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EFFECTS OF GAS PRESSURES ON GRANULAR STRUCTURE'S FOR MATION OF ALUMINUM FILMS PREPARED BY PVD PROCESS

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ABSTRACT

In order to investigate the influence of gas pressure in PVD deposition conditions, aluminum films were prepared by vacuum evaporation and ion plating. The crystal orientation and morphology of the films affected by argon gas pressures were characterized by using X-ray diffraction (XRD) and scanning electron micrography (SEM) respectively. With the increasing of argon gas pressure, the preferred orientation of aluminum films exhibited (200) and the diffraction peaks of the films became less sharp and broadened. Film's morphology changed from columnar structure to granular structure with the increase of gas pressure. And the properties of these films on corrosion behaviors were estimated by measuring anodic polarization curves in deaerated 3% NaCl solution. The aluminum films which exhibited granular structure with (200) preferred orientation showed good corrosion resistance.

INTRODUCTION

The films, particularly those deposited from plasma-assisted vacuum coating process, are usually quite different from the respective bulk material as to their structures and properties(1). For this reason, the use of plasma-assisted process, e. g. physical vapour deposition such as ion plating technique, has spread into various types of industrial applications(2, 3).

The properties of the deposited film depend on the deposition condition and these, in turn depend critically on the crystal orientation and morphology of the films. Therefore, it is important to clarify that the formation mechanism for the morphology and orientation of the film affected by deposition parameters, e. g. the substrate temperature, the nature and pressure of the gas and bias voltage etc..(4)

The influence of the substrate temperature on the micro structure of evaporated thick coatings has been examined by B.A.Movchan and A.V.Demchishin(5) who reported the structure zone model. J.A.Thornton(6, 7) extended the structure zone model to sputter deposition by including the sputtering gas pressure. However, the structure zone models only provide an information about the morphology of the deposited film. That is, the data in the literature on the effects of deposited films are scanty and usually refer to only a narrow range of evaporation conditions.

In this paper Aluminum films are prepared by vacuum evaporation and ion plating technique in order to investigate the influence of gas pressure on the crystal orientation and morphology of the films. Finally we have found some interesting orientation and morpholog-ical effects and their corrosion resistance relation in deposited aluminum films prepared by changing the argon gas pressure.

EXPERIMENTAL PROCEDURES

The ion plating apparatus consist of three main parts, i.e. (1) a metal evaporator, (2) an ionization system and (3) a substrate holder. A resistance heating system was used to evaporate aluminum metal. The purities of alumi-num used in this experimental were 99.99%. In order to enhance the ionization effiency, a filament of tantalum wire 0.8mm in diameter was set a level of 2cm above the evaporator and negative bias voltage of 250V was supplied on the ionization filament against evaporator. The cold-rolled steel plates used as substrates were progressively polished to a final abrasive size of 0.05μm Al_2O_3 and then ultrasonically cleaned in a bath of acetone for 30min, prior to mounting in the vacuum chamber. The source-to-substrate distance was 7.5cm.

Prior to the evaporation process, the system was initially evacuated to a pressure in the region of 7.0×10^{-3} Pa. The substrate was ion cleaned in an argon glow discharge at a pressure of 1.3Pa with a bias voltage of -1.0kV for about 10min to remove an residual oxides from the surface. After the ion cleaning, the system was pumped down to a base pressure of 7.0×10^{-3} Pa again. Argon gas pressures of 10^{-3}, 10^{-2}, 10^{-1} and $10^{0} \times 7.3$ Pa and bias voltages of 0, -0.2, -0.5 and -10kV were used in ion-plating arrangement. The ion plating process lasted typically 20min with consideration rates of about 1μm min^{-1} resulting in coatings of 17±5μm thickness. The purities of argon gas used in this exprement were 99.8%. The substrate temperature during deposition was lower than 200℃ without any controlling.

The top surface and cross section of the obtained films were examined by scanning electron microscopy(SEM). X-ray diffractometer was used to syudy the crystal structure and the preferred orientation of the films. Anodic polarization measurements carried out in the starting form the rest potential, at 2mV/sec in measured versus SCE(saturated calomel electrode).

