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## Enhanced hardness in epitaxial TiAlScN alloy thin films and rocksalt TiN/(Al,Sc)N superlattices

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High hardness TiAlN alloys for wear-resistant coatings exhibit limited lifetimes at elevated temperatures due to a cubic-AlN to hexagonal-AlN phase transformation that leads to decreasing hardness. We enhance the hardness (up to 46 GPa) and maximum operating temperature (up to 1050 °C) of TiAlN-based coatings by alloying with scandium nitride to form both an epitaxial TiAlScN alloy film and epitaxial rocksalt TiN/(Al,Sc)N superlattices on MgO substrates. The superlattice hardness increases with decreasing period thickness, which is understood by the Orowan bowing mechanism of the confined layer slip model. These results make them worthy of additional research for industrial coating applications. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4898067]

Hardness is a measure of how readily dislocations are formed within a material and how easily these dislocations propagate under an applied stress. Hardness is directly associated with a material's plastic properties, and is only indirectly associated with its elastic constants.<sup>1,2</sup> Researchers have often wondered whether it is possible to design a material with a hardness approaching or greater than that of diamond (the hardest known material). The design and realization of superhard materials would prove beneficial in abrasion/wear-resistant applications like cutting tools, bearings, and tribology.<sup>3–6</sup>

Transition metal nitrides are attractive as coating materials in many technological applications<sup>7,8</sup> since they are hard, chemically stable at high temperatures, exhibit high melting temperatures, and are readily deposited on tooling substrates via both reactive sputtering and cathodic arc deposition. Titanium nitride (TiN) is a leading coating material<sup>9,10</sup> which is used for edge retention and corrosion resistance on machine tooling, such as drill bits and milling cutters, often improving tool lifetime by a factor of three or more. However, the hardness of TiN is relatively low ( $\approx$ 20–24 GPa) and the oxidation resistance of TiN in air is limited to temperatures below 700 °C, beyond which TiN forms TiO<sub>2</sub> and nitrogen bubbles.<sup>11</sup> Several ternary and quaternary alloy systems of TiN (e.g., (Ti,Al)N, (Ti,C)N, and (Ti,Al,V)N) have been developed to increase hardness and oxidation resistance. (Ti,Al)Nbased coatings<sup>12</sup> are the most commonly employed industrial tool coating with hardness greater than that of TiN and exhibiting greater oxidation resistant than TiN. Despite its superior properties, (Ti,Al)N-based coatings have a limited maximum operating temperature and lifetime due to the formation of hexagonal AlN grains at high temperatures.<sup>13</sup>

Thin-film multilayers and superlattices are a potential configuration that may realize extraordinarily hard materials with long lifetime at high operating temperatures. Koehler<sup>14</sup> proposed in the 1970s that the interfaces in superlattices should act as high energy barriers for dislocation motion, thereby increasing hardness. Based on their suggestion,

several superlattice systems<sup>15–17</sup> (e.g., TiN/NbN, TiN/VN, and TiN/CrN) have been developed that show improved hardness compared to TiN and (Ti,Al)N. However, all of the nitride superlattices mentioned above are miscible at temperatures exceeding 800 °C, which significantly limits their usefulness in cutting tool applications where the surface temperature can reach as high as 1000 °C during the cutting process. Cubic (rocksalt)-TiN/AlN superlattices have been developed<sup>18</sup> to overcome the miscibility problem since TiN/AlN superlattices are immiscible up to ~1000 °C.<sup>19</sup> TiN/AlN superlattices also exhibit excellent oxidation resistance, relatively high hardness compared to TiN, and they are already used commercially as a coating material.

However, TiN/AIN superlattice coatings have a significant drawback that limits their practical applications. The hardness of TiN/AIN superlattices is around 33–35 GPa when the thickness of the AIN layers is less than 2–3 nm, but decreases sharply to 23–24 GPa as the AIN layer thickness is increased. This large reduction in hardness is attributed to the transition from the epitaxially stabilized metastable c-AIN phase to the stable wurtzite-AIN phase when the AIN layer thickness exceeds the critical thickness of 2–3 nm.<sup>18,20,21</sup> The formation of wurtzite-AIN breaks the epitaxial relationship with c-TiN leading to polycrystalline grain growth and a significant hardness reduction. The same c-AIN to wurtzite-AIN transition is also the cause for deteriorating hardness in industrial TiAIN tool coatings.

