CHAPTER 7       STRUCTURES AND PROPERTIES OF AlTiN ALLOY AND MULTILAYERS

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7.1 Abstract

Here we present a novel method to grow uniform Al\textsubscript{x}Ti\textsubscript{1-x}N alloys (x up to 70%) and highly aligned TiN/AlN superlattices by pulsed laser deposition. In this method TiN and AlN targets are arranged in a special configuration that they can be ablated in sequence. As the concentration of these two targets varies, the as-grown films either have layer by layer growth of TiN(1nm)/AlN(4nm) superlattice structures (x>80%), or form very uniform alloys (x up to 70%). X-ray diffraction and transmission electron microscopy (TEM) analysis showed the cubic structure for both nanoscale multilayers and alloys. Microstructure and uniformity for the superlattice structures and alloys were studied by TEM (cross-section and plan-view) and Scanning transmission electron microscopy with Z-contrast (STEM). Nanoindentation results suggested high hardness for these new structures and four point probe electrical resistivity measurements showed overall insulating behavior for both alloys and superlattices.
7.2 Introduction

Superhard thin films and coatings are needed for applications such as cutting tools that require improved surface resistance to wear, friction, oxidation and corrosion. Binary component coating materials exhibit interesting structural and mechanical properties which can fit in above requirements.\textsuperscript{1,2} For example, transition metal nitride thin films, especially titanium nitride (TiN), have served as the most practical and economical protective coatings, because TiN exhibits a metallic character with golden color and high hardness, high temperature stability, and abrasion resistance. However, TiN gets oxidized above 500°C to form a rutile-structure which limits its applications in high speed cutting tools.\textsuperscript{2, 3} AlN thin layers have remarkable hardness, thermal and chemical stability and high electrical resistivity. TiN-AlN binary-component coatings can integrate their functionalities and show much higher oxidation resistance, lower internal stresses and better adhesion.\textsuperscript{4} TiN-AlN binary-components can be formed in two types of structures. One is uniform alloy which AlN concentration is lower than 60%.\textsuperscript{5, 6} If AlN concentration is higher than 60%, phase separation results which may lead to precipitation hardening.\textsuperscript{7} The other type is multilayer structure where there is no reaction between TiN and AlN. Especially, nanometer-scale multilayer structures attract a lot of interest due to their special interfacial structure which may leads to novel structural and mechanical properties.\textsuperscript{8, 9} In this paper we present a novel method to grow highly aligned TiN/AlN superlattice and Al\textsubscript{x}Ti\textsubscript{1-x}N alloys by pulsed excimer laser. In this method TiN and AlN targets are arranged in a special configuration that they can be ablated in sequence. As the concentration of these two targets varies, the as-grown films either have layer by layer growth of TiN(1nm)/AlN(4nm) superlattice structures, or form very uniform alloys. The structure of AlN in these structures is determined to be cubic.
which is metastable and stabilized by the TiN thin buffer layer. And the phase separation concentration is increased to 80% which is higher than 60% reported values.

7.3 Experimental

The depositions of TiN buffer layer and Al\(_x\)Ti\(_{1-x}\)N alloys were performed in a multitarget chamber with a KrF excimer laser (Lambda Physik 210 \(\lambda = 248\) nm, 10 Hz). The targets were hot-pressed stoichiometric TiN and AlN obtained from CERAC Inc. The target for Al\(_x\)Ti\(_{1-x}\)N alloys deposition is specially arranged, which is shown in Fig. 1. The ratio of the area of two targets can determine the concentration of these as-deposited films and finally determine the structure of films. For superlattice case, by varying the target rotation speed and laser ablation frequency, the thickness of TiN/AlN superlattice layers can be engineered. TiN buffer layer and all three concentration Al\(_x\)Ti\(_{1-x}\)N samples were deposited at a base pressure of about \(1 \times 10^{-7}\) Torr and substrate temperature 650\(\pm\)10°C. Crystal structure of these films was determined by X-ray diffraction using a Rigaku X-ray diffractometer with CuK\(_\alpha\) radiation and Ni filter. Microstructural characterization of these films was performed by high resolution transmission electron microscopy (HRTEM, plan-view and cross-section) and scanning transmission electron microscopy (STEM) using a JEOL-2010F analytical electron microscope with point to point resolution of 0.18 nm(TEM) and 0.12 nm(STEM). The surface morphology of these films was studied by SEM. The hardness ‘H’ and elastic modulus ‘E’ of the films were measured by using a nanoindenter method. The resistivity of the multilayers was measured by Four-point probe technique.
7.4 Result and discussion