RESULT AND DISCUSSION

The X-ray diffraction patterns as a function of argon gas pressure at the different bias voltages for the deposited aluminum films are shown in Fig. 1. From Fig. 1, it can be seen that the crystal orientation of the films cha-nged with the increase of argon gas pressure. The diffraction patterns of the aluminum films deposited at the no bias voltage of 0 kV were similar to the value of American Society for Testing and Materials (ASTM) card regardless of the argon gas pressures. The crystal orientation of the films deposited at the negative of bias voltage of 0.2kV had a strong (200) prepared orientation regardless of the gas pressures. From the bias voltages of -0.5, -1.0kV in Fig. 1, the films deposited at low argon gas pressures

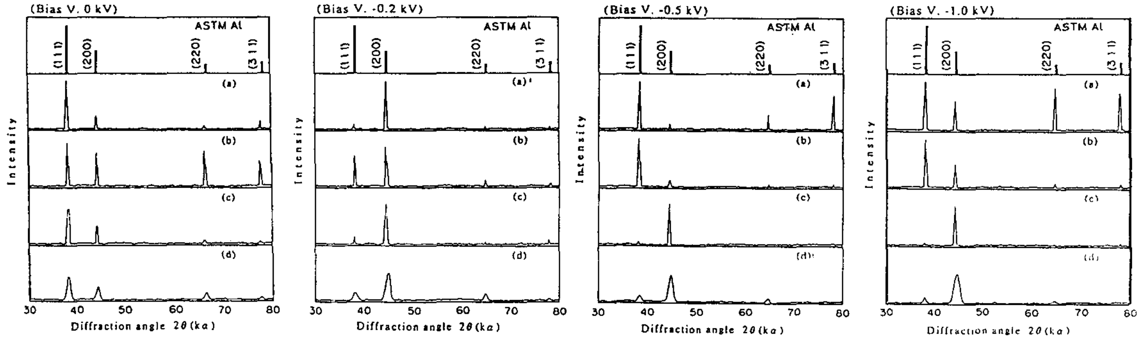


Fig. 1 X-raydiffraction patterns of aluminum films deposited at various argon gas pressures of (a) 7.3×10^{-3} Pa, (b) 7.3×10^{-2} Pa, (c) 7.3×10^{-1} Pa, (d) 7.3 Pa.

such as 7.3×10^{-3} and 7.3×10^{-2} Pa exhibited (111) preferred orientation. The X-ray diffraction peak of (111), however, decreased and the intensity of (200) peak increased as the argon gas pressures increased up to 7.3×10^{-1}Pa. As shown in Fig. 1, the diffraction peaks became less sharp and broadened at 7.3Pa argon pressure. And it can be seen that the crystal orientation of the films was also influenced by substrate bias voltage.

The SEM photographs of top surface and cross section for deposited aluminum films as a function of argon gas pressure at the different bias voltages are shown in Figs. 2(A) and 2(B). It can be seen that the surface and cross sectional morphology of these films varied with deposition conditions such as argon gas pressure and substrate bias voltage. All the aluminum films which were deposited by vacuum evaporation of no bias voltage exhibited a granular structure with porosity and defects. The morphology of the ion plated films deposited at the bias voltage of -0.2kV changed from a granular structure (without defects or pinholes) with the increase of argon gas pressure. This related to the broadened diffraction peaks of the film shown in Fig. 1. From the bias voltages of -0.5, -1.0 kV, the film ion plated at low argon gas pressure exhibited clearly columnar structures. However, column width of the films become smaller with the argon gas pressure increased up to 7.3×10^{-1} Pa. From the results of Fig. 2(A) and 2(B), it can be seen clearly the effect of increasing bias voltage will be similar to that of decreasing argon gas pressure.