We overcome the significant critical thickness limitation of TiN/AlN superlattices by alloying the AlN layers with scandium nitride (ScN). We previously reported on epitaxially stabilized c-(Al,Sc)N films deposited on TiN/MgO substrates with critical thickness values exceeding 200 nm.<sup>22</sup> The resulting c-TiN/(Al,Sc)N superlattices exhibit enhanced hardness values compared to traditional TiAlN coatings and are stable at higher temperatures (up to 4 h at 1050 °C). The confined layer slip model is used to explain the hardness enhancement in the superlattices. Surprisingly, a Ti<sub>0.5</sub>Al<sub>0.36</sub>Sc<sub>0.14</sub>N alloy thin film, whose composition represents the average composition of the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices studied herein, exhibits the highest hardness value (46 GPa) of all our films, even exceeding the hardness of the superlattice films. The alloy result is promising given the simplicity of deposition and high temperature stability afforded to alloy films versus superlattices.

In addition to MgO (001) substrates, alloy and superlattice films were also deposited on Si (001) and sapphire (0001) substrates. Microstructural characteristics and mechanical properties of these films are presented in the supplementary material<sup>35</sup> with the remainder of the paper focused on films deposited on MgO.

In order to deposit single-crystalline defect-free TiN/ (Al,Sc)N superlattices, the (Al,Sc)N alloy was lattice matched with TiN using 72% AlN mole fraction. The TiN/  $Al_{0.72}Sc_{0.28}N$  superlattices discussed herein are single crystalline and coherent. The crystallographic and microstructural characteristics of the TiN/ $Al_{0.72}Sc_{0.28}N$  superlattices are briefly described and the mechanical properties are discussed in greater detail to show the usefulness of TiN/ (Al,Sc)N superlattices as well as Ti<sub>0.5</sub>Al<sub>0.36</sub>Sc<sub>0.14</sub>N alloys as hard-coating materials. The individual thin film and the superlattices are deposited with a reactive dc-magnetron sputtering technique inside a high vacuum chamber. Details of the superlattice growth, x-ray diffraction, and TEM analysis are presented in the experimental details section of the supplementary material.<sup>35</sup>

The x-ray diffraction spectra of TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices (Fig. 1(a)) show that the superlattices grow with a 002-orientation on MgO (001) substrates. The superlattices exhibit a small degree of mosaicity indicated by an extremely small rocking curve full-width-at-half-maximum (FWHM) of 0.065° for the 002 diffraction peak. Such a small rocking curve FWHM value suggests that the superlattices are nearly single crystalline. A reciprocal space x-ray map from the 10 nm/10 nm TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattice (Fig. 1(b) adapted from our previous publication (Ref. 23)) suggests that the superlattices are pseudomorphic on MgO (001) substrates. The 024 superlattice diffraction peak, the 024 MgO diffraction peak, and the interference fringes are all aligned vertically indicating that the in-plane lattice constants of both TiN and  $Al_{0.72}Sc_{0.28}N$  are fixed with that of MgO (4.21Å). The out-of-plane lattice constants for TiN and Al<sub>0.72</sub>Sc<sub>0.28</sub>N are 4.23 Å and 4.26 Å, respectively. The interference fringes in both Figs. 1(a) and 1(b) are distinct and sharp, indicating atomically abrupt interfaces. X-ray reflectivity (XRR) measurements (not presented here, see Ref. 24 for detailed analysis) and subsequent data fitting suggest that the interface roughness values are on the order of 0.2-0.4 nm, which corresponds to one to two atomic layers.

The  $Ti_{0.5}Al_{0.36}Sc_{0.14}N$  alloy thin film (lattice constant = 4.24 Å) also grows with a 002-orientation on MgO (001) substrates as shown in the symmetric  $2\theta$ - $\omega$  x-ray diffraction spectrum of Figure 1(c). The rocking curve FWHM of the 002 diffraction peak is about 0.04°, indicating that the alloy is nominally single crystalline, and exhibits improved crystal quality compared to the superlattices.

