RELAXATION OF RESIDUAL STRESSES IN THIN FILMS INVESTIGATED USING SYNCHROTRON RADIATION

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ABSTRACT
The crystal structure and residual stresses of TiN thin films deposited by arc ion plating (AIP) on a steel substrate were investigated using a synchrotron radiation system which emitted ultra-intense X-rays. In a previous study, the crystal structure of TiN films deposited by AIP was found to be strongly influenced by the bias voltage during deposition. However, for film thickness of approximately 200 nm, TiN films deposited under bias voltages of –100 V and 0 V had a preferred orientation of {110}. In the present study, the two-tilt method was used to evaluate the residual stresses in TiN films by measuring lattice strains in two directions determined by the crystal orientation. The TiN films deposited under a bias voltage of –100 V were found to have a compressive residual stress of –8.0 GPa. This was observed to decrease with increasing annealing temperature, and reached a value of –3.5 GPa at 800°C. On the other hand, TiN films deposited under a bias voltage of 0 V had a compressive residual stress of –6.5 GPa, which was reduced to –5.2 GPa following annealing at 800°C.

Keywords: TiN film, Arc ion plating, Crystal structure, Residual stress, Surface morphology, Synchrotron radiation

INTRODUCTION
Since surface modifications are used extensively in industrial applications, film-coating technologies play an important role in the manufacture of many types of products, including semiconductors, engines and machine components. Large residual stresses develop in coated films due to intrinsic or thermal stress produced by a mismatch between the thermal contractions of the film and the substrate [1, 2]. It is important to identify the factors that generate residual stresses since they exert a strong influence on the mechanical properties of the coated materials. Considerable effort has gone into measuring residual stresses in various ceramic coatings [3, 4]. X-ray stress measurements have proved useful for the non-destructive analysis of coated films. Recently, further advances have been made in stress analysis of thin films by using high-intensity synchrotron radiation.

In a previous report [5], it was shown that {110}-oriented TiN thin films could be deposited by an arc ion plating (AIP) system, regardless of the bias voltage. This present study uses the ultra-intense X-rays emitted from a synchrotron radiation system to investigate changes in the
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residual stresses of \{110\}-oriented TiN films caused by annealing. In addition, the surface morphology of the heat-treated films was studied using field emission scanning electron microscopy (FESEM).

EXPERIMENTAL DETAILS

SPECIMENS
The substrates used were stainless-steel (JIS: SUS304) plates having a diameter of 25 mm and a thickness of 7.0 mm. An arc ion plating (AIP) system (Kobe Steel Co.) was used to deposit TiN films on these substrates. As shown in Figure 1, the substrate surface was positioned parallel to the Ti target. After degassing, nitrogen gas was injected into the chamber to a pressure of 1.0 Pa.

Prior to deposition, the substrate was ion-cleaned two times using Ti ions to remove impurities. Each cleaning step was carried out for 1 min using an arc current of 60 A and a bias voltage of \(-700\) V. An arc current of 60 A and bias voltages of 0 and \(-100\) V were used for deposition. The specimen temperature was always less than 200ºC during cleaning and deposition. The final films were found to have thicknesses of approximately 200 nm.

![Figure 1  Schematic illustration of the apparatus for arc ion plating](image)

ANNEALING TREATMENT
In order to investigate the effect of heat treatment on the morphology and residual stress, the specimens were heated in a vacuum furnace to temperatures of 200, 400, 600 and 800ºC at a rate of 5.0°C min\(^{-1}\). They were maintained at each temperature for 60 min and subsequently cooled to room temperature. All measurements were performed at room temperature.