The result from corrosion test of the deposited aluminum films as a function of argon gas pressure is shown in Fig. 3(A) and 3(B). It shows the anodic potentiodynamic polarization curves for the films measured in deaerated 3% NaCl solution. When scaned from the rest potential, most of the films appeared to show the active/passive polarization behaviors. Thus Fig. 3(A) presents the dependence of the pitting potential of all the films tend to shift in the positive direction by the increase of argon gas pressure. From Fig. 3(B), it can be also seen that the pitting limiting current density of aluminum films measured at the steady potential of 1.0V tend to exhibit low values with the increase of argon gas pressure. Eventually, corrosion-resistance

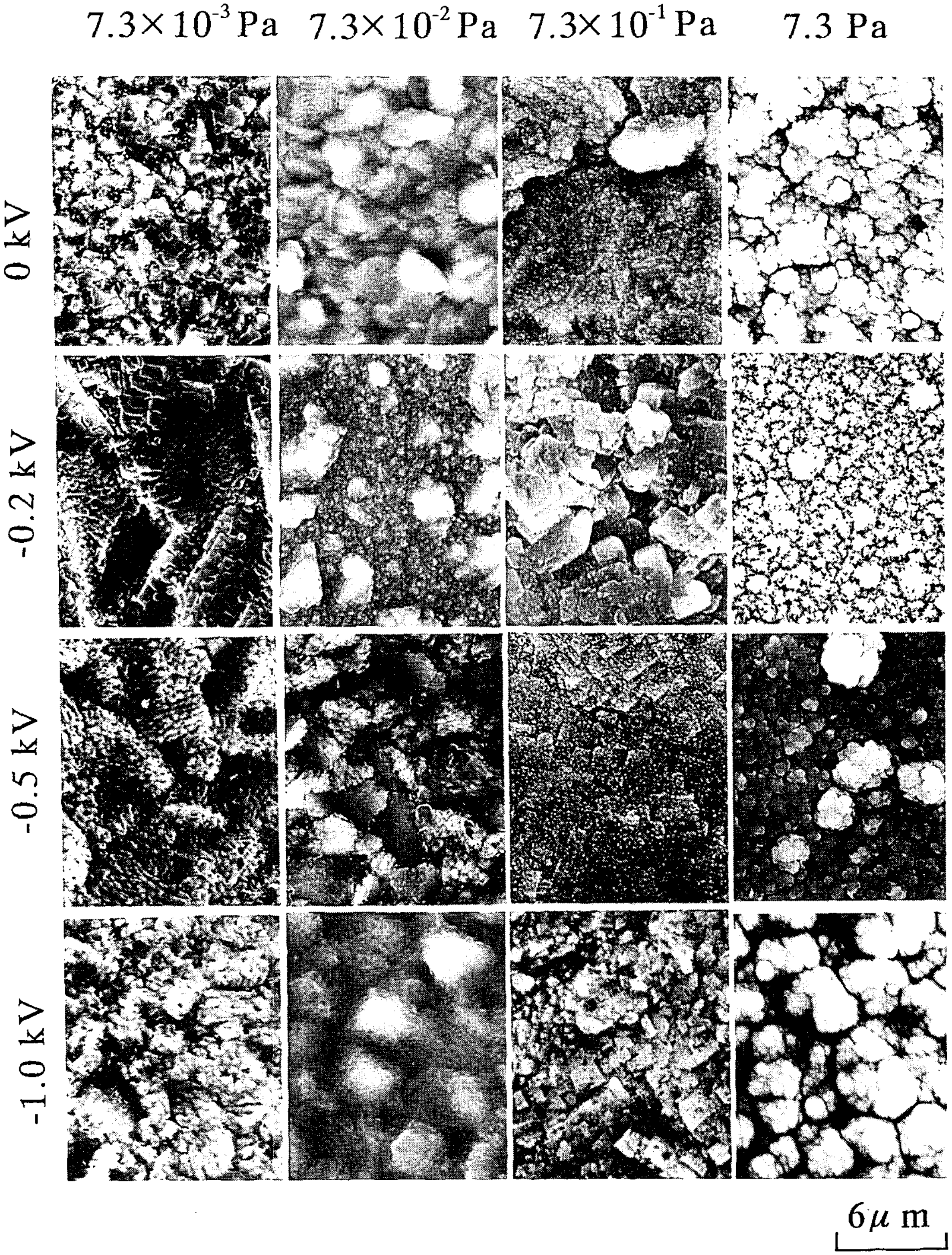


Fig. 2 (A) SEM photographs of top surface of aluminum films deposited at different argon gas perssures and bias voltages.

