Epitaxial Ti$_{1-x}$W$_x$N alloys grown on MgO(001) by ultrahigh vacuum reactive magnetron sputtering: Electronic properties and long-range cation ordering


Materials Science Department and the Frederick Seitz Materials Research Laboratory, University of Illinois, 104 South Goodwin Avenue, Urbana, Illinois 61801

(Received 12 June 2002; accepted 7 October 2002; published 4 December 2002)

Epitaxial Ti$_{1-x}$W$_x$N alloys with 0.0≤x≤0.6 were grown on MgO(001) substrates at 500 °C by ultrahigh vacuum reactive magnetron sputtering from Ti and W targets in pure N$_2$. X-ray diffraction, transmission electron microscopy (TEM), and cross-sectional TEM show that the 0.3-μm-thick Ti$_{1-x}$W$_x$N(001) alloys are single crystals with the B1-NaCl structure. Rutherford backscattering spectroscopy investigations indicate that alloys with x≥0.05 are slightly overstoichiometric with N/(Ti + W) = 1.06±0.05. The alloy lattice parameter a$_{\perp}$ along the film growth direction is 4.251 Å, irrespective of the WN concentration, for x≤0.41 and decreases slightly at higher concentrations. TEM analyses show that Ti$_{0.5}$W$_{0.5}$N(001) alloys have long-range CuPt-type atomic ordering on the cation sublattice. The room-temperature resistivity increases linearly from 13 μΩ cm for TiN to 287 μΩ cm for Ti$_{0.6}$W$_{0.4}$N due primarily to alloy scattering while the temperature coefficient of resistivity is positive in Ti$_{1-x}$W$_x$N alloys with x≤0.21 and negative for x>0.21 due to weak charge carrier localization. The superconducting critical temperature $T_c$ of Ti$_{1-x}$W$_x$N alloys initially increases with x, due to a larger density of states at the Fermi level, consistent with valence band x-ray photoelectron spectroscopy measurements. $T_c$ reaches a maximum of 6.67 K at x=0.21 and decreases for larger x values. © 2003 American Vacuum Society. [DOI: 10.1116/1.1525818]

I. Introduction

Transition-metal nitrides are well known for their remarkable physical properties including high hardness, mechanical strength, chemical inertness, high-temperature stability, and electrical resistivities that 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, optical coatings, and superconducting thin films. Here, we focus on the Ti$_{1-x}$W$_x$N alloy system which has received relatively little attention in this alloy system. While understoichiometric, polycrystalline, and multiphase, the Ti$_{1-x}$W$_x$N and, $\beta$-WN rich Ti$_{1-x}$W$_x$N N alloys with x≥0.41 and decreases slightly at larger x values. The room-temperature resistivity $\rho$ increases linearly with increasing x in Ti$_{1-x}$W$_x$N(001) alloys, while the temperature coefficient of resistivity (TCR) is positive in layers with x≤0.21 and negative for x>0.21 due to weak charge carrier localization. The superconducting critical temperature $T_c$ initially increases with x, reaches a maximum of 6.67 K at x=0.21, and decreases at larger x values.

II. EXPERIMENTAL PROCEDURE

All Ti$_{1-x}$W$_x$N(001) layers were grown in a load-locked multichamber UHV stainless steel dc-magnetron sputtering system described in detail in Ref. 6. The pressure in the sample introduction chamber was reduced to less than 5×10$^{-8}$ Torr (7×10$^{-6}$ Pa), using a 50 l s$^{-1}$ turbomolecular pump (TMP), prior to initiating substrate exchange into the deposition chamber which has a base pressure of 5×10$^{-10}$ Torr (7×10$^{-8}$ Pa), achieved using a 170 l s$^{-1}$
The water-cooled 7.5 cm diam Ti (99.999%) and W (99.99%) targets, 12.5 cm from the substrate, were mounted at an angle of 45° with respect to the substrate normal and 90° with respect to each other.

