 3.58$ g/cm$^3$). Two of the parameters, the VN $c_{12}$ and $c_{44}$ elastic constants, are unknown; however, the SAW velocity $v_{\text{SAW}}$ is only sensitive to $c_{44}$ (the $v_{\text{SAW}}$ sensitivities to $c_{12}$ and $c_{44}$ are $-0.01$ and 0.25). This reduces the SAW propagation velocity to a function of a single parameter, $v_{\text{calc}}(c_{44})$. To obtain $c_{44}$, we estimate $c_{44}$, compute $v_{\text{calc}}(c_{44})$, compare $v_{\text{calc}}(c_{44})$ to our measured $v_{\text{SAW}}$ value, input a new estimate for $c_{44}$, and continue this iterative procedure until we obtain agreement between the calculated and measured SAW propagation velocities. The result is $c_{44} = 126 \pm 3$ GPa and, from Eqs. (5b) and (5c), the remaining VN elastic constant $c_{12}$ is 178 $\pm$ 33 GPa.

The VN elastic constants are compared to more commonly reported isotropic modulus values obtained from polycrystalline bulk samples following the Voigt-Reuss-Hill approach. Polycrystalline shear moduli $G_{\text{poly}}$ are bound by the Voigt isostrain shear modulus $G_V = (c_{11} - c_{12} + 2c_{44})/5$ (Ref. 63) and the Reuss isostress shear modulus $G_R = 5/(4s_{11} - 4s_{12} + 5s_{44})$, in which the elastic compliance $[s_i] = [c_{ij}]^{-1}$, so that the Voigt-Reuss-Hill shear modulus $G_{\text{VRH}} = (G_V + G_R)/2 \sim G_{\text{poly}}$. Similarly, polycrystalline elastic moduli $E_{\text{poly}}$ are approximated by the Voigt-Reuss-Hill elastic modulus $E_{\text{VRH}} = (E_V + E_R)/2$, for which the Voigt/Reuss elastic modulus $E_V/R = 9K_{\text{VRH}}/(3K + G_{\text{VRH}})$ and the bulk modulus $K_{\text{VRH}} = K_V = K_R = (3c_{11} + 6c_{12})/\rho$. From the three independent VN elastic constants ($c_{11}$, $c_{12}$, and $c_{44}$) obtained here, $E_{\text{VRH}} = 393$ and $K_{\text{VRH}} = 313$ GPa, in reasonable agreement with published VN modulus values $E_{\text{poly}} = 357$ GPa (Ref. 45) and $K_{\text{poly}} = 267$ (Ref. 65) and 300 $\pm$ 6 GPa (Ref. 66) from bulk polycrystalline samples.

The isotropic VN Poisson ratio, defined as $\nu = (E_{\text{VRH}}/(2G_{\text{VRH}})) - 1$, is 0.29. Non-isotropic Poisson ratios obtained through the relationships:

$$\nu_{001} = \frac{c_{12}}{c_{11} + c_{12}}$$

$$\nu_{011} = \frac{c_{11} + 2c_{12} - 2c_{44}}{2(c_{11} + 2c_{12} + c_{44})}$$

$$\nu_{111} = \frac{\frac{3}{2}c_{11} + c_{11}c_{12} - c_{12} - 2c_{11}c_{44} + 8c_{12}c_{44}}{3(c_{11} + c_{11}c_{12} - c_{12} - 2c_{11}c_{44})}$$

are $\nu_{001} = 0.23$, $\nu_{011} = 0.32$, and $\nu_{111} = 0.30$ and used in Sec. III A to determine relaxed VN lattice parameters from HR-RLM measurements. The VN elastic anisotropy $A = 2c_{44}/(c_{11} - c_{12}) = 0.62$.

IV. CONCLUSIONS

Fully dense stoichiometric VN films are grown at $T_s = 430 ^\circ C$ by magnetically unbalanced reactive magnetron sputter deposition onto 001-, 011-, and 111-oriented MgO substrates. The combination of XRD $\omega$-2$\theta$, $\varphi$-scans, and pole figures, together with SAED and XTEM analyses show that VN(001), VN(011), and VN(111) overlayers are NaCl-structure single-crystals with film substrate orientation relationships: $\langle 001 \rangle_{\text{VN}}||\langle 001 \rangle_{\text{MgO}}$ with $\langle 110 \rangle_{\text{VN}}||\langle 110 \rangle_{\text{MgO}}$ and $\langle 111 \rangle_{\text{VN}}||\langle 111 \rangle_{\text{MgO}}$ with $\langle 110 \rangle_{\text{VN}}||\langle 110 \rangle_{\text{MgO}}$. Relaxed lattice parameters determined from HR-RLMs, $a_0 = 0.4134$ nm, are consistent with mass densities, $\rho = 6.1$ g-cm$^{-3}$, obtained from RBS and indicate that the films are fully dense. Moreover, $a_0$ and $\rho$ are equal to reported values for bulk VN crystals.

VN longitudinal sound velocities along [001], [011], and [111] directions are determined using sub-picosecond ultrasonic optical pump/probe techniques as $v_{001} = 9.8$, $v_{011} = 9.1$, and $v_{111} = 9.1$ km/s. The surface acoustic wave velocity, $v_{\text{SAW}} = 4420$ m/s, is measured by optically-modulating the surface of VN/MgO(001) films. Combining these results with the mass density yield the fundamental VN elastic constants $c_{11} = 585 \pm 30$, $c_{12} = 178 \pm 33$, and $c_{44} = 126 \pm 3$ GPa, as well as the VN elastic anisotropy $A = 0.62$, isotropic Poisson ratio $\nu = 0.29$, and anisotropic Poisson ratios $\nu_{001} = 0.23$, $\nu_{011} = 0.32$, $\nu_{111} = 0.30$.

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