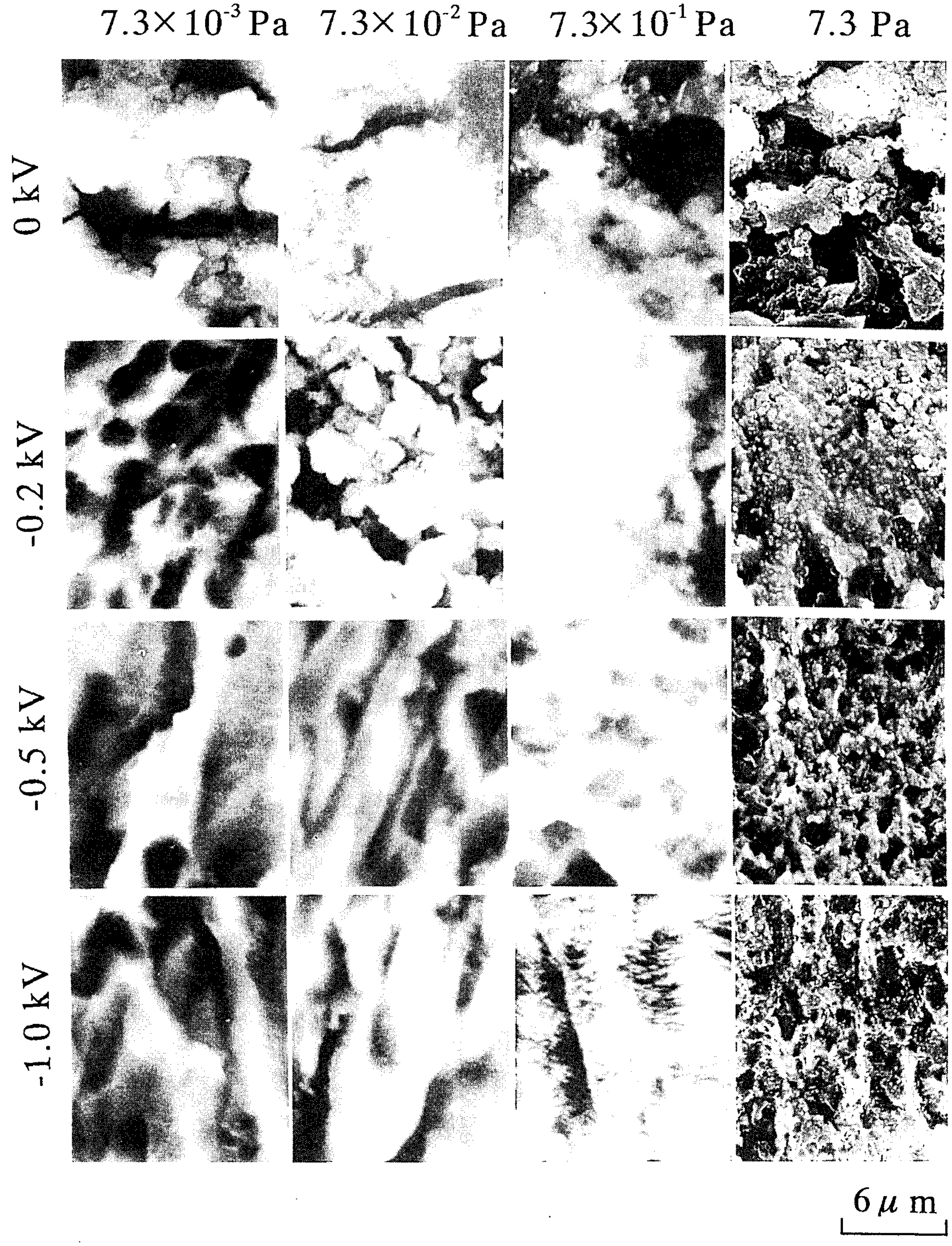


Fig. 2(B) SEM photographs of aluminum films deposited at different argon gas pressures and bias voltages.

