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Properties of (Ti, Al)N films prepared by ion beam assisted deposition[†]

Tsuneo SUZUKI*, Yuichi SETSUHARA**, Yukio MAKINO**, Shoji MIYAKE***, Takao SAKATA**** and Hirotaro MORI*****

Abstract

A study was performed to investigate the properties of (Ti, Al)N films prepared by ion beam assisted deposition (IBAD). The films were synthesized by depositing Ti and Al metal vapour under simultaneous bombardment with nitrogen ions in the energy range of 0.2-20 keV with the N/(Ti+Al) transport ratio in the range of 0.2-1.0. The films were grown on Si(111) wafers at room temperature. From the result of x-ray diffraction and selected area electron diffraction, the crystalline structure of the (Ti_{0.7}Al_{0.3})N films was found to be a metastable single-phase B1-NaCl structure and the interplanar distance d_{200} decreased with increasing N/(Ti+Al) transport ratio. With a increase in Al content, (Ti_{0.2}Al_{0.8})N films were found to have a wurtzite structure phases. The ion-beam-induced crystallization effects in the early stage of the single-phase (Ti_{0.7}Al_{0.3})N film growth was also examined using transmission electron microscopy. Preliminary results were obtained for the samples prepared with 5- and 20-keV N ions with the transport ratio kept constant at 0.5, which suggest that the ion energy can significantly affect the crystallite growth but has less effects on the nucleation site density. The oxidation resistance at an elevated temperature was also examined. TiN films began to oxidize at a temperature of about 700°C in air, whereas the (Ti, Al)N films did not oxidize at temperatures as high as 900°C.

KEY WORDS: (Ion beam assisted deposition) (Titanium-aluminum nitride) (Microstructure) (Oxidation)

1. Introduction

TiN and metastable (Ti, Al)N exhibit high mechanical hardness and low friction coefficients towards steels and TiN is used extensively as wear-protective coatings on cutting tools, die molds, and so on. TiN began to oxidize already at temperature above 500°C. Recent studies of the synthesis of (Ti, Al)N films have attracted an increasing interest as a means of obtaining wear-protective coatings with higher oxidation resistance at elevated temperatures^{1,2)} and an improved performance in machining operations³⁾. The (Ti, Al)N coatings with such desirable properties may provide a promising alternative to conventionally used TiN coatings⁴⁾. The (Ti, Al)N films are deposited with various type of chemical vapour deposition(CVD) and physical vapour deposition(PVD)²⁻⁷⁾. However, in conventional PVD and CVD processes, there are some disadvantages such as high processing temperature, insufficient adhesion of coating, etc. The films deposited by IBAD technique is expected to have high adhesion to the substrate in a near room-temperature processing.

In the Ti-Al-N ternary-phase equilibrium diagram, Ti, Al and N appear to have essentially no solubility in AlN, TiN and TiAl, respectively, and Ti₂AlN, Ti₃AlN and Ti₃Al₂N are the only equilibrium ternary phases⁸⁾. So far the investigations on the variation of the microstructure and the metastable phases in the (Ti,Al)N films by PVD techniques have been mainly discussed as a function of the overall Al content in the films, and the effects of ion bombardment on the formation of the metastable phases have not been revealed in detail.

This study is designed to investigate the microstructure of the (Ti, Al)N thin films which are prepared using IBAD technique, which exhibits advantages in the controllability of the energy and the ion to atom ratios over a variety of PVD methods, and also to discuss the ion-beam irradiation effects on the properties of the metastable phases. The (Ti, Al)N films are prepared by vapour deposition of Ti-Al alloy under simultaneous bombardment with N ions in the energy range of 2-20 keV. Crystalline structure of the films was characterized by using x-ray diffraction (XRD) and selected area electron diffraction (SAED). In addition,

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preliminary investigations are presented regarding the ion-beam-induced crystallization effects in the early stage of the film growth. Furthermore, oxidation resistant tests of (Ti, Al)N film at elevated temperatures up to 1000°C are carried out using the thermogravimetric-differential thermal analysis method, and the results are compared with those obtained from TiN film.