Sputter deposition was carried out in pure N₂ (99.99%) discharges at 10 mTorr. N₂ gas is 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 power to each of the targets was varied between 60 and 500 W to maintain a constant deposition rate of 0.04 Å s⁻¹, using predetermined calibration curves, and to obtain a film thickness of 0.3 μm for all samples. Lateral film thickness and composition uniformities of better than 99% were achieved using selectively transmitting shields which were first coated with target material to prevent film contamination.

Plasma characteristics in the vicinity of the substrate during film growth were determined from probe measurements described in detail in Ref. 6. The present film growth experiments were carried out using an ion-to-metal ratio incident at the substrate varying from ≈2 for TiN(001) to 1 for Ti₀.₄W₀.₆N(001) with an incident ion energy of 28 eV. The vast majority of the ions incident at the substrate and growing film during deposition experienced the full sheath potential since the mean-free path for charge-exchange collisions, ≈1.5 cm, was more than the sheath width estimated from the Child–Langmuir equation.

The substrates were polished 10×10×0.5 mm³ MgO(001) wafers cleaned with successive rinses in ultrasonic baths of trichlorethane, acetone, ethanol, and deionized water and blown dry in N₂. The wafers were then mounted on resistively heated Ta platen using Mo clips and inserted into the sample introduction chamber for transport to the growth chamber where they were 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. Immediately prior to initiating deposition, the target was sputter etched for 5 min with a shutter shielding the substrate. All Ti₁₋ₓWₓN(001) layers were grown at Tₛ = 500 °C, including the contribution due to plasma heating.

Ti₁₋ₓWₓN(001) layer compositions were determined by Rutherford backscattering spectroscopy (RBS). The probe beam consisted of 2 MeV He⁺ ions incident at an angle of 22.5° relative to the sample surface with the detector set at a 150° scattering angle. Backscattered spectra were quantified using the RUMP simulation program. The layers were also analyzed for impurities by Auger electron spectroscopy measurements, the ion flux consists primarily different offsets in a high resolution diffractometer with Ge(220) four-crystal and three-crystal monochromators in the primary and secondary x-ray axes, respectively. With Cu Kα₁ radiation (λ = 0.154 059 7 nm), this arrangement provides an angular beam divergence of ≈12° arc sec with a wavelength spread Δλ/λ of 7×10⁻⁵. TEM and XTEM observations were carried out in a Philips CM12 microscope operated at 120 kV. XTEM samples were prepared by gluing two samples film-to-film and then cutting a vertical section which was thinned by mechanical grinding to a thickness of ≈25 μm. Final thinning to electron transparency was done by Ar⁺ ion milling in which the incident beam angle and energy were progressively reduced from 15° to 9° and 5 to 3.5 keV in order to obtain samples with relatively uniform thickness distributions.

The electronic structure of the Ti₁₋ₓWₓN(001) alloys was investigated by x-ray photoelectron spectroscopy (XPS) using a PHI Model 5600 MultiTechnique system with a monochromatized Mg Kα₁(hν = 1253.6 eV) source. The spectra were obtained at a take-off angle of 45° from the sample surface, using a pass energy of 35 eV and a resolution of ≈1 eV, after 5 min of sputter etching with a 3 keV, 0.30 mA cm⁻² Ar⁺ ion beam incident at 58° to the sample normal. Elemental binding energy (BE) values are corrected for charging using the C 1s peak at 284.8 eV from adventitious adsorbed surface C.

Four-point probe measurements were used to determine room-temperature resistivities ρ₃₀₀ K. Temperature-dependent (4–300 K) resistivities, the Hall coefficient, as well as the critical temperature for the superconducting transition, were obtained using a Quantum Design physical property measurement system. For this purpose, Al contacts in a van der Pauw pattern were deposited by evaporation.

