Enhanced mechanical and electrochemical properties of TiN$_x$ thin films prepared by magnetron sputtering with an anode layer ion source

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ABSTRACT
An anode layer ion source (ALIS) is used in magnetron sputtering to deposit TiN films. The effects of the ion source discharge current ($I_s$) on the microstructure, mechanical, and electrochemical properties, and adhesion characteristics of the deposited films are studied. By coupling with magnetron sputtering discharge ($I_1$) and varying the ALIS discharge current, the ion energy ($E_i$) and ion flux density ($J_f$) can be increased to 180 eV and $3.5 \times 10^{16}$ ions cm$^{-2}$ s$^{-1}$, respectively. The preferred orientation of the films changes from (200) to mixed (111) & (200) and finally to (111) with increasing $I_s$. The microstructure changes from a columnar to dense one and the residual stress in all the films is compressive. The stress increases initially and then decreases slightly with the (111) orientation and the hardness and fracture toughness depend on the residual stress with the hardness increasing from 14.5 GPa to 27.0 GPa and fracture toughness increasing to 70%. As shown by the Rockwell C adhesion test, the films deposited by varying the ion source discharge current show improved adhesion. Electrochemical studies reveal reduced corrosion current density and increased impedance by an order of magnitude. The results reveal for the first time significant changes in the mechanical and electrochemical properties of films deposited by magnetron sputtering with ALIS assistance. This hybrid technique has the advantages that the film structure and mechanical and electrochemical properties can be readily adjusted.

1. Introduction

Magnetron sputtering is extensively used in research and industry to deposit transition metal (TM) nitrides due to easy control of the film microstructure and properties, low cost, and reliability [1,2]. Films deposited by magnetron sputtering generally have a columnar structure which may not be preferred in some applications. For example, the columnar morphology tends to increase the brittleness, reduces the fracture toughness, and provide channels for easy penetration of external corrosive media into the substrate to cause early corrosion [3]. In ion beam assisted deposition (IBAD), the two parameters of ion energy and flux play critical roles [4] and it has been shown that by coupling an evaporator source with the ion source, surface migration of adatoms is enhanced at a relatively low temperature and the microstructure, crystallinity, and anisotropy can be optimized [5,6].

Kaufman ion sources are frequently used because of the independent control of the ion energy and flux. In fact, these ion sources can be operated in the high energy and low flux mode but scaling up to meet industrial demand is challenging [7,8]. Hence, in addition to magnetic confinement, other sources such as ICP sources powered by RF [9] and ECR sources [10], which are collectively called ionized-physical vapor deposition (IPVD) sources, have been proposed [11,12]. The ion flux and energy can be controlled effectively and the inherent columnar morphology can be altered by these methods, but adoption by the tool industry is still limited. The anode layer ion source (ALIS), a type of closed drift thruster, is used industrially to etch substrates before deposition to enhance film adhesion [13]. ALIS can be operated in two different modes, high-flux low-voltage mode and low-flux high-voltage mode and switching between the two modes is possible by varying the pressure. This source offers the advantage of one single source for a specific application and ALIS can be readily scaled up to meet large-area deposition demanded by the industry [7]. However, there are very few studies on the use of the high-flux, low-voltage mode of ALIS in magnetron sputtering as well as resulting changes in the structural, mechanical, and electrochemical properties of the films.

TiN, which is widely used in the industry for the superior...
mechanical and anti-corrosion properties [14], is appealing as an anti-wear coating on cutting tools [15] and anti-corrosion coating on biomedical implants [16]. The properties depend on the microstructure and morphology of the deposited film [17]. In this work, the high-flux, low-voltage mode of ALIS is implemented in magnetron sputtering to deposit TiN thin films with a thickness of 275 ± 25 nm. The maximum average ion energy (Ei) is up to 180 eV and the ion flux density (Ji) can be varied. The important properties such as the residual stresses, hardness, elastic modulus, fracture toughness, adhesion, and corrosion resistance are investigated systematically. Our results show that these properties depend on the ALIS discharge current which alters the film structure, morphology, and internal stress.

