Chemical Modification of Titanium Nitride Films via Ion Implantation

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Titanium nitride, TiN is a typical ceramic coating film for cutting tools and dies; it often suffers from low oxidation temperature and high friction coefficient and wear volume. Its wearing and oxidation resistance is drastically improved by chemical modification via ion implantation. Carbon-, aluminum- and chlorine-ion implantation is introduced to describe the difference in the modified microstructure at the vicinity of surface. Ion-plated TiN films on a high-speed tool steel substrate are employed as a common specimen to be implanted. Each modified titanium nitride has its intrinsic, as-implanted nanostructure to the selected species. In the carbon implantation, the near-surface structure of TiN film is modified to have the layered bonding state with Ti-C/C-C/Ti-C. The Al-implantation modifies TiN to have non-equilibrium solid solution phase of (Ti, Al) N and metallic aluminum cluster. No change is seen in the chlorine implanted TiN except for increase of dislocations or point defects. The wear resistance is improved by the above as-implanted nano-structuring in the case of carbon implantation. Al- and Cl-implantation significantly improves the original oxidation and wearing resistance of TiN by the post-implantation nano-structuring. The stable, dense aluminum oxide layer is in-situ formed as a tight protective shield during the oxidation test by surface reaction between penetrating oxygen and diffusing aluminum. The lubricious titanium oxide film is also in-situ formed in the wear track at the presence of chlorine to sustain low friction and wear rate even in dry, severe wearing conditions.

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Keywords: surface nano-structuring, ion implantation, titanium nitride film, chemical modification, wear and oxidation resistance

1. Introduction

Ion implantation is a typical tool in the material processing related to the silicon technology. Various kinds of doping element or chemical species are implanted into the originally pure silicon to modify its intrinsic properties in electronics. Furthermore, the kinetic energy, the amount of doses, or, the penetration depth profile for implanted species, can be controlled by varying the process parameters. These advantageous merits are also attractive to surface modification for structural parts and components. The previous research works for application of ion implantation to surface modification1–3 were categorized into two groups. Most of heavy ion implantation studies aim at investigation of irradiation damage effects or the intense ion beam solid interactions. On the other hand, light element ion implantation might well be favorable for physical modification of near-surface structure of materials. Being free from the excessive damage of solid materials, light-element physical modification is effective in hardening, strengthening of solids via ion implantation. In particular, since the ion implantation can be used as a simulator to investigate the role of alloying elements or species in the coating design, various studies have been reported in the surface modification of metallic and ceramic coating films. Table 1 summarized the recent works related to the light-element ion implantation to titanium nitride films. Most of studies aim at improvement of the wear resistance by surface strengthening and hardening via ion implantation. Generation of high dislocation density induces the work hardening at the vicinity of surface.

As partially included in Table 1, the authors6–14,14–17 have proposed the importance of chemical surface modification to accommodate the self-protection and self-lubrication to coating films. In a similar manner to the conventional physical modification via the argon implantation, a significant amount of dislocations are induced with enhancement of implanted atom doses. In this approach, however, much concern of importance is placed on the chemical interactions of implanted species or atoms with the constituent atoms of matrix, or, with other pre-implanted species. These chemical interactions mainly take place at about 100–200 nm in depth from the surface; however, wear or oxidation resistance can be significantly improved via this chemical modification. In other words, a preferable surface nano-structured zone to improve material performance is accommodated into metallic and ceramic coating films via the light element ion implantation. Two types of nano-structuring are considered in this paper: as-implanted nano-structuring and post-implantation nano-structuring. In the former, original features of ion implantation reflect on the formation of unique microstructure as shown in Fig. 1. At first, the original chemical bonding state is modified or changed to form a new chemical bonding state in the coating film. In the second,
clusters of implanted atoms are formed in the coating film, having their loose interaction with the constituent atoms. In the third, mobile species are distributed in the film without formation of new compounds and chemical interactions with constituent atoms in the matrix. In the latter, autonomous change of microstructure is induced when the implanted materials are subjected to severe circumstance. If the implanted species are completely reacted with constituent matrix or matrix is only physically modified, the mass gain or wear volume could be reduced during severe oxidation or wearing but microstructure remains unchanged. On the contrary, the nano-structured materials often change their microstructure in posterior to ion implantation to accommodate the self-protection of original matrix materials and the self-lubrication of contact interface. In the present paper, the above nano-structuring is introduced via the carbon, the aluminum and the chlorine ion implantation into titanium nitride films. Through accommodation of nano-structuring via ion implantation, the essential nature of chemical modification can be understood. In particular, much importance of materials science lies in the change of nano-structured system during the wearing or the oxidation tests. Owing to high mobility or chemical reactions of implanted species, the original titanium nitride films are self-protected from further oxidation, or, they are self-lubricated to significantly reduce its wear volume and friction coefficient. On this basis, new materials design for die-sets or cutting tools is proposed toward dry forming and dry machining.