The thermal stability of the superlattices were investigated via *ex-situ* annealing treatments in forming gas (5%  $H_2$ :95%  $N_2$ ) followed by synchrotron based x-ray diffraction with a 2D-detector. A detailed treatment of the annealing study is beyond the scope of this article and will be presented in a separate report. However, we have observed that the TiN/ Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices are stable at 1050 °C for 4 h. As the annealing time is increased, the metastable Al<sub>0.72</sub>Sc<sub>0.28</sub>N



FIG. 1. (a) Symmetric  $2\theta$ - $\omega$  x-ray diffraction spectra of the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices as a function of superlattice period. The superlattices grow with 002-orientation on the MgO (001) substrates with small a degree of mosaicity. (b) Reciprocal space x-ray 024 diffraction map of the 10 nm/10 nm superlattice suggesting the pseudomorphic and epitaxial nature of superlattices when deposited on MgO (001) substrates. (c) Symmetric  $2\theta - \omega$  x-ray diffraction spectrum of the Ti<sub>0.5</sub>Al<sub>0.36</sub>Sc<sub>0.14</sub>N alloy thin film deposited on an MgO (001) substrate. The smaller rocking curve FWHM value for the alloy thin film compared to the superlattice films indicates higher crystal quality in the alloy thin film (Adapted from Ref. 23).

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 136.152.38.197 On: Mon, 09 Feb 2015 20:05:26 undergoes a rocksalt to wurtzite structural phase transformation that is captured in our synchrotron analysis.

The microstructures of the superlattices are characterized by high resolution transmission electron microscopy (HRTEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) based techniques. The HRTEM image in Fig. 2(a) shows a high quality TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattice with sharp interfaces where the TiN layer thickness is kept constant at 20 nm and the Al<sub>0.72</sub>Sc<sub>0.28</sub>N layer thickness is varied from 2 nm to 80 nm. Even the 2 nm  $Al_{0.72}Sc_{0.28}N$  layer is clearly visible in Fig. 2(a). The high magnification image of the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N interface (Fig. 2(b)) shows a cube-on-cube epitaxial relationship of TiN (001)[100]||MgO (001)[100] and Al<sub>0.72</sub>Sc<sub>0.28</sub>N (001)[100]||TiN (001)[100]. The interfaces are latticematched and pseudomorphic. We do not see any signature of a misfit dislocation at the interface as far as we can verify. The fast Fourier transformation (FFT) from the Al<sub>0.72</sub>Sc<sub>0.28</sub>N region indicates a rocksalt (cubic) diffraction pattern, which demonstrates the stabilization of the metastable rocksalt phase of Al<sub>0.72</sub>Sc<sub>0.28</sub>N between TiN layers. An HAADF-STEM image (Fig. 2(c)) shows TiN layers (light layers) and Al<sub>0.72</sub>Sc<sub>0.28</sub>N layers (dark layers) along with some V-shaped structural defects that originate at the substrate surface and propagate through the superlattice.

The mechanical properties of the superlattices and individual reference thin films were measured via nanoindentation with a Hysitron Triboindenter 950 equipped with a Berkovich probe with a radius of approximately 150 nm. Forty-nine indents, arrayed in a square, were made in each sample using a load controlled, partial-unloading method with a peak load of 2000  $\mu$ N. Indents were spaced 20  $\mu$ m apart so that the plastic zone of a previous indent did not influence the subsequent indent. The contact radius of each indent at maximum load was less than half of the total film

## thickness, thus substrate mechanical properties should not drastically impact the measured film properties.

The hardness values of the individual component films, c-TiN (300 nm on MgO) and cubic-Al<sub>0.72</sub>Sc<sub>0.28</sub>N (200 nm on 20 nm TiN/MgO), are shown as horizontal dashed lines in Figure 3(a). The reduced modulus is first calculated from the unloading slope of each indentation load-displacement record according to the following equation:<sup>25,26</sup>

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A}.$$

Here, stiffness, dP/dh, is experimentally measured from the upper portion of the unloading curve, A is the projected area of the elastic contact, and reduced modulus,  $E_r$ , is defined as

$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i},$$

where  $\nu$  and E are Poisson's ratio and the elastic modulus of the sample, respectively, and  $\nu_i$  and  $E_i$  are Poisson's ratio (0.7) and elastic modulus (1147 GPa) of the diamond indenter, respectively. Hardness is computed by dividing the maximum indentation load,  $P_{max}$ , by the projected area, A. Representative load-displacement curves are presented in Figure 3(b).

