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Growth and mechanical properties of epitaxial NbN(001) films on MgO(001)

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ABSTRACT

NbN_x layers were deposited by reactive magnetron sputtering on MgO(001) substrates in 0.67 Pa pure N_2 at $T_s = 600–1000$ °C. $T_s \geq 800$ °C leads to epitaxial layers with a cube-on-cube relationship to the substrate: $(001)_{NbN}||(001)_{MgO}$ and $[100]_{NbN}||[100]_{MgO}$. The layers are nearly stoichiometric with $x = 0.95–0.98$ for $T_s \leq 800$ °C, but become nitrogen deficient with $x = 0.81$ and 0.91 for $T_s = 900$ and 1000 °C. X-ray diffraction reciprocal space maps indicate a small in-plane compressive strain of -0.0008 ± 0.0004 for epitaxial layers, and a relaxed lattice constant that decreases from 4.372 Å for $x = 0.81$ to 4.363 Å for $x = 0.98$. This unexpected trend is attributed to increasing Nb and decreasing N vacancy concentrations, as quantified by first-principles calculations of the lattice parameter vs. point defect concentration, and consistent with the relatively small calculated formation energies for N and Nb vacancies of 1.00 and -0.67 eV at 0 K and -0.53 and 0.86 eV at 1073 K, respectively. The N-deficient $NbN_{0.81}(001)$ layer exhibits the highest crystalline quality with in-plane and out-of-plane x-ray coherence lengths of 4.5 and 13.8 nm, attributed to a high Nb-adatom diffusion on an N-deficient growth front. However, it also contains inclusions of hexagonal NbN grains which lead to a relatively high measured hardness $H = 28.0 \pm 5.1$ GPa and elastic modulus $E = 406 \pm 70$ GPa. In contrast, the nearly stoichiometric phase-pure epitaxial cubic $NbN_{0.98}(001)$ layer has a $H = 17.8 \pm 0.7$ GPa and $E = 315 \pm 13$ GPa. The latter value is slightly smaller than 335 and 361 GPa, the isotropic elastic modulus and the [100]-indentation modulus, respectively, predicted for NbN from the calculated $c_{11} = 641$ GPa, $c_{12} = 140$ GPa, and $c_{44} = 78$ GPa. The electrical resistivity ranges from 171 to 437 μΩ cm at room temperature and 155–646 μΩ cm at 77 K, suggesting carrier localization due to disorder from vacancies and crystalline defects.

1. Introduction

Transition metal nitrides have many useful physical properties such as a high hardness, chemical inertness, corrosion resistance, excellent thermal stability and electrical resistivities which vary from metallic to semiconducting [1–7]. As a result, they are widely used as hard wear-resistant coatings, diffusion barriers, and optical thin films [3,4]. Niobium nitride (NbN) has not been studied as extensively as some other transition metal nitrides like TiN. However, it has attracted considerable attention due to its high superconducting transition temperature of 17.3 K [8], and its related potential applications in superconducting electronics including single-photon detectors and tunnel junctions [9,10]. In addition, NbN has potential as a hard protective coating [11,12]. Therefore various researchers have studied the microstructure and mechanical properties of NbN coatings deposited using ion beam assisted deposition [13], pulsed laser deposition [14], cathodic arc deposition [11,12], and reactive magnetron sputtering [15–19]. Deposition using a high ion flux, as obtained by unbalanced magnetron sputtering results in a strong 111 preferred orientation [20], and increasing the nitrogen partial pressure in a Ar/N_2 mixture during deposition leads to an increasing N/Nb ratio in the NbN_x films from $x = 0.61$ to 1.06 and a transition from a pure cubic δ-NbN rocksalt structure to a mixed phase structure including a hexagonal δ′-NbN phase [15]. The reported hardness *H* of NbN ranges from 7 to 48.5 GPa [11,12,14–18,21]. We attribute this large range to a combination of microstructural effects including open grain boundaries, layer density, texture, and intrinsic stress, but is likely also related to the phases and the N/Nb-ratio, as a transition from the δ to the δ′ phase with an associated increase in *x* from 0.92 to 1.08 is reported to cause an increase in *H* from 25 to 40 GPa [15], while an even higher hardness of 48.5 GPa is reported for highly stressed cathodic arc deposited layers [12]. Also, an increase in the nitrogen flow rate or the substrate bias from floating to −200 V yields a transition from cubic-111 to hexagonal-110 preferred orientation, an increase in the biaxial compressive stress from 0.2 to 7.2 GPa, and a transition from δ to δ′, resulting in an increase in *H* from 14.5 to 37.9 GPa [16,18].