2. Experimental Procedure

Substrate samples with the size of $15 \times 15 \times 2 \text{ mm}^3$ were cut from high-speed tool steel AISI M 36. They were subsequently ground, polished, hardened and cleaned by argon bombardment before coating. TiN films were deposited on all the surfaces of these substrates by a commercial-type hollow cathode discharge ion plating (HCD-IP) at temperatures around 723 to 773 K. In this preparation of TiN films, the pre-deposited titanium was used as an interlayer between TiN and substrate. The thickness of TiN films was about 1 \text{ m}. This TiN had columnar structure with the preferred orientation of (111). Its average grain size was 30 to 70 nm and its aspect ratio, 3 to 4.

Ion implanter (ULVAC IMX-3500) was utilized for preparation of samples, which was equipped with a mass separator and a beam scanner. An ion beam was generated from liquid or gaseous materials in the Freeman type with a vaporizer and mass-selected to yield a single, positive-charged ion beam. The incident angle was fixed in normal to the sample surface and the vacuum was controlled to be less than $2 \times 10^{-5} \text{ Pa}$ during implantation. To suppress the ion beam heating, the beam current density was limited to 0.03 to 0.05 A/m$^2$ throughout the process. The further details of this implanter and experimental set-up for light element ion implantation were seen in elsewhere. The standard ion implantation conditions are listed in Table 2. The depth profile of implanted atoms is mainly determined by the atomic number or mass and the acceleration energy. In general, the maximum penetration depth decreases with increasing the atomic number, and, monotonically increases with acceleration energy. As had been discussed in Ref. 20), TRIM code helps to estimate the depth profile of implanted atoms. In the ideal case where the implanted atoms with perfectly constant energy have no chemical interactions with a solid, the depth profile might be shaped in the Gaussian profile. Otherwise, it is much affected by the ion implantation conditions. In fact, as partially discussed in Ref. 21), this profile was modified to have a trapezoidal shape by varying the implantation energy.

![Fig. 1](image_url)

**Table 2** Standard ion implantation conditions in the present study.

<table>
<thead>
<tr>
<th>Ion source</th>
<th>Freeman type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion species</td>
<td>Gas</td>
</tr>
<tr>
<td>Vaporizing temperature</td>
<td>Up to 873 K</td>
</tr>
<tr>
<td>Mass separation</td>
<td>Static magnetic field</td>
</tr>
<tr>
<td>Acceleration energy</td>
<td>Up to 180 keV</td>
</tr>
<tr>
<td>Ion beam current</td>
<td>Up to 300 mA</td>
</tr>
<tr>
<td>Irradiation area</td>
<td>$2.5 \times 10^{-3} \text{ m}^2$</td>
</tr>
<tr>
<td>Target chamber pressure</td>
<td>1 to $1.5 \times 10^{-3} \text{ Pa}$</td>
</tr>
</tbody>
</table>
and wear testing was conducted with a pin-on-ball tribometer. Austenitic stainless steel balls of AISI 304 with a diameter of 6 mm were used as a counter material. The normal load was kept constant, 2 N, and the relative sliding velocity, 0.1 m/s. The tests were done in the normal temperature of 275–278 K, and, the relative humidity of 55–65% without lubrication. The friction coefficient was online monitored by division of measured tangential stress by normal pressure. The wear volume of counter materials was measured after 500 m sliding test.