2. Experimental

A compact IBAD system with a bucket-type 2.45-GHz electron-cyclotron-resonance ion source and an electron beam evaporation source was used for the preparation of the (Ti, Al)N films. Details of the deposition system has been described elsewhere⁹. Acceleration voltage of the extracted nitrogen ions was varied in the range of 2-20 kV. The ion current measured using a Faraday cup with an entrance aperture of 3-cm diameter was typically 0.7 mA; i.e., the ion current density onto a substrate was 100 $\mu\text{A}/\text{cm}^2$. For characterization of the extracted ion beam, mass spectra of the extracted ions were measured using a analyzing magnet mounted on the other side of the ion source and the ratio of the atomic to the molecular ion species ($\text{N}^+ : \text{N}_2^+$) was approximately 1:2. The base pressure of the deposition system, evacuated with a 1500-l/s cryopump, was 9×10^{-5} Pa. The working pressure of nitrogen during the ion source operation was $2\text{--}3 \times 10^{-3}$ Pa. The substrate temperature was controlled to be less than 250°C by water cooling system.

The (Ti, Al)N thin films were prepared on Si (111) wafers by depositing the vapourised titanium aluminide alloy under simultaneous bombardment with N ions. Details of the deposition procedures for the vapourised titanium aluminide alloy were described in the previous study¹⁰. The elemental composition of the deposited films was measured using Rutherford backscattering (RBS) spectrometry, energy-dispersive x-ray spectroscopy (EDS) and x-ray fluorescence (XRF) analysis. The atomic percent of Al in the films was found to be higher than that in the evaporation source, possibly because of the lower melting temperature for Al compared with Ti. Due to this selective evaporation of Al out of the source, every preparation of the film was carried out after exchanging the source material for a brand-new piece of alloy in order to perform reproducible experiments. Furthermore, non-uniformity of the Ti- to Al-flux ratio during the deposition process was also evaluated using RBS spectrometry and was found to be insignificant ($\pm 3\%$) within the range of experiments in our present study. The transport ratio $\text{N}/(\text{Ti}+\text{Al})$ was varied in the range of 0.2-1.

The crystalline structure of the films were characterized using XRD and SAED. XRD measurements were performed with a Cu anode. Glancing-incidence thin-film

optics were employed with the theta drive locked at 2.00°. Films for SAED measurements were first formed on NaCl-crystal substrate with a film thickness of 1000-2000 Å and were finally mounted on Mo mesh by dissolving the NaCl substrate in water.

Plan-view TEM observation was also performed to investigate the ion-beam-induced crystallization effects in the early stage of the single-phase $(\text{Ti}_{0.7}\text{Al}_{0.3})\text{N}$ film growth. For this investigation, films with a thickness of ~ 600 Å were deposited on electron-transparent Si (111) substrates. Preparation of this specific substrate was accomplished before the film deposition, which consisted of grinding, followed by etching in hydrofluoric acid to obtain electron-transparent specimens. This method for preparing TEM samples has advantages over that requiring thinning processes after the deposition of the films. The method allows plan-view observations in a very thin layer (possibly ~ 500 Å) of as-deposited films without degrading and/or changing the microstructure through chemical-etching and/or ion-milling processes. In the present study, we are particularly interested in the ion-beam-induced effects in the early stage of the film growth, and the post-thinning process with ion milling techniques may simply add significant ambiguities to the examinations of the microstructure resulting from the ion-beam irradiation during film growth. TEM observations and SAED measurements were performed in a HITACHI H800 electron microscope operated at 200kV. High-resolution TEM (HRTEM) examinations were also conducted in a HITACHI H9000 electron microscope with an acceleration voltage of 300 kV.

The weight-gain resulting from oxidation of TiN and $(\text{Ti}_{0.7}\text{Al}_{0.3})\text{N}$ films was measured using the thermogravimetric-differential thermal analysis method. The films with a thickness of ~ 7000 Å were deposited on pure platinum (99.98%) substrates with 20-keV nitrogen ions at a transport ratio $\text{N}/(\text{Ti}+\text{Al})$ of 0.5. Platinum was used as a non-oxidation substrate. The specimens were heated in air at a heating rate of 5K/min.