2. Experimental details

The substrates were 500 μm thick Si (100) and 1 mm thick stainless steel (SS) sheets and cut to dimensions of 10 × 30 mm² and 10 × 10 mm², respectively. They were ultrasonically cleaned in ethanol and methanol for 10 min each and dried in nitrogen. Deposition was carried out on the industrial-scale plasma immersion ion implantation and deposition (PIII&D) instrument in the Plasma Laboratory of City University of Hong Kong. It was equipped with two middle frequency magnetron sputtered targets, one gridless linear anode layer ion source, and 200 V DC power supply and the schematic of the PIII&D system is shown in Fig. 1. The angle between the deposition flux and ionic flux from ALIS was kept at 45°. The TiN target (7.5 × 34.5 cm²) in the reactive mode in a mixed Ar (99.999%) & N₂ (99.999%) environment. The Ar/N₂ ratio, temperature, and magnetron ratio is between 0.65 and 0.8 by varying the ALIS discharge current (Iₜ) of 0.6 to 1.0 and have the single-phase NaCl lattice. In this study, the N/Ti ratio and ALIS were connected to current control pulsed power units operated at a frequency of 40 kHz and duty cycle of 80%. Before deposition, the instrument was evacuated to a base pressure of 1.0 × 10⁻³ Pa and the important processing parameters are listed in Table 1.

X-ray diffraction (XRD) was performed on the Rigaku XRD machine in the Bragg and Brentenno geometry with Cu Kα radiation (45 kV, and 196 mA, and 1.5406 Å). The average grain size (D) was calculated by Scherer formula [18]:

$$D = \frac{0.9 \lambda}{B \cos \theta}$$

(1)

where λ is the wavelength of the Cu Kα X-ray (1.5406 Å), B is the full-width at half-maximum (FWHM) of the diffraction peak, and θ is the diffraction angle. Field-emission scanning electron microscopy (FE-SEM, FEI XL 30) and energy-dispersive X-ray spectroscopy (EDS, EDAX, Phoenix) were utilized to study the surface and cross-sectional morphologies as well as composition.

The mechanical properties were determined on a microhardness Tester (Fisheroscope, HM2000XYp; Fischer Technology, Inc. Windsor) with a Berkovik tip in the constant load mode. A load of 1 mN was selected to limit the maximum depth to 50 nm and the data represented the average of six readings with the distance between each indentation being ≥ 200 μm. The MTS nano-indenter was used to determine the film hardness to confirm the results and the continuous stiffness measurement (CSM) mode was adopted in the hardness evaluation. The residual stress in the films was calculated by measuring the radius of curvature of the silicon substrate before and after deposition using Stoney's equation [19]:

$$\sigma = \frac{E_s t_o}{6(1 - v)} \frac{R}{t_f} \left( \frac{1}{R_i} - \frac{1}{R_f} \right)$$

(2)

where, E₀, t₀, R₀ and Eₕ are the young's modulus, thickness, radius of curvature of the bare substrate, and Poisson's ratio of the substrate, respectively. The radius of curvature was measured by contact mode surface profilometry (Taylor Hobson Ltd., Leicester, United Kingdom) at a scanning rate of 0.5 mm/s over a scanned length of 25 mm. Three readings were taken before and after deposition and the averages were calculated. The fracture toughness was measured by indenting the film using a micro hardness tester equipped with a microscope and Vickers indenter at a constant load of 0.98 N. The adhesion strength of the coatings was evaluated by the Rockwell indentation test according to the VDI standards 3198 with a HRC diamond indenter, normally classified as a destructive qualitative test for coating materials. The detailed principle of the Rockwell ‘C’ adhesion analysis can be found in Ref. [20]. The coated specimen was then examined by optical microscopy and adhesion was assessed by distinguishing between the different adhesion classes ‘HF’ between HF 1 to HF 4 (sufficient adhesion) and HF 5-HF 6 (insufficient adhesion).

The corrosion rate of the films on stainless steel was determined in a 3.5% NaCl solution on the Zahner Zennium electrochemical workstation based on the three-electrode technique in which platinum and Hg/Hg₂Cl₂ were the counter and reference electrodes, respectively. The exposed sample surface area was 0.5 cm². Potentiodynamic polarization was performed at a scanning rate of 1 mV/s from −1.0 V in the cathodic direction to +1.2 V in the anodic direction based on the open circuit potentials (OCPs) after immersion for 45 min. The electrochemical impedance spectra (EIS) were collected at the respective OCPs after stabilization in the solution for 45 min using a sinusoidal potential of 5 mV and frequency range between 100 kHz and 10 MHz.