III. RESULTS AND DISCUSSION

Ti₁₋ₓWₓN(001) layer compositions are plotted in Fig. 1 as N/(Ti+W) versus x. All layers, with the exception of pure TiN(001) and Ti₀.₉₅W₀.₀₅N(001), are slightly overstoichiometric with N/(Ti+W) = 1.06 ± 0.05. We attribute this primarily to trapping of energetic neutral N atoms backscattered from the W target. From previous glow discharge mass spectroscopy measurements, the ion flux consists primarily

![Fig. 1. Nitrogen fraction N/(Ti+W) in epitaxial Ti₁₋ₓWₓN alloys grown on MgO(001) as a function of the composition x.](image)
(<96%) of N$_2^+$.\(^{11}\) TRIM Monte Carlo simulations\(^{12}\) show that for 350 eV N$_2^+$ ions (28 amu) dissociatively bombarding a W target (183.9 amu), the average energy of backscattered N atoms is 70 eV. This value, as well as the N backscattering yield are more than a factor 2.5 larger in the case of the W target, since W is nearly four times heavier than Ti. All Ti$_{1-x}$W$_x$N(001) alloys, 0≤x≤0.6, were found to be single crystals with the Bi–NaCl structure as judged by XRD and TEM. The only XRD features observed over the 2θ range between 20° and 80° are the 002 Ti$_{1-x}$W$_x$N and MgO peaks. A typical ω–2θ scan, in this case from a Ti$_{0.74}$W$_{0.26}$N(001) alloy, is shown in the inset of Fig. 2. It was obtained by using a 1° offset along ω in order to isolate the film peak from the 002 MgO substrate peak at 42.910°. The nitride alloy peak is located at 2θ=42.560°, corresponding to a lattice parameter $a_\parallel$ along the film direction of 4.248 Å, approximately equal to the value obtained for TiN(001), $a_\parallel = 4.249$ Å, but slightly above the relaxed lattice constant $a_\parallel$ of 4.226 Å. Thus the TiN(001) layer is in a mild state of in-plane compressive strain with $\varepsilon_\parallel = 0.002$. The residual compressive strain, in TiN(001) and presumably in the Ti$_{0.74}$W$_{0.26}$N(001) layer as well, is due to differential thermal contraction during sample cooling following film growth at $T_s = 500$ °C. The thermal-expansion coefficients of TiN and MgO are 9×10$^{-6}$ K$^{-1}$ (Ref. 14) and 1.3×10$^{-5}$ K$^{-1}$ (Ref. 15), respectively.

Figure 2 is a plot of the out-of-plane lattice parameter $a_\perp$ of Ti$_{1-x}$W$_x$N(001) alloys as a function of the WN concentration x. We find that within experimental uncertainty, $a_\perp$ remains approximately constant at 4.251 Å for alloys with WN concentrations up to x = 0.41. This indicates that metal–nitrogen bond lengths remain essentially unchanged as W is substituted for Ti cations, consistent with the fact that Ti and W have very similar covalent radii, 1.32 and 1.30 Å, respectively. We do, however, observe a small decrease in $a_\perp$ at higher WN concentrations with a weak minimum near x = 0.5, for which $a_\perp = 4.226$ Å, even though the N to metal ratio in these layers remains constant as shown in Fig. 1. We attribute the minimum in $a_\perp(x)$ to strong CuPt ordering at

\[ Ti_{1-x}W_xN(001) \] compositions around x = 0.5 as discussed below.

A typical HRRLM around the 002 Bragg reflection from a Ti$_{0.77}$W$_{0.23}$N/MgO(001) layer is shown in Fig. 3. Diffracted intensity distributions are plotted as isointensity contours as a function of the reciprocal lattice vectors $k_\parallel$ parallel and $k_\perp$ perpendicular to the surface. The intense peak corresponds to the MgO(001) substrate with a relaxed lattice constant $a_\parallel$ of 4.212 Å. The transverse diffraction intensity distribution along the $\Delta \omega$ direction in the substrate peak is due to mosaicity which is typically quite large in bulk MgO crystals.\(^{16}\) The wide feature below the MgO(001) substrate corresponds to the Ti$_{0.77}$W$_{0.23}$N(001) layer, with a vertical separation between film and substrate diffracted intensity distributions yielding $a_\perp = 4.249$ Å, in excellent agreement with the XRD measurement. The center of the film peak is shifted by 0.015 Å$^{-1}$ in $k_\parallel$, indicating that the layer is tilted $\approx 0.25\degree$ with respect to the MgO(001) substrate. This is most likely due to an imbalance, arising from surface miscut, in the number of dislocations formed on the [110] and [110] glide systems.