Single-crystalline c-TiN films grown on MgO (001) substrates exhibit a hardness of 23 GPa and reduced elastic modulus of 301 GPa, consistent with previously published results.<sup>9,10</sup> The measured hardness of the cubic-Al<sub>0.72</sub>Sc<sub>0.28</sub>N film is 31 GPa with a reduced elastic modulus of 324 GPa. The hardness value of the cubic-Al<sub>0.72</sub>Sc<sub>0.28</sub>N alloy thin film is higher than both cubic-ScN and wurtzite-AlN thin films. We cannot accurately use the rule-of-mixtures method to predict the hardness of the Al<sub>0.72</sub>Sc<sub>0.28</sub>N alloy since the



FIG. 2. (a) HRTEM image of a TiN/ Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattice where the 2 nm Al<sub>0.72</sub>Sc<sub>0.28</sub>N layer is clearly visible. The interfaces are sharp and abrupt. The TiN layers are uniform with a thickness of 20 nm. (b) High magnification TEM image of the TiN/ Al<sub>0.72</sub>Sc<sub>0.28</sub>N interface showing cubeon-cube crystal growth. FFT of the TiN and Al<sub>0.72</sub>Sc<sub>0.28</sub>N layers show that both layers are cubic (c) HAADF-STEM image of the superlattice where the TiN layers appear light while the  $Al_{0.72}Sc_{0.28}N$  layers appear dark. The  $2 \text{ nm Al}_{0.72} \text{Sc}_{0.28} \text{N}$  layer is also clearly visible in the image.

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FIG. 3. (a) Superlattice hardness as a function of the superlattice period thickness for superlattices deposited on MgO (001) substrates. The hardness of superlattices deposited on MgO increases with decreasing superlattice period. (b) Representative load vs. depth curves during the nano-indentation measurement using the partial-unloading method.

hardness of metastable cubic-AlN thin films is unknown. However, given that the hardness of wurtzite-AlN (Ref. 27) is between 11 and 15 GPa and the hardness of cubic-ScN (Ref. 28) is about 21 GPa, the measured hardness of the cubic-Al<sub>0.72</sub>Sc<sub>0.28</sub>N alloy is reasonable as other researchers have reported nanoscale system hardness values on the order of 2–3 times greater than the rule-of-mixtures estimates based on the constituent materials.<sup>29</sup> The hardness enhancement is probably due to the fact that the Al<sub>0.72</sub>Sc<sub>0.28</sub>N alloy is lattice matched with the TiN/MgO substrate and grows as an epitaxial single crystal film with a low density of defects and dislocations.

The measured hardness values of the epitaxial singlecrystalline superlattices grown on MgO (001) substrates are plotted as a function of superlattice period in Figure 3 (hardness values of superlattices grown on Si (001) and sapphire (0001) substrates are reported in the supplementary material<sup>35</sup>). The indentation moduli of all the superlattices grown on MgO (001) substrates are in the range of 350 GPa  $\pm$  30 GPa and the moduli do not vary significantly with superlattice period thickness. A slight increase in the modulus with decreasing lattice period may be due to the hardening of the film leading to more bending (i.e., a drumhead) rather than fully plastic indentation throughout the film.<sup>30</sup>

The hardness of the superlattices increases monotonically with decreasing superlattice period thickness. We obtain a maximum hardness of 42 GPa for a 1.5 nm/1.5 nm TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattice, which is 82% greater than that of TiN and 65% greater than a superlattice hardness of 27 GPa predicted from the rule-of-mixtures. Previous studies on TiN/NbN and TiN/VN superlattices showed that superlattice hardness exhibits a maximum value at a superlattice period of about 8 nm, after which the hardness decreases with decreasing period thickness. The authors of these papers identified intermixing at the superlattice interfaces as a possible reason for such behavior. However, we do not observe any decrease in hardness with decreasing period thickness primarily due to the fact that our superlattices have an interface roughness of about 0.2-0.4 nm, and therefore lack any significant intermixing. The measured hardness of the superlattices is higher than that predicted by the rule-of-mixtures for superlattice periods of 3 nm, 6 nm, 10 nm, and 15 nm. However, the hardness of the superlattices converges to the hardness of TiN (23 GPa) when the superlattice period is increased to 20 nm.

Increasing hardness with decreasing period thickness in TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices follows the trend observed in nanoscale metallic multilayers of Cu and Ni as described by Misra *et al.*<sup>31</sup> The authors report a hardness increase of nearly three times when the period thickness of a Cu-Ni system decreases from 200 nm to 10 nm; this strength enhancement is consistent with the breakdown of Hall-Petch behavior in nanoscale materials and suggests that deformation behavior is no longer controlled by dislocation pile-ups. The period thicknesses and similar crystallography of the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices investigated in this work suggest that single-dislocation-based strengthening mechanisms likely control deformation in this system.