3. Results and discussion

The TiN films contain different ratios of nitrogen to titanium from 0.6 to 1.0 and have the single-phase NaCl lattice. In this study, the N/Ti ratio is between 0.65 and 0.8 by varying the ALIS discharge current (Iₜ).
which alters the ion energy and flux. Fig. 2(a) shows the composition of the deposited films determined by EDS and Fig. 2(b) and (c) displays the XPS depth profiles (estimated sputtering rate of 30.5 nm/min for samples A and D and see Table 1). It has been shown that deposition of TiN during ion bombardment using a separate ion source can increase sorption of nitrogen and the N/Ti ratio [4,5,30].

The XRD patterns of the films deposited at a magnetron discharge current \(I_t\) of 3.5 A and different ALIS discharge currents \(I_s\) are presented in Fig. 3. The structure of titanium nitride resembles the rock salt B1 structure. At \(I_s = 0\) (NIBA-MS), the peak from TiN (200) is observed. As the ALIS discharge current \(I_s\) is increased, peak broadening is observed and the (200) preferred orientation gradually changes to the mixed (111) + (200) one. The largest discharge current produces the (111) orientation. The values of \(E_i\) and \(J_i\) in each stage are shown in Table 1. The average crystallite size decreases from 26.9 nm to 5.2 nm.

Mayrhofer et al. [21] have shown that during deposition of TiN by magnetron sputtering employing an additional magnetic confinement to increase \(J_i\), a larger ion flux density and energy \(> 50\) eV can alter the preferred orientation to [111] after transforming through the mixed [111] + [100] orientation. The phenomenon is attributed to enhanced re-sputtering of Ti adatoms on [100] grains resulting in the preferred [111] orientation. Fig. 4 shows the planar and cross-sectional FE-SEM images of the films deposited under different conditions. The NIBA-MS film shows a faceted and columnar morphology resembling Zone 1c with a faceted morphology [17]. A larger ALIS discharge current, \(I_s\), increases both \(J_i\) and \(E_i\) and the change of \(I_s\) transforms the surface morphology from a faceted one to round granular one and finally smooth morphology corresponding to energies and ionic fluxes of 80 eV and \(4.3 \times 10^{15}\) ions cm\(^{-2}\) s\(^{-1}\), 95 eV and \(1.2 \times 10^{16}\) ions cm\(^{-2}\) s\(^{-1}\), and 170 eV and \(3.0 \times 10^{16}\) ions cm\(^{-2}\) s\(^{-1}\) respectively. The inherent columnar structure is destroyed with ALIS assistance during film deposition. A similar phenomenon has been observed by Tian et al. [3] from CrN films deposited by IBAD with assistance of ions up to an energy of 1200 eV. Our results further show that when the ion energy is increased from 95 eV to 170 eV together with an increased ion flux density, the film is further densified and the granular morphology transforms into a smoother one as shown in Fig. 4(d). Moreover, no grain coarsening is observed here. The reason for the smooth morphology and reduced crystallite size is believed to be energetic ion bombardment at a larger ion flux density partially dissociating the

<table>
<thead>
<tr>
<th>Sample number</th>
<th>ALIS discharge current (I_s) (A)</th>
<th>Negative bias voltage (V)</th>
<th>Maximum average energy of ions, (E_i) (eV)</th>
<th>Average ion flux density, (J_i) (\times 10^{16}) (ions cm(^{-2}) s(^{-1}))</th>
<th>Average crystallite size (nm)</th>
<th>Average thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>–50</td>
<td>50 (biasing)</td>
<td>–</td>
<td>26.9</td>
<td>271.12 ± 12</td>
</tr>
<tr>
<td>B</td>
<td>1.5 A</td>
<td>0</td>
<td>Up to 80</td>
<td>0.43</td>
<td>7.3</td>
<td>268.15 ± 13</td>
</tr>
<tr>
<td>C</td>
<td>3.5 A</td>
<td>0</td>
<td>90–95</td>
<td>1.2</td>
<td>6.8</td>
<td>272.18 ± 9</td>
</tr>
<tr>
<td>D</td>
<td>7.0 A</td>
<td>0</td>
<td>170–180</td>
<td>3.0</td>
<td>5.2</td>
<td>273.95 ± 12</td>
</tr>
</tbody>
</table>

Table 1

Important processing parameters.

Table 2

Miscellaneous fixed parameters:

<table>
<thead>
<tr>
<th>Working pressure</th>
<th>Temperature</th>
<th>Magnetron discharge current, (I_t) (A)/Power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4.5 \times 10^{-1}) Pa</td>
<td>180 °C</td>
<td>3.5 A/1500 W</td>
</tr>
<tr>
<td>(1.0 \times 10^{-3}) Pa</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Fig. 2. (a) Semi-quantitative composition analysis by EDA of the TiN films deposited at different ALIS discharge currents \(I_s\) and XPS depth profile (estimated sputtering rate of 30.5 nm/min) of (b) Sample A and (c) Sample D.

