Formation of Protection Layer during Oxidation of Al-Implanted TiN Coating

Thananan Akhadejdamrong1, *1, *2, Atsushi Mitsuo2, Chihiro Iwamoto3, Takahisa Yamamoto4, Yuichi Ikuhara5 and Tatsuhiko Aizawa1

1Research Center for Advanced Science and Technology, The University of Tokyo, Tokyo 153-8904, Japan
2Tokyo Metropolitan Industrial Technology Research Institute, Tokyo 115-8586, Japan
3Engineering Research Institute, The University of Tokyo, Tokyo 113-8656, Japan
4Department of Advanced Materials Science, The University of Tokyo, Tokyo 113-8656, Japan
5Department of Material Science, The University of Tokyo, Tokyo 113-8656, Japan

A protective nanocrystalline aluminum oxide layer forms during oxidation of Al-implanted TiN thin film coating on stainless steel substrate. TiN itself has poor chemical stability at elevated temperatures in an oxidizing atmosphere. Implantation of Al-ions to a TiN film, prepared by hollow cathode discharge ion plating (HCD-IP), at 4.5 × 1017 ions·cm⁻² has greatly improved thermal oxidation resistance at temperatures up to 973 K and for periods up to 20 h in a pure oxygen atmosphere. Al-implantation significantly reduced the oxidation rate of the TiN. The apparent activation energy for oxidation increased with increasing Al-dose. At the initial stage of oxidation, free metallic aluminum and/or more likely (Ti,Al)N-reacted with oxygen prior to oxidation of TiN. The thin aluminum oxide layer formed on the implanted samples was dense and free from surface flaws. This layer is thought to act as a barrier to oxygen migration protecting the TiN film from further oxidation. The diffusion of Al-atoms was a driving mechanism to activate the protection of TiN at high oxidation temperatures. The alteration of the oxidation kinetics and mechanism of the implanted TiN in an oxygen atmosphere is a consequence of the effective modification of oxide properties through Al incorporation.

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1. Introduction

Thermal stability of the metal nitrides has grown an important issue in practice because of their widespread applications. Wear protective coating for tools, mechanical components, electrical contacts, and diffusion barrier in electronic devices at elevated temperature are typical target for R&D. The most investigated nitride films with respect to high temperature resistance are TiN, CrN, AlN, and ZrN. Regarding their performances and deposition processes; a major success in the field of industrial coatings was obtained in titanium nitride (TiN). It has been widely used as a protective coating for cutting tools and automotive parts such as inserts, cutting blades, and bearings because of its excellent mechanical properties. However, TiN film has one serious disadvantage: thermal limitation. It cannot be used in air at temperatures above 723 K because it is easily oxidized to titanium dioxide (TiO₂) resulting in a significant degradation of performance. In order to improve the oxidation resistance of TiN, the researchers mostly focused on housing additive elements during deposition process. 1–3) The examples of this modification are seen as (Ti, Al)N, (Ti, Al)ON, Ti–Si–C–N, (Ti, Hf)N or (Ti, Al, Zr, Si)N. The films can be prepared by many processes. 4–7) It is generally known that Al can have a beneficial effect on an oxidation resistance of (Ti, Al)N film. However, the resulting oxide scale of such (Ti, Al)N has been composed of mixed TiO₂/aluminum oxide Al₂O₃ that has less oxidation resistance than pure crystalline Al₂O₃. 8–9) TiO₂ is a fast growing oxide of non-protective type at 973 K, while Al₂O₃ belongs to a slow growing protective type. In other words, a better oxidation resistance could be achieved if Al₂O₃ is formed selectively.

A powerful technique for modifying the surface of TiN is ion implantation because it has many advantages such as no change in the original dimension or solid solubility limit. Ion implantation is one of a number of surface modification processes that is emerging as an economical and viable process for improving near surface properties. Otherwise, there are a few works, which clearly explain the role of implanted elements concerning the improvement in the oxidation resistance by ion implantation. 10–12)

Therefore, the main aspect of this work is to modify the TiN film by incorporation of reactive-Al by ion implantation process. It is expected to achieve better oxidation resistance of TiN film without degrading either strength or toughness of the original TiN in oxidizing atmosphere. In this study, a TiN thin film was deposited on a stainless steel substrate with about 1 μm thickness. Al-ions were implanted normal to the TiN surface. The implanted samples were oxidized in a pure oxygen atmosphere. Through a precise analysis by X-ray diffraction (XRD), electron spectroscopy for chemical analysis (ESCA) and transmission electron microscope (TEM) observation, the development of Al₂O₃ is observed and described.

