Influence of bias voltage on the hardness and toughness of CrAlN coatings via magnetron sputtering

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Chromium aluminum nitride (CrAlN) coatings were prepared via magnetron sputtering in a mixed Ar and N2 ambient. The effect of negative bias voltage (Vb) on the microstructure was investigated using a spectrum of characterizing techniques in terms of Glancing Angle X-ray Diffractometry, Field Emission Scanning Electron Microscopy and Transmission Electron Microscopy. As Vb increased from 50 to 260 V, hardness was improved from 10 to 26 GPa. Toughness grew at the same time and maximized at around 2 MPa·m1/2 when Vb = 210 V. Simultaneous improvements in hardness and toughness were attributed to the densified microstructure with refined grains and increased compressive stress.

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1. Introduction

Due to the improved wear [1,2], corrosion [3] and oxidation resistance [4,5], chromium aluminum nitride (CrAlN) was considered a promising alternative to the traditional CrN as a protective coating. Recent studies demonstrated that the enhanced strength originated from the solid solution hardening as a result of Al incorporation, which rendered the metastable face-centered-cubic (fcc) structure of Cr1−xAlxN. Theoretical calculation indicated that the stability range of fcc-Cr1−xAlxN could be x = 0.48–0.75, depending on the sublattice population [6]. Beyond this critical solubility, the emergence of a separated wurtzite AlN would lead to a drastic degradation in the strength [7].

CrAlN coating can be synthesized by means of physical vapor deposition techniques, such as cathodic arc ion plating [2,8,9], reactive magnetron sputtering [5,10,11], and beam plasma-assisted physical vapor deposition [12]. To optimize its mechanical properties, many tried to directly alter the Cr/Al chemical concentration ratio [1,5,9,13–15]. Others changed the deposition conditions, such as processing pressure (i.e. N2 partial pressure or Ar + N2 total pressure) [16–18] and the negative bias voltage (Vb) [11,19,20]. Out of these researches, results regarding the toughness are of great paucity. It was once reported that the fracture toughness (KIC) of CrAlN coatings, deposited on the AISI H13 steel substrate, was 7.02–16.69 MPa·m1/2 when Vb varied from 0 to 120 V [20]. However, details that concerned this increment were not provided.

To fill this gap, the microscopic investigation on the CrAlN coatings, which were prepared at varied negative bias voltage via magnetron sputtering, was carried out in details in this study. It was revealed that the tendencies of hardness and toughness were strongly related to the microstructure and the stress variation. The results also indicated that with proper tailoring of negative bias voltage, improved hardness and enhanced toughness could be obtained simultaneously.

2. Experimental setup

2.1. Sample preparation

Deposition of the CrAlN coatings was conducted on the Si (100) wafer via magnetron sputtering in a mixed Ar and N2 ambient. Cr and Al targets (6 in. in diameter, 99.9% in purity) were mounted about 150 mm above the substrate holder, which was allowed to rotate evenly and controllably during depositing process. The base pressure in the sputtering chamber was better than 1.3 × 10−5 Pa and the processing pressure was maintained at 0.4 Pa (Ar: 40 sccm and N2: 20 sccm). The deposition temperature was set at 400 °C. The power density on the Cr and Al targets was set at 2.2 W/cm2 and 3.3 W/cm2, respectively. The radio frequency (r.f.) negative bias voltage was varied from 50 to 260 V. The thickness of all the samples was controlled at around 1 μm. Before loading, the Si wafer substrates were ultrasonically cleaned for 20 min in acetone followed by 10 min in ethanol for 3 cycles, and finished up with ultrasonic cleaning for 5 min in de-ionized water. Prior to the deposition, a 15 min Ar+ plasma etching was conducted at Vb = 160 V to remove the oxides and the contaminants that may still cling on the surface. To avoid unnecessary thermal stress, all the samples...
were cooled down to the room temperature (25 °C) before taking out of the chamber.