Benefit from the special arranged target assembly for TiN/AlN deposition, the ratio of the area of two targets can determine the concentration of these superlattice or alloy structures. As we vary the concentrations from 60% AlN, to 70%AlN, final to 80% AlN, the Al\textsubscript{x}Ti\textsubscript{1-x}N films changed from uniform alloys to superlattice structure. The detailed deposition information is listed in Table 1. The resultant concentrations are measured by RBS profile and fitted with simulation results, which is close to the concentrations proposed. (see table 1)

X-ray diffraction pattern (intensity vs. 2\(\theta\)) of Al\textsubscript{0.6}Ti\textsubscript{0.4}N alloy and AlN/TiN (Al\textsubscript{0.8}Ti\textsubscript{0.2}N) multilayers on Si (100) using TiN as buffer layers are shown in Fig.2 (a) and (b) respectively. In both of the X-ray patterns, the two TiN peaks centered at 42.42\(^o\) and 93.18\(^o\) are indexed as (200) and (400), respectively, suggesting that TiN buffer layers have grown highly textured on
Si(100). For $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}$ alloy, $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}$ (200) peak almost merged with TiN(200) peak, because $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}$ alloy has very close lattice parameter with TiN which indicates the AlN has mixed into TiN lattice site and formed very uniform alloy. For $\text{Al}_{0.7}\text{Ti}_{0.3}\text{N}$, the X-ray diffraction is very similar to $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}$ diffraction showing the uniform alloy formed even at 70% AlN. For $\text{Al}_{0.8}\text{Ti}_{0.2}\text{N}$, in stead of the alloy peak, the B1 cubic AlN(200) peak showed at 43.92° which indicates that the AlN did not mix with TiN and metastable B1 cubic AlN has been stabilized by the cubic TiN buffer layer and thin TiN multilayers in the superlattice configuration. The lattice parameter of this cubic AlN layer is calculated to be 0.412nm, which is slightly larger than 0.408nm of the cubic-phase AlN reported by Madan et al.\textsuperscript{10}

<table>
<thead>
<tr>
<th>Target Concentration</th>
<th>Laser Energy</th>
<th>Temperature °C</th>
<th>RBS</th>
<th>Result Structure</th>
<th>Uniformity and Structure</th>
</tr>
</thead>
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<tr>
<td>$\text{Al}<em>{0.6}\text{Ti}</em>{0.4}\text{N}$</td>
<td>600mJ</td>
<td>650°C</td>
<td>$X=0.57\pm0.05$</td>
<td>$\text{Al}<em>{0.6}\text{Ti}</em>{0.4}\text{N}$ alloy /TiN/Si</td>
<td>Uniform and Cubic structure</td>
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<tr>
<td>$\text{Al}<em>{0.8}\text{Ti}</em>{0.2}\text{N}$</td>
<td>600mJ</td>
<td>650°C</td>
<td>$X=0.78\pm0.05$</td>
<td>TiN(1nm)/AlN(4nm) superlattice /TiN/Si</td>
<td>Phase separation and Cubic structure</td>
</tr>
</tbody>
</table>

Table 1. Comparisons of various deposition concentrations and resultant structures.
Figure 2. XRD patterns (intensity vs. 2θ) from (a) Al$_{0.6}$Ti$_{0.4}$N alloy and (b) superlattice structure (Al$_{0.8}$Ti$_{0.2}$N), showing (200) and (400) peaks TiN buffer layer and (200) peak from cubic Al$_{0.6}$Ti$_{0.4}$N and cubic AlN, respectively.
In order to study the microstructure and uniformity of these alloys and nanoscale multilayer structures, low magnification and high magnification TEM were performed on all three different concentration samples. Figure 3(a) shows the low magnification <110> cross-section TEM of Al_{0.6}Ti_{0.4}N alloy on Si(100) by TiN as buffer layer. It is very clear that uniform Al_{0.6}Ti_{0.4}N alloy formed throughout the whole sample and no indication of any precipitations. TiN buffer layer is about 20nm which is used to accommodate the cubic Al_{0.6}Ti_{0.4}N alloy and make AlN fit in TiN lattice site to form uniform alloys. High magnification image of the same area from <110> cross-section sample of Al_{0.6}Ti_{0.4}N / TiN / Si(100) is shown in figure 3(b). Both of the TiN/Al_{0.6}Ti_{0.4}N and TiN/Si interfaces are quite sharp without any indications of interface reaction. Near the interface of TiN/Al_{0.6}Ti_{0.4}N, the alloy lattice is matching with TiN. But above certain thickness, it starts to have misorientations and forms smaller grain.