2. Experimental Method

Rectangular substrate samples with dimension of 10 mm × 20 mm × 2 mm were prepared from AISI 304 austenitic stain-
less steel by laser cutting, ground, polished, hardened, and cleaned by Ar-bombardment before coating. TiN films were deposited on all surfaces of these substrates by a manufacturing hollow cathode discharge ion plating (HCD-IP) type at temperatures about 723 to 773 K. Implantation was performed by an ion implanter which is equipped with a mass separation and a magnetic beam scanning. The samples were mounted on a target manipulator and irradiated by a scanning beam of Al-ions at 100 kV. Ion beam was generated from AlCl3 in an ion source with a vaporizer and mass-selected for a single-charged Al. Doses of implanted-Al were varied from 1.0 × 1017 to 4.5 × 1017 ions·cm−2. The incident angle was fixed normal to the sample surface and the vacuum was better than 2 × 10−5 Pa during implantation. To suppress the heating by ion beam itself, the beam current density was limited to 0.03–0.05 A·m−2 throughout the process.

High temperature oxidation tests were carried out in a thermo gravimetric analysis (TGA) in a dry oxygen atmosphere at temperatures of 873 to 1273 K, for 20 h holding time. The heating rate was 20 K·min−1, and the flow rate of oxygen was 20 cm3·min−1. Furthermore, the continuous oxidation behavior was also observed by increasing temperature from room temperature to 1273 K at a heating rate of 1 K·min−1. The mass gain of each specimen was recorded simultaneously with time when heating the specimen to the test temperature, soaking and cooling down to room temperature.

The crystallographic structures were identified by XRD with one-degree incident angle and the chemical bonding state of elements was determined by ESCA. Depth profiles of targeting elements were obtained by intermittent surface sputtering with 2.0 kV Ar-ions and etching rate of 2.0 nm·min−1. The Gaussian-like distribution curve fitting method was used to determine the chemical bonding state of detected elements. The cross-sectional microstructure of oxidized sample was observed by a scanning electron microscope (SEM). In order to determine the nature of the oxide layer, the thin foil specimen was prepared by a focused ion beam (FIB) method and subsequently observed by TEM operating at both 200 kV and 400 kV. Energy dispersive X-ray spectroscopy (EDS) was used for chemical analysis.

3. Results

3.1 Influences of Al-dose on TiN film

Crystallographic structures of TiN thin films before and after ion implantation were characterized by XRD. TiN exhibits new phases when increasing the Al dose up to 4.5 × 1017 ions·cm−2 as shown in Fig. 1. For the lower implantation dose, the TiN peak becomes a little broader but no new phase was synthesized.

ESCA was used to quantitatively describe the chemical bonding state as well as the depth distribution of elements. Figure 2 demonstrates that the surface of Al-implanted sample with the highest dose consists of Al2O3 (75.4 eV), and partially TiO2 (458.9 eV). The oxygen content decreased drastically from the top of surface and become approximately constant at about 5.0 at% in the inner region. This level is a standard background in the HCD-IP TiN film because a similar spectrum was also obtained from the unimplanted samples. The binding energy spectrum of Ti2p peaks at deeper region is just only corresponding to TiN (455.5 eV). The Al2p peak splits into a metallic state (72.6 eV) and a bound state. Two different bound states can be seen: binding energies of 73.8 eV and 75.7 eV are referred to the peaks for AlN and Al2O3, respectively. The binding energies of N1s and O1s also confirmed the nitride and oxide states.