Figure 4 shows a typical XTEM image from an epitaxial Ti$_{0.77}$W$_{0.23}$N/MgO(001) layer. The 100 zone-
axis cross-sectional selected area electron diffraction (SAED) pattern exhibits symmetric single-crystal reflections revealing a cube-on-cube epitaxial relationship: Ti$_{1-x}$W$_x$N(001) $\parallel$ MgO(001) with Ti$_{1-x}$W$_x$N(100) $\parallel$ MgO(100). The image, obtained close to the 100 zone axis, shows that the film/substrate interface is abrupt. The most prominent features in the layers are 2-nm-wide nanopipes along the [001] growth direction. The nanopipes are underdense regions which appear bright when the image is underfocused, as is the case for the micrograph in Fig. 4, but appear dark when viewed in overfocused conditions. The surface exhibits a periodic mound structure with an average mound height $\langle h \rangle = 13$ nm and a mound-to-mound spacing of $\approx 24$ nm. Our TEM investigations suggest that the formation of nanopipes is directly related to the presence of the surface cusps separating adjacent periodic growth mounds. The overall surface morphology is characteristic of kinetic roughening previously observed in cubic semiconductor, metal, and TM nitride films grown at relatively low homologous temperatures. The local deposition rate at the bottom of the cusps is reduced due to atomic shadowing which, in combination with limited adatom mobility, gives rise to the formation of nanopipes similar to those previously observed in epitaxial ScN(001), TaN(001), and CrN(001) layers.

Plan-view TEM and XTEM SAED patterns from Ti$_{1-x}$W$_x$N(001) alloys with $x > 0.2$ revealed 1/2$\{111\}$ superstructure reflections in the 013, 011, 112, and 114 zone axes. The superstructure reflections are strongest in Ti$_{0.5}$W$_{0.5}$N(001) alloys and are found to occur only in zone axes containing $\{111\}$ reflections. The set of 001, 013, 011, 112, 114, and $\{111\}$ diffraction patterns, corresponding to a stereographic triangle about the 001 pole of the NaCl structure, are presented in Figs. 5(a)–5(f) for Ti$_{0.50}$W$_{0.50}$N(001).

Half-order superstructure reflections, the signature of long-range atomic order, between fundamental reflections along (111) and (131) directions appear in the 011, 013, 112, and 114 SAED patterns, whereas there are no additional reflections in the 001 and 111 patterns. This is indicative of a doubling of the real-space lattice parameter along $\{111\}$ directions consistent with the formation of CuPt ordering. Since (111) is a polar direction in the NaCl crystal structure, CuPt ordering in Ti$_{1-x}$W$_x$N(001) corresponds to alternating Ti-rich and W-rich $\{111\}$ planes. This structure was confirmed by comparing the experimental SAED patterns with simulated patterns (also shown in Fig. 5) obtained using the DIFFRACT computer program in which alternating $\{111\}$ planes in the cation sublattice are occupied by all Ti and all W atoms. The experimental and simulated patterns exhibit excellent agreement in all zone axes. Minor differences in relative fundamental and superstructure intensity ratios can be ascribed to less than perfect $\{111\}$ cation segregation.