For the average grain size study, the low magnification bright field and high magnification TEM were performed on plan-view sample of Al_{0.6}Ti_{0.4}N/TiN/Si (100) and shown in figure 4(a) and 4(b), respectively. Bright field image clearly indicate the size of the dark grains ranges from 10 to 20 nm. High magnification image from the same area shows some smaller grains exist in between those larger grains and the size is around 5-10 nm. The relatively small grain size is thought to be that, each of TiN deposition is followed by AlN deposition, then the excess AlN can not form Al_{0.6}Ti_{0.4}N with TiN and act as a new nucleation site which may have different orientation with underlying layer. When second TiN covers this misorientated AlN nucleation site and forms a new layer of Al_{0.6}Ti_{0.4}N alloy.
Figure 3(a) Low magnification TEM and (b) high magnification TEM from <110> cross-section sample of Al$_{0.6}$Ti$_{0.4}$N on TiN/Si(100).
Figure 4(a) Low magnification TEM and (b) high magnification TEM from plan-view sample of $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}$ on TiN/Si(100) showing the average grain size is in the range of 10-20nm.
Figure 5 (a) Selected area diffraction pattern of Al$_{0.6}$Ti$_{0.4}$N from plan-view sample of Al$_{0.6}$Ti$_{0.4}$N/TiN/Si(100) showing slightly texture formed in nano grains. (b) Selected area
diffraction pattern of $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}/\text{TiN}/\text{Si}(100)$ from $<110>$ cross-section sample of $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}$ on $\text{TiN}/\text{Si}(100)$, showing the texture relations.

The diffraction from the corresponding large area of plan-view TEM sample is shown in figure 5(a). The fine-lined diffraction pattern also proved the grain size of $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}$ alloy is in the nano range. Slightly arc shape of the diffraction pattern indicates that texture is forming. Texture formation is much clear in figure 5(b), the diffraction pattern of $<110>$ cross-section TEM sample of $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}/\text{TiN}/\text{Si}(100)$. After indexing those diffraction patterns, the lattice parameter of $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}$ is found to be a little smaller than $\text{TiN}$ lattice parameter ($a=0.424\text{nm}$). That is the reason from X-ray diffraction, $\text{TiN}$ and $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}$ (002) peaks are almost identical. Besides the $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}$ diffraction rings, no other phases found in plan-view diffraction pattern, which proved no precipitations and other phase formation in large area.

Scanning electron microscopy imaging technique also was used as surface morphology and uniformity study. Figure 6(a) is the surface morphology of $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}$ alloy by normal SEM imaging technique. Besides few particles showing on the top surface, the whole surface is very flat and uniform. Figure 6(b) is elemental map of the whole surface by back scattering imaging technique which the contrast is proportional to $Z$ (atomic number). It is very clear that uniform alloy formed through out the whole samples and no clear indications of precipitation formation.
Figure 6(a) SEM image and (b) back scattering image from the surface of Al$_{0.6}$Ti$_{0.4}$N alloy.
As we increase AlN target concentration to 70%, the uniform Al\textsubscript{0.7}Ti\textsubscript{0.3}N alloy formed and microstructures are very close to Al\textsubscript{0.6}Ti\textsubscript{0.4}N. While when AlN target concentration increased to 80%, instead of Al\textsubscript{0.8}Ti\textsubscript{0.2}N alloy, the highly aligned AlN/TiN superlattice formed throughout the sample thickness. The low magnification TEM image of AlN/TiN superlattice/TiN/Si(100) were performed from large area of the film and shown in figure 7(a). The thickness of individual TiN and AlN nanoscale layers is determined to be 1nm and 4nm, respectively. The layer thickness is uniform throughout the whole superlattice structure. The total thickness of the superlattice layer is about 500nm. A STEM-Z contrast image from <110> cross-section of superlattice clarified the sharp interfaces of AlN/TiN without any indication of interfacial reactions, as shown in figure 7(b). The TiN layer shows the brighter contrast compared to AlN, because the STEM-Z contrast is proportional to Z\textsuperscript{2} and the atomic number of Ti is 22, which is larger than those of Al (13). Fast Fourier Transformation (FFT) from cross-section sample of the AlN/TiN nanoscale multilayers shows superlattice characteristics from the satellite diffractions in figure 8(a). The corresponding selected-area-diffraction pattern from <110> cross-section of TiN buffer layer on Si (100) suggests epitaxial relation of TiN <110> // Si<110> in figure 8(b).