3. Surface Structuring by Chemical Bonding Modification

The carbon mono-oxide was used as an ion source to generate the carbon ion beam. The carbon doses were varied from $1.0 \times 10^{21}$ to $5.0 \times 10^{21}$ ions/m$^2$ with the implantation energy of 50 and 90 keV. The maximum carbon concentration reached 60 at% and 45 at% for the implantation energy of 50 and 90 keV, respectively. On the other hand, the average projected ranges for 50 and 90 keV were estimated to be 76 and 130 nm, respectively by using the TRIM code. Fraction of area with high carbon concentration enlarges in TiN by increasing the energy. In the case of carbon implantation into TiN, no peaks other than TiN single phase can be seen in the XRD profiles even with increasing the carbon dose, irrespectively of the acceleration energy. Neither alloyments, compounds, or, precipitates were detected by XRD. Although TiN peak intensity was reduced up to $5.0 \times 10^{21}$ ions/m$^2$, C-C bonds became more dominant in the spectrum. The chemical bonding state between the implanted carbon and the lattice constitutive element, titanium, or between implanted carbon atoms is controlled by the carbon concentration. When increasing the carbon dose up to $5.0 \times 10^{21}$ ions/m$^2$, C-C bonds became more dominant in the spectrum.

Figure 2 compares the C$_{1s}$ spectra obtained from the C-implanted TiN film for various carbon doses. Besides Ti-N bonding, only Ti-C bonds were observed for the C-implanted TiN films, while, only Ti-C bonds were formed with decreasing the carbon concentration.

Figure 3 depicts the variation of the wear volume of the stainless steel ball after 500 m sliding test. When the Ti-C bonding is combined with the original Ti-N bonding, the wear volume is reduced to the level, measured for TiC coating films. Further reduction of wear volume was recognized with increasing the carbon doses. This steep reduction of wear volume is attributed to the increase of graphitic layers in the inside of TiN structure.

4. Surface Structuring by Heterogeneous Reaction

As an ion source, AlCl$_3$ with the purity of 99.99% was used to generate the Al ion beam. In this case, the implantation energy was chosen to be constant, 100 keV to utilize the positive trivalent ions of Al$^{3+}$. The Al doses were varied from $1.0 \times 10^{21}$ to $4.5 \times 10^{21}$ ions/m$^2$. The implantation dose rate became constant by $3.0 \times 10^{17}$ ions/(m$^2$.s). As partially reported in Ref. 16), the implanted Al atom distribution has relatively good correlation to the Gaussian profile to the maximum penetration depth of 100 nm. This
might be because that the implanted Al atoms have a constant energy and rather weak interactions with the TiN lattices. Maximum Al concentration was varied to be 16 at%, 25 at% and 34 at%, respectively, when increasing the dose to $1.0 \times 10^{21}$, $2.9 \times 10^{21}$ and $4.5 \times 10^{21}$ ions/m$^2$.