CuPt ordering has been attributed to a variety of mechanisms in different materials systems. It is widely observed in III–V semiconductor pseudobinary alloys, for which calculations have indicated that the ordered phase forms in heteroepitaxially grown alloys in order to reduce the misfit strain. Thus, the degree of CuPt ordering in III–V pseudobinary alloys is highest for alloys with the highest misfit. Since most of these studies are carried out for alloys grown on substrates corresponding to one of the constituents (e.g., In$_{1-x}$Ga$_x$P on GaP(001)), maximum ordering is obtained for alloys with maximum difference in bond lengths. However, as we have shown in Fig. 3, TiN and WN have very similar bond lengths. Thus CuPt ordering in Ti$_{1-x}$W$_x$N(001) is more likely due to a Bethe–Peirls instability caused by Fermi-surface-nesting as observed in CuPt alloys.
nied by a 0.6% reduction in the electronic structure in Ti$_{1-x}$W$_x$N(001) ordered phase. Long-range ordering in Ti$_{0.5}$W$_{0.5}$N is accompanied by a 0.6% reduction in the $a_\perp$ lattice parameter due to a corresponding increase in bond strength in the more stable ordered phase.

We use valence-band XPS to investigate changes in the electronic structure in Ti$_{1-x}$W$_x$N(001) alloys as a function of $x$. Measured photoelectron spectra from alloys with $x=0$, 0.23, 0.40, and 0.60 are plotted (offset to avoid overlap) in Fig. 6 over the binding energy range $-4 \leq E_b \leq 20$ eV. The layers are metallic, as indicated by the nonzero density of states (DOS) at the Fermi edge (located at $E_b=0$ and broadened by $\approx 1$ eV, the energy width of the x-ray source). The three features in the TiN spectrum located near 0.6, 6, and 16.7 eV are attributed to the Ti 3$d$ states, hybridized N 2$p$/Ti 3$d$ states, and N 2$s$ states, respectively. The small feature at 10.8 eV is associated with the presence of oxygen in the nanopipes, whose internal surfaces adsorb oxygen upon air exposure.

TiN has a total of nine valence electrons per formula unit. Therefore the N 2$s$ and hybridized N 2$p$/Ti 3$d$ valence bands are fully occupied, containing 2 and 6 electrons per unit formula, respectively, while the remaining electron per formula unit partially fills the 3$d$ conduction bands. The Ti$_{1-x}$W$_x$N(001) alloy spectra closely resemble the TiN(001) XPS spectrum, exhibiting the same three primary features without significant energy shifts. This is not surprising since, with increasing $x$, Ti cations are replaced by W, in the same crystal structure. W has two more $d$ electrons than Ti, leading to an increase in the number of valence electrons with increasing $x$. These extra electrons occupy states in the $d$ conduction bands. Since, the $d$ bands contain 1, 1.5, 1.8, and 2.2 electrons per formula unit for Ti$_{1-x}$W$_x$N(001) with $x=0$, 0.23, 0.40, and 0.60, respectively, we observe an increase in the intensity of the peak associated with the metal $d$ bands, relative to that from the hybridized $p-d$ and the N 2$s$ states, with increasing $x$. The hybridized $p-d$ bands near 6 eV, which primarily determine the cation–anion bond strengths, remain essentially unchanged. This is in agreement with our XRD results showing that the alloy lattice parameter remains constant as a function of $x$. Even the slight decrease in $a_\perp$ at $x=0.50$ attributed to CuPt ordering corresponds to only an average decrease of 0.6% in bond length. This is too small of a change to be observed by XPS.

The room-temperature resistivity $\rho$ of single crystal Ti$_{1-x}$W$_x$N(001) alloys is plotted versus $x$ in Fig. 7(a). $\rho$ is $13 \, \mu\Omega \cdot \text{cm}$ for TiN(001), in agreement with previously published values for single crystal layers, and increases linearly with $x$ to $287 \, \mu\Omega \cdot \text{cm}$ for Ti$_{0.42}$W$_{0.58}$N(001). We attribute the increase in $\rho$ with $x$ primarily to a combination of alloy scattering and a flattening of the bands at the Fermi level.

