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# Optimization of (Al, Ti) N Thin Film Formation Process by Ion Beam Assisted Deposition <sup>†</sup>

Yasuo TAKAHASHI\*, Shuguang LI\*\*, Tomoyuki IMAKITA\*<sup>†</sup>, Akihiro IMATANI\*<sup>†</sup> and Katsunori INOUE\*\*\*

## Abstract

Ternary (Al, Ti) N film was produced by using the ion beam assisted deposition method (IBAD). The ternary (Al, Ti) N film gives a significant improvement in wear-resistance and corrosion protection compared with conventional binary nitrides and the mechanical properties depend on the composition. In the present study, the formation process was optimized by proposing an objective function, designed to evaluate the mechanical properties when searching for the optimal process conditions for a film which has higher hardness and finer surface roughness as possible.

The atom arrival ratio  $R_1 = Ti/(Ti+Al)$  and the ion-atom arrival ratio  $R_2 = (Ti+Al)/N$  were adopted as the controlling process factors.  $R_1$  and  $R_2$  were changed in the range of 0~1.0 and 0.5~1.5, respectively, keeping the ion current density (0.10mA/mm<sup>2</sup>) and the ion energy (2.0keV) constant.

Two steps of the global searching and the local searching were adopted for the experimental optimization. The local domain for a good process was obtained by the global searching, which was around  $R_1 = 0.2$  and  $R_2 = 1.0$ . The optimal process condition, which was finally found at the point of  $[R_1, R_2] = [0.25, 1.0]$  by the steepest descent method. It was found that the ternary film (Al, Ti) N around the optimal process condition shows a fine structure of two phase coexistence (AlN+TiN), the average composition of which was expressed by  $(Al_{1-x}Ti_x)N_{1.25}$  where  $x = 0.23$ , i.e., this represents a non-stoichiometric composition.

**KEY WORDS:** (Optimization)( Ion-beam-assisted deposition) (Thin film) (Aluminium nitride)  
(Titanium nitride) (Hardness) (Surface roughness)

## 1. Introduction

Binary TiN coating has been widely used in mechanical parts or cutting tools for high wear resistance because of its excellent tribological characteristics but it does not show high protection against corrosion<sup>1)</sup>. On the other hand, AlN has been noted for its thermal and chemical stability and electric conductivity<sup>2)</sup>. Therefore, Ternary (Al, Ti) N coating might present much higher hardness and much better characteristics than conventional binary metal nitrides. Some methods of physical vapor deposition (PVD)<sup>3-6)</sup> and chemical vapor deposition (CVD)<sup>7-8)</sup> have been applied to obtain the films with good properties. Also, ion-beam-assisted deposition (IBAD) has an advantage in producing stronger interfacial adhesion. In IBAD processing, low ion energy is usually used and the substrate temperature is kept at relative low temperatures so that meta stable characteris-

tics can be obtained. Some physical phenomena, such as ion implantation and sputtering occur during IBAD to improve the mechanical properties of coated films<sup>9-10)</sup>.

(Al, Ti) N films produced by IBAD exhibit structures and the properties which are very dependent on process conditions, such as ion current, ion energy and, especially, arrival ratios between metal vapor and nitrogen ion<sup>11-12)</sup>. Therefore, in the present study, the atom arrival ratio  $R_1 = Ti/(Ti+Al)$  and the ion-atom arrival ratio  $R_2 = (Ti+Al)/N$  are adopted as the controlling process factors and the optimal process condition of (Al, Ti) N film formation is determined by changing these two factors. The purpose of the present study is to search for the optimal process condition producing higher hardness and smaller surface roughness, and to investigate the film properties and its structure produced at the optimal condition.

