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Nitrization of Aluminium by Using ECR Nitrogen Plasma

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Abstract

Numerous nitrization 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 nitrization. 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 nitrization, 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, AIN, was formed by the present plasma nitrization.

1. Introduction

For thin film coatings and surface modifications, low temperature plasma has been very aggressively employed in numerous fields1)-10). In the nitrization 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 nitrization significantly depends on the state of nitrogen plasma, and the substrate conditions such as temperature and bias voltage9)-11).

In the present study, a systematic plasma nitrization experiment for alminium 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℃. Thus, the nitrization based on the thermal process is believed to be considerably difficult12). Even when using a nitrogen plasma, the surface nitrization 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 far13), since the penetration depth of the nitrogen ion becomes larger than the oxide thickness. In order to successfully nitrize 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 nitrizations by changing the substrate temperature and the bias voltage. These results were compared with each other.

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2. Experimental

For the nitrization of alminium, 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℃ during the irradiation. In addition, bias voltage is applicable. For the purpose of the plasma diagnostics, an opti-

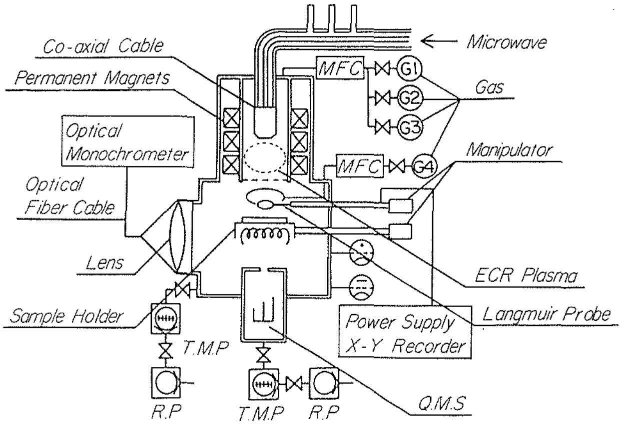

Fig. 1 ECR plasma process device.

Table 1 Nitrization conditions

Case	Discharge Gas	Pressure (Pa)	Microwave Power (W)	Substrate Temperature (℃)	Applied Bias (V)	Irradiation Time (min)	Comment
1	N_2	1	0	ⓐRT,ⓑ300,ⓒ500	0	120	Thermal Nitrization
2	N_2	1	200	RT	0	120	Plasma Nitrization(RT)
3	N_2	1	200	RT	−1000	120	Plasma Nitrization with Negative Bias (RT)
4	Ar N_2	1 1	200 200	RT RT	−1000 0	30 120	Plasma Nitrization after Ar Ion Etching (RT)
5	Ar N_2	1 1	200 200	RT ⓐRT,ⓑ300,ⓒ500	−1000 −1000	30 120	Plasma Nitrization with Negative Bias (RT, 300℃, 500℃) after Ar Ion Etching

cal monochrometer and an electrostasic 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 nitrization, 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 tharmal nitrizations, the thermal nitrization experiment is carried out without the injection of the microwave power. The nitrization 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 nitrization of aluminium.

3. Results and Discussions

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

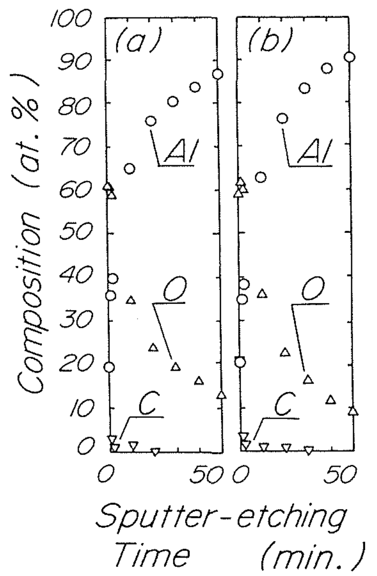

Fig. 2 Depth composition profiles, (a) before nitrization (as received) and (b) after thermal nitrization.

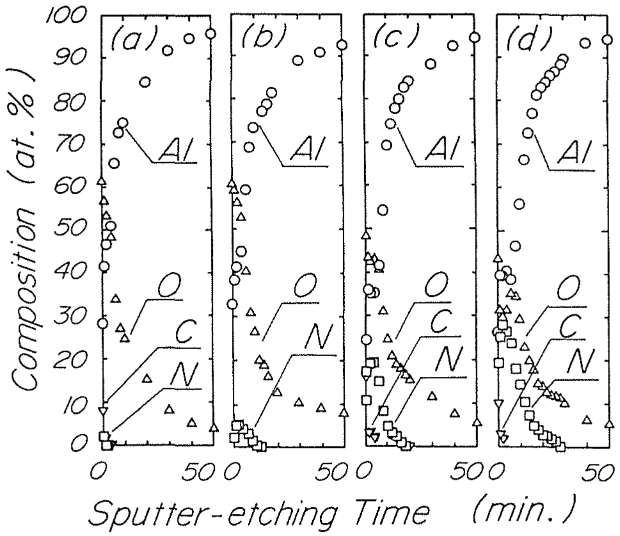

Fig. 3 AES depth profiles of nitrized samples.
(a) Without Ar plasma treatment (OV, RT). (Case 2)
(b) With Ar plasma treatment before nitrization (OV, RT) (Case 4)
(c) With Ar plasma treatment before nitrization (−1kV, RT) (Case 5 ⓐ)
(d) With Ar plasma treatment before nitrization (−1kV, 500℃) (Case 5 ⓒ)

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 nitrization, the nitrogen content was considerably enhanced. However, the nitrogen concentration was still very low (~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 nitrization[9,10]. 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 −1kV, and the temperatures were RT and 500℃, 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 approsimately 4 times increased (Fig. 3(c)). When the substrate temperature was 500℃, the nitrogen content was largely enhanced because of the nitrogen diffusion into the bulk.

From above plasma nitrization 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 nitrogen process.

In order to observe the formation of aluminium nitride, AlN, the XPS analyses were carried out for the sample of Case 5 ⓐ and ⓑ. 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.

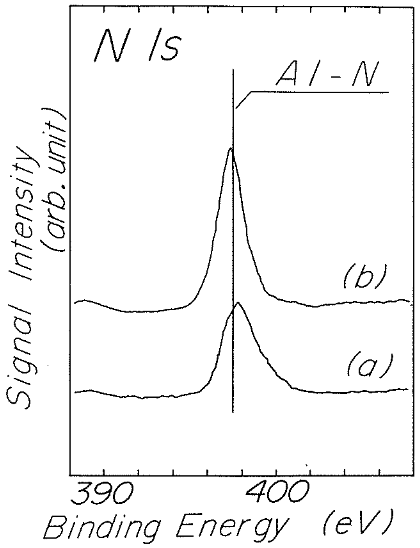

Fig. 4 XPS spectra of N1s for nitrized surfaces, case 5 ⓐ and ⓑ (a) RT, (b) 300℃

4. Conclusions

The aluminium surface was successfully nitrized by using the Ar ion etching treatment before the nitrization due to the nitrogen plasma. Without this pretreatment the nitrization was observed to be quite poor. Since the nitrogen ion species, N_2^+, largely contributes to the nitrization, 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 nitrization and the nitrization with a substrate negatively biased are necessary for the surface nitrization of the aluminium.

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