Temperature dependence for nitridation of aluminum films by sub-atmospheric pressure discharge

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Abstract. Characteristics of aluminum (Al) films exposed to helium/nitrogen (He/N\textsubscript{2}) mixture plasma under sub-atmospheric pressure were investigated using X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), and scanning electron microscopy (SEM). After nitridation, the Al-N component became a dominant constituent element on the Al films through Al-N bonding due to exposure to He/N\textsubscript{2} mixture plasma. The content of the Al-N component with respect to temperature was almost constant at more than 0.6 up to 573 K. However, the Gaussian width of the Al-N component corresponding to disorder of aluminum nitride (AlN) crystal tended to become narrower with the elevation of the temperature. At a high temperature of 673 K, where the nitridation process may be easily promoted, an AlN 0002 reflection peak appeared in the XRD pattern, and crystals composed of collections of tiny white dots started to be observed in SEM images.

1. Introduction

Nondestructive inspection with an electromagnetic acoustic transducer (EMAT) employing permanent magnets is expected to detect cracks and wastage in pipes of a fast-breeder reactor under a moderate temperature of about 473 K [1]. Recently, in order to achieve more safety and reliability in the reactor, an ultrasonic inspection technique is strongly required under the high-temperature environment of 823 K during reactor operation.

A novel EMAT equipping the piled electronic circuits with a layer of insulation instead of permanent magnets has been proposed [2, 3]. However, the polyimide films widely used for insulating coatings are limited to a temperature under about 523 K.

Aluminum nitride (AlN) is well known to show excellent properties, such as high resistivity and high thermal conductivity [4, 5]. The properties of AlN films have been clarified using various techniques, such as magnetron sputtering, RF sputtering, and ECR resonance techniques at a low pressure condition below about 1 Pa [6-8]. However, experiments have been rarely performed for the aluminum nitridation process under high pressure, though the high deposition rate of silicon has been obtained using an atmospheric pressure plasma process technique [9]. If the mechanism of the aluminum nitridation process for the interaction between the high-density plasma and the surface is elucidated, it might be suitable for the coating of electronic circuits.

In this study, the basic growth process of the AlN film fabricated by exposing aluminum (Al) films to helium/nitrogen (He/N\textsubscript{2}) mixture plasma under sub-atmospheric pressure was investigated from the viewpoint of the substrate temperature. Characteristics of these films were investigated using X-ray
photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental

Al films used in the nitridation experiments were made in advance as follows. Al films were deposited onto a copper-tungsten substrate by an RF wave magnetron sputtering apparatus. In order to remove adsorption molecules such as water and oxygen molecules from the wall of the reaction chamber, the chamber was evacuated to a pressure of $1 \times 10^{-4}$ Pa using turbo-molecular pumps. A disk of pure Al (99.99% in purity) 3 inch in diameter and 2 mm thick was set as a target material. Argon (Ar) gas as a source gas was accurately introduced into the chamber using a gas mass flowmeter. The deposition process of the Al film by Ar sputtering was performed under a pressure of $7 \times 10^{-1}$ Pa at room temperature. During sputtering, the flow rate of the Ar gas was kept constant at 6 sccm. The prepared Al films were taken out from the magnetron sputtering apparatus at atmospheric pressure.

Next, nitridation of the deposited Al films was performed using an atmospheric pressure plasma apparatus with helium/nitrogen (He/N$_2$) mixture plasma under sub-atmospheric pressure, as shown in Figure 1. After fixing the Al films on the substrate holder, the reaction chamber was evacuated to a pressure of $1 \times 10^{-4}$ Pa to remove oxygen influence. The Al film was heated by a resistive heater mounted inside the sample holder, which was kept within $\pm 5$ K of set values of 373 K, 473 K, 573 K and 673 K. Mixture gases of He and N$_2$ as source gases were accurately introduced into the chamber using a gas mass flowmeter. The Al film was exposed to He/N$_2$ mixture plasma at a pressure of $1 \times 10^3$ Pa, where the gap length between the RF electrode and the substrate holder was kept at several millimeters. During discharge, the flow rate of He and N$_2$ gases were kept at constant values of 50 sccm and 20 sccm, respectively.

The XPS measurement of the Al films exposed to He/N$_2$ mixture plasma was performed using an X-ray photoelectron spectrometer (Shimadzu Co. Ltd./Kratos Analytical Ltd.; AXIS-165). A magnesium target as an X-ray source was employed. An X-ray beam with an energy of 1253.6 eV obtained by an applied voltage of 12 kV and a current of 10 mA was irradiated on the sample. Photoelectrons emitted from the sample were detected by a hemispherical electron analyser. The pass energy employed was 40 eV. In this system, the total resolution has been estimated to be $\sim 850$ meV. The vacuum of the analysis chamber was kept below $1 \times 10^{-7}$ Pa. Photoelectron spectra in an Al 2p region of the films were measured by detecting the photoelectrons emitted from the surface region of the samples.