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### 2. Objective function for optimization

An objective function is necessary to evaluate the film properties depending on the two process factors  $R_1$  and  $R_2$ . The objective function is given by

$$F(\mathbf{x}) = w_h \left\{ \frac{h(\mathbf{x}) - h_{\max}}{h_c} \right\}^2 + w_r \left\{ \frac{r(\mathbf{x}) - r_{\min}}{r_c} \right\}^2 \quad (1)$$

where  $h(\mathbf{x})$  and  $r(\mathbf{x})$  are, respectively, Vickers hardness and the average surface roughness of the film. And also,  $h_{\max}$  is an ideal maximum hardness which was set at 6000 Kg/mm<sup>2</sup> of the diamond value, and  $r_{\min}$  is an ideal surface roughness, which was defined as zero. Vector  $\mathbf{x}$  is given by  $\mathbf{x} = [R_1, R_2]^T$ . The two parameters,  $h_c$  and  $r_c$  are necessary for non-dimensionalization of two terms in eq. (1) and  $w_h$  and  $w_r$  are the weights of these terms. Equation (1) has been applied to the optimization against two factors with different dimensions.

In the present study, the parameters,  $h_c$  and  $r_c$ , were set at 6000 Kg/mm<sup>2</sup> and 0.25  $\mu\text{m}$ , respectively and both the weights,  $w_h$  and  $w_r$ , were set at 0.5, so that the values of the two terms in eq. (1) can be in same order. Also, the process factors,  $R_1$  and  $R_2$  were changed in the regions of  $0 \leq R_1 \leq 1.0$  and  $0.5 \leq R_2 \leq 1.5$ , respectively.

### 3. Experimental procedure

The optimization process consists of two steps; global and local investigations. Firstly the global searching was carried out by dividing the investigation conditions into 8x8 points over the total region. The information about rough profile of the objective function was obtained by the global searching. The local searching was carried out based on this information. In that stage, the steepest descent

method was applied in a local domain where the objective function  $F(\mathbf{x})$  became low and its profile was concave. The local searching was started from one point [  $R_1, R_2$  ] in the local domain to the direction given by

$$\text{grad } F(\mathbf{x}) = \frac{\partial F(\mathbf{x})}{\partial R_1} \mathbf{i} + \frac{\partial F(\mathbf{x})}{\partial R_2} \mathbf{j} \quad (2)$$

where  $\mathbf{i}$  and  $\mathbf{j}$  are the unit vectors for the factors,  $R_1$  and  $R_2$ , respectively. The further local searching was repeated by the same way<sup>13)</sup> until the local minimum  $F(\mathbf{x})$  was obtained.

The IBAD equipment is illustrated in Fig. 1

The ion energy  $E_i$  and the ion current density  $r_i$  were kept constant in all experiments. Al (99.99 mass %) and Ti (99.99 mass %) were used as the deposited material. They were vaporized from crucibles by electron beams, under nitrogen ion irradiation in the vacuum chamber at less than  $3 \times 10^{-3}$  Pa. Silica substrates were water cooled, so that the substrate temperature was kept about at 250 °C during deposition. The thickness of coated film was kept at about 1.5  $\mu\text{m}$  by the deposition monitor (quartz oscillator). Some additional thick films of 6.5  $\mu\text{m}$  were also deposited to observe the substructure of bulk film (fine grain size) and to measure the precision Vicker's hardness of bulk film. The applied load for hardness measurement was from 20 to 25 g. The surface roughness was measured by a surface profile measurement system with a diamond pin. The average compositions of the film were measured by an electron probe microanalyzer (EPMA). The interior structures were examined by X-ray diffraction (XRD). Scanning Electron Microscopy (SEM) was also applied to examine the fine grain structure of the film. The deposition conditions for (Al, Ti)N film formation by IBAD are indicated in Table 1.