Mismatch between the thermal contraction rates of the film and the substrate generates stress in the films. Assuming that there is no stress at the deposition temperature, the thermal
residual stress \((\sigma_{th})\) is given by

\[
\sigma_{th} = \frac{E_f}{1 - \nu_f} \left( \alpha_f - \alpha_s \right) \Delta T
\]  \hspace{1cm} (1)

where \(E_f\) is Young’s modulus, \(\nu_f\) is Poisson’s ratio for the film, \(\Delta T\) is the temperature difference between the deposition temperature and room temperature, and \(\alpha_f\) and \(\alpha_s\) are the thermal expansion coefficients of the film and the substrate, respectively. In the present case, \(E_f\) is 327 GPa \([6]\), \(\alpha_f\) is 9.35\(\times\)10\(^{-6}\) ℃\(^{-1}\) and \(\alpha_s\) is 18.7\(\times\)10\(^{-6}\) ℃\(^{-1}\) \([7]\).

**MEASUREMENT OF RESIDUAL STRESS IN THE TiN FILMS USING LABORATORY X-RAY AND ULTRA-HIGH-INTENSITY SYNCHROTRON RADIATION**

The film textures were measured using a laboratory X-ray diffraction system (lab. X-ray) emitting CuK\(\alpha\) radiation, with a tube voltage of 40 kV and a current of 20 mA. The residual stresses in the films were measured using synchrotron radiation (SR) from the BL13XU beam line at the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI). The SR energy was 12.4 keV, which corresponds to an X-ray wavelength of 0.1 nm. The dimensions of the incident SR beam were 1.0\(\times\)1.0 mm\(^2\). Stress values were determined by measuring the TiN220 diffractions \((2\theta = 38.9^\circ)\).

The two-tilt method \([8]\) represented by Eq. (2) was used for stress evaluation since an adequate diffraction intensity could be obtained only for the angular values of \(\psi = 0^\circ\) and 60\(^°\) for \{110\}-textured films \([9]\). The stresses in the TiN films were determined using the following equation \([8]\),

\[
\sigma = \frac{E}{2(1 + \nu)} \frac{\epsilon_{\psi 1} - \epsilon_{\psi 2}}{\sin^2 \psi_1 - \sin^2 \psi_2}
\] \hspace{1cm} (2)

where \(E\) and \(\nu\) are the Young’s modulus and the Poisson’s ratio of the film respectively, and \(\psi\) is the angle between the normal to the lattice plane and the normal to the film surface.

Expressing the lattice strain, \(\epsilon\), in terms of the diffraction peak angle, \(2\theta\), Eq. (2) becomes:

\[
\sigma = \frac{E}{2(1 + \nu)} \frac{\pi \cot \theta_0}{180} \frac{2\theta_{\psi 1} - 2\theta_{\psi 2}}{\sin^2 \psi_1 - \sin^2 \psi_2} = KM
\] \hspace{1cm} (3)

where \(K\) is a stress constant and \(M\) is the gradient of the \(2\theta / \sin^2 \psi\) plot. The values of \(E\) (391 GPa) in the \{110\}-planes of TiN were assumed to be the average values for the Voigt \([10]\) and Reuss \([11]\) models for the elastic compliance of a TiN single crystal \([12]\). In addition, the measured residual stress value was about the same in an arbitrary measurement course on the specimen surface.
RESULTS AND THE DISCUSSION

Several particles on the surface of the TiN\textsubscript{0V} and the TiN\textsubscript{−100V} as-deposited film can be observed in the FESEM images shown in Figures 2a and 2b, respectively. Although annealing at 800°C produced no observable change to the surface morphology of the TiN\textsubscript{0V} film (Figure 2c), the growth of new crystals can be observed on the surface of the TiN\textsubscript{−100V} film (Figure 2d).

Figures 3a and 3b show typical X-ray diffraction (XRD) patterns from the TiN\textsubscript{0V} and the TiN\textsubscript{−100V} film, respectively. Because of the strong \{110\} texture in both films, the only intense peaks detected in the as-deposited films were due to 220 diffraction. Annealing at 800°C produced a small increase in the 220 peak intensity for the TiN\textsubscript{0V} films (Figure 3a) and a much larger increase for the TiN\textsubscript{−100V} films (Figure 3b).

