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$V_{0.5}Mo_{0.5}N_x$/MgO(001): Composition, nanostructure, and mechanical properties as a function of film growth temperature

H. Kindlund [a, *], G. Greczynski [a], E. Broitman [a], L. Martínez-de-Olcoz [a, b], J. Lu [a], J. Jensen [a], I. Petrov [a, c], J.E. Greene [a, c], J. Birch [a], L. Hultman [a]

[a] Thin Film Physics Division, Department of Physics (IFM), Linköping University, SE-58183, Sweden
[b] Grupo de Capas Finas e Ingeniería de Superficies, Facultad de Física, Universidad de Barcelona, Dep. Física Aplicada y Óptica, 08028, Barcelona, Spain
[c] Department of Materials Science, Fredrick Seitz Materials Research Laboratory, University of Illinois, 104 South Goodwin, Urbana, IL, 61801, USA

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$V_{0.5}Mo_{0.5}N_x$/MgO(001) alloys with the B1-NaCl structure are grown by ultra-high-vacuum reactive magnetron sputter deposition in 5 mTorr mixed Ar/N_2 atmospheres at temperatures T_s between 100 and 900 °C. Alloy films grown at $T_s \leq 500$ °C are polycrystalline with a strong 002 preferred orientation; layers grown at $T_s \geq 700$ °C are epitaxial single-crystals. The N/Metal composition ratio x ranges from 1.02 ± 0.05 with $T_s = 100–500$ °C to 0.94 ± 0.05 at 700 °C to 0.64 ± 0.05 at $T_s = 900$ °C. N loss at higher growth temperatures leads to a corresponding decrease in the relaxed lattice parameter a_o from 4.212 Å with x = 1.02 to 4.175 Å at x = 0.94 to 4.120 Å with x = 0.64. $V_{0.5}Mo_{0.5}N_x$ nanoindentation hardnesses H and elastic moduli E increase with increasing T_s from 17 ± 3 and 323 ± 30 GPa at 100 °C to 26 ± 1 and 370 ± 10 GPa at 900 °C. Both polycrystalline and single-crystal $V_{0.5}Mo_{0.5}N_x$ films exhibit higher toughnesses than that of the parent binary compound VN. $V_{0.5}Mo_{0.5}N_x$ films deposited at higher T_s also exhibit enhanced wear resistance. Valence-band x-ray photoelectron spectroscopy analyses reveal an increased volume density of shear-sensitive $d\text{-}t_{2g} - d\text{-}t_{2g}$ metallic states for $V_{0.5}Mo_{0.5}N_x$ compared to VN and the density of these orbitals increases with increasing deposition temperature, i.e., with increasing N-vacancy concentration.

1. Introduction

Transition-metal (TM) nitrides are hard refractory ceramics which exhibit excellent wear and corrosion resistance and are therefore used as, for example, protective coatings on cutting tools and in automotive applications [1]. Enhancing hardness in ceramic films has been a major goal in materials science for several decades [2–7]. However, hardness alone is not sufficient to prevent failure in ceramic coatings exposed to high stresses since increased hardness is usually accompanied by an increase in brittleness. In order to avoid film cracking, the coating material must be *both* hard and ductile, i.e. tough. However, TM nitrides, as most ceramics, generally exhibit low ductility and hence poor toughness.

We have previously shown that single-crystal $V_{0.5}Mo_{0.5}N_x$/MgO(001) thin films deposited at 700 °C are not only harder than the parent binary compound VN/MgO(001), but also exhibit increased toughness; that is, increased resistance to crack formation [8,9]. While all indents in reference VN and TiN epitaxial layers exhibit severe cracking along ⟨110⟩ directions, epitaxial $V_{0.5}Mo_{0.5}N$ layers do not crack [8].

The enhanced toughness of $V_{0.5}Mo_{0.5}N$ was predicted by density functional theory (DFT) calculations [10], based upon a high valence electron concentration which optimizes the occupancy of shear-sensitive $d\text{-}t_{2g}$ metallic bonding states. This is an important step toward obtaining new families of hard, yet tough, refractory thin films [11]. However, the relatively low temperatures, high deposition rates, and polycrystalline nature of the substrates required for large-scale synthesis of hard coatings used in industrial applications results in polycrystalline films which may have quite different properties than epitaxial layers. As an initial step in developing hard, tough polycrystalline TM nitride films, we investigate the effect of growth temperature T_s over a wide range, from 100 to 900 °C, on $V_{0.5}Mo_{0.5}N$ film composition, nanostructure, and mechanical properties.