3. Results and discussion

The phase composition of (Ti, Al)N films with high and low Al content was investigated using SAED. Typical SAED patterns from (Ti, Al)N films with 30 and 80 atomic percent Al are shown in Fig. 1(a) and (b), respectively. Here the films were prepared with 20-keV N ion beam at a transport ratio $\text{N}/(\text{Ti}+\text{Al})$ of 0.5, and the atomic percent of Al in the films was obtained from EDS measurements.

The SAED pattern from the film with 30 atomic percent Al shows a single-phase B1-NaCl structure typical for the titanium-based nitrides. It should be noted that the Ti-Al intermetallic alloy phases are not observed, which is in

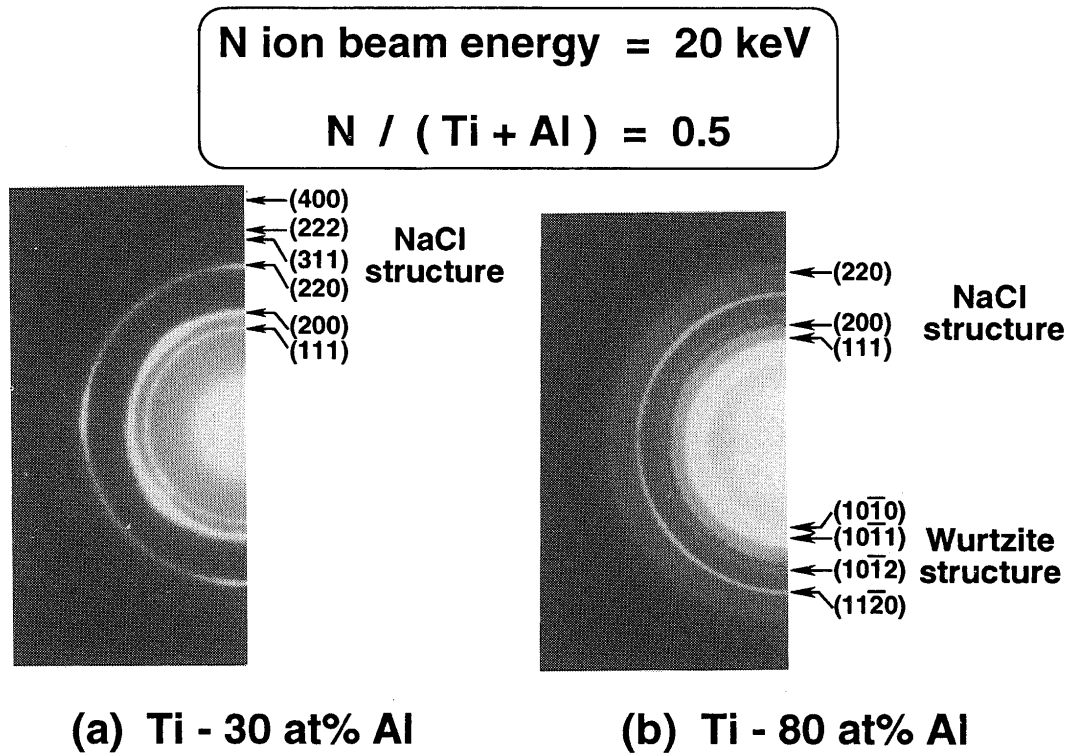


Fig. 1. SAED patterns from (Ti, Al)N films with (a) 30 at% Al and (b) 80 at% Al. The films are prepared with 20-keV N ion beam at a transport ratio $N/(Ti+Al)=0.5$.

contrast to our previous IBA study¹⁰⁾ to prepare the Ti-Al films with (Ti+Al) vapour deposition under simultaneous Ar-ion-beam bombardment. Possibly, this is because of the reactivity of N ions, which may tend to stabilize the Ti-Al-N system in a metastable nitride phase rather than in a multi-phase mixture composed of the intermetallics phases together with nitride phases. A question then arises whether Al is actually incorporated in the single-phase NaCl structure typical for TiN. To answer this question, elemental mappings constructed from Ti and Al signals in EDS are compared with the plan-view TEM images from the films. As a result the spatial distributions of Ti and Al atoms are found to be homogeneous over the entire film region and obviously consistent with the plan-view TEM images.