3.2 Oxidation Kinetics

Figure 3 shows the typical mass gain per unit surface area versus the exposure time in flowing oxygen at 873 to 1073 K. For accuracy purpose, the mass gains of all Al-implanted samples are subtracted by the calculated mass gain obtained from edge areas of the unimplanted TiN sample (relative area ~23%) in equal time and temperature, and then divided by the total implantation affected surface area. For 4.5 × 1017 Al-implanted samples, the mass gains are rather small during the exposure period and shaped like linear rate at 873 K, two-step kinetic rate except for initial stage at 973 K, and parabolic rate with a breakaway stage (at 12 h) at 1073 K, respectively. This implies that a protective aluminum oxide layer of Al-implanted sample is developed rapidly and stable up to 973 K. In contrast, the unimplanted samples show higher mass gain for all temperatures. It indicates that oxides containing Ti and Fe or Cr are developing continuously with time. The oxidation rate constant can be determined by applying a power law:

\[
\log(\Delta M/S) = \log(K) + n \cdot \log(t)
\]

where \(\Delta M\) is the mass gain, \(S\) the oxidation area and \(n\) the index relating to the law.

To deduce the activation energy, the oxidation rate constants are calculated after transient stage (about 1 h exposure period) and the \(K\) obeys the Arrhenius relation:

\[
K = K_0 \cdot e^{-E_a/RT}
\]

where \(K_0\) is the rate coefficient, \(E_a\) the activation energy, \(R\) the gas constant and \(T\) the absolute temperature.

Figure 4 shows the Arrhenius plot for the rate constants. There is a significant difference in the oxidation kinetics between the unimplanted TiN and the Al-implanted ones.
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Fig. 2 ESCA spectra profiles of O$_{1s}$, Ti$_{2p}$, Al$_{2p}$, and N$_{1s}$ of $4.5 \times 10^{17}$ Al·cm$^{-2}$ implanted TiN at 100 kV, respectively.

Fig. 3 TGA mass gain curves of the oxidation of (a) TiN as-deposited and (b) $4.5 \times 10^{17}$ Al·cm$^{-2}$ at 873 K, 973 K and 1073 K for 20 h.

Fig. 4 Arrhenius plot of oxidation rate constants $K$ for the temperatures range 873 to 1073 K.

Unimplanted TiN exhibits a high oxidation rate with apparent activation energy of 167 kJ·mol$^{-1}$ whereas Al-implanted TiN shows a significantly reduced oxidation rate with activation energies in the range of 286–364 kJ·mol$^{-1}$ depending on the dose. The activation energy is increased with increasing the Al-dose. However, there is no significant difference in values between $1.0 \times 10^{17}$ ions·cm$^{-2}$ and $2.9 \times 10^{17}$ ions·cm$^{-2}$ compared to $4.5 \times 10^{17}$ ions·cm$^{-2}$.

3.3 Reaction compounds through oxidation

The temperature effects are listed in Table 1, which shows the identified compounds after 20 h holding at oxidation tem-
Table 1  Temperature dependence and the phase evolution after oxidation for 20 h in oxygen atmosphere.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Deposited TiN</th>
<th>1.0 × 10^{17} ions·cm^{-2}</th>
<th>2.9 × 10^{17} ions·cm^{-2}</th>
<th>4.5 × 10^{17} ions·cm^{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>873</td>
<td>TiN</td>
<td>TiN</td>
<td>TiN; (Ti, Al)N</td>
<td>TiN; (Ti, Al)N</td>
</tr>
<tr>
<td>973</td>
<td>TiO_2</td>
<td>TiN; (Ti, Al)N</td>
<td>TiN; (Ti, Al)N</td>
<td>TiN; (Ti, Al)N</td>
</tr>
<tr>
<td>1073</td>
<td>TiO_2; Fe_2O_3</td>
<td>TiO_2; TiN</td>
<td>TiO_2; Fe_2Ti_2O_5; Fe_3O_5</td>
<td>TiO_2; Fe_2Ti_2O_5; Fe_3O_5</td>
</tr>
</tbody>
</table>

Fig. 5  Cross-sectional SEM images with Al-line profile: the films were changed to oxide scale, resulting in a change of thickness and adhesion after rapid oxidation at 1273 K.