The XRD measurement of the Al films exposed to He/N$_2$ mixture plasma was performed using a powder X-ray diffractometer (Rigaku Co. Ltd.; RINT-2000). A copper target as an X-ray source was employed. An X-ray beam with an energy of $\sim 8$ keV obtained by an applied voltage of 40 kV and a

![Figure 1. Schematic of atmospheric pressure plasma apparatus.](attachment:figure1.png)
A current of 30 mA was monochromatized by means of a graphite monochromator and was irradiated on the sample. Two Soller slits each were positioned in the incident X-ray beam in front of the divergent slit and in the diffracted X-ray beam in front of the graphite monochromator. The diffracted X-ray beam intensity was recorded using a NaI scintillation counter mounted on the 20 arm. Diffraction patterns were obtained by scanning the 20 in the angular range from 31° to 42°.

The surface morphology of the Al films exposed to He/N2 mixture plasma was observed using SEM (Hitachi High-Technologies Co.; S-2150). An electron beam emitted thermally from an electron gun equipped with a tungsten filament was accelerated at an acceleration voltage of 20 kV in the section of an electrostatic lens. The accelerated electron beam was focused by condenser lenses to a spot of ~5 nm in diameter and irradiated on the sample. SEM images of the films were obtained at 3000 magnification through monitoring reflection electrons emitted by scanning the electron beam.

3. Results and discussion

Figure 2 shows a typical Al 2p core-level photoelectron spectrum for the Al film exposed to He/N2 mixture plasma. In the Al 2p photoelectron spectrum, a broad peak containing several components was observed. The spectrum is divided into four peaks with consideration of chemical shift after Shirley background subtraction. A dominant peak observed at 73.4 eV is assignable to Al-N bonding [10-12].

![Figure 2. An Al 2p core-level photoelectron spectrum for an Al film exposed to He/N2 mixture plasma.](image)

![Figure 3. I_{Al-N}/I_{all} ratio as a function of temperature.](image)
Peaks obtained in a lower binding energy region of 71.6 eV and 71.9 eV are assignable to Al-Al bonding corresponding to metallic aluminum [13]. Another peak centered at a higher binding energy region of 74.2 eV is ascribable to Al-O bonding originating from native oxide [14, 15]. It is noted that a typical spectrum for native aluminum oxide/aluminum is only observed before nitridation (not shown).

The ratio of the area intensity for the Al-N component to that for all divided components ($I_{\text{Al-N}}/I_{\text{all}}$) is plotted as a function of the temperature in Figure 3. The $I_{\text{Al-N}}/I_{\text{all}}$ ratio is almost constant at more than 0.6. However, at 673 K, the Al 2p spectrum was difficult to detect because of the surface charge-up effect.

On the other hand, the Gaussian width of the Al-N component derived from the Al 2p spectra is plotted as a function of the temperature in Figure 4. The Gaussian width tends to become gradually narrower with temperature, suggesting formation of crystalline AlN.

Figure 5 shows X-ray diffraction patterns for the Al films nitrided at temperatures from 373 K to 673 K. For the film fabricated at 673 K, an AlN 0002 reflection peak at 35.5° starts to appear, though its reflection peak width is broad.

Figure 6 shows the surface morphology of the as-deposited film and the films exposed to He/N$_2$ mixture plasma at 473 K and 673 K. Especially, Figure 6 (d) displays the magnification of the area indicated by the square in Figure 6 (c). On the as-deposited film, the collection of spherical particles, which would be the Al particles, was observed. No change of the surface morphology arose up to 473 K. However, the surface morphology was drastically varied at 673 K. Tiny white dots, the characteristic phenomena of charge-up of insulating materials, were observed. This phenomenon is in good agreement with results from the XPS measurement and XRD measurement.
Figure 6. The surface morphology of Al films after nitridation by He/N₂ mixture plasma.

It is revealed that the Al film exposed to He/N₂ mixture plasma is dominantly composed of the Al-N component by progress of the nitridation. In spite of the fact that the I_{Al-N}/I_{all} ratio is more than 0.6 at temperatures from 373 K to 573 K, the surface charge-up phenomenon hardly occurred. However, at 673 K, a significant charge-up phenomenon is observed for XPS and SEM, as observed in insulating materials. It is considered that the disordered components decreased and the crystalline AlN increased on the film by the sufficient thermal energy of 673 K. Moreover, from the results of XRD patterns, it is indicated that the AlN crystal itself has a long-period structure with increasing temperature, though grain size of the AlN crystal is still small. Therefore, a temperature of more than 573 K would be required in order to form the AlN crystal with both a long-period structure and a large grain size.

4. Conclusions
The characteristics of Al films exposed to He/N₂ mixture plasma under sub-atmospheric pressure were investigated using XPS, XRD and SEM. The films exposed to He/N₂ mixture plasma are composed of Al-Al, Al-N and Al-O components. The I_{Al-N}/I_{all} ratio is almost constant up to 573 K. However, the Gaussian width of the Al-N component tends to become narrower with the elevation of the temperature. From the XRD patterns, the weak and broad AlN 0002 peak indicating growth of the AlN crystal is observed at 673 K. Moreover, on the Al film after nitridation at 673 K, a collection of tiny white dots appeared over the surface of the film. It is revealed that a temperature of more than 573 K would be required in order to form the AlN crystal with both a long-period structure and a large grain size.

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