2.2. Microstructure characterization

The chemical compositions of Cr, Al, N and O were analyzed using Field Emission Electron Probe Micro-Analyzer (FE-EPMA, JEOL JXA-8500F) with the aid of the ZAF-corrected program. The accelerating voltage was 12 kV to achieve a detection depth of around 1 μm. The bond strengths were determined using X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra) with a monochromatic Al Kα (1486.71 eV) X-ray radiation (15 kV/10 mA). All the results were referenced to C 1s line of the adventitious carbon at 284.6 eV. The crystalline structure was analyzed using Glancing Angle X-ray Diffractometry (GAXRD, Panalytical X’Pert Pro) with a Cu-Kα 40 kV/30 mA X-ray source (wavelength λ = 0.15406 nm). The glancing incidence was set at 1° and the scanning range was from 20° to 90° at a step size of 0.02° with 0.5 s per step.

The surface and cross-sectional morphology were investigated using Field Emission Scanning Electron Microscopy (FESEM, JEOL JSM-6700F) and Transmission Electron Microscopy (TEM, JEOL JEM-2100F). The root mean square of surface roughness (Rq) was evaluated using Atomic Force Microscopy (AFM, Vecco Dimension 3000) operated under the tapping mode at a scanning frequency of 1.0 Hz. In particular, the resolution was set at 512 pixels × 512 pixels and the scanning area was constrained in a 10 × 10 μm² square.

2.3. Mechanical property evaluation

The residual stress (σ) was measured using surface profiler (TALYSCAN 150, Taylor Hobson) and then calculated according to the Stoney’s equation:

\[
\sigma = \frac{E_s}{6(1-v_s)} \cdot \left( \frac{1}{R_1^2} - \frac{1}{R_2^2} \right)
\]

where, Es/(1 – vs) is the substrate biaxial modulus (180.5 GPa for Si (100) wafer); ts and tc are respectively the Si substrate thickness (400 μm) and the coating thickness (1 μm); R1 and R2 are the curvature radius of the Si substrate before and after deposition, respectively.

The hardness and Young’s modulus were evaluated from Nanoindenter (Hysitron TI-900 Tribolindenter) under depth-control mode. The tip area function was calibrated by indenting a standard fused silica. The indent depth was controlled less than 1/10 (i.e. 0.1 μm) and the coating thickness was determined using scanning electron microscopy. The toughness was calculated by the minimization of free energy of the coatings, including surface and strain energies. In the normal condition, the vertical build of the coating possesses structure with large columnar grains of V shape. In the fracture condition, the melting temperature (Tm) of CrAlN is around 2445 K [26].

3. Results and discussion

3.1. Chemical concentrations and bonding state

Table 1 summarizes the results of chemical concentrations. The results show that N ranges from 53 to 57 at.% and the content ratio of Al/(Al + Cr) ranges from 0.37 to 0.40, indicating that increased Vb poses no significant influence on the chemical concentrations. Inevitable oxygen is due to the residual gasses in the spectrometer chamber or the ionic transport via impurities in the Ar or reactive N2. Bonding state analyses of the XPS narrow scan (Fig. 1) confirm the existence of Cr–N and Al–N, respectively [22]. Al 2p spectra (Fig. 1(c)) reveal the Al–N bond with peaks centered at 74.1 eV, higher than the reported value of AlN (73.6 eV) [23]. This is attributed to the chemical shift of Al since it forms CrAlN solid solution rather than the pure segregated AlN.

3.2. Crystalline structure

Typical fcc structure can be identified from the diffraction of peaks (111), (200), (220) and (311) (Fig. 2). No peaks of wurtzite AlN phase can be observed. Together with the results of XPS, formation of CrAlN solid solution is confirmed.

Growth orientations of CrAlN coatings are strongly related to the negative bias voltage. In general, the orientation evolution is determined by the minimization of free energy of the coatings, including surface and strain energies. In the normal condition, the vertical build of the coating possesses no significant influence on the chemical concentrations. Inevitable oxygen is due to the residual gasses in the spectrometer chamber or the ionic transport via impurities in the Ar or reactive N2. Bonding state analyses of the XPS narrow scan (Fig. 1) confirm the existence of Cr–N and Al–N, respectively [22]. Al 2p spectra (Fig. 1(c)) reveal the Al–N bond with peaks centered at 74.1 eV, higher than the reported value of AlN (73.6 eV) [23]. This is attributed to the chemical shift of Al since it forms CrAlN solid solution rather than the pure segregated AlN.