The $V_{0.5}Mo_{0.5}N_x$ layers are deposited by reactive magnetron

* Corresponding author.
E-mail address: hanki@ifm.liu.se (H. Kindlund).

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sputtering and analyzed using x-ray diffraction (XRD), transmission electron microscopy (TEM), Rutherford backscattering spectrometry (RBS), scanning electron microscopy (SEM), scanning probe microcopy (SPM), nanoindentation techniques, and x-ray photoelectron spectroscopy (XPS). Berkovich nanoindentation results show that the hardnesses of all $V_{0.5}Mo_{0.5}N_x$ alloy films are higher than that of the parent compound VN ($H = 16 \pm 1$ GPa for epitaxial layers) [8], and increase with increasing growth temperature. The latter effect is attributed to vacancy-induced hardening [9,12].

SEM and SPM images of cube-corner nanoindentations in polycrystalline $V_{0.5}Mo_{0.5}N_x$ films deposited at 100 and 300, as well as in epitaxial layers grown at 700 and 900 °C show no cracks, i.e., in addition to exhibiting high hardnesses, the films are ductile (tough). Valence-band XPS measurements carried out using single-crystal $V_{0.5}Mo_{0.5}N_x$ samples show, in agreement with DFT predictions [10], that the volume density of shear-sensitive d-t_{2g} − d-t_{2g} metallic bonds is enhanced compared to VN, and increases with increasing deposition temperature. That is, the metallic states are increasingly populated at higher N-vacancy concentration, resulting in enhanced toughness.

2. Experimental procedures

$V_{0.5}Mo_{0.5}N_x$ thin films are deposited on polished MgO(001) substrates by dual-target reactive magnetron sputtering in a stainless-steel ultra-high-vacuum (UHV) system with a base pressure of ~2×10^{-9} Torr. The targets are 76-mm-diameter V (99.95% purity) and Mo (99.95% purity) discs. Sputtering is carried out in mixed N_2/Ar atmospheres at a total pressure of 5 mTorr, as measured by a capacitance manometer. The nitrogen partial pressure is maintained constant at 3.2 mTorr by an automatic mass-flow controller. Film growth temperatures T_s are varied between 100 and 900 °C in separate experiments. Target powers are 260 W for V and 120 W for the Mo target, yielding film growth rates R_{VMoN} of ~70 Å/min. The substrate holder is rotated at 30 rpm to provide lateral film thickness uniformity, and a substrate bias potential of −30 V is applied during deposition.

The MgO(001) substrates are ultrasonically cleaned in sequential acetone and 2-propanol baths for 5 min, blown dry in N_2, mounted in the UHV system, and degassed at 900 °C for 45 min, a procedure shown to provide sharp MgO(001)1 × 1 diffraction patterns as determined by reflection high-energy electron diffraction [13], before initiating deposition at the selected T_s value. The targets are separately sputter cleaned, with shutters protecting the substrate and the opposite target, prior to deposition.

$V_{0.5}Mo_{0.5}N_x$ film compositions are obtained by RBS using a 2 MeV He^+ beam incident at 10°, with a 172° scattering angle. Results are quantified using the SIMNRA software [14].

The nanostructure and phase composition of as-deposited alloys are determined by XRD, cross-sectional TEM (XTEM), and selected-area electron diffraction (SAED). XRD θ/2θ scans are acquired in a Bragg-Brentano diffractometer with Cu K_α radiation and 0.5° slits. Relaxed lattice parameters are obtained from reciprocal-space maps (RSM) around *113* reflections using a four-axis x-ray goniometer equipped with a hybrid-mirror monochromator. RSM measurements follow the protocol described in Ref. [15]. XTEM and SAED analyses are carried out in an FEI Tecnai G2 TF20 UT microscope equipped with a field-emission gun operated at 200 kV.

Nanoindentation measurements are performed in a Hysitron TI 950 Triboindenter with a Berkovich 142.3° diamond tip (radius of ~150 nm) whose area function is calibrated using a fused silica reference sample. Indentations are carried out in load-controlled mode to a maximum indentation depth ≲10% of film thicknesses, ~300 nm, in order to minimize substrate effects. Film hardness and indentation modulus values are determined, from load-displacement data, following the method of Oliver and Pharr [16].