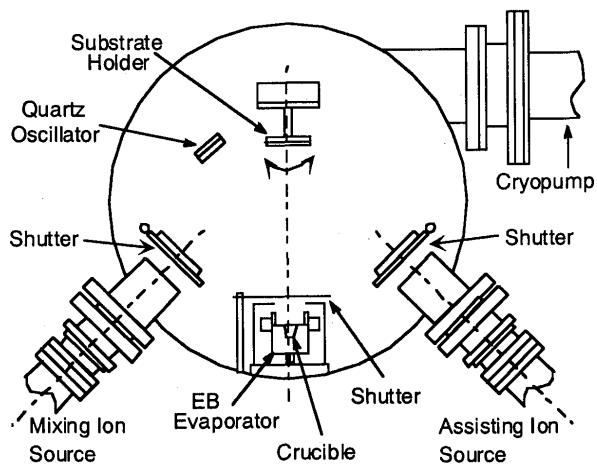


Fig. 1 Schematic illustration of IBAD equipment..

Table 1 Deposition condition of (Al, Ti) N coating by IBAD.

Vacuum pressure before deposition	$< 3 \times 10^{-4}$ Pa
Vacuum pressure during deposition	$\sim 3 \times 10^{-4}$ Pa
Ion incident angle $\theta_i$	0 °
Ion energy $E_i$	2.0 keV
Ion current density $r_i$	0.10 mA/mm <sup>2</sup>
Evaporated substance	99.999mass% Al, 99.99mass% Ti
Substrate	Silica
Substrate rotary velocity	6 r.p.m.
Substrate temperature during deposition	250 °C
Atom arrival ratio $R_1 = \text{Ti}/(\text{Al}+\text{Ti})$	0 ~ 1.0
Atom/ion arrival ratio $R_2 = (\text{Al}+\text{Ti})/\text{N}$	0.5 ~ 1.5

## Results and discussion

Fig. 2 shows the overall profile of the objective function distribution produced by global searching under the conditions indicated in Table 1. As seen in Fig. 1, the objective function value becomes small and exhibits a concave profile in the local domain around  $[R_1, R_2] = [0.2, 1.0]$ . The optimal process condition must therefore exist in this domain, where the steepest descent searching mentioned above was carried out to obtain the film with the optimal properties, i.e., the smallest value of  $F(x)$ .

Finally, the optimal condition was located at  $[R_1, R_2] = [0.25, 1.0]$  for the fixed condition of nitrogen ion energy (2.0 keV) and the nitrogen ion beam current density (0.10 mA/mm<sup>2</sup>). The Vicker's hardness<sub>25g</sub> of this optimal condition was 1340 kgf/mm<sup>2</sup> (for the thin film of 1.5  $\mu\text{m}$ ), and the average surface roughness  $R_a$  was 0.02  $\mu\text{m}$ . Also, the objective function  $F(x)$  value was 0.30. The hardness of the thin film was influenced by the substrate hardness (about 1000 kgf/mm<sup>2</sup>), because the depth of indentation for Vicker's hardness was often greater than about 1.5  $\mu\text{m}$ . The hardness of the thick film was then measured. It was found that the real film hardness is upto 1900 kgf/mm<sup>2</sup>, which is much higher than the hardness value (1000 ~ 1200 kgf/mm<sup>2</sup>) of TiN film produced by IBAD<sup>1)</sup>. In addition, as seen in Fig. 2, there may exist a lowest point for  $F(x)$  at  $[R_1, R_2] = [0.17, 1.2]$ , but the film has locally large etch pits (craters). This point was thus omitted for the optimal condition. This

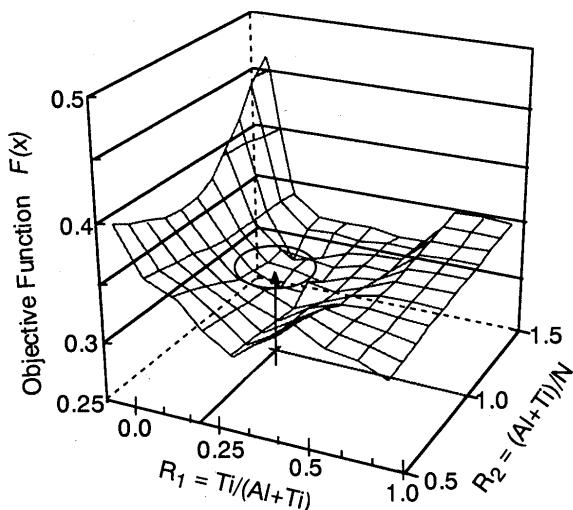


Fig. 2 Objective function profile obtained by direct searching. The objective function  $F(x)$  is determined from Vickers hardness<sub>25g</sub> and average surface roughness  $R_a$  of (Al,Ti)N films deposited under the conditions of ion current density of 0.10 mA/mm<sup>2</sup> and ion energy of 2.0 keV.

detail reason is not known.