With increasing Al content, the film with 80 atomic percent Al shows a two-phase mixture consisting of NaCl and wurtzite crystalline phases, as can be seen in Fig. 1(b). The variation of the crystalline state phases from the B1-NaCl to the two-phase mixture (NaCl and wurtzite structures) with increasing Al content in the Ti-Al-N system is consistent with that obtained from the films deposited using the cathodic arc ion plating⁶⁾ and the dual-target magnetron sputtering⁷⁾.

Detailed investigations were then performed on the microstructure of the films with 30 atomic percent of Al. The $(Ti_{0.7}Al_{0.3})N$ films were prepared with 2-20 keV N

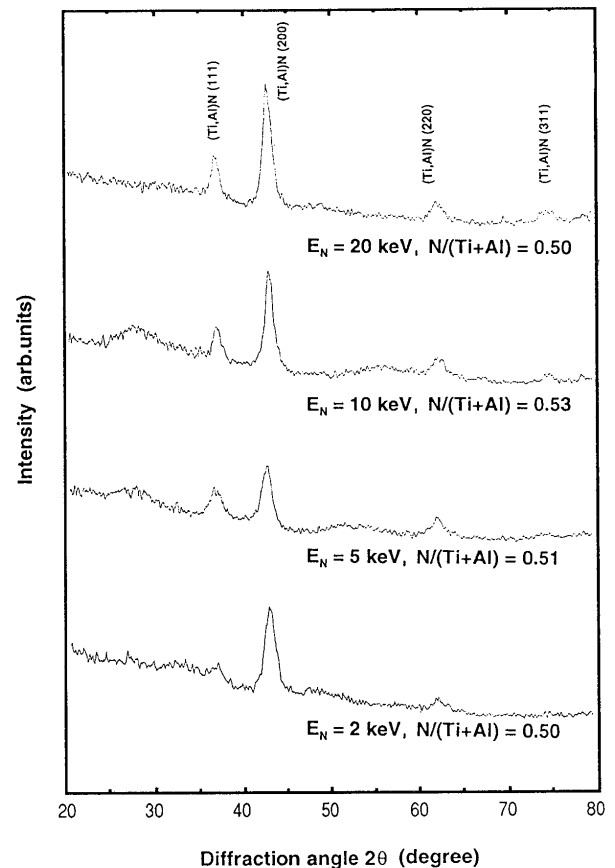


Fig. 2. XRD patterns from $(Ti_{0.7}Al_{0.3})N$ films prepared with 2-20-keV N ion beam at a transport ratio $N/(Ti+Al)$ kept nearly constant at 0.5.

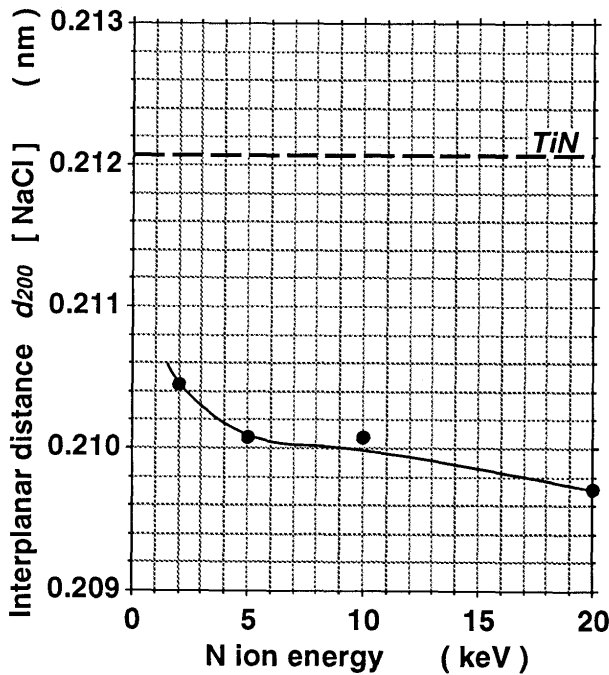


Fig. 3. Interplanar distances d_{200} for single-phase NaCl-structure (Ti, Al)N films prepared at a transport ratio $N/(Ti+Al)$ kept constant at 0.5 as a function of N ion energy. The broken line shows the corresponding value for bulk TiN¹¹⁾.