Figure 7(b) shows typical resistivity $\rho$ versus temperature $T$ curves for single crystal Ti$_{1-x}$W$_x$N(001) alloys. Above the superconducting transition at $T_c=5.5$ K, the TiN ($x=0$) resistivity remains approximately constant at $\rho=0.84 \, \mu\Omega \cdot \text{cm}$ up to $\approx 50$ K, then increases linearly with $d\rho/dT=5.6 \times 10^{-8} \, \mu\Omega \cdot \text{cm} \cdot \text{K}^{-1}$ due primarily to phonon scattering. $\rho(T)$ curves for Ti$_{1-x}$W$_x$N(001) alloys with $x \leq 0.21$ also...
exhibit metallic behavior, similar to that of TiN(001), with constant resistivity values $\rho_0$ at low temperatures followed by the onset of phonon scattering near 50 K. $\rho_0$ increases with $x$ due to alloy scattering. However, the data in Fig. 7(b) indicates that the major component, 94%, of the room-temperature resistivity for TiN(001) is due to phonon scattering. The percentage drops steeply with the addition of WN to temperature resistivity for TiN.

Figure 7(b) shows that Ti$_{1-x}$W$_x$N alloys with $x>0.21$ exhibit a negative temperature coefficient of resistivity (TCR). We attribute this to a weak localization of conduction electrons as a result of the perturbation in the periodic crystal potential associated with the randomly distributed W atoms. This is also true for samples exhibiting CuPt ordering, indicating that, as mentioned above, even the ordered phase contains a considerable fraction of scattering centers, consistent with the fact that we do not observe an anomalous change in $\rho_{300 \text{ K}}$ with $x$ near 0.5 in Fig. 7(a).

The low-temperature Ti$_{1-x}$W$_x$N(001) resistivity $\rho_0$ increases from 170 $\mu$Ω cm at $x=0.26$ to 361 $\mu$Ω cm with $x=0.58$ due to a decrease in the electron scattering length, and hence stronger localization, with increasing WN concentrations.

Hall measurements have been performed on Ti$_{1-x}$W$_x$N/MgO(001) alloys at temperatures ranging from $T_c$ to 300 K. For TiN ($x=0$), the Hall coefficient $R_H$ is equal to $-1.1 \times 10^{-4}$ cm$^3$C$^{-1}$ at low temperature and increases linearly to $-0.8 \times 10^{-4}$ cm$^3$C$^{-1}$ as $T$ is ramped from 100 to 300 K. For the alloys, however, $R_H$ values are nearly independent of temperature over the entire measurement range, $10 \leq T \leq 300 \text{ K}$. This behavior is consistent with the resistivity results presented in Fig. 7(b) showing that the resistivity, which is the temperature-dependent part of the resistivity, constitutes the dominant contribution to the overall resistivity value only for alloys with $x$ near zero.

Room-temperature $R_H$ values are plotted in Fig. 8 for Ti$_{1-x}$W$_x$N(001) alloys as a function of WN composition $x$. $R_H$ for TiN ($x=0$) is $-0.8 \times 10^{-4}$ cm$^3$C$^{-1}$, in excellent agreement with the previously reported value. The negative sign indicates $n$-type charge carrier conduction as expected due to the partially-filled $d$ bands in TiN. $R_H$ remains equal to $-0.8 \times 10^{-4}$ cm$^3$C$^{-1}$ for Ti$_{0.87}$W$_{0.13}$N alloys. For alloys with $x \geq 0.21$, however, $R_H$ becomes positive (the layers are $p$ type) and decreases continuously with $x$ from $R_H = 0.70 \times 10^{-4}$ cm$^3$C$^{-1}$ for Ti$_{0.79}$W$_{0.21}$N(001) to 0.26 $\times 10^{-4}$ cm$^3$C$^{-1}$ for Ti$_{0.3}$W$_{0.7}$N(001). The change in $R_H$ can be explained using the calculated TiN band structure. The conduction band of TiN consists of one low-lying band which contains the majority of carriers while two higher-lying bands are only sparsely occupied. Therefore, as the number of carriers in Ti$_{1-x}$W$_x$N increases linearly with $x$, as indicated by our XPS results, the Fermi level increases and the lowest lying band becomes more than half full giving rise to $p$-type behavior. We expect the transition from $n$ to $p$ type to occur at a filling of $\approx 1.4$ conduction electrons per unit formula, corresponding to a Ti$_{1-x}$W$_x$N with $x=0.2$, in good agreement with the data shown in Fig. 8.

