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# Nitritization of Aluminium by Using ECR Nitrogen Plasma

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## Abstract

Numerous nitritization experiments for Al were carried out using ECR nitrogen plasma. Since the aluminium surface is covered by a stable oxide, the surface was etched by Ar plasma bombardment before the nitritization. By this pretreatment, the nitrogen content on the surface was largely increased. Since it was observed from the emission spectroscopy analysis that the nitrogen ion,  $N_2^+$ , was effective for the nitritization, the nitrogen ion flux was enhanced by applying a negative bias to the substrate. The nitrogen content was increased several times by negative voltage, compared with the case of free voltage. It was also found by the XPS analysis that the aluminium nitride, AlN, was formed by the present plasma nitritization.

## 1. Introduction

For thin film coatings and surface modifications, low temperature plasma has been very aggressively employed in numerous fields<sup>1)-10)</sup>. In the nitritization of metal surfaces, the application of nitrogen plasma has several advantages, i. e. low substrate temperature and high deposition rate due to a large quantity of reactive particles. The plasma nitritization significantly depends on the state of nitrogen plasma, and the substrate conditions such as temperature and bias voltage<sup>9)-11)</sup>.

In the present study, a systematic plasma nitritization experiment for aluminium was carried out by using an ECR plasma process device. The aluminium surface is covered by a stable oxide, alumina ( $Al_2O_3$ ). In addition, the melting point is very low, namely 660°C. Thus, the nitritization based on the thermal process is believed to be considerably difficult<sup>12)</sup>. Even when using a nitrogen plasma, the surface nitritization is not easy since the oxide is more stable than the nitride. Only the use of nitrogen ion beam with energy of MeV enables us to use nitride on the aluminum so far<sup>13)</sup>, since the penetration depth of the nitrogen ion becomes larger than the oxide thickness. In order to successfully nitritize the aluminium by nitrogen plasma, we tried to etch the oxide layer prior to the nitrogen plasma bombardment. The effect of the preetching was examined. We also conducted nitritizations by changing the substrate temperature and the bias voltage. These results were compared with each other.

## 2. Experimental

For the nitritization of aluminium, the ECR plasma process device shown in Fig. 1 was used. The device consists of two chambers, the ECR plasma chamber and the irradiation chamber. The ECR plasma is produced by launching the microwave with frequency of 2.45 GHz into the region with a resonance magnetic field. As the magnetic field, a hexapole field made by the array of permanent magnets formed in the plasma chamber. For the discharge, the nitrogen gas is supplied into the plasma chamber. The gas flow rate is adjusted by a mass flow controller. Typical microwave power and discharge pressure were 200W and 1 Pa, respectively.

In the irradiation chamber, the aluminium sample with a purity of 99.999% is placed on the sample holder. The sample can be heated up to 800°C during the irradiation. In addition, bias voltage is applicable. For the purpose of the plasma diagnostics, an opti-

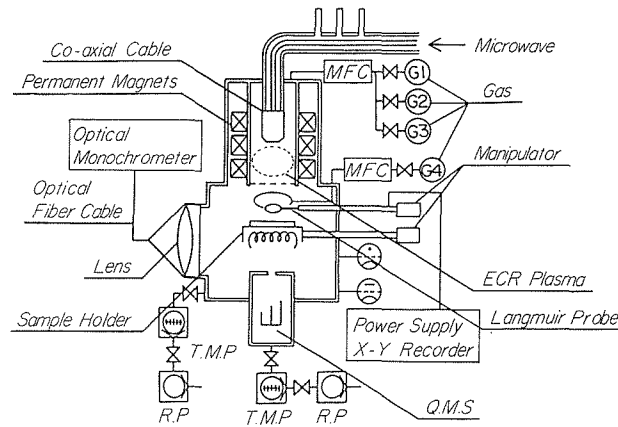


Fig. 1 ECR plasma process device.

