Atomic Force Microscope Observations of the Corroded Surfaces of Aluminum Nitride Thin Films

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Aluminum nitride (AlN) thin films have been prepared by ion-beam assisted deposition method on silicon single crystal substrates and the change in the surface morphology of AlN thin films during the early stage of corrosion by acid (pH 1 HCl) and alkaline (pH 12 NaOH) solutions has been observed by atomic force microscopy (AFM). To study the effects of nitrogen ion beam energy during preparation on the corrosion process, AlN films were prepared with different nitrogen ion energy of 0.2 keV and 1.5 keV. AFM observations reveal that in the case of corrosion by acid solutions the surface roughness of the film prepared with the 0.2 keV ion beam increases rapidly compared with that of the film prepared with the 1.5 keV ion beam, while in the case of corrosion by alkaline solutions the film prepared with the 1.5 keV ion beam degrades faster than the film prepared with the 0.2 keV ion beam. These results suggest that the corrosion process is different between the acid and alkaline solutions and the corrosion behavior is dependent on the nitrogen ion beam energy during preparation.

1. INTRODUCTION

Aluminum nitride (AlN) thin films have arrested widespread attention because of their outstanding properties, such as high hardness, good thermal conductivity, and electrical resistivity. Owing to these unique properties, AlN thin films is an attractive electronic material including surface acoustic wave (SAW) devices.[1] In addition, recently, AlN films are considered to be an excellent candidate for (1) silicon-on-insulator (SOI) materials[2], (2) metal-insulator-semiconductor (MIS) materials[3] and (3) cap layers for GaAs substrates.[3]

AlN thin films have been prepared by various methods including reactive sputtering[2-4], chemical vapor deposition[5], laser ablation deposition[6], ion-beam assisted deposition (IBAD)[7] and ion-beam sputtering deposition(IBSD)[8]. Among these deposition methods, the deposition techniques using ion beams, IBAD and IBSD, have the advantage of an independent and well defined control of the ion bombardment parameters, such as ion beam kinetic energy, ion beam current density and an incident angle to the substrate.[9]

In a previous paper, the present authors prepared AlN thin films at low temperatures (around room temperature and 473K) using IBAD method[10], and studied the influence of nitrogen ion beam energy on crystalline microstructure, surface morphology and optical properties.[11-13] According to the previous results, AlN films with different microsctructures, surface roughness or optical properties can be prepared by controlling the nitrogen ion beam energy, and the similar effects of the ion beam energy on structure, stress and hardness of this material are also reported by J. H. Edger *et al.*[14]

On the other hand, in the case of applying AlN films to practical usage, corrosion resistivity of the film is of importance. To understand a corrosion process, it is essential to study the initial stage of the corrosion. For this purpose, observations of surface changes during corrosion are useful because they provide a record of the corrosion process. Atomic force microscopy (AFM) has the potential to characterize the surface morphology on the nanometer scale and has the advantage of stable measurements for insulating materials like AlN.

The purpose of the present paper is to try to observe changes in the surface morphology of AlN thin films during corrosion by acid and alkaline solutions, focusing on the behavior in the early stage of the corrosion process. In addition, the effect of the film structure on the corrosion behavior is studied for the films with different structures prepared with varying the nitrogen ion beam energy.

2. EXPERIMENTAL

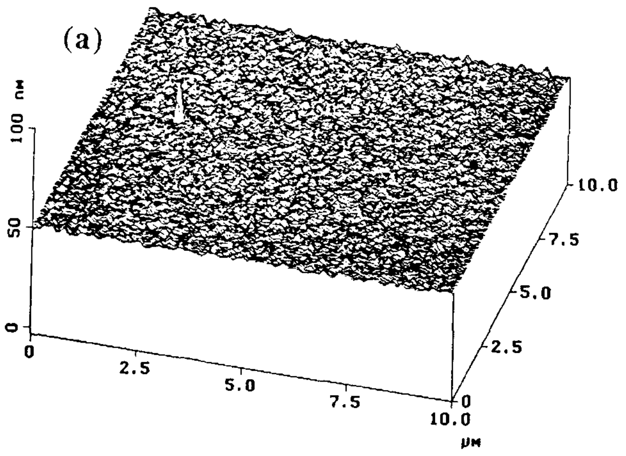
AlN thin films were prepared from nitrogen gas (99.999% pure) and aluminum (99.99% pure) with the IBAD method. The schematic drawing of the IBAD apparatus and the detailed descriptions of the experimental procedures were given in the literature.[15] The substrate used in this study was a silicon single crystal, Si (100), kept at around room temperature. A nitrogen ion beam was obtained with the electric field lenses for focusing and accelerating. The accelerating voltage was kept at 0.2 keV or 1.5 keV and the current density of the ion beam was adjusted so as to obtain the arrival ratio of nitrogen to aluminum to be equal at the substrate. The films grew to be approximately 300 nm.