Ti$_{1-x}$W$_x$N(001) superconducting critical temperatures $T_c$ are plotted as a function of alloy composition $x$ in Fig. 9. $T_c$ for pure TiN(001) is 5.5 K, within the range of previously reported values, 4.6–6.0 K. For Ti$_{1-x}$W$_x$N(001) alloys, $T_c$ gradually increases with increasing $x$ to reach a maximum at $T_c=6.67$ K with $x=0.21$. We attribute the shape of the $T_c$ versus $x$ curve to the competition between two primary effects. Increasing WN concentrations lead, as observed in our valence-band XPS measurements, to an increasing DOS at the Fermi level and, consequently, to higher $T_c$ values. However, at larger WN concentrations ($x \geq 0.21$), this effect is increasingly compensated by the localization of vibrational modes which reduces the phonon-mediated long-range effective electron–electron coupling. In addition to these two competing effects, the increase in $T_c$ at low $x$ is also partially due to the replacement of Ti on the cation sublattice by the much heavier W atoms causing increased electron–phonon coupling.

**IV. CONCLUSIONS**

Epitaxial B1-NaCl structure Ti$_{1-x}$W$_x$N(001) alloys with $0 \leq x \leq 0.6$ were grown on MgO(001) substrates at 500 °C by UHV reactive magnetron sputtering from Ti and W targets in pure N$_2$. The layers are slightly overstoichiometric, with $\text{N/(Ti+W)}=1.06 \pm 0.05$ for $x \geq 0.05$, due to the trapping of
energetic N atoms backscattered from the W target. TEM and XTEM analyses show that Ti$_{0.42}$W$_{0.58}$N(001) alloys exhibit long-range CuPt atomic ordering on the cation sublattice. Ti$_{1-x}$W$_x$N(001) lattice parameters $a_\perp$ along the growth direction are equal to 4.251 Å, irrespective of alloy composition for $x \leq 0.41$, but exhibit a weak minimum, $a_\perp = 4.226$ Å at $x = 0.5$, due to ordering. Valence band XPS measurements indicate that the addition of WN to TiN results in continuous filling of the $d$ bands, leading to a larger DOS at the Fermi level. Room-temperature resistivities increase linearly from $\rho = 13 \ \mu \Omega \ cm$ for TiN(001) to 287 $\mu \Omega \ cm$ for Ti$_{0.42}$W$_{0.58}$N(001) while the TCR is positive for the DOE, at the University of Illinois. Microanalysis of Materials, which is partially supported by the DOE, reaches a maximum of 6.67 K at T$_c$, initially increases with x, reaches a maximum of 6.67 K at x = 0.21, and decreases at larger x values. The maximum T$_c(x)$ results from the competition between an increasing DOS at the Fermi level and a reduction of the phonon-mediated long-range effective electron–electron coupling due to the localization of vibrational modes.

**ACKNOWLEDGMENTS**

This work was supported by the U.S. Department of Energy, Division of Materials Science, under Grant No. DEFG02-ER9645439 through the University of Illinois Frederick Seitz Materials Research Laboratory. The authors also appreciate the use of the facilities of the FS-MRL Center for Microanalysis of Materials, which is partially supported by the DOE, at the University of Illinois.

30. The diffraction calculation program, “Diffracl v. 1.2,” was distributed by Virtual Laboratory, Albuquerque, NM.