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In summary, the different microstructures in reported polycrystalline NbN layers strongly affect the measured mechanical properties. Therefore, it is challenging to determine the intrinsic mechanical properties of NbN from existing studies. An effective approach to deconvolute the intrinsic properties from microstructural effects is to perform property measurements on well characterized single-phase epitaxial layers, as has been previously done for TiN(001) [22], ScN(001) [23], TaN(001) [24,25], HfN(001) [26,27], CrN(001) [28], WN(001) [29], and CeN(001) [30]. Barnett et al. have reported on superlattice hardening in epitaxial Mo/NbN and W/NbN superlattice films [31,32], while the mechanical properties of pure epitaxial NbN(001) layers are not known yet. In contrast, the superconducting properties of epitaxial NbN(001) layers have been studied by various researchers [33–41]. The most common approaches are the growth on MgO(001) substrates by reactive magnetron sputtering [34,38,42] or pulsed laser deposition [43–45]. Extensive work has been done to optimize growth conditions to maximize the critical temperature for superconductivity T_c and achieve a low normal-state resistivity. For example, Wang et al. reported a strong dependence in T_c as a function of the total processing gas pressure and the N_2 partial pressure in an Ar/N_2 gas mixture during sputter deposition at room temperature [42], while Chockalingam et al. studied the effect of sputtering power and N_2 partial pressure during growth at 600 °C [34]. In addition, the lattice parameter of the cubic NbN phase has been found to increase with increasing N_2 partial pressure [34,42,43,46], which can be attributed to a decreasing density of N-vacancies or the possible formation of an ordered phase with both cation and anion vacancies [43,47]. However, details regarding point defects in NbN are still unclear and motivate the first-principles calculations of defect formation energies in our present study. Also, in contrast to the existing investigations on epitaxial NbN(001) that focus primarily on optimizing the superconducting properties, the present work investigates epitaxial NbN(001) as a hard coating material. Correspondingly, opposite to previous studies on NbN(001), growth conditions are chosen in the range commonly used for the epitaxial growth of hard transition metal nitrides, that is, high temperature and pure N_2 gas.

In this paper, we present the results of an investigation on the growth and mechanical properties of epitaxial NbN_x layers deposited on MgO(001) by dc reactive magnetron sputtering in 5 mTorr (0.67 Pa) pure N_2 at substrate temperatures $T_s = 600–1000$ °C. A combination of energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD) shows that layers grown at $T_s = 800–1000$ °C are epitaxial single crystals with an N/Nb ratio $x = 0.81–0.98$ that depends on T_s and causes a decrease in the relaxed lattice constant with increasing x. First-principles calculations of lattice constants vs. point defect density indicate that this decrease can be attributed to increasing Nb and decreasing N vacancy concentrations. Both vacancy types have relatively small formation energies and therefore form due to kinetic constraints during growth. The hardness, elastic modulus, and electrical resistivity are also a function of T_s, due to an increasing crystalline quality with $T_s \leq 900$ °C and a considerable N-vacancy concentration for $T_s \geq 900$ °C.