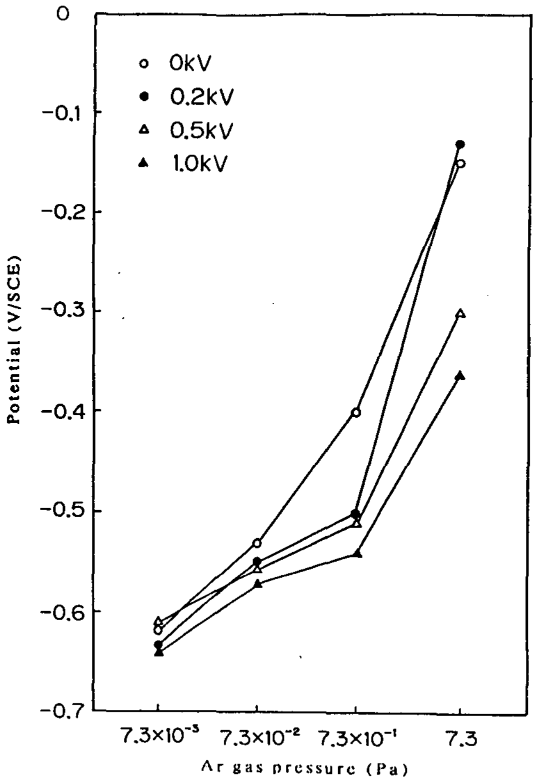


Fig. 3(A) Pitting potential of aluminum films deposited at different argon gas pressures.

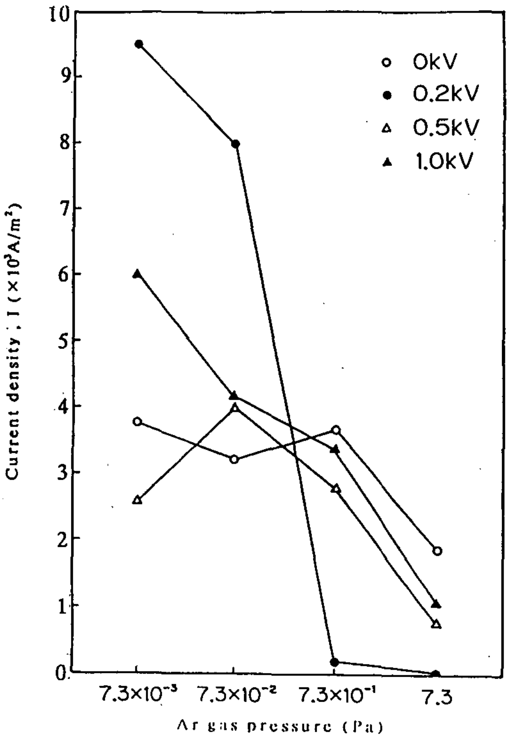


Fig. 3(B) Pitting limiting current density of aluminum films deposited at different arg-on gas pressures.(Steady-potential; 1.0V/SCE)

of the films obtained in this experiment exhibited at high argon gas pressure such as 7.3×10^{-1} and 7.3×10^{0} Pa. That is the aluminum films which had granular structure with (200) preferred orientation showed good corrosion resistance.

From the experimental results, the aluminum films which had granular structure with (200) preferred orientation showed good corrosion resistance. The morphology of structures of aluminum films tend to change from columnar structure to a granular structure with the increase of argon gas pressure, although the substrate temperature was constant. In this case, the preferred orientation of the films exhibited (200) and the diffrection peaks of the films became less sharp and broadened. Fig. 4 shows relation between argon gas pressures and X-ray diffraction peak shift of aluminum film ion plated at negative bias voltage of 1kV. Compared to the peaks of ASTM card, X-ray peak shifts of crystal faces in the deposited aluminum films increased with the increase of the argon gas pressure. In these caseis, all the films exhibited columnar structures and the columnar widths became smaller with the increase of the argon gas pressures as shown in Fig. 5. In these results it is obvious that the argon gas pressure plays a large part in affecting the for-