Fig. 3 shows the SEM photograph of the film surface prepared under the optimal condition. The surface is very fine without craters. The surface profile is shown in Fig. 4. The maximum roughness is smaller than 0.2  $\mu\text{m}$  as seen in Fig. 4. It was found that the film surface roughness becomes coarse with decreasing  $R_2 = (Al+Ti)/N$  as shown in

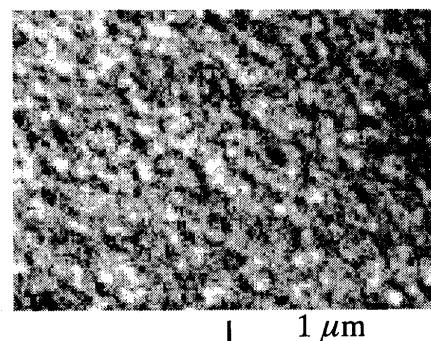


Fig. 3 SEM observation of (Al, Ti) N film surface produced under the optimal condition.

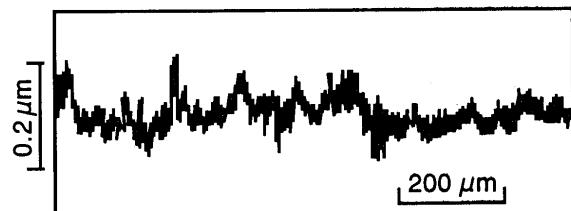


Fig. 4 Surface profile curve of optimal film.

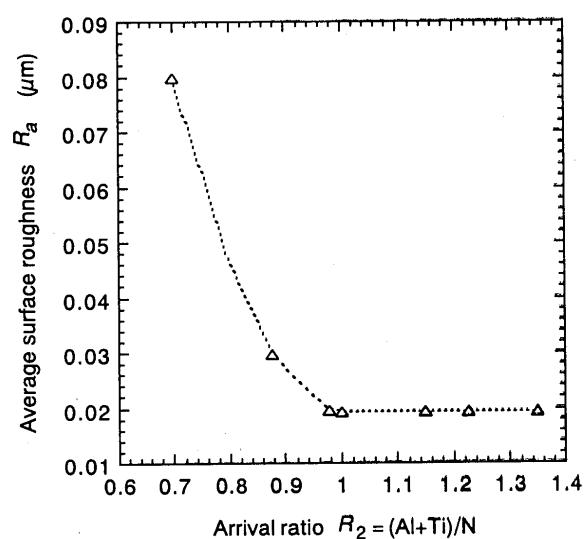


Fig. 5 Average surface roughness  $R_a$  of (Al,Ti)N films, depending on  $R_2 = (Ti+Al)/N$ ,  $r_i = 0.10 \text{ mA/mm}^2$  and  $E_i = 2.0 \text{ keV}$ .  $R_1$  is kept at 0.25.

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**Fig. 5.** This is a result by the ion sputtering effect. Also, it was found from XRD analysis that the optimal film consists of two phase coexisting crystalline grains, AlN and TiN, as shown in **Fig. 6**. This agrees with the results reported previously<sup>12)</sup>. The (Al,Ti)N film produced by IBAD has higher hardness if two phases of AlN and TiN coexist. In addition, the optimal film has a lot of fine grains smaller than 0.2  $\mu\text{m}$ .

