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Epitaxial growth and properties of cubic WN on MgO(001), MgO(111), and Al_2O_3(0001)

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ABSTRACT

Tungsten nitride layers, 1.45-μm-thick, were deposited by reactive magnetron sputtering on MgO(001), MgO(111), and Al_2O_3(0001) in 20 mTorr N_2 at 700 °C. X-ray diffraction ω-2θ scans, ω-rocking curves, φ scans, and reciprocal space maps show that all layers exhibit a cubic rock salt structure, independent of their N-to-W ratio which ranges from $x = 0.83$–0.93, as determined by energy dispersive and photoelectron spectroscopies. Growth on MgO(001) leads to an epitaxial WN(001) layer which contains a small fraction of misoriented grains, WN(111)/MgO(111) is an orientation- and phase-pure single-crystal, and WN/Al_2O_3(0001) exhibits a 111-preferred orientation containing misoriented cubic WN grains as well as N-deficient BCC W. Layers on MgO(001) and MgO(111) with $x = 0.92$ and 0.83 have relaxed lattice constants of 4.214 ± 0.005 and 4.201 ± 0.031 Å, respectively, indicating a decreasing lattice constant with an increasing N-vacancy concentration. Nanoindentation provides hardness values of 9.8 ± 2.2, 12.5 ± 1.0, and 10.3 ± 0.4 GPa, and elastic moduli of 240 ± 40, 257 ± 13, and 242 ± 10 GPa for layers grown on MgO(001), MgO(111), and Al_2O_3(0001), respectively. Brillouin spectroscopy measurements yield shear moduli of 120 ± 2 GPa, 114 ± 2 GPa and 108 ± 2 GPa for WN on MgO(001), MgO(111) and Al_2O_3(0001), respectively, suggesting a WN elastic anisotropy factor of 1.6 ± 0.3, consistent with the indentation results. The combined analysis of the epitaxial WN(001) and WN(111) layers indicate Hill's elastic and shear moduli for cubic WN of 251 ± 17 and 99 ± 8 GPa, respectively. The resistivity of WN(111)/MgO(111) is 1.9×10^{-5} and 2.2×10^{-5} Ω-m at room temperature and 77 K, respectively, indicating weak carrier localization. The room temperature resistivities are 16% and 42% lower for WN/MgO(001) and WN/Al_2O_3(0001), suggesting a resistivity decrease with decreasing crystalline quality and phase purity.

1. Introduction

Transition metal nitrides are known for their high hardness, wear and corrosion resistance, and high temperature stability [1–3], and are therefore widely used as hard wear-protective coatings, diffusion barriers in microelectronics, and optical or decorative coatings [4,5]. There is a great interest in accurate values for the intrinsic mechanical properties like hardness and elastic modulus for all transition metal nitrides. These properties are, in general, a function of composition, phase, and orientation. However, the measured coating properties are typically also strongly affected by the microstructure including grain size, intrinsic strain, porosity and roughness [6]. It is challenging to determine the intrinsic properties using measurements on polycrystalline films, since they depend on the microstructure which, in turn, strongly varies with deposition conditions [7]. An effective approach to deconvolute the intrinsic properties from microstructural effects is to perform property measurements on well characterized single-phase epitaxial single crystal layers, as has previously been done for HfN [8], TiN [9], TaN [10], ScN [11], CrN [12], ZrN [13], and VN [14] and is done in this study for tungsten nitride.

Tungsten nitride has been reported to crystallize in a variety of phases, with the most common being a stoichiometric hexagonal δ-WN or a cubic W_2N with a rock salt structure where 50% of the N-sites are vacant [15,16]. In addition hexagonal and rhombohedral W_2N_3 and cubic W_3N_4 phases have also been reported, using high pressure and high temperature synthesis methods [17]. Polycrystalline tungsten nitride layers have been deposited by reactive DC magnetron sputtering [18–24], but also by reactive pulsed laser deposition [23,25], RF sputtering [26], cathodic arc deposition [27], atomic layer deposition [28], and chemical vapor deposition [29–32], and have been used to determine the mechanical properties by nanoindentation [21–27]. Reported values for the WN_x elastic modulus E range from $E = 240$–430 GPa [21,23,26], where an increase in the N-to-W ratio from $x = 0.61$–0.71 leads to a decrease in E from 305–275 GPa [26], or for $x = 0.43$, 0.89, and 1.38 to $E = 380$, 380, and 325 GPa [21], with the latter value being further reduced through strain relaxation upon annealing to $E = 285$ GPa [21]. Relatively small N concentrations yield a reduced modulus $E_r = 279$–224 GPa for samples with $x = 0.17$–0.5 deposited by PLD [23] and $E_r = 313$–277 GPa for sputtered WN_x with $x = 0.11$–