Considering the above factors and the fact that the coating thickness is kept constant, the dominant growth on the (220) plane and suppressed growth on (111) plane when Vb increases from 50 to 210 V could be caused by the driving force to decrease the overall energy. However, when Vb further increases to 260 V, random growth of crystallites takes place. It is believed that the re-arrangement of adatoms is facilitated by the enhanced thermal energy(471,913),(914,964)
while the substrate temperature ($T_s$) is assumed around 673 K at lower bias voltage (i.e. 50 and 160 V). This gives rise to $T_s/T_m$ of 0.28. At an ideal condition depicted by the basic model of the forming phenomena in polycrystalline coatings [27], the self surface diffusion of crystallites is remarkable while the grain boundary migration is strongly limited when $0.2 < T_s/T_m < 0.4$. In consequence, the coating structure is inhomogeneous along the coating thickness, composing V-shaped grains owing to the competitive growth of differently oriented neighboring crystals. When $V_b$ further increases, however, the ionized particles in the plasma are able to deliver high momentum to the substrate and create more chance of crystal re-nucleation. As such, the grain boundary migration and restructuration become prevalent and lead to the less textured dense structure. In light of these interactions, the morphology evolution is attributed to a sputter-induced redistribution of adatoms during growth process.

To clearly observe the grain boundaries, TEM is employed and reveals the similar results. The width of the columnar grains in CrAlN coatings prepared at $V_b = 50$ V is around 60 nm (Fig. 4(a)), while finer columnar grains with width of less than 30 nm (Fig. 4(b)) are observed in ones deposited at $V_b = 160$ V. In particular at $V_b = 50$ V, large gaps are observed between the columns, indicating the defects during coating growth (as pointed by the arrows in Fig. 4(a)). However, such defects no more exist when $V_b = 160$ V and above. Grain size calculated using Williamson–Hall method is summarized in Table 1. As bias voltage increases, grain size decreases accordingly from 52 to 13 nm. This refinement is caused by the intensive bombardment of incident ions with increased kinetic energy [21]. These ions with enhanced incident energy result more defects on the growth surface, thereby increasing the number of nucleation sites and thus the decrease of the grain size [28].

### 3.4. Mechanical properties

The residual stress as a function of bias voltage is demonstrated in Fig. 5. The compressive residual stress increases from $-0.7$ to $-1.4$ GPa (the minus sign indicates that the stress is “compressive”) as $V_b$ increases from 50 V to 260 V. A rapid increase of residual stress is observed when $V_b$ ranges from 50 to 210 V. This is attributed to the ion peening effect as in the case of TiC coatings synthesized by a filtered cathodic arc technique [29] and in the case of magnetron sputtered TiN [30] and TiC [28] coatings. With sufficient kinetic energy, incoming atoms knock atoms

![Fig. 1. XPS core-level spectra of (a) Cr 2p (b) N 1s and (c) Al 2p.](image1)

![Fig. 2. GAXRD results of CrAlN coatings at different $V_b$.](image2)