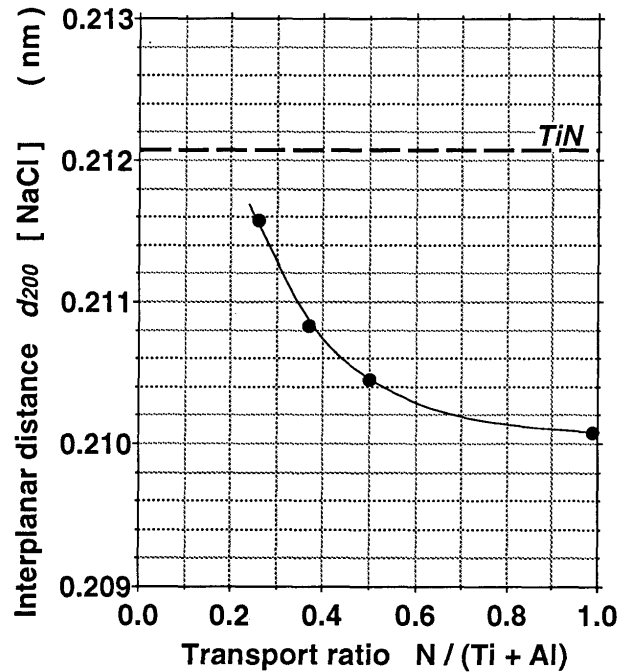


Fig. 4. Interplanar distances d_{200} for single-phase NaCl-structure (Ti, Al)N films prepared with 2-keV N ion beam as a function of transport ratio $N/(Ti+Al)$. The broken line shows the corresponding value for bulk TiN¹¹⁾.

ions at transport ratios $N/(Ti+Al)$ in the range of 0.2-1. Typical XRD patterns from the films prepared with 2-20 keV N ions are shown in Fig. 2, where the transport ratio $N/(Ti+Al)$ is kept nearly constant at 0.5. The XRD patterns show only a single-phase B1-NaCl structure, which is consistent with the SAED result in Fig. 1(a). In addition the (200) peak positions are found to be higher than the corresponding bulk value for TiN¹¹⁾ and are shifting towards higher 2θ values with increasing ion energy. XRD patterns from the films, prepared at a constant ion energy of 2 keV with a variation of the transport ratio in the range 0.2-1, also revealed only a single-phase B1-NaCl structure, and the (200) peak positions shifted towards higher 2θ values with increasing transport ratio.

The variations of the interplanar distance d_{200} as determined from XRD are plotted in Figs. 3 and 4 as a function of the N ion energy and the transport ratio, respectively. Here it should be noted that the broken lines in Figs. 3 and 4 show the d_{200} value for bulk TiN¹¹⁾ as a reference to be compared with the corresponding values obtained in the present study.

First, the interplanar distances d_{200} in the films are found to be reduced from the corresponding value for the bulk TiN. One possible mechanism for this reduction, compared with the bulk TiN value, has been explained by the substitutional replacement of Ti in the cubic B1 lattice with Al atoms of smaller ionic radius²⁾. Wahlström *et*

al., however, reported that this reduction can not be completely suggested as the substitutional replacement and they pointed out the role of the complex bonding in transition-metal nitrides⁷⁾.

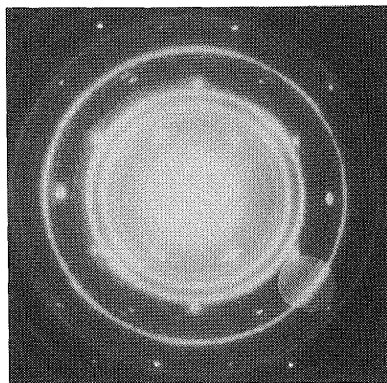
Second, the interplanar distance d_{200} in Figs. 3 and 4 is found to decrease slightly with increasing N ion energy and monotonically with increasing $N/(Ti+Al)$ transport ratio. The variation of the d_{200} as a function of the N ion energy, however, is found to be quite small, so that further investigations are in progress to clarify the effect. The decrease in the interplanar distance, and thus in the unit cell dimension, has also been reported for increasing atomic percent of Al in the other PVD processes^{6,7)}, where this decrease has been attributed to the higher content of Al incorporated in the lattice forming a single-phase NaCl structure. Following these published works, the results in Fig. 4 suggest that the energy transfer to the films from the ion beam has significant effects on the enhancement of the atomic mixing in Ti-Al-N system to form the single-phase metastable structure. This can be explained by the fact that the average kinetic energy per deposited Ti or Al atom, transferred from incident N ions through the collision cascade, becomes larger with increasing transport ratio.