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0.25 [23]. In addition, phase and intrinsic stress also affect E, for example, hexagonal $WN_{1.17}$ with a compressive stress of −12.6 GPa exhibits a high $E = 430$ GPa [26]. The hardness H of WN_x has been reported to range from 5–39 GPa [22–27]. This large range is attributed to variations in microstructure, nitrogen content, layer density, and phase content. For example, H decreases from 32 to 26 GPa as x increases in cubic WN_x from 0.35 to 0.7, but H increases again with increasing $x > 0.75$ due to the formation of hexagonal phase inclusions [26]. In addition, H is reported to increase with deposition power and nitrogen partial pressure but decrease with total gas pressure, providing a large range from 6–30 GPa in a single study [22].

In this paper, we report on the growth and characterization of tungsten nitride layers to determine the mechanical properties of the relatively unexplored cubic phase. For this purpose, epitaxial and polycrystalline WN layers with a cubic phase and a measured N-to-W ratio of 0.83–0.93 were deposited on single crystal MgO(001), MgO(111), and Al_2O_3(0001) substrates by DC reactive magnetron sputtering, yielding 001 and 111-oriented epitaxial layers on the MgO substrates, and 111-oriented polycrystalline WN layers on Al_2O_3(0001), with the latter containing some misoriented WN as well as bcc W grains. Nanoindentation results show hardness values and elastic moduli that are lower than reported in most previous literature [21–23,25–27], with the exception of the particularly low hardness reported in Refs. [22] and [25] that can be attributed to underdense microstructures. Our approach of growing epitaxial thin films reduces or eliminates the effects of grain boundaries and different crystal orientations on property measurements. Complementary characterizations by nanoindentation and Brillouin spectroscopy provide both Young's and shear moduli. Electrical resistivity measurements at room temperature and 77 K indicate a negative temperature coefficient, suggesting weak charge carrier localization in WN, while the W grains in WN/Al_2O_3(0001) reduce the overall thin film resistivity.

2. Experimental procedure

All WN layers were deposited in a load-locked ultra-high vacuum (UHV) dc magnetron sputtering system with a base pressure of $<10^{-9}$ Torr [33,34]. Polished 10 × 10 × 0.5 mm^3 MgO(001), MgO(111) and Al_2O_3(0001) wafers were cleaned in successive rinses of trichloroethylene, acetone, isopropanol, and deionized water, blown dry with dry N_2, attached to a Mo block with silver paint, loaded into the system through the load-lock chamber, and thermally degassed at 900 °C for 1 h. This procedure has previously been successfully applied to grow epitaxial CrN(001)/MgO(001) [35–37], ScN(001)/MgO(001) [33], Cu(001)/MgO(001) [38–40], Ag(001)/MgO(001) [34], and $Al_{1-x}Sc_xN$(0001)/Al_2O_3(0001) layers [41,42]. The target was a 51-mm-diameter, 6-mm-thick water-cooled 99.95% pure W disk positioned 9.3 cm from the substrate at a 45° angle. Before each deposition, the target was sputter etched for 5 min with a shutter shielding the substrate. Depositions were performed at 20 mTorr 99.999% pure N_2, using a constant dc power of 300 W applied to the magnetron source, yielding a deposition rate of 375 nm/h. All layers were deposited at 700 °C, as measured by a thermocouple below the sample stage that was cross-calibrated with a pyrometer focused on the sample surface. This temperature was chosen to provide the best crystalline quality for all layers.