Table 1 Nitritization conditions

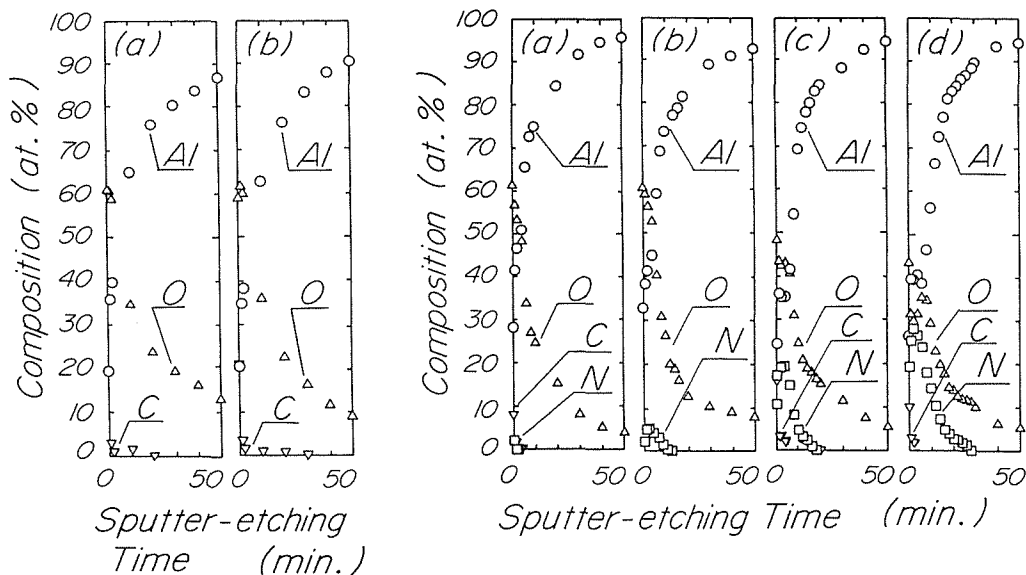
Case	Discharge Gas	Pressure (Pa)	Microwave Power (W)	Substrate Temperature (°C)	Applied Bias (V)	Irradiation Time (min)	Comment
1	N <sub>2</sub>	1	0	®RT, ®300, ®500	0	120	Thermal Nitritization
2	N <sub>2</sub>	1	200	RT	0	120	Plasma Nitritization(RT)
3	N <sub>2</sub>	1	200	RT	-1000	120	Plasma Nitritization with Negative Bias (RT)
4	Ar N <sub>2</sub>	1	200	RT	-1000	30	Plasma Nitritization after Ar Ion Etching (RT)
		1	200	RT	0		
5	Ar N <sub>2</sub>	1	200	RT	-1000	30	Plasma Nitritization with Negative Bias (RT, 300°C, 500°C) after Ar Ion Etching
		1	200	®RT, ®300, ®500	-1000		

cal monochrometer and an electrostatic probe are attached to the irradiation chamber. In particular, from the emission spectrum obtained by the monochromer, the gas species which is effective to the nitritization, can be identified.

The pre-etching due to Ar plasma can be carried out, by changing the discharge gas species from nitrogen to argon and by applying a negative bias voltage to the substrate. In order to examine the difference between the plasma and the thermal nitritizations, the thermal nitritization experiment is carried out without the injection of the microwave power. The nitritization experiments with different substrate bias is readily carried out just by merely changing the voltage from the power supply. Table 1 shows the experimental conditions for the surface nitritization of aluminium.

### 3. Results and Discussions

We first tried to nitritize the aluminium by the thermal process (Case 1). As shown in Fig. 2, the depth atomic profiles after the thermal nitritization with temperature of 300°C, (b), which was obtained by Auger Electron Spectroscopy (AES), remained the same as that before nitritization, (a). It is seen that the surface can not be nitritized by the thermal process. It is known that the excited species of nitrogen plays a role of nitritization in the thermal process. Then, it was verified that the excited species does not contribute to the nitritization of the aluminium.