TEM cross-sectional bright field micrograph of Al-implanted TiN is shown in Fig. 4 together with its selected area electron diffraction (SAED) pattern. Before implantation, the columnar TiN structure as well as grain boundaries, were distinctly seen in the TEM micrograph. The implanted zone in Fig. 4 was highly disordered and grain boundaries cannot be distinguished in this region. Precise analysis of SAED pattern indicated that satellites next to TiN spots should correspond to (Ti, Al) N. This is consistent with observation and analysis in Ref. 24). With high resolution SEM, the surface morphology, as well as grain size, were measured. The round grain boundaries were formed by the sputtering effect via Al-implantation and the average grain size was 40 to 100 nm. XRD profiles were depicted in Fig. 5 for as-deposited TiN, Al-implanted TiN and (Ti, Al) N reference sample. With increasing the Al dose, XRD peak of TiN (111) was shifted to a higher angle. For the lower implantation dose, the TiN peak became a little broader but no new phase was detected. When increasing the Al-dose up to $4.5 \times 10^{21}$ ions/m$^2$, additional peaks were seen at about 38°. These peaks correspond to (Ti, Al) N reference sample. Lattice parameters of TiN were calculated both for as-deposited and Al-implanted samples: 0.42520 nm for as-deposited TiN, and, 0.42275 nm for $1.0 \times 10^{21}$ ions/m$^2$, 0.42253 nm for $2.9 \times 10^{21}$ ions/m$^2$, 0.42250 nm for $4.5 \times 10^{21}$ ions/m$^2$. Linear reduction of lattice parameter with increasing the AlN mol% in (Ti, Al) N was seen in the case of the co-deposition of TiN and AlN. This reduction of TiN unit cell dimension might be caused by substitutional replacement of Ti sub-lattice by Al atoms due to kick-off mechanism in the Al-implantation. In addition to the smaller atomic radius of implanted Al, decrease of charge transfer between Ti/Al and N leads to reduction of effective size of N sub-lattice in TiN.

When increasing the Al dose into TiN, various bonding state can be introduced in the TiN lattice. Figure 6 depicts the four energy spectra for Ti$_{2p}$, Al$_{2p}$, N$_{1s}$ and O$_{1s}$ in the highest Al-dose sample. Due to natural oxidation of TiN, only the top surface of Al-implanted sample consists of Al$_2$O$_3$ (75.4 eV) and TiO$_2$ (458.9 eV). The oxygen concentration drastically decreases from the top surface and approaches an almost constant level at about 5 at% in the inner region. This content is a standard background detected in the as-deposited TiN films. The bonding energy of Ti$_2p$ peaks corresponds to TiN (455.5 eV). Except for Al$_2$O$_3$ at the top surface, Al$_{2p}$ peak splits into two states: metallic state (72.6 eV) and AlN (73.8 eV). The peak ratio of AlN to metallic Al in the XPS profiles significantly varies with Al-dose. In the case of $1.0 \times 10^{21}$ ions/m$^2$, no metallic Al phase was detected in the XPS profiles and only cubic AlN was first synthesized to form the solid solution of (Ti, Al) N. As had been discussed
in Ref. 26), formation of meta-stable fcc-structured solid solution is a main reaction in the physical vapor deposition methods for relatively wide concentration of AlN in TiN up to 60 mol%. Hence, when the ion implantation energy is increased enough to activate the kick-off mechanism of implanted Al atoms and to replace titanium atoms, (Ti, Al) N is synthesized during Al-implantation into TiN with high volume fraction. Once the Al concentration in the implanted region exceeds the solubility limit, the implanted Al atoms precipitate as a metallic phase.

As had been reported in Ref. 16), TiN has low oxidation resistance so that as-deposited TiN usually should be reacted to TiO$_2$ at the holding temperature above 673 K. Table 3 compares the activation energy in oxidation between the as-deposited and Al-implanted TiN films with the reference data.$^{27,28}$ With increasing Al dose, the activation energy was increased, or, the oxidation resistance was promoted. Except for the initial stage in the oxidation test, the activation energy for (Ti, Al) N is far lower than those for Al-implanted TiN films. This suggests that only formation of solid solution phase should never be responsible for this high oxidation resistance by Al-implantation. Figure 7 compares the cross-sectional nano-structure for the Al-implanted TiN film before and after the oxidation test. As before mentioned, Al atoms distributed in the Gaussian depth profile with the maximum relative concentration of about 60 at% at 70 nm from the surface in the inside of Al-implanted TiN film. After oxidation test, Al concentration became null or very small in the trace level in the original TiN film. Instead of that, a layer with high Al concentration formed on the original surface. This externally formed layer was a corundum, dense /C11/Al$_2$O$_3$. The in-situ formation of stable, dense /C11/Al$_2$O$_3$ during the oxidation test must be responsible for enhancement of activation energy in oxidation or for promotion of oxidation resistance. In the deeper regions away from the affected zone by ion implantation, the same columnar /C11/TiN was seen in Fig. 7. The affected TiN zone by Al-implantation was completely changed: the columnar /C11/TiN structure turned to be equi-axis /C11/TiN nanostructure.