AlN thin films were immersed into acid (pH 1 HCl) and alkaline (pH 12 NaOH) solutions in proper time and then rinsed with pure water. Changes in the surface morphology were observed by AFM (NanoScope III). AFM observations were performed by the tapping mode in air with commercial silicon tips. The AFM images were acquired at 256 x 256 points per frame and corrected by subtraction of the background slope.

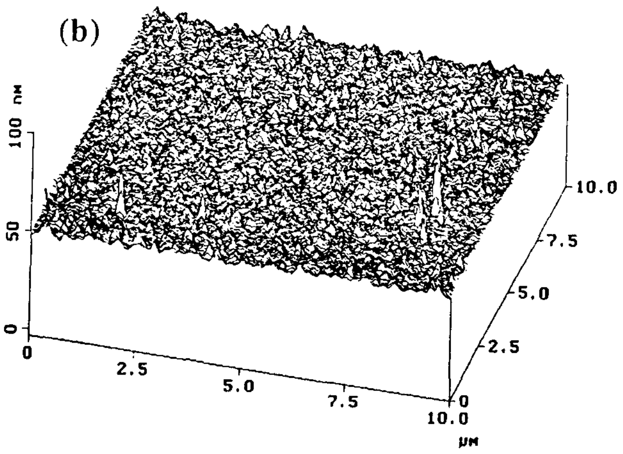
3.RESULTS AND DISCUSSION

Figures 1 (a) and (b) show the typical AFM images of the surface of as-deposited AlN films prepared with the nitrogen ion beam of 0.2 keV and 1.5 keV respectively. From these images, it can be seen that (1) the surfaces of both films are uniform and (2)the surface of the film prepared with the 0.2 keV ion beam is much smoother than that of the film prepared with the 1.5 keV ion beam energy. The surface average roughness, *R*a, is calculated from these images and evaluated to be 0.57 and 1.05 nm, respectively. The tendency of increasing of the surface roughness with increasing of the ion beam energy is in good agreement with the previous results.[16] Cross sectional observations by scanning electron microscope have shown that the AlN film on fused silica prepared with 0.2 keV ion beam has the columnar structure and the film on fused silica prepared with 1.5 keV does not show the columnar but the densely packed structure.[17] The difference in the surface roughness is probably related to the difference in the film structure.

Figures 2(a) and (b) show the typical AFM images of the corroded surfaces of the AlN films prepared with the nitrogen ion beam of 0.2 keV and 1.5 keV. Both films were immersed in acid solutions (pH 1 HCl) for 60 minutes. From these images, it can be said that (1) the surfaces of both films become rough compared with the as-deposited films and (2) the remarkable difference in the surface morphology is hardly observed between these two films.

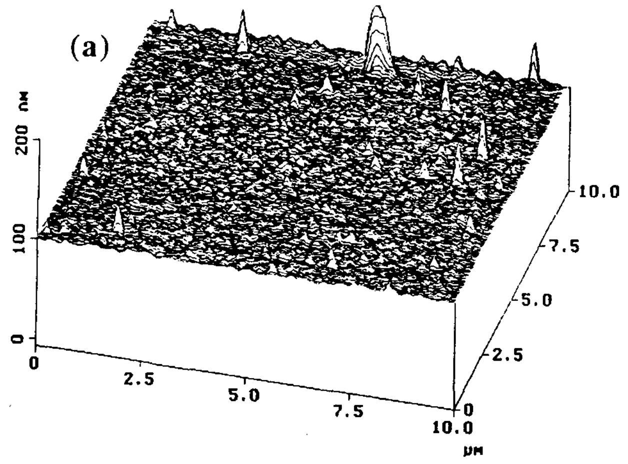


300–nm AlN films, 0.2 keV, as–deposited

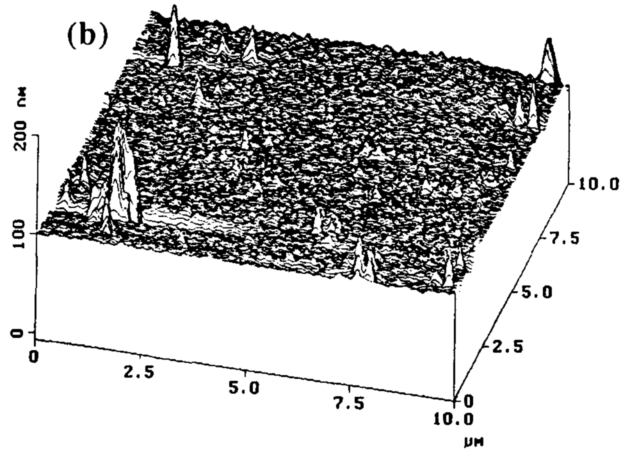


300–nm AlN films, 1.5 keV, as–deposited

Fig. 1 AFM images of the surfaces of the as-deposited AlN thin films prepared with the nitrogen ion beam of (a) 0.2 keV and (b) 1.5 keV.