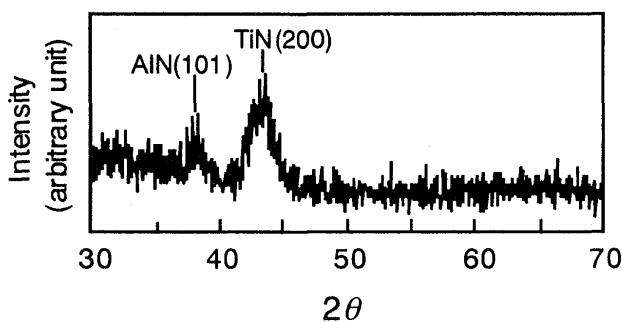
**Fig. 7** shows the fractured section (SEM photo) of the film produced under the optimal process condition. Although the grain boundary is not so clearly recognized, many fine grains are observed. In other words, the optimal film is not amorphous. The grain size of ternary (Al,Ti)N is much smaller, compared with a binary coating AlN<sup>2)</sup>. Also, no voids are observed in the (Al, Ti) N films around the optimal condition, i. e., they have a dense structure.

The effect of the atom-ion arrival ratio  $R_2 = (\text{Al}+\text{Ti})/\text{N}$  on the internal structure was investigated by keeping the atom arrival ratio  $R_1 = \text{Ti}/(\text{Al}+\text{Ti})$  at 0.25. As  $R_2$  decreases, less than unity, the peaks of the X-ray pattern become smaller and finally disappear. This implies that the grain size becomes finer, or an amorphous structure is formed. On the other hand, as the ratio  $R_2$  increases greater than unity, metal

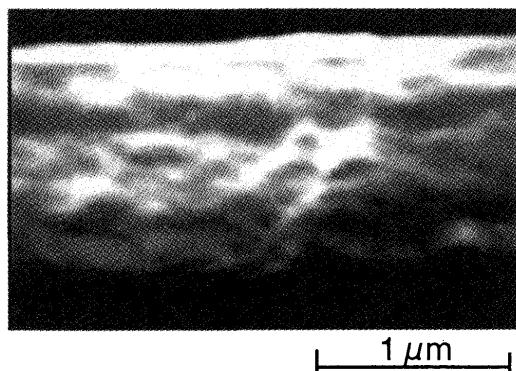
peaks appear in the x ray diffraction pattern and the nitride peaks become lower. Metallic Al occurs in the vicinity of the film surface as  $R_2$  increases. It is unfavorable for the fine crystalline growth of the (Al,Ti) N system if  $R_2 = (\text{Al}+\text{Ti})/\text{N}$  becomes too high or too low ( $R_2 \sim 1$  is the best). In addition, as the atom arrival ratio  $R_1 = \text{Ti}/(\text{Al}+\text{Ti})$  increases under the condition of  $R_2 = (\text{Al}+\text{Ti})/\text{N} \sim 1.0$ , the diffraction peaks of TiN appear, as reported in other studies<sup>7, 11)</sup>.

The film structure in the vicinity of the surface has an influence on the color of the film surface. The film color produced under the optimal process condition was light brown, which was reflected by the two phases coexisting fine grain structure. The color depends on the atom arrival ratio  $R_1$ . As the Ti dosage increases, the color of the film surface becomes a light yellow or golden color, which corresponds to the NaCl structure. On the other hand, as  $R_1$  decreases lower than unity (Al dosage increases), the color becomes dark brown or like graphite, because of an AlN Wurtzite structure<sup>12)</sup>. The color of the film surface became brown with light green under the condition where  $R_1 = 0.25$  and  $R_2 = 0.7$ . This implies that super saturation of nitrogen in the film can have a serious influence on the surface color because the film structure deviates from the NaCl structure of TiN.