Fig. 3. X-ray diffraction spectra of TiN films deposited at different ALIS discharge currents \(I_s\) and constant magnetron discharge \(I_t\) of 3.5 A on the Si substrate with a native oxide layer at 180 °C.
islands. Hence, some dislodged atoms together with adatoms form new islands and nucleation sites are increased, while the crystallite size decreases.

Fig. 5(a) shows the residual stress in the film determined by the curvature method for different $I_s$. All the deposition conditions lead to net compressive residual stress and larger stress values are observed from films deposited with the ALIS discharge current than the NIBA-MS. The stress arises from ion peening. Bombardment of the film with energetic ions in conjunction with increased ion source discharge current ($I_s$) causes densification and increases the in-plane compressive stress due to the sub-plantation effects. The maximum compressive residual stress observed from a polycrystalline film is $-3.0$ GPa and further increase in the discharge current reduces the compressive stress slightly. The XRD patterns show a shift to the [111] orientation that tends to change the stress. Fig. 5(b) shows the hardness and elastic modulus evolution with ALIS discharge currents. The hardness of the NIBA-MS film is about 14.8 GPa and increases with ion bombardment. The maximum hardness of a polycrystalline film with a mixed orientation is 27.0 GPa and the inset shows the hardness of the same film determined by nano-indentation in the CSM mode. The higher hardness can be attributed to various mechanisms including increase in plane compression, reduction in crystallite size, densification, and so on [5,22]. In this case, the crystallite size decreases with increasing discharge current reaching 5.2 nm for $I_s$ of 3.5 and 7.0 A while the film becomes monotonically more densified as indicated in Fig. 4. The stress in the film deposited at $I_s$ of 3.5 A is the largest (compression) and it

Fig. 4. SEM micrographs showing the surface and cross-sectional morphology: (a) Sample A, (b) Sample B, (c) Sample C, and (d) Sample D.

Fig. 5. (a) Average residual stress in the TiN films as a function of ALIS discharge currents ($I_s$), and (b) average harness and elastic Modulus of the TiN film as function of ALIS discharge currents ($I_s$) with the inset showing the hardness of sample C determined by nano-indentation performed in the CSM mode for result validation.
may be the main reason for the increased hardness. Our results are similar to previous research [21,23]. For example, Mayrhofer et al. [21] observed that for magnetically enhanced ionization confinement during sputtering, an increase in the ionized flux along with energy tends to reduce slightly the internal residual stress with developing [111] texture. This reduction in the residual stress decreases the hardness.

The fracture toughness which is related to the ability to absorb energy before cracking is an important mechanical attribute. In our measurements, a radial crack is introduced to the film by micro Vickers indentation at a load of 0.98 N. The length of the crack is measured during indentation and confirmed by microscopy. The typical crack at a normal force of 0.98 N is shown in Fig. 6(a). The fracture toughness is determined by the following equation [24]:

$$K_{IC} = \alpha \left( \frac{E}{H} \right)^{1/2} \frac{P}{c^{3/2}}.$$  \hspace{1cm} (3)

where \( P \) is the peak load, \( c \) is the crack length, \( \alpha \) is the empirical constant depending on the type of indenter and that of the Vickers indenter is 0.016, and \( E \) and \( H \) are the elastic modulus and hardness of the film. A schematic of the radial crack formation is shown in the inset in Fig. 6(a). Fig. 6(b) shows the fracture toughness as a function of discharge currents and the radial cracks are also shown. The fracture toughness increases from 0.68 MPa\cdot m^{1/2} to 1.15 MPa\cdot m^{1/2} as the discharge currents are increased from 0 A to 3.5 A. For a discharge current of 7 A, the fracture toughness is reduced to 1.09 MPa\cdot m^{1/2}. The SEM images of the cracks on samples A and C are depicted in Fig. 5(c) and (d). The crack on sample A is quite long compared to sample C indicating that sample C has better characteristics. The trend shows similarity with the in-plane residual stress and hardness indicating the dominant role of residual stress in the mechanical properties. The increase in toughness is ascribed to larger in-plane compression that resists deformation and crack formation, but it is saturated in the polycrystalline film. As the structure changes to the [111] orientation, both the residual stress and fracture toughness decrease. L. Zhang et al. [24] have shown that residual stress changes from compression to tensile with increasing TiN film thickness giving rise to reduced fracture toughness. After a crack is initiated, it propagates under the action of the tensile component at the tip and compressive in-plane stress can help disintegrate this tensile component. The crack can only grow if the tensile component at the tip is greater than the compressive stress in the film and hence, higher in-plane compressive stress leads to greater fracture toughness.