During the initial stages of superlattice plastic deformation, glide dislocations are confined to slip in a single layer. A dislocation loop nucleated within a layer will glide by the Orowan bowing mechanism parallel to the interface, leaving behind misfit dislocations along the interface as it moves. When a layer yields plastically, load is transferred to the next elastically deforming layer; full plasticity in the composite occurs once sufficient load is transferred so as to allow slip transmission across the interface and yielding of the adjacent layer. The strength of multilayer systems scales<sup>32</sup> with ln(h)/h, where *h* is the period thickness. As period thickness decreases, the Orowan stress confined to a single layer increases, leading to an overall increase in the hardness of the superlattice.

Coherency stresses resulting from lattice parameter mismatch<sup>33,34</sup> and Koehler images forces resulting from shear modulus mismatch<sup>14</sup> have been invoked to explain strength increases in certain coherent nanoscale metallic multilayers. However, below a critical thickness for coherency loss, the coherency stress is typically independent of layer thickness.<sup>33</sup> Additionally, in the current superlattice system, TiN and Al<sub>0.72</sub>Sc<sub>0.28</sub>N are nearly lattice matched, reducing the likelihood of misfit dislocations at the interface. Thus, it is unlikely that coherency stress effects contribute significantly to the observed hardening. Furthermore, the shear moduli of the TiN and  $Al_{0.72}Sc_{0.28}N$  layers do not differ greatly; it is unlikely that substantial strengthening is derived from the development of Koehler image forces between layers. Therefore, hardening of TiN/ Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices as period thickness decreases is likely best described by the Orowan bowing mechanism of the confined layer slip model.

The hardness of a  $Ti_{0.5}Al_{0.36}Sc_{0.14}N$  alloy thin film (Fig. 3(a)) was also measured since it represents the equivalent

alloy of the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices. Surprisingly, the hardness of this alloy is about 46 GPa, which is higher than the maximum hardness exhibited by any of the superlattices. The elastic modulus of this alloy sample is also high ( $\approx$ 410 GPa). X-ray analysis indicates that the crystal quality of the Ti<sub>0.5</sub>Al<sub>0.36</sub>Sc<sub>0.14</sub>N alloy thin film is better than that of the superlattices, which is manifested by a smaller rocking curve FWHM value. Therefore, the high hardness could be due to an extremely low density of defects and dislocations; the strengthening mechanism in this novel crystalline alloy with high impurity content but low line or area defects is likely different than the Orowan mechanism that is the suspected hardening method in the multilayer. Further, microstructural analysis is needed to help explain the details of high hardness of this alloy film. Nevertheless, an alloy film with hardness higher than a superlattice of the same constituent materials is desirable as an industrial hard coating due to the alloy's enhanced mechanical properties, the ease of deposition for alloys compared to superlattices, and the enhanced long-term thermal stability compared to superlattices whose layered structure may break down via diffusion mechanisms.

In conclusion, an epitaxial Ti<sub>0.5</sub>Al<sub>0.36</sub>Sc<sub>0.14</sub>N alloy thin film and epitaxial rocksalt-TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices are developed that show significant hardness enhancement compared to TiN and industrial-based TiAlN hard coatings. Incorporation of scandium increases the critical thickness of the metastable cubic-Al<sub>0.72</sub>Sc<sub>0.28</sub>N phase in TiN/ Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices and results in higher hardness values compared with TiN/AlN superlattices. The hardness of the superlattices increases monotonically with decreasing superlattice period and the equivalent Ti<sub>0.5</sub>Al<sub>0.36</sub>Sc<sub>0.14</sub>N alloy thin film exhibits the highest hardness value. The TiN/ Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices grow with 002-orientation on MgO (001) substrates with sharp interfaces, and are stable in the cubic phase at 1050 °C for 4 h, after which the cubic Al<sub>0.72</sub>Sc<sub>0.28</sub>N layers begin to transform into the thermodynamically stable wurtzite phase. The high hardness and excellent thermal stability make the  $Ti_{0.5}Al_{0.36}Sc_{0.14}N$  alloy thin films and TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices attractive hard-coating candidates for cutting tool applications. The Ti<sub>0.5</sub>Al<sub>0.36</sub>Sc<sub>0.14</sub>N alloy is particularly attractive and deserves further study using industrial-relevant tooling substrates such as cemented carbide.

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