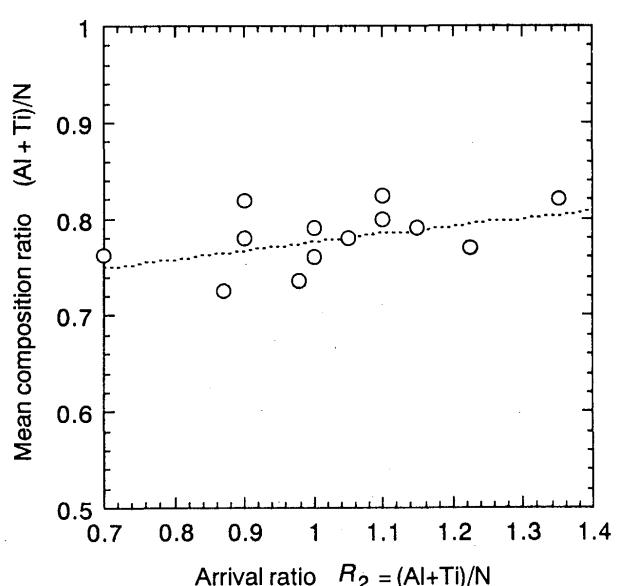
As  $R_1$  decreases, the film becomes brittle, and this was observed at the film composition ratio  $\text{Ti}/(\text{Al}+\text{Ti})$  less than 15 at%. On the other hand, as the film composition ratio  $\text{Ti}/(\text{Al}+\text{Ti})$  becomes greater than 20 at%, the ductility was improved because of the NaCl structure.



**Fig. 6** Result of X ray diffraction for optimal film.



**Fig. 7** Typical SEM photograph of film's section fractured. The film was deposited around the optimal process condition.  $\rho_i = 0.10\text{mA/mm}^2$  and  $E_i = 2.0\text{keV}$ .



**Fig. 8** Effect of atom-ion arrival ratio  $R_2$  on the atomic composition ratio  $(\text{Ti}+\text{Al})/\text{N}$  of (Al,Ti)N films.  $R_1$  is kept at 0.25.  $\rho_i = 0.10\text{mA/mm}^2$  and  $E_i = 2.0\text{keV}$ .

**Fig. 8** shows the average atomic composition (Ti+Al)/N with the change in  $R_2$  from 0.7 to 1.4. The average atomic composition (Ti+Al)/N of the film does not largely depend on  $R_2$  and is close to 80 at% around the optimal condition. Also, the atomic composition, synthesized around the optimal condition can be expressed by  $(Al_{1-x}, Ti_x)N_{1.25}$ , where  $x \approx 0.23$ . This is supported by Auger analysis<sup>11)</sup> in AlN film under the condition of  $[R_1, R_2] = [0.06, 1.0]$ . This also suggests that nitrogen atoms are easily supersaturated in the (Al,Ti)N film produced by IBAD.

### Conclusions

The optimal (Al, Ti) N films have been synthesized by ion-beam-assisted deposition (IBAD), based on an optimization function to search for the best condition of hardness and surface roughness. The optimal process condition exists for the atom arrival ratio  $R_1 (=Ti/(Al+Ti)) = 0.25$ , and the atom-ion arrival ratio  $R_2 (= (Al+Ti)/N) = 1.0$ , when the ion current density and ion energy are kept at 0.10 mA/mm<sup>2</sup> and 2.0 keV, respectively. The optimal film exhibits an average surface roughness of 0.02  $\mu$ m and a maximum roughness less than 0.2  $\mu$ m and also, with a Vicker's hardness of 1900 kg/mm<sup>2</sup> (the bulk film) is much higher than that of binary AlN or TiN film.

The film structure coated at the optimal process condition consists of coexisting crystalline AlN and TiN. As the dosage of nitrogen ions decreases or increases from the optimal condition, the condition for the growth of crystalline structures becomes unfavorable. Compared with binary AlN film synthesized by IBAD, the ternary (Al,Ti)N films are dense and grain sizes smaller than 0.2  $\mu$ m are obtained around the optimal condition.

The average composition of the film around the optimal process condition can be expressed by  $(Al_{1-x}Ti_x)N_{1.25}$ , where  $x \approx 0.23$ .

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