Fig. 6  Cross-sectional TEM images of Al-implanted TiN films before and after oxidation. As shown in (a), the cross-sectional TEM micrograph of Al-implanted TiN film shows a typical dense columnar structure with grain diameter 30–60 nm and aspect ratio 3–4. The grain boundaries cannot be clearly seen due to the strong strain contrast. This might be due to a lot of defects or dislocations in that region.
resulting from implanted-Al. The bright contrast is just corresponding to the high aluminum concentration zone. Since the aluminum concentration is shaped Gaussian, this bright contrast zone is an affected layer by Al-implantation. In Fig. 6(b), there are two layers over the retained TiN columnar: a thin aluminum oxide layer and a layer that have granular structure with grain size in the range of 20–40 nm. The Al-concentration determined by EDS is shifted close to the surface. This profile is in very good agreement with the oxide thickness. Oxidation at 873 K drove very fast diffusion of Al-atoms outward to the surface.

As analyzed from the electron diffraction pattern, for this aluminum oxide layer, Fig. 7 shows the scattering of small spots. This reveals that fine grain-sized crystallines have randomly oriented in the observed plane. A measured lattice distance is matched with the corundum α-Al₂O₃ (JCPDS 46-1212).

4. Discussion

The implanted-Al in the columnar TiN coating has various phases and structures, depending on the Al-dose. As shown in Fig. 2, the peak ratio of (Ti, Al)N to metallic aluminum in the XPS profiles varied with the Al-dose. Figure 8 shows the metastable PVD diagram in the TiN–AlN system. In the low temperature range, the formation of fcc solid solution is a main reaction for the AlN which has concentration up to 60 mol%. This reveals that mutual solid solubility of TiN and AlN is significantly large. Hence, the first reacted matter or AlN during Al-implantation is thought to form a solid solution with the TiN as (Ti, Al)N. When Al-concentration has exceeded the maximum solubility limit, however, Al-metals might exist at grain boundaries of TiN or even substitute the Ti-sublattice by kick-off mechanism. Therefore, the formation of metallic aluminum has also become dominant in the implanted zone (IZ).

Fig. 6 Bright field micrograph of cross-sectional 4.5 × 10¹⁷ Al·cm⁻² implanted TiN film: (a) before oxidation and (b) after oxidation at 873 K for 20 h. EDS analysis shows the change of Al-concentration profile from the outer surface.

Fig. 7 Selected area electron diffraction (SAED) pattern obtained from the top layer shows α-crystalline Al₂O₃ (corundum).

Fig. 8 Schematic metastable PVD phase diagram of the pseudobinary system TiN–AlN, after Ref. 13).
Al-implantation to the TiN thin film significantly improved oxidation resistance. An extensive XRD analysis demonstrated that the composition of oxides is influenced by the Al-dose and oxidation temperature. Oxidation protection has no longer existed for the unimplanted TiN, since it was completely oxidized to brittle crystallized TiO₂. In case of Al-implantation, the crystalline Al₂O₃ layer formed on the top of TiN acted as a barrier to oxygen diffusion. It protects the resident TiN at temperatures up to 973 K in a pure oxygen atmosphere. Here, the oxidation resistance is strongly dependent on the Al-dose, reaction temperature, and holding time. The kinetic mechanism seems to be different from that for typical (Ti, Al)N or Ti–Al coating since the irradiation effect by ion implantation can induce a large number of defects to the TiN, causing higher diffusion rate of Al than normal case.

In principle, four oxidation-protection mechanisms can be considered: (1) modification of the oxide defect structure, (2) modification of the protective layer by incorporation of reactive elements, (3) blocking mechanisms, and (4) modification of the oxide plasticity. The detail was described elsewhere. 14) Observation of oxidation protection behavior on some related materials15–17 supported the above classification of protection mechanism.

For oxidation of (Ti, Al)N8–9 and Ti–Al intermetallic alloy18–20 materials, the TiO₂ was co-formed with Al₂O₃ scale. This typical scale cannot prevent further penetration of oxygen to the film. The volume change of TiN to TiO₂ might be relatively large to cause scale expansion and to induce defects and stress concentration between interfaces. The oxide may crack and tend to promote the failure of scale.