### Table 3 Comparison of activation energy in oxidation among the Al-implanted TiN and various (Ti, Al) N reference films.

<table>
<thead>
<tr>
<th>Material</th>
<th>Atmosphere</th>
<th>Activation Energy (kJ/Mol)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>Dry Oxygen</td>
<td>167</td>
<td>Present</td>
</tr>
<tr>
<td>TiN</td>
<td>Air</td>
<td>136</td>
<td>Ref. 27</td>
</tr>
<tr>
<td>(Ti90Ti10) N</td>
<td>Air</td>
<td>185</td>
<td>Ref. 27</td>
</tr>
<tr>
<td>(Ti60Al40) N</td>
<td>Air</td>
<td>265</td>
<td>Ref. 27</td>
</tr>
<tr>
<td>(Ti, Al) N</td>
<td>Air</td>
<td>187</td>
<td>Ref. 28</td>
</tr>
<tr>
<td>TiN + 1.0 x 10$^{21}$ ions-m$^{-2}$</td>
<td>Dry Oxygen</td>
<td>309</td>
<td>Present</td>
</tr>
<tr>
<td>TiN + 2.9 x 10$^{21}$ ions-m$^{-2}$</td>
<td>Dry Oxygen</td>
<td>286</td>
<td>Present</td>
</tr>
<tr>
<td>TiN + 4.5 x 10$^{21}$ ions-m$^{-2}$</td>
<td>Dry Oxygen</td>
<td>364</td>
<td>Present</td>
</tr>
</tbody>
</table>

5. Surface Structuring by Distribution of Mobile Species

In the Cl ion implantation, AlCl$_3$ was also utilized as an ion source to generate the single, positively charged ion beam of Cl$^+$. The Cl ion doses were varied from 1.0 x 10$^{20}$ to 1.0 x 10$^{21}$ ions/m$^2$. Implantation energy was constant, 100 keV. The maximum Cl penetration depth was estimated
to be about 200 nm by using TRIM code. Figure 8 compares the XRD profiles of cubic TiN structure before and after the Cl-implantation. Since no change was detected between the two cases, no new compounds or phases were synthesized by this Cl-implantation. Even by increasing the Cl dose up to \( \frac{1.0 \times 10^{21}}{2} \) ions/m\(^2\), no new peaks were detected in the XRD profiles. Different from the previous two cases, the implanted atoms have little or no capability to modify the chemical bonding state in the lattice of TiN. Figure 9(a) depicts TEM observation of the Cl-implanted TiN film in the cross-section. In its plan view, the original assembly of TiN columnar grains was also detected even after Cl-implantation. Even by increasing the Cl dose up to \( 1.0 \times 10^{21} \) ions/m\(^2\), no new peaks were detected in the XRD profiles. Different from the previous two cases, the implanted atoms have little or no capability to modify the chemical bonding state in the lattice of TiN.