In regard to the ion-irradiation effect on the variation of the (200) interplanar distance, a question may arise about the elemental-composition deviations in the films caused by the sputtering process during film growth, since

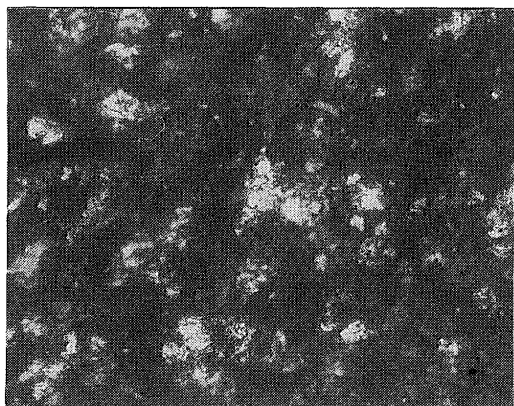
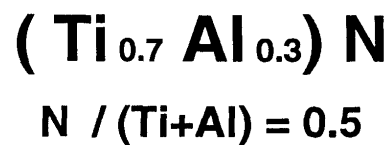
the early works^{6,7)} using PVD processes have suggested that the unit cell dimension of the (Ti, Al)N metastable phase decreases linearly with increasing atomic percent of Al in the films. To answer this question we performed XRF measurements on the elemental composition of the prepared films. The XRF measurements revealed that the atomic percent of Al in the films deviated by 9.8% towards smaller values with increasing transport ratio from 0.25 to 1. Furthermore the TRIM¹²⁾ calculations on the sputtering yields also supported this tendency, which can also be expected from the mass numbers in this atomic system; *i.e.*, the sputtering yield of Al atoms is slightly higher than that of Ti atoms. As has been suggested by the earlier works^{6,7)} using PVD processes, the slight depletion of Al content with increasing transport ratio may lead to films with larger unit-cell dimensions. However, the experimental results in Fig. 4 suggests otherwise. This discrepancy indicates that the decrease in

the unit-cell dimension with increasing N/(Ti+Al) transport ratio is inherently attributed to the enhancement of the atomic mixing in Ti-Al-N system rather than the elemental-composition deviations caused by the sputtering process.

In order to further investigate the ion-beam-induced crystallization effects, early stages of the single-phase (Ti_{0.7}Al_{0.3})N film growth were also examined using TEM observations. Preliminary experiments were performed on the samples prepared with 5- and 20-keV N ions with the transport ratio kept constant at 0.5 to study the effect of the ion energy on the nucleation site density and the crystallite growth. Prior to the TEM observations of the prepared films, a benchmark test was performed on a (Ti_{0.7}Al_{0.3})N_x film (x<1) prepared with the ion-source plasma in operation but without N ion-beam irradiation, to examine the microstructure of the films in absence of the ion-irradiation. Both SAED patterns and HRTEM images from the benchmark-test samples revealed an amorphous structure.

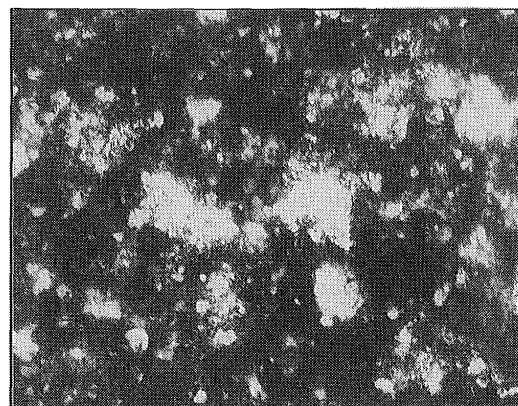


(a) SAED pattern



50 nm

(b) N beam energy = 5 keV



50 nm

(c) N beam energy = 20 keV

Fig. 5. Plan-view dark-field TEM images from the samples prepared at a transport ratio N/(Ti+Al) kept nearly constant at 0.5 with (b) 5- and (c) 20-keV N ions. The images are taken from the (220) diffracted electrons as-selected in the electron diffraction for (220), which is depicted in (a) as a white circle on the (220) diffraction ring.