Figure 4 shows the variations in the full-width at half-maximum intensity (FWHM) and the integrated intensities (I\textsubscript{int}) as functions of the annealing temperature. These data were obtained from the TiN220 diffraction of the TiN\textsubscript{0V} and TiN\textsubscript{−100V} TiN films at an angle $\psi = 0^\circ$. In case of the TiN\textsubscript{0V} film (Figure 4a), annealing at 800°C produces a small increase in I\textsubscript{int} as the annealing temperature increased. No change in the FWHM is observed up to 600°C, but a suddenly decrease occurs at 800°C. In contrast, for the TiN\textsubscript{−100V} film (Figure 4b), annealing at temperatures above 400°C causes a relatively large reduction in the FWHM, but
Figure 3  X-ray diffraction pattern of TiN film deposited by arc ion plating

(a) Bias voltage of 0V  
(b) Bias voltage of -100V

Figure 4  Change in FWHM with increasing annealing temperature

(a) Bias voltage of 0V  
(b) Bias voltage of -100V

I_{int} remains unchanged up to 600ºC, after which it suddenly increases.

It is conjectured that the reduction in the FWHM value for the annealed TiN_{−}100V film is caused by relaxation of the third kind of residual stress. In addition, the increase in I_{int} is believed to be the result of the growth of TiN grains in the film. These new crystals are observable in the FESEM images of the TiN_{−}100V films that were annealed at 800ºC.

Figures 5a and 5b show the residual stresses measured in the TiN_0V and the TiN_{−}100V films, respectively. The thermal residual stresses (Eq. (1)) derived from the differences in the thermal contractions of the TiN film and the substrate [11] are also plotted. In the case of the TiN_0V films, the as-deposited films have a highly compressive residual stress of −6.5 GPa. This was found to decrease to −5.2 GPa as the annealing temperature was increased to 800ºC. On the other hand, the residual stress of −8.5 GPa in the as-deposited TiN_{−}100V films decreased to −3.5 GPa at an annealing temperature of 800ºC.

The development of residual stresses in films depends on the deposition conditions, including ion energy and temperature. The residual stress values of −8.5 and −6.5 GPa of the
The existence of large compressive residual stress was previously reported for TiN films deposited by arc ion plating. It is likely that this stress is mainly due to the intrinsic stress produced by ion bombardment during film deposition, and that stress reduction during annealing is the result of the relaxation of the strain associated with this intrinsic stress. As mentioned previously, it is conjectured that the reduction in the FWHM of the annealed TiN_{-100V} film is caused by relaxation of the third kind of residual stress. Following annealing at 800ºC, the TiN_{0V} films had higher residual stresses (−5.2 GPa) than the TiN_{-100V} films (−3.5 GPa). Since the only difference between this two films is the bias voltage, the residual stress is thought to originate not only from ion bombardment but also from crystal growth during film deposition. However, further research is required to clarify the mechanism involved.

**SUMMARY**

The crystal orientation and residual stress of TiN films deposited by arc ion plating were investigated. Films deposited using bias voltages of −100 V (TiN_{-100V} film) and 0 V (TiN_{0V} film) were found to have strong {110} textures. No significant change in the appearance of the surface of the TiN_{0V} films was observed following annealing below 800ºC. However, in case of the TiN_{-100V} films, recrystallized TiN grains appeared on the surface when the specimens were annealed at 800ºC. A large decrease in the FWHM of the 220 XRD peaks was found to occur during annealing of the TiN_{-100V} films, whereas for the TiN_{0V} films only a slight decrease was observed above 600ºC. In addition, the FWHM of TiN_{-100V} films were about twice the value of the TiN_{0V} films. The as-deposited TiN_{-100V} and TiN_{0V} films were to have compressive residual stresses of −8.2 GPa and
–6.5 GPa, respectively. This stress became relaxed during annealing, and the rate of stress relaxation was greater for the TiN_100V film than the TiN_0V film.

REFERENCES