In the Rockwell indentation test, the indenter geometry under the load of 1.471 kN induces high shear stress in the vicinity of the coating/substrate interface. Only well adherent coatings can tolerate such a high level of shear stress and do not delaminate. Fig. 7 shows the optical micrographs of the samples deposited with different ALIS discharge currents after the indentation test. The NIBA-MS film (sample A) shows a very small proportion of spallation at the periphery as shown in Fig. 7(a). Since the proportion of spallation is not large enough, adhesion is within the acceptable level. All the other samples deposited with different ALIS discharge currents show improved adhesion and can be classified into the HF1 category. Some pile-up of the substrate materials is seen from the periphery but the coating is still intact. This also
verifies the increased toughness discussed earlier. The buildup of internal stress caused by the peening effect adversely affects adhesion [25]. Increase in the ALIS discharge current leads to increment in the assisted energy that modifies the interface between the deposited coating and substrate. Similar effects have been observed from IPVD processes in which the energetic plasma gives rise to strong interfacial bonding as well as enhanced adhesion [11].

Although hard coatings like TiN have good corrosion resistance [26], a columnar morphology can provide open channels for the external medium to access the substrate [3]. The potentiodynamic polarization results acquired at different \( I_s \) values are shown in Fig. 8. \( E_{corr} \), \( I_{corr} \), and \( \beta_c \) are calculated by Tafel extrapolation from the linear cathodic polarization region and summarized in Table 2. The corrosion current density is an important parameter and use of ALIS during magnetron sputtering decreases \( I_{corr} \) by an order of magnitude due to the dense and non-columnar structure created by ion bombardment. To further investigate the corrosion behavior, EIS spectra are obtained after immersion in a 3.5% NaCl solution for 45 min and the Bode impedance, phase angle, and Nyquist plots are presented in Fig. 9. The films show one time constant in the entire range indicating the absence of additional processes during immersion [27,28]. PVD films typically have pores and prolonged immersion allows the solution to penetrate the pores. In this study, the outcome of the films produced at different ALIS discharge currents is monitored but the prolonged effects are not considered. According to the Bode impedance results, the film impedance increases with ALIS discharge currents. The impedance at low frequencies is considered a valuable parameter to study corrosion protection and a higher impedance at low frequencies implies better performance as it corresponds to mass transportation of dissolved ions [29]. In this respect, the ALIS modified films show impedance that is an
order of magnitude larger than that of the NIBA-MS film indicating better performance. The phase angles are also larger between $10^1$ and $10^2$ Hz indicating a dominant capacitive behavior. These results are consistent with those reported previously [27, 28]. The behavior is attributed to a constant phase element (CPE) of the equivalent circuit as a capacitor in series with the solution resistance due to a very large value of parallel resistance $R_p$ (~5 MΩ cm$^2$) and occurs with the absence of porosity in the films [27]. Our results revealing increased impedance with ALIS discharge currents are in accordance with the observed decrease in the corrosion current density and related to the change in the columnar structure and reduced crystallite size.

4. Conclusion

The objective of this study is to combine the high-flux and low-voltage mode of the anode layer ion source (ALIS) with magnetron sputtering to control the structure and morphology of TiN films to improve mechanical and electrochemical properties. The influence of the ALIS discharge current ($I_d$) is studied systematically. The maximum ion energy is 180 eV and ion flux density is $3.5 \times 10^{16}$ ions·cm$^{-2}$·s$^{-1}$. Our results show that ALIS operated in the high-flux, low-voltage mode in combination with magnetron sputtering is an effective means to control the structure and morphology of the TiN films. The fracture toughness and hardness are improved from 0.68 MPa m$^{1/2}$ and 14.5 GPa to 1.15 MPa m$^{1/2}$ and 27.0 GPa, respectively. Moreover, adhesion is enhanced, as the ALIS discharge current is increased and the corrosion resistance in 3.5% NaCl also increases by an order of magnitude. The mechanical properties depend on the residual stress arising from the peening effect, whereas the improved electrochemical properties are related to the reduced crystallite size and evolution of a non-columnar structure. This hybrid technique that can be scaled up readily to satisfy industrial demand enables easy control of the film microstructure and properties.

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References