Figures 5(b) and (c) show the plan-view dark-field TEM images from the samples prepared with 5- and 20-keV N ions, respectively. Here the images are taken from the (220) diffracted electrons as selected in the electron diffraction for (220), which is shown in Fig. 5(a) as a white circle on the (220) diffraction ring. The small dots in Fig. 5(a) correspond to the net patterns from the electron-transparent Si substrate. The nucleation site density for these specific images was measured to be $(1.9 \pm 0.2) \times 10^{11} \text{ cm}^{-2}$ and $(1.7 \pm 0.1) \times 10^{11} \text{ cm}^{-2}$, respectively, for 5- and 20-keV samples, which are found to be statistically equivalent. In contrast the qualitative comparison of the crystallite size appears to be larger for the 20-keV sample than for the 5-keV. In order to explicitly exhibit the difference, an image-processing routine was carried out on these TEM images over a 400nm-by-400nm area to obtain Fig. 6, showing the cumulative fraction of the nucleation sites as a function of the crystallite size. The average crystallite sizes are found to be comparable for both of the energies, which are 7.0nm and 10.1nm for 5- and 20-keV N ions, respectively. On the other hand, the maximum crystallite sizes are found to be much larger for the 20-keV case (44nm) than that for the 5-keV case (18nm). In this study we have presented rather preliminary results on the ion-beam-induced nucleation and crystallization in the early stage of film growth. Further investigations are still in progress for better understanding of the mechanisms involved in these effects.

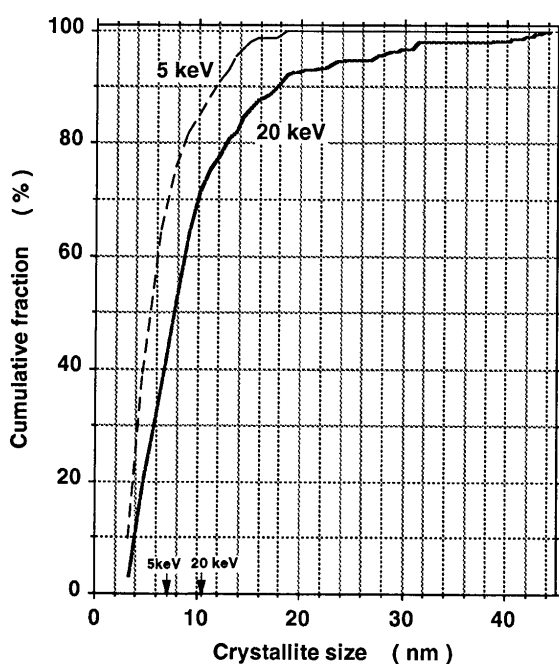


Fig. 6. Cumulative fraction of the nucleation sites as a function of the crystallite size for the TEM images shown in Figs. 5 (b) and (c).

Figure 7 shows the oxidation curves of $(\text{Ti}_{0.7}\text{Al}_{0.3})\text{N}$ and TiN films measured using thermogravimetric-differential thermal analysis method. The TiN film began to oxidize at a temperature of about 973K, while $(\text{Ti}_{0.7}\text{Al}_{0.3})\text{N}$ film did not show any weight-gain up to 1173K. It was considered that protective layers of Al oxides formed on the surface of the (Ti, Al)N films during oxidation tests protected the films from further oxidation. But the initiation of oxidation of the (Ti, Al)N films was not clear. Ikeda *et al.* reported that $(\text{Ti}_{0.75}\text{Al}_{0.25})\text{N}$ films prepared with the cathodic arc ion plating method began to oxidize at 750°C⁶. It is not so easy to compare the oxidation behavior of these two (Ti, Al)N films which were formed in different methods, but it is considered that this difference resulted from the difference of microstructure and the way of measurement.