Figure 9(a) depicts TEM observation of the Cl-implanted TiN film in the cross-section. In its plan view, the original assembly of TiN columnar grains was also detected even after Cl-implantation. In the middle of depth, the zone affected by implantation was seen in this TEM micrograph. Three regions were selected from this image to investigate the change of original crystallographic structure in the cross-section: the vicinity of surface, the affected zone by implantation and the deeper zone far from the affected zone. As seen in Fig. 9(b), no distinct change of crystallographic structure was detected for all the three regions. In fact, the measured lattice constant (0.4245 nm) in common is nearly equal to the reference data (0.4252 nm). As corresponding to Fig. 8, no chemical bonding state is induced by this Cl implantation into TiN film. As studied in Ref. 30), many dislocations were generated via this Cl-implantation in the similar manner to the conventional Ar implantation. In the case of excessive implantation condition with the energy of 100 keV and the dose of \( 1.0 \times 10^{21} \) ions/m\(^2\), the scalar dislocation density on \( \{111\} \) plane of Cl-implanted TiN was measured by using the Fast-Fourier Transport method for the above selected three regions: \( 1.6 \times 10^{17} \) m\(^{-2}\), \( 7.0 \times 10^{17} \) m\(^{-2}\) and \( 1.7 \times 10^{17} \) m\(^{-2}\), in the direction of depth. This suggests that implanted Cl atoms might be trapped at the generated dislocations or point defects in the affected region of TiN film. Figure 10 depicts the concentration profile of implanted Cl atoms in the inside of TiN film. No difference was seen in the Cl concentration both in the intergranular and transgranular regions. The implanted Cl atoms are mainly trapped at the crystalline defects, irrespectively of intra-grains and grain boundaries. The implanted chlorines are expected to diffuse with high mobility through defects or grain boundaries.

There are two aspects, which distinctly differ the Cl-implantation from the physical modification to the same TiN film. Recent studies on the Ar- and N-implantation into TiN stressed that surface hardening or strengthening becomes a main effect of physical modification via the ion implantation. Hence, these implanted TiN films have higher stiffness and hardness than original TiN in the nano-indentation. As had been partially discussed in Refs. 29-31), the Cl-implanted TiN indicates softer response than the original TiN films and this softness is enhanced with increasing the Cl dose. This softening via Cl-implantation to TiN is completely opposite to the conventional hardening effect via the physical modification. The second difference lies in enhancement of oxidation for TiN films in the presence of implanted Cl atoms. Figure 11 compares the oxygen concentration profiles between the as-deposited and the Cl-implanted TiN films.
The maximum penetration depth of oxygen during ion plating is almost limited by around 10 nm. Since the ion implantation takes place in much higher vacuum atmosphere, no additional oxidation occurs in the conventional processes. Much oxygen penetration observed in Fig. 11 for Cl-implanted TiN films implies that oxidation reaction at room temperature in air should be enhanced and that increase of Cl dose should lead to activation of this low-temperature oxidation.

Table 4 compares the tribological properties among the as-deposited, the Ar-implanted and the Cl-implanted TiN films. No significant difference was seen between the as-deposited and Ar-implanted TiN films. On the contrary, the wear volume was reduced by two to three orders and the friction coefficient was reduced by about 1/10 for the Cl-implanted TiN films. Chemical modification via Cl-implantation must be responsible for this significant improvement of tribological properties. Figure 12(a) depicts the XPS spectrum by narrow scanning. Only TiO$_2$ was detected with relatively
Since no TiN was detected, the whole TiN surface was completely oxidized to TiO₂. In the case of Cl-implantation, TiN was detected with the same intensity as TiO₂. In addition, the intermediate oxides were also detected with significant intensities between two peaks for TiN and TiO₂.

That is, these intermediate oxides were in-situ synthesized in the wear track at the presence of Cl during the wear test. Figure 12(b) shows SAED patterns of the wear debris particles collected from the wear track. In the EDX analysis, only Ti and Cl were detected besides O and N. Hence, the materials identified by this pattern should be in-situ synthesized in the wear track. TiO₂ was only synthesized by 17% in the whole population of oxides. Most of yielded materials in the wear track must be intermediate titanium oxides or Magneli phase oxides. Hence, their plastic deformation under high normal pressure, is responsible for direct reduction of friction coefficient and wear volume. The implanted Cl atoms are necessary to change the triboc-chemical reaction and to form the lubricous oxides.