High Resolution <110> cross-section images of the AlN/TiN superlattice structure and TiN/Si(100) interface are shown in Figure 9(a) and 9(b), respectively. The interfaces of TiN/AlN are quite sharp without any indication of interfacial reaction layer in figure 9(a). It has been reported earlier that beyond a certain substrate temperature, some interfacial reactions occur leading to the formation of ternary and binary phases such as Ti\textsubscript{3}Al\textsubscript{2}N\textsubscript{2}, Ti\textsubscript{3}AlN, Ti\textsubscript{2}N etc.\textsuperscript{11,12} To avoid this problem, the substrate temperature for the superlattice structure was
maintained at 650±10°C, which is lower than the temperature for interfacial reaction. Moreover, because of the nonequilibrium nature of the pulsed laser deposition process, we obtained high quality films even at this low temperature. The lattice constant of TiN and cubic AlN is 4.24Å and 4.12Å obtained from X-ray results, respectively. The calculated lattice misfit is about 2.8% which is in the range of lattice matching epitaxy. The small lattice misfit provides the possibility for accommodating the metastable cubic AlN phase in between these thin layers of TiN.

AlN/TiN superlattice grown on MgO substrate for lattice matching was reported by Madan et al. Here the TiN buffer layer grown on Si(100) substrate was used to provide the template for AlN/TiN superlattice growth. The reasons for selecting TiN as buffer layer are that: first, TiN buffer layer proves the structural capability to grow these superlattices on top of TiN coatings for future cutting tools; second, it provides the possibility to grow these superlattices on silicon substrate which make the superlattice structure integrated with Si for electronic device applications, such as packaging coatings. In figure 9(b), {111} lattice planes of TiN buffer layer and Si are well aligned. Because of the large lattice mismatch along the interface of TiN(a=4.24Å) /Si(a=5.43Å), the strain energy is sufficient to overcome the activation energy for nucleation of dislocation at the free surface. In figure 9(b), misfit dislocations are clearly visible along the interface of TiN/Si and marked as two sets of extra half planes by white arrows. The short ordering of these extra half planes is clearly observed as 3:4 relationship, which means that 4 atomic planes of TiN (111) align with 3 atomic planes of Si(111), according to domain matching epitaxy. And every two set of extra half planes compose one 90° dislocation as shown in figure 9(b). These 90° dislocations are orderly distributed along the
interface and burgers vector of these misfit dislocation is identified as $\frac{a}{2} < 110 >$. We observed that the quality of the TiN buffer layer directly affects the growth quality of these superlattice structures.

Figure 7 (a). Low magnification $<110>$ cross-section image of superlattice of AlN(4nm)/TiN(1nm) on TiN/Si(100).
Figure 7 (b) STEM-Z contrast image from <110> cross-section sample shows the uniformity of supperlattice structure.

Fig. 8 (a) Fast Fourier Transformation (FFT) from superlattice showing satellite diffraction characteristics; (b) Selected-area-diffraction pattern of TiN on Si(100), cross-section of TiN <110> // Si<110>.
Fig. 9 (a) High Resolution <110> cross-section image at interface of superlattice / TiN showing the atomic structure of superlattice; (b) High Resolution <110> cross-section image of epitaxial
TiN on Si(100), the white arrows marked the extra half planes. The misfit dislocations are marked along the interface.

Mechanical properties of all the Al\(_{x}\)Ti\(_{1-x}\)N (x up to 70%) alloys and superlattice structures were studied by nanoindentation technique. Figure 10 (a) and (b) show the experimental and simulated results for the ratio of hardness between film and substrate for the Al\(_{0.6}\)Ti\(_{0.4}\)N and AlN/TiN superlattice structure respectively. The hardness, yield stress, and Young’s modulus of the substrate, indent depth and thin film thickness are all considered in simulation procedure in order to subtract the effect of the substrate. One can refer to reference 14 for detailed information. It can be seen that this ratio varies with the ratio of indent depth and film thickness. The calculated hardness and Young’s modulus for three different concentrations are listed in table 2 and compared with rule-of-mixtures values.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Measured Hardness (GPa)</th>
<th>Rule-of-mixtures hardness (GPa)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(<em>{0.6})Ti(</em>{0.4})N</td>
<td>22.8</td>
<td>16.4</td>
<td>314</td>
</tr>
<tr>
<td>Al(<em>{0.7})Ti(</em>{0.3})N</td>
<td>20.3</td>
<td>16.2</td>
<td>285</td>
</tr>
<tr>
<td>Al(<em>{0.8})Ti(</em>{0.2})N (AlN/TiN Superlattice)</td>
<td>18.2</td>
<td>15.8</td>
<td>248</td>
</tr>
</tbody>
</table>