Although the available data on Al-diffusion in TiN indicated high diffusivities of Al in TiN films,21,22 in case of the oxidation-protection mechanism by ion implantation, the enhanced diffusion process by irradiation becomes another major factor. The driving force of mobile defects such as dislocation and vacancy plays an important role to accelerate the diffusion of implanted-Al at the temperature range between 0.2–0.6 Tₘ. In general, grain boundaries and dislocations act as paths for rapid diffusion of O-ions during oxidation. However, implanted Al-ions have a higher diffusivity than the O-ions and host Ti-ions, because their energetic is increased due to radiation enhanced diffusion phenomena. Thus, the transports of Al prevailed and move faster toward the outer surface of TiN film and react with oxygen before Ti. Because of the larger affinity to oxygen, based on the standard Gibbs’ free energy,23 the Al₂O₃ layer is formed by the selective oxidation mechanism (b) and (c).

\[
\begin{align*}
a) & \quad \text{TiN} + \text{O}_2 \rightarrow \text{TiO}_2 + \frac{1}{2}\text{N}_2 \\
& \quad (\Delta G_o = -770 \text{kJ mol}^{-1} \text{ at } 973 \text{ K}) \\
b) & \quad 2\text{Al} + 3/2\text{O}_2 \rightarrow \text{Al}_2\text{O}_3 \\
& \quad (\Delta G_o = -910 \text{kJ mol}^{-1} \text{ at } 973 \text{ K}) \\
c) & \quad 2(\text{Ti, Al})\text{N} + 3/2\text{O}_2 \rightarrow 2\text{TiN} + \text{Al}_2\text{O}_3
\end{align*}
\]

Several types of Al₂O₃ have been found on Al₂O₃-forming material, such as γ-Al₂O₃, δ-Al₂O₃, θ-Al₂O₃, and α-Al₂O₃. However, the work of An et al. showed that the α-Al₂O₃ is a good protective oxide among of those because of its thermodynamic stability.24 In our study, only α-Al₂O₃ is found. It implies that the oxide layer is stable and has good oxidation resistance.

The observed equiaxed grains beneath the Al₂O₃ layer can be explained in terms of recrystallization; it is very probable that atomic displacements during implantation produce changes in the TiN lattice. It resembled grain refinement inside each of columnar grain. While the oxide layer is forming and become thicker during oxidation, the Al depletion region becomes distinct due to the fast outward diffusion of the Al from the implanted zone. This leads to a recrystallization of refined TiN to a well-defined grain boundary with equiaxed shape. Otherwise, pores are formed at grain boundaries in this region due to agglomeration of many vacancies generated after Al-movement from the TiN lattice toward the surface. In general, the recrystallization of the nitrides is usually not considered due to the large difference between melting temperature of the material and the temperature of application. However, the small grain size with large level of stress can offer significant driving forces for recrystallization at relatively low temperatures. Through the effective defect annihilation, equiaxed grains with equilibrium phase fraction take place inside columnar grain after oxidation for 20 h at 873 K.

The apparent activation energy for the Al-implanted TiN derived from this study is close to that of (Ti, Al)N and Ti–Al alloy which were reported by a group of researchers3,25 as listed in Table 2. In spite of the fact that higher Eₐ value can be translated into lower value of diffusion and such behavior is temperature dependent. Then it implies that suitable Al-dose can cause stable protective Al₂O₃ which resulting in more difficulties for oxygen to diffuse through the oxide.

### Conclusion

The oxidation mechanism for an Al-implanted TiN film has been established. The governing step is diffusion of oxygen through the Al₂O₃ layer with activation energy of 280–360 kJ mol⁻¹. The oxide layer decreases the oxidation rate of TiN. This is reflected by an increase in the activation energy of oxidation. The implantation of Al-ions to TiN thin films at the highest dose greatly improves the oxidation resistance at temperatures up to 973 K, for 20 h in a pure oxygen atmosphere. During the initial oxidation stages, free metallic aluminum and/or (Ti, Al)N reacts with oxygen prior to oxidation of the TiN. The Al₂O₃ layer on top of the dense polycrystalline TiN acted as an oxygen diffusion barrier to protect the inner TiN. In this study, three important factors affecting oxidation resistance are modification of the protective layer by incorporation of reactive Al-ions, radiation-enhanced diffusion, and oxygen blocking mechanism. It is found that the
activity of Ti is significantly lower than that of Al, and then the Al₂O₃ barrier can be selectively formed during oxidation. This crystalline Al₂O₃ is obviously very fine, dense and has a good adhesion on residual TiN. It is possible to conclude that implanted-Al has generated finer crystal size of Al₂O₃ than of which dissociated-Al from general (Ti, Al)N or Ti–Al alloy materials.

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