4. Summary

(Ti, Al)N films were prepared by depositing Ti-Al vapour deposition and simultaneous bombardment with N ions in the energy range of 2-20 keV with the transport ratio in the range of 0.2-1. The $(\text{Ti}_{0.7}\text{Al}_{0.3})\text{N}$ films revealed a metastable single-phase B1-NaCl structure and the interplanar distance d_{200} decreased with increasing N/(Ti+Al) transport ratio. With increasing Al content, $(\text{Ti}_{0.2}\text{Al}_{0.8})\text{N}$ films were found to be a two-phase mixture consisting of NaCl and wurtzite structure phases. The ion-beam-induced crystallization effects in the early stage of the single-phase $(\text{Ti}_{0.7}\text{Al}_{0.3})\text{N}$ film growth were also examined using transmission electron microscopy. Preliminary results to study the ion-beam-induced crystallization effects in early stage of film growth suggest

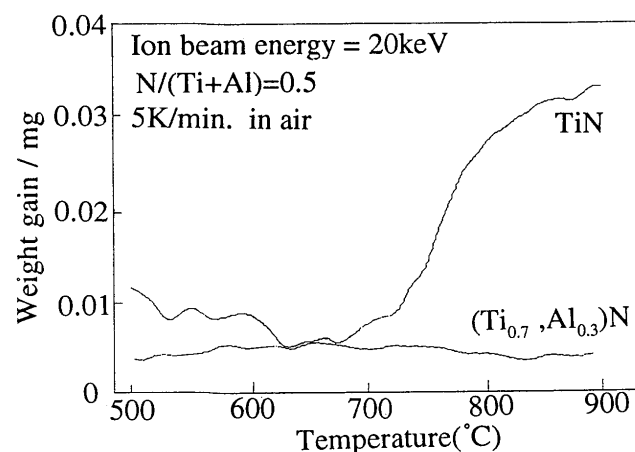


Fig. 7. Oxidation curves of $(\text{Ti}_{0.7}\text{Al}_{0.3})\text{N}$ film compared with that of TiN film as a function of temperature.

that ion energy may have a significant effects on the crystallite growth but less on the nucleation site density. An oxidation test shows that (Ti, Al)N films have superior antioxidation characteristics at elevated temperature, up to 900°C, compared with TiN films.

Acknowledgment

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References

- 1) M. Wittmer, J. Noster, and H. Melchior, *J. Appl. Phys.* 52 (1981) 6659.
- 2) O. Knotek, M. Böhmer, and T. Leyendecker, *J. Vac. Sci. Technol. A4* (1986) 2695.
- 3) T. Leyendecker, O. Lemmer, S. Esser, and J. Ebberink, *Surf. Coat. Technol.* 48 (1991) 175.
- 4) W. D. Münz, *J. Vac. Sci. Technol. A4* (1986) 2717.
- 5) H. Ichimura, and A. Kawana, *J. Mater. Res.*, 8 (1993) 1093
- 6) T. Ikeda and H. Satoh, *Thin Solid Films* 195 (1991) 99.
- 7) U. Wahlström, L. Hultman, J.-E. Sundgren, F. Adibi, I. Petrov, and J. E. Greene, *Thin Solid Films* 235 (1993) 62.
- 8) J. C. Schuster and J. Bauer, *J. Solid State Chem.* 53 (1984) 260.
- 9) S. Miyake, K. Honda, T. Kohno, Y. Setsuhara, A. Chayahara, and M. Satou, *J. Vac. Sci. Technol. A10* (1992) 3253.
- 10) Y. Setsuhara, H. Ohsako, Y. Makino, and S. Miyake, *Surf. Coat. Technol.* 66 (1994) 495.
- 11) Powder Diffraction File, JCPDC International Center for Powder Diffraction Data, Swarthmore, PA, 1989: TiN (6-642).
- 12) J. F. Ziegler, J. P. Biersack and U. Littmark, *The stopping and Ranges of Ions in Solids* (Pergamon, New York, 1985).