300–nm AlN films, 0.2 keV, HCl 60 min.



300–nm AlN films, 1.5 keV, HCl 60 min.

Fig. 2 AFM images of the corroded surfaces of the AlN thin films by immersion in pH1 HCl solutions. The films were prepared with the nitrogen ion beam of (a) 0.2 keV and (b) 1.5 keV.

The value of *Ra* of the films is plotted as a function of the immersion time by the acid solution and shown in Fig. 3. This figure displays that the value of *Ra* of the film prepared with 0.2 keV gradually increases with increasing of the immersion time, while the value of *Ra* of the film prepared with 1.5 keV does not change drastically.

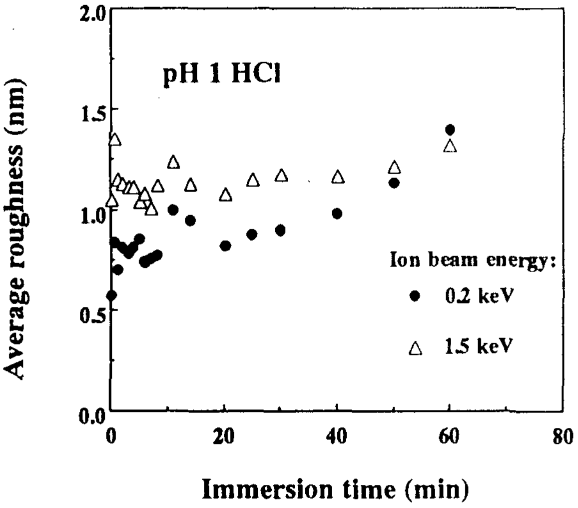
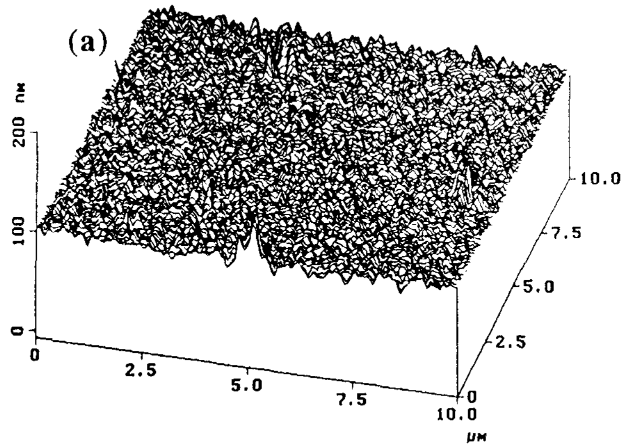
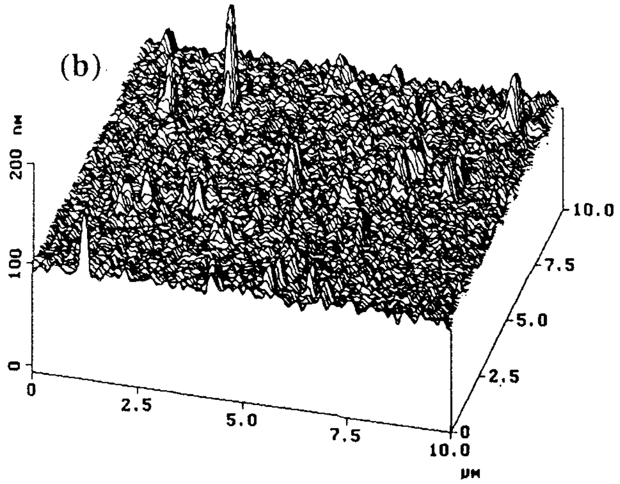


Fig. 3 Relation between the average roughness of the AlN films and immersion time in pH 1 HCl solutions.

Figures 4(a) and (b) show the typical AFM images of the corroded surfaces of the AlN films prepared with the nitrogen ion beam energy of 0.2 keV and 1.5 keV, which were immersed in alkaline solutions (pH 12 NaOH) for 7 and 2.5 minutes, respectively. It is found that both films are corroded more severely than in the acid solutions. In addition, the film prepared with the 1.5 keV ion beam has much rougher surface than the film prepared with the 0.2 keV ion beam, in spite of shorter immersion time in the NaOH solution. Furthermore, many protrusions, which seem to be reaction products between AlN and NaOH solution, are observed on the surface of the film prepared with the 1.5 keV ion beam. These two figures indicate that the films prepared with the 0.2 keV ion beam show better corrosion resistivity for NaOH solutions.