Table 2. Hardness, rule-of-mixtures hardness and Young’s modulus of three different concentrations.
It is obvious that all the hardness values for three concentrations are much higher than the corresponding rule of mixtures values. The increase in the hardness of Al\textsubscript{x}Ti\textsubscript{1-x}N alloy (x up to 70\%) may be contributed to the metastable cubic phase of Al\textsubscript{x}Ti\textsubscript{1-x}N. The lattice constant of these metastable cubic phases is relatively smaller than that of TiN, which may cause the film under tension and therefore increase the hardness. Another reason is that the average grain size of Al\textsubscript{x}Ti\textsubscript{1-x}N alloys is about 10-20nm which may not be able to accommodate a single dislocation within one grain. The dislocation motion is harder and hardness increased in nanocrystalline materials. According to our previous study on hardness of nanocrystalline TiN, as the grain size decreases below a critical value, materials softening may happen which is normally known as negative Hall-Petch relation. This suggests that further increase the grain size by varying deposition parameters may increase the hardness of these Al\textsubscript{x}Ti\textsubscript{1-x}N alloys. The hardness of AlN/TiN superlattice structure is also higher than the rule-of-mixtures, which is due to the special structure of superlattice. The superlattices are reported to have high hardness, which is explained as elastic-moduli difference between different layers. The modulus difference may cause the dislocations gliding from one layer to another layer or gliding within a single layer get more difficult and further enhance the hardness of the superlattice structures. Both of AlN and TiN have B-1 rock-salt cubic structures in this superlattice structure, but they have different lattice parameter and elastic modulus and their bilayer thickness is only 5nm. Therefore, the hardness is increased. The hardness of superlattice structure is relatively lower than those alloy hardness which may caused by the lower TiN concentration in superlattice structure.
Electrical resistivity of all the alloys and superlattice structure were measured by four point probe. The room-temperature resistivity of $\text{Al}_{0.6}\text{Ti}_{0.4}\text{N}$ and $\text{Al}_{0.7}\text{Ti}_{0.3}\text{N}$ are measured to be 1500 cm and 310 O-cm, respectively. The relative high resistivity is caused by high concentration of AlN which has high resistivity $10^{11}$ O-cm. The resistivity of superlattice is determined to be 4500 O-cm which is even higher than both of the alloys. The resistivity increasing is due to higher AlN concentration and layer-contact resistivity of superlattice structure. It could be interesting to study the effects of the thickness of TiN layer in the superlattice on the mechanical and electrical properties of the whole structure.
For Al$_{0.6}$Ti$_{0.4}$N:
- $H_f/H_s = 1.75$
- $E_f/E_s = 1.9$
- $\sigma_f/\sigma_s = 1.75$
- $E_f = 314$ GPa
- $H_f = 22.8$ GPa

For Al$_{0.8}$Ti$_{0.2}$N:
- $H_f/H_s = 1.4$
- $E_f/E_s = 1.5$
- $\sigma_f/\sigma_s = 1.1$
- $E_f = 248$ GPa
- $H_f = 18.2$ GPa
Fig.10. The ratio of hardness of films and substrate vs. the ratio of the indent depth and film thickness for (a) Al$_{0.6}$Ti$_{0.4}$N, (b) superlattice of AlN/ TiN. (Al$_{0.8}$Ti$_{0.2}$N)

7.5 Conclusion

Uniform cubic Al$_x$Ti$_{1-x}$N (x up to 70%) alloys and highly aligned TiN/AlN superlattice structures (x>80%) were synthesized on Si(100) using TiN buffer layer by pulsed laser deposition. Uniformity of these alloys and superlattice structures has been proved by transmission electron microscopy, scanning electron microscopy and scanning transmission electron microscopy (STEM, or Z-contrast). Al$_x$Ti$_{1-x}$N (x up to 70%) alloys are determined to be cubic structured nanocrystalline with slightly texture. For superlattice structure, it was observed that individual layers of AlN(4nm) and TiN(1nm) are highly textured cubic phases with no interface reaction. X-ray diffraction and TEM analysis proved the cubic Al$_x$Ti$_{1-x}$N (x up to 70%) alloys and cubic TiN/AlN nanoscale multilayers have been stabilized by thin layer of TiN buffer layer. Mechanical and electrical property studies suggest that Al$_x$Ti$_{1-x}$N (x up to 70%) alloys and AlN/TiN superlattices (x>80%) could be a promising candidate for coatings in high speed cutting tool and electronic packaging. Further studies on the stability of these metastable cubic Al$_x$Ti$_{1-x}$N (x up to 70%) alloys and TiN/AlN superlattice structure are needed for these future applications.
Reference