6. Discussion

In the dependent manner on the implanted species, the chemical modification induces a unique nanostructure. In the case of C-implantation, TiN is modified to have a sandwich layered structure with Ti-C/C-C/Ti-C bonding state at the vicinity of its surface. This as-implanted nanostructure directly leads to reduction of the wear volume. During the wear testing, titanium carbide and graphite were detected as wear debris particles together with TiN. Once the implanted carbon forms titanium carbide or graphite, no further reaction takes place to modify the as-implanted nanostructure in the wear track during the post-implantation testing. Al-implanted TiN has a modified phase of cubic solid solution, (Ti, Al) N, and metallic aluminum cluster for an as-implanted nanostructure inside TiN. Under oxidation condition, these phases decompose themselves to release Al atoms. They are sufficiently free to diffuse from depth to surface for reaction with the penetrating oxygen atoms at the surface, so that a dense, stable α-Al₂O₃ layer should be in-situ formed as a protective shield against further oxidation. In this case, since the implanted Al atoms have weaker bonding with the constituents of TiN, mobile Al atoms are supplied to the surface for reaction with oxygen atoms. The implanted Al atom works as an active constituent in the TiN frame to change its as-implanted nanostructure to the preferable post-implantation nanostructure to improvement of oxidation resistance.

On the other hand, in the case of Cl-implantation, TiN is physically modified to increase the dislocation and point defect density. No chemically modified nanostructure can be seen: the as-implanted microstructure is nearly the same as the original TiN film. Under dry, severe wearing condition, since Cl atoms diffuse toward the surface of wear track, a part of TiN film near the surface is oxidized even at low flash temperature. That is, the tribo-chemical reaction of TiN to oxides advances in sluggish and intermediately terminates in the wear track. The formed oxide layer has a crystallographic structure of TiOₓ (1 < x < 2) with shear deformability in plasticity. In this case, the implanted Cl atoms work as catalysis to preserve gradual, low-temperature oxidation of TiN to lubricious oxide layer during wearing. Original columnar structure of TiN film can be chemically modified to have various microstructure not only by ion implantation but also by post-implantation conditions. As-implanted nano-

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Table 4 Comparison of wearing test results among as-deposited, Ar-implanted and Cl-implanted TiN films against the same counter material of AISI 304 stainless steel.

<table>
<thead>
<tr>
<th>Wear mode</th>
<th>As-Deposited TiN</th>
<th>Ar-Implanted TiN</th>
<th>Cl-Implanted TiN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of debris</td>
<td>Much</td>
<td>Middle</td>
<td>Very little</td>
</tr>
<tr>
<td>Friction coefficient</td>
<td>0.8 ~ 1.2</td>
<td>~1.0</td>
<td>0.1 ~ 0.2</td>
</tr>
<tr>
<td>Wear coefficient</td>
<td><del>10⁻³</del>10⁻⁴</td>
<td>~10⁻⁴</td>
<td><del>10⁻⁷</del>10⁻⁶</td>
</tr>
<tr>
<td>Wear volume</td>
<td>~10⁻¹¹ m³</td>
<td>~10⁻¹⁰ m³</td>
<td>~10⁻¹³ m³</td>
</tr>
</tbody>
</table>

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Fig. 12 *In-situ* formation of transient titanium monoxides and Magneli phase oxides during the abrasive wearing: (a) XPS analysis on the surface of wear track, and, (b) SAED analysis of wear debris particles ejected from the wear track.

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structuring provides us a wide surface material selection via direct chemical modification of metallurgical coating and thin films. Post-implantation nano-structuring also helps us to significantly improve the material performance of coated tools.

7. Conclusion

Two types of nano-structuring are introduced into the titanium nitride films: as-implanted nano-structuring and post-implantation nano-structuring. In the former approach, new bonding state is built in, or, new non-equilibrium phase compounds are synthesized inside TiN films to form characteristic as-implanted nano-structure to each species. In the latter, as-implanted nanostructure changes itself in the oxidation or wearing conditions to significantly improve the oxidation and wear resistance. Stable, stiff oxide block layer, which was *in-situ* formed during the oxidation process, works as a self-protection barrier against further oxidation of TiN films. Lubricious oxide layer is *in-situ* formed on the wear track with aid of mobile implanted species in TiN to preserve low friction and wearing state. This self-lubrication process is unique to accommodate the workability for dry machining and forming to die/tool materials and their coating films via ion implantation.

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