Film ductility is assessed, via SEM and SPM, based upon analyses of material pile-up around the indent edges following nanoindentation experiments carried out with a sharp cube-corner tip to a depth of 400 nm. That is, the cube-corner nanoindentations extend into the substrate by ~100 nm. The SEM is operated at 5 kV with a secondary-electron detector and an aperture of 30 μm.

A Hysitron TI 950 Triboindenter with a 60°, 5-μm-diameter, conical diamond tip is used to measure microscale friction and wear. The diamond tip with a normal load of 1000 μN, is dragged across the sample surface at a velocity of 0.5 μm/s in a reciprocal motion consisting of 28 cycles. Each individual line scan is 5 μm in length. Wear rates are determined by comparing SPM images of the wear track before and after each experiment. Friction coefficients are measured at normal loads of 10, 100, and 1000 μN. The adhesion between tip and film is characterized by pull-off tests, in which the tip approaches the sample from 50 nm above the surface at 5 nm/s, indents into the film to a depth of 2 nm, and is withdrawn from the sample at the same speed.

$V_{0.5}Mo_{0.5}N_x$ valence-band XPS spectra are acquired in an Axis Ultra DLD instrument from Kratos Analytical using monochromatic Al K_α radiation ($h\nu = 1486.6$ eV). Prior to analysis, contamination due to air exposure is removed using a 2 min Ar^+ sputter etch at 4 keV and 11.5 mA/cm^2. The ion beam is incident at 70° with respect to the sample normal and rastered over a 3×3 mm^2 area. The area analyzed is 0.3×0.7 mm^2 at the center of a 320 Å-deep crater. The XPS spectrum obtained from single-crystal VN/MgO(001) with N/V = 0.89 ± 0.05, grown following the procedure described in Ref. [8], is used for comparison.

3. Results and discussion

RBS results indicate that all film compositions are $V_{0.5}Mo_{0.5}N_x$, for which the N fraction x decreases with increasing T_s. Stoichiometric films ($x = 1.02 \pm 0.05$) are obtained at $T_s \leq 500$ °C, while at $T_s = 700$ and 900 °C, the films are understoichiometric as shown in Fig. 1(a). x decreases to 0.94 ± 0.05 at $T_s = 700$ °C and 0.64 ± 0.05 with $T_s = 900$ °C. The reduced N uptake with increased substrate temperature is expected due to increased nitrogen desorption [17] and the relatively wide single-phase fields of B1-NaCl-structure TM nitrides [18].

Fig. 1(b) is a series of XRD θ/2θ scans, over the 2θ range 40–50°, from ~300-nm-thick $V_{0.5}Mo_{0.5}N_x$/MgO(001) layers grown as a function of T_s. All $V_{0.5}Mo_{0.5}N_x$/MgO(001) films have the NaCl structure (see also cross-sectional TEM (XTEM) and selective-area electron diffraction (SAED) results below). The MgO *002* peak occurs at 42.95° corresponding to a lattice constant of 4.21 Å, in agreement with previous reports [19]. Layers deposited at $T_s \geq 700$ °C exhibit only one XRD film peak: VMoN *002* at 43.32° with $T_s = 700$ °C and 43.80° for $T_s = 900$ °C. Film θ/2θ XRD reflections from $V_{0.5}Mo_{0.5}N_x$/MgO(001) layers grown at $T_s \leq 500$ °C are unresolvable from the high-intensity MgO substrate peak.

In-plane $a_{||}$ and out-of-plane $a_\perp$ $V_{0.5}Mo_{0.5}N_x$ lattice parameters are obtained from RSMs acquired around asymmetric *113* reflections. For a 001-oriented NaCl-structure crystal, $a_{||}$ and $a_\perp$ are given by

$$a_{||} = \sqrt{2}\Big/q_{||} \text{ and } a_\perp = 3/q_\perp, \tag{1}$$

in which $q_{||}$ and $q_\perp$ are the reciprocal lattice vectors parallel and perpendicular to the surface, respectively. Fig. 2 shows typical *113* RSMs from $V_{0.5}Mo_{0.5}N_x$/MgO(001) layers grown at 500 and 900 °C. XRD intensities corresponding to films deposited at $T_s < 500$ °C cannot be resolved from the substrate peak. However, for the