**Fig. 2** Depth composition profiles, (a) before nitritization (as received) and (b) after thermal nitritization.

**Fig. 3** AES depth profiles of nitritized samples.

- (a) Without Ar plasma treatment (OV, RT). (Case 2)
- (b) With Ar plasma treatment before nitritization (OV, RT) (Case 4)
- (c) With Ar plasma treatment before nitritization (-1kV, RT) (Case 5 (a))
- (d) With Ar plasma treatment before nitritization (-1kV, 500°C) (Case 5 (c))

When the aluminium was exposed to the nitrogen plasma, only at the surface the nitrogen content of several percent was observed, as shown in Fig. 3 (a). In the case where the Ar ion etching was attempted before the plasma nitridation, the nitrogen content was considerably enhanced. However, the nitrogen concentration was still very low ( $\sim 5\%$ ). It has been already shown that the nitrogen ion species,  $N_2^+$ , is very effective compared with the excited nitrogen species,  $N_2^*$ , to the nitridation<sup>9,10</sup>. Thus, negative bias voltage was applied to the substrate in order to enhance the quantity of the ion species in the sheath region. Figures 3 (c) and (b) show the depth atomic profiles when the substrate bias was  $-1\text{kV}$ , and the temperatures were RT and  $500^\circ\text{C}$ , respectively. As a result of emission spectroscopy, the enhancement of the ion species was confirmed. By the application of this negative voltage, the nitrogen content was approximately 4 times increased (Fig. 3(c)). When the substrate temperature was  $500^\circ\text{C}$ , the nitrogen content was largely enhanced because of the nitrogen diffusion into the bulk.

From above plasma nitridation experiments, it was found that the acceleration and enhancement of the nitrogen ion species are important in addition to the Ar ion etching before the nitridation process.

In order to observe the formation of aluminium nitride, AlN, the XPS analyses were carried out for the sample of Case 5 (a) and (b). Figure 4 shows the XPS spectra. It was clearly seen that the electron emission peak existed at the Al-N peak. Then, it can be regarded that the aluminium nitride was formed in the aluminium surface.

#### 4. Conclusions

The aluminium surface was successfully nitridated by using the Ar ion etching treatment before the nitridation due to the nitrogen plasma. Without this pretreatment the nitridation was observed to be quite poor. Since the nitrogen ion species,  $N_2^+$ , largely contributes to the nitridation,

the application of a negative voltage to the substrate was attempted. By the acceleration of ion species toward to the substrate and the enhancement of the quantity of ion species, the nitrogen content was remarkably enhanced. In this case, the high substrate temperature caused a larger quantity of nitrogens compared with the case of RT, since the injected nitrogen may be transferred into the bulk by the enhanced diffusion. In summary, both the Ar ion etching before the nitridation and the nitridation with a substrate nega-

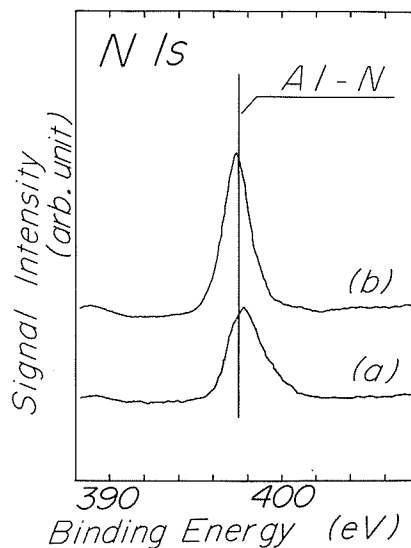


Fig. 4 XPS spectra of N1s for nitridated surfaces, case 5 (a) and (b) (a) RT, (b)  $300^\circ\text{C}$

tively biased are necessary for the surface nitritization of the aluminium.

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