<table>
<thead>
<tr>
<th>Negative bias voltage ($V_b$)</th>
<th>Concentrations [at.%]</th>
<th>Grain size (nm)</th>
<th>$R_q$ (nm)</th>
<th>H (GPa)</th>
<th>E (GPa)</th>
<th>$K_{IC}$ (MPa·m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>Al</td>
<td>N</td>
<td>O</td>
<td>G</td>
<td>P</td>
<td>X</td>
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<tr>
<td>50</td>
<td>27.9</td>
<td>16.8</td>
<td>54.4</td>
<td>0.9</td>
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<td>18</td>
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<tr>
<td>160</td>
<td>28.5</td>
<td>17.4</td>
<td>52.7</td>
<td>1.4</td>
<td>33</td>
<td>16</td>
</tr>
<tr>
<td>210</td>
<td>28.9</td>
<td>17.2</td>
<td>53.1</td>
<td>0.8</td>
<td>17</td>
<td>9</td>
</tr>
<tr>
<td>260</td>
<td>24.8</td>
<td>17.1</td>
<td>57.4</td>
<td>0.7</td>
<td>13</td>
<td>6</td>
</tr>
</tbody>
</table>
out of their lattice position and bring about atom-collision cascades. As such, re-arrangement of lattice atoms takes place and leads to the resultant internal stress [31]. However, residual stress no more increases remarkably when \( V_b \) further increases to 260 V. This is due to the enhanced dynamic annealing since intensive ion ballasting may render much increased temperature at the substrate.

The tendencies of hardness and Young's modulus are plotted in Fig. 6. Hardness and Young's modulus grow as \( V_b \) grows. Lowest hardness of 10.4 GPa and Young's modulus of 235 GPa are observed in coatings prepared at \( V_b = 50 \) V. Comparable lower hardness is mainly due to the large grains (i.e. around 52 nm) and less compact microstructure with large amount of defects. At \( V_b = 260 \) V, grain size reduces to 13 nm and maximum hardness of 25.8 GPa as well as Young's modulus of 368 GPa are reached. Generally, decreased grain size brings about increased grain boundary fraction and provides additional obstacles for lattice dislocations thus the strength enhancement [32–34]. In parallel, the increased residual stress also contributes to the strength improvement as a result of the stress hardening [31].

Fig. 7 demonstrates the toughness as a function of the indent depth. The indent depth decreases from 2.8 to 1.6 \( \mu \)m. Below 1.6 \( \mu \)m, there were no measurable radial cracks as the force falls below the crack threshold [35]. However, even at 1.6 \( \mu \)m, it is over-indent thus includes much of the substrate influence. It is commonly accepted that the substrate influence can be considered null when the indentation depth is less than 1/10 of the coating thickness. Therefore, an interpolation is used against the indentation depth to 1/10 of the coating thickness for an estimation of the property of the coating (i.e. with minimized substrate effect). Here, linear interpolation was used for simplicity, which may not be the case as the depth of the indent becomes very small: the substrate effect at larger indentation (higher
slope) would be more than that at smaller indentation (lower slope). Treating the influence as linear from the large-force indentation (thus higher slope) would therefore result in overestimation of the property. As there is no information regarding the slope change with respect to indentation depth, linear interpolation is used as the first degree of estimation.

As shown in Fig. 7, with growth of \( V_{bs} \), the toughness increases from 1.67 to 2.02 MPa-m\(^{1/2}\). One reason that accounts for the improvement is the densified structure with refined grains. Densified structure decreases the amount of defects among columnar grains thus less chance of through thickness cracking. Reduced grain size, at the same, brings about more complicated grain boundary. This gives rise to the crack bending or branching, resulting in more energy being consumed to allow cracks to propagate [36]. In addition, bias voltage induced compressive stress also contributes to the toughness enhancement since certain level of compressive stress allows coatings to sustain more tensile strain before fracture [31]. To sum, the toughness increment is a synergetic contribution of dense structure, refined grains and proper level of increased compressive stress.

4. Conclusion

The dependences of microstructure, hardness and toughness on the negative bias voltage \( (V_{bs}) \) are explored in the magnetron sputtered chromium aluminum nitride (CrAlN) coatings. With increased \( V_{bs} \) from 50 to 260 V, coatings become dense and compact with fewer defects. In parallel, the compressive stress increased from −0.7 to −1.4 GPa. Owing to the synergetic contributions of refined structure with fewer defects and increased compressive stress, hardness increases from 10 to 26 GPa and toughness improves from 1.67 to 2.02 MPa·m\(^{1/2}\). This indicates that the simultaneous increment of hardness and toughness is achievable if the negative bias voltage is properly controlled.

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References