300–nm AlN films, 0.2 keV, NaOH 7 min.



300–nm AlN films, 1.5 keV, NaOH 2.5 min.

Fig. 4 AFM images of the corroded surfces of the AlN films by immersion in pH12 NaOH solutions. The films were prepared with the nitrogen ion beam of (a) 0.2 keV and (b) 1.5 keV.

The relation between the surface roughness and the immersion time is shown in Fig. 5. Figures 3 and 5 indicate that the AlN films are corroded faster in alkaline solutions than in acid solutions.

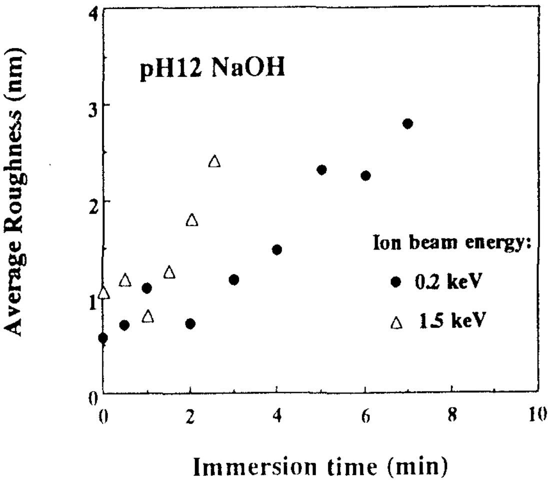


Fig. 5 Relation between the average roughness of the AlN films and the immersion time in pH12 NaOH solutions.

Furthermore, in the case of the corrosion by alkaline solutions, the film prepared with the 1.5 keV nitrogen ion beam severely degrades compared with the film prepared with the 0.2 keV nitrogen ion beam energy, which is contrast to the corrosion by acid solutions. These results suggest that the corrosion process of AlN films immersed in acid solutions is different from corrosion by alkaline solutions and the corrosion behavior is dependent on the film structure.

According to the results of the corrosion tests by C. D. Young *et al.* [18], violent chemical reactions between the AlN substrates and alkali solutions (NaOH and KOH) were observed and only several atomic layers of AlN substrates were etched off in acid solutions (HCl and so on). They proposed that (1) in the case of corrosion by alkali solutions AlN grains are attacked randomly and rapidly due to the violent chemical reactions, and (2) in the case of corrosion by acid solutions AlN grains are etched homogeneously and the etching rate depends on the crystal orientation.

Suppose their model can be applied to thin films, the present results are explained as follows: (1) the film prepared with the 1.5 keV ion beam has rougher surface than the film prepared with the 0.2 keV ion beam and this means the surface area of the former film is larger than that of the latter film, (2) in the corrosion by alkali solutions, the larger surface area the film has, the faster the film is etched off, because violent chemical reactions occur on the surface randomly, and (3) in the corrosion by acid solutions, the difference in the etching rate between two films is due to the different crystal orientation. It should be noted that the crystal orientation is different between these two films; the preferential growth is the (10•0) and (00•2) planes for the film prepared with the 0.2 keV nitrogen ion beam, while the (10•0) plane for the film prepared with the 1.5 keV nitrogen ion beam.[11, 13]

Although it is difficult to establish the corrosion mechanism of AlN films immersed in solutions from the results of the present study only, it is found that the AlN films prepared with the 1.5 keV nitrogen ion beam offer good corrosion resistivity for acid solutions and thus they will be used for coating materials used in the atmosphere, because water vapor in the atmosphere usually shows neutral or weak acid due to acid rain.

4. CONCLUSIONS

Aluminum nitride thin films have been prepared by the IBAD method, and the corrosion process of the film surface immersed in acid and alkaline solutions has been observed by AFM. AFM observations reveal that in the corrosion by acid solutions the surface roughness of the film prepared with the 0.2 keV ion beam increases rapidly compared with that of the film prepared with the 1.5 keV ion beam, while in the corrosion by alkaline solutions the films prepared with the 1.5 keV ion beam degrades more rapidly than the film prepared with the 0.2 keV ion beam. These results will give some clue to understand the corrosion mechanism of the AlN films immersed in solutions.

ACKNOWLEDGMENT

This work was performed by means of the ion vapor deposition apparatus in the Advanced Materials Laboratory of the National Defense Academy.

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Received March 1, 1997
Accepted March 19, 1997