2. Sample preparation and characterization

The NbN_x films were deposited in a load-locked ultrahigh vacuum DC magnetron sputter deposition system with a base pressure of 10^{-9} Torr (10^{-7} Pa) [48] onto one-side polished 10 × 10 × 0.5 mm^3 MgO(001) wafers that were ultrasonically cleaned in subsequent baths of trichloroethylene, acetone and isopropyl alcohol, rinsed in deionized water, blown dry with dry nitrogen, mounted onto a substrate holder using silver paint, inserted into the deposition system, and degassed for 1 h at 1000 °C using a radiative pyrolytic graphite heater [49]. The heater current was adjusted to reach the desired substrate temperature $T_s = 600–1000$ °C, as measured with a pyrometer that was cross-calibrated by a thermocouple underneath the substrate holder. 99.999% pure N_2 was further purified with a MicroTorr purifier and introduced into the chamber with a needle valve to reach a constant pressure of 0.67 ± 0.01 Pa (= 5 mTorr), which was measured with a capacitance manometer and was chosen based on the reported range of 0.4–2.7 Pa for growth of epitaxial transition-metal nitride layers in pure N_2 by reactive sputtering [29,50–61]. A 5-cm diameter 99.95% pure Nb target was positioned 9 cm from a continuously rotating substrate at an angle of 45°, and a constant magnetron power of 300 W was applied, yielding a growth rate of 12 nm/min and a layer thickness after 180 min of deposition of 2.2 ± 0.2 μm, as determined using thickness measurements from scanning electron micrographs of cross-sectional specimens.

The film composition was determined by energy dispersive spectroscopy (EDS) using a FEI Helios Nanolab scanning electron microscope operated with a 0.69–1.4 nA 5.0 keV primary beam and a working distance of 5.0 mm. The spectra were acquired using an Oxford Instruments X-Max^N 80 silicon drift detector which is designed to improve on the typically low light-element sensitivity of EDS quantification. This system has been calibrated using the single beam current Oxford Instruments QCAL approach which takes into account width, position, and shape of each peak profile. The quantitative analysis has been tested with Micro-Analysis Consultants Ltd. produced BN and CaSiO3 standards, indicating an accuracy of the measured N-to-metal ratios of ±2.3%.

X-ray diffraction (XRD) was done using a Panalytical X'pert PRO MPD system with a Cu source and a PIXcel line detector. A divergent beam configuration was used for Ω–2θ scans, while Ω-rocking curves were acquired with an incident parallel beam using an x-ray mirror and limiting the detector receiving angle to 0.27°. XRD ϕ scans were obtained in the parallel-beam mode with Ω and 2θ angles set to detect the NbN 113 reflections at an Ω-offset of 25.153°. Reciprocal space maps around asymmetric 113 reflections were obtained using a hybrid mirror two-bounce monochromator that provides Cu Kα_1 radiation with a 0.0068° divergence, and a small (~10°) angle between the sample surface and the reflected beam to reduce the beam width which facilitates fast and high-resolution parallel detection over 256 channels in 2θ with the line detector.

Nanoindentation measurements were done using a Hysitron Triboindenter with a maximum load of 10 mN. The area function of the triangular Berkovich diamond tip was calibrated using fused silica, following the procedure described in Ref. [62]. Ten indent sequences were applied for each sample. Each loading-unloading curve was evaluated to detect possible anomalies associated with, for example, particle (dust) surface contamination. As a result, a small fraction (<10%) of outlier curves were excluded from the subsequent data analysis. The resistivity of the coatings was measured using a spring loaded linear four point probe with the sample in air at room temperature (290 K) or immersed in liquid N_2 at 77 K, using a Keithley current source operating at −4.0 to +4.0 mA.

3. Calculations

3.1. Computational approach

First-principles density functional calculations were performed using the Vienna ab initio simulation package (VASP), employing periodic boundary conditions, a plane wave basis set, the Perdew–Burke–Ernzerhof generalized gradient approximation exchange correlation functional [63], and the projector-augmented wave method [64]. All computational parameters are chosen such that calculated total energy differences are converged to within 1 meV/atom. This includes a 500 eV cut-off energy for the plane-wave basis set expansion and a Γ-centered 20 × 20 × 20 k-point grid for an 8-atom conventional unit cell. Nb 4*s*, 4*p*, and 4*d* electrons are explicitly calculated, that is, they are not included in the core of the pseudo potential. Rocksalt niobium nitride NbN_x with $x = 0.75–1.0$ was simulated using a cubic supercell with 32 Nb atoms and 24–32 N atoms that were randomly distributed on anion