X-ray diffraction was done with a PANalytical X'Pert PRO MPD system with a Cu Kα source and a two-bounce two-crystal Ge(220) monochromator, yielding a parallel incident beam with a wavelength of $\lambda = 1.5406$ Å, a divergence of 0.0068°, and a width of 0.3 mm. Sample alignment included height adjustment as well as correction of the ω and χ tilt angles were done by maximizing the substrate peak intensity. Symmetric ω-2θ scans were obtained using a 0.27° slit and a 0.04 radian Soller Slit before the diffracted X-ray beam entered a PW1964/96 scintillation point detector. ω-rocking curves and φ scans were obtained using constant 2θ angles corresponding to WN 111 or 113 reflections and using the same parallel beam geometry as used for ω-2θ scans. Asymmetric reciprocal space maps around 113 reflections were obtained using a MediPix2 PIXcel solid-state line detector and a geometry with a small diffracted beam exit angle of 8–12° with respect to the sample surface to cause a beam narrowing which increases the 2θ resolution. In addition, ω-2θ scans with a divergent beam Bragg–Brentano geometry and the PIXcel line detector were acquired over a large 2θ range from 5–90° in order to detect small inclusions of possible secondary phases or misoriented grains.

The N-to-W composition ratio of each sample was determined using a combination of X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS). XPS spectra were acquired using Al Kα radiation (1486.7 eV) in a PHI VersaProbe system with a hemispherical analyzer and an 8-channel detector. All high resolution spectra were collected using a pass energy of 23.5 eV and a step size of 0.2 eV. The surfaces were analyzed by XPS without sputter cleaning. EDS spectra were collected in a FEI Helios Nanolab SEM with an accelerating voltage of 5.0 kV, a working distance of 5.0 mm, and an Oxford Instruments X-Max^N 80 silicon drift detector which is particularly well suited for light element analysis. The EDS spectra were analyzed with the Oxford Instruments AZtec EDS software, and the system was calibrated using the single beam current Oxford Instruments QCAL approach and tested with Micro-Analysis Consultants Ltd. produced BN and $CaSiO_3$ standards, indicating an accuracy of the measured N-to-metal ratios of ±2.3%.

The hardness and elastic modulus were measured using a Hysitron TI 900 Triboindenter nanoindenter with a diamond Berkovich tip with a nominal tip radius of 150 nm. Ten indents were performed for each maximum load of 2, 4, 6, 8, and 10 mN, after which loading–unloading curves were inspected for anomalies related to surface contamination or roughness. As a result, a maximum of 1–2 indents were excluded from the data analysis for each set of ten indents [43]. The instrument was calibrated using a fused quartz standard of known hardness and elastic modulus. H and E of the layers were determined with the Oliver and Pharr method [44], using an elastic modulus of 1140 GPa and a Poisson's ratio of 0.07 for the diamond indenter tip [45], and assuming a Poisson's ratio $\nu = 0.25$ for WN.

The sheet resistance of each layer was measured at both room temperature (293 K) and liquid nitrogen temperature (77 K) using a linear four point probe with 1-mm inter-probe spacings, a Keithley 2182A Nanovoltmeter, and a Keithley 6220 Precision Current Source providing 3 mA. The resistivity was calculated using the layer thickness of 1.45 ± 0.05 μm, as measured by cross sectional SEM on cleaved samples, and correcting for the substrate geometry according to Ref. [46].

Brillouin light scattering (BLS) spectra were obtained using a six-pass high contrast Fabry–Perot interferometer from JSR Scientific Instruments and a monochromatic $\lambda = 532.18$ nm Verdi V2 DPSS green laser providing a 65 mW beam that was focused on the sample surface with an average incident angle $\theta = 60 \pm 1°$ relative to the surface normal. A 1-inch achromatic doublet lens (f = 76.2 mm, NA = 0.15, 90% clear central aperture) was used for laser delivery with TM polarization. The laser light was scattered from surface (Rayleigh) acoustic phonons [47] and collected using the same lens, using a shutter to block most of the intense unshifted light. The surface Rayleigh wave velocity V_R was determined from the measured frequency shift Δf using $V_R = \lambda \Delta f / (2\sin\theta)$ [47]. For analysis, the layers are considered semi-infinite media [47,48], since their thickness of 1.45 ± 0.05 μm is much larger than the wavelength of the surface acoustic wave of 0.3 μm. The local strain associated with a surface wave is primarily a shear strain perpendicular to the direction of wave propagation. Therefore, the measured surface wave velocity is related to the transverse bulk wave velocity V_t through $V_R = \beta V_t$ [49], where the factor β is a value close to but smaller than unity, and is a function of the surface orientation and the wave propagation direction and is affected by the elastic anisotropy and the ratio of the effective shear modulus vs bulk modulus. For the analysis in this report we assume a constant $\beta = 0.94$, which is within the reported typical range of 0.90–0.97 [48] and corresponds to the value that has been reported for the analysis of sputter deposited $Zr_{1-x}Ta_xN$