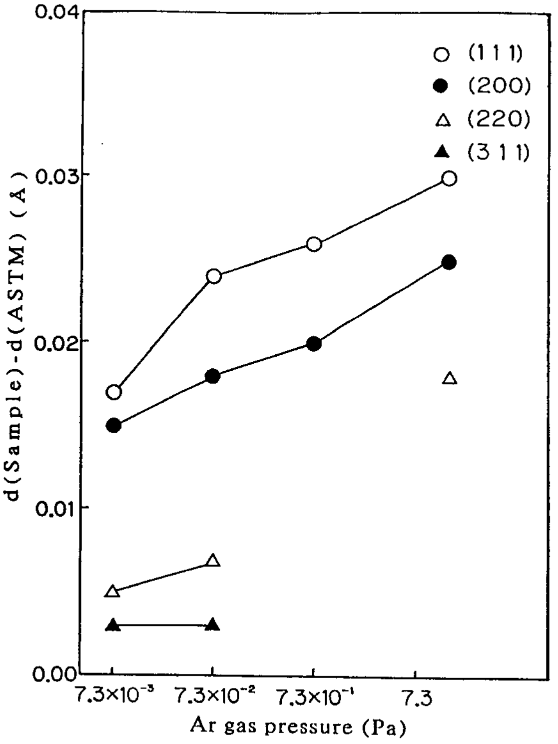
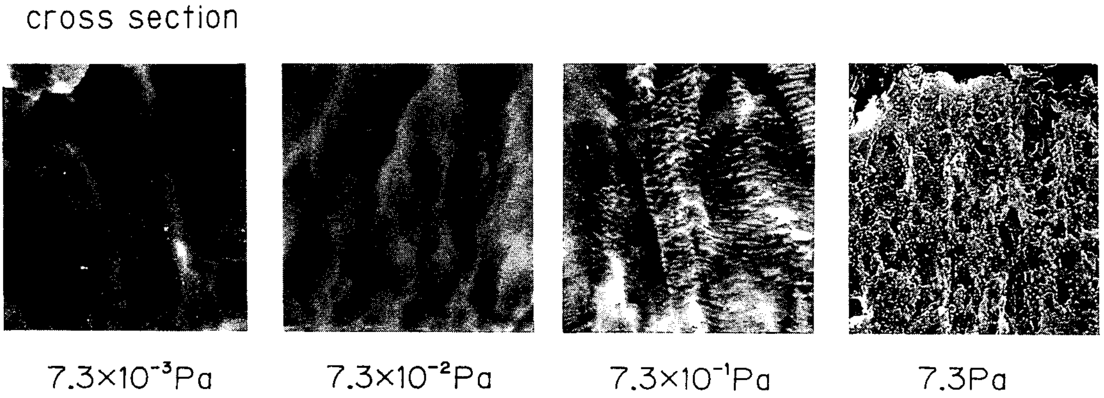


Fig. 4 Relation between argon gas pressures and X-ray peak shifts.

mation of the crystal orientation and morphology of deposited films. We think that the adsorption or occulusion of argon atoms on the growing film surface during the deposition may be play an important role in this case, because such gas adsorbates could also change the growth mechanism of nuclei.

Because the cold rolled steel plate of substrate which was used in this work is polycrystal, the orientation of the nuclei would have been random at the early growth stages. Consequently the film orientation depends on the growth of the nuclei. Generally the differences of growth rate of different crystal planes are expected to be small at low substrate temperature. However, ion plating system is essentially a vapour deposition process in which the substrate surface is cathode of a glow discharge system. Therefore ion bombardment during depsition will cause an increase in the bulk temperature and especially in the surface temperature of the growing film(8−9). The adatom mobilities can be enhanced by such ion bombardment, although the substrate temperature may be relatively low. In this case, it is possible that the growth rate of different crystal planes become different. Aluminum has the face cubic structure, and the relative order of its surface energy is as follows: $\gamma_{(200)} > \gamma_{(111)}$. When the aluminum



cross section

7.3×10⁻³Pa　7.3×10⁻²Pa　7.3×10⁻¹Pa　7.3Pa

Fig. 5 SEM photographs of aluminum films deposited at different argon gas presssures. (Bias volatage: -1.0kV) film was deposited by ion plating at high vacuum (low argon gas pressure as there were little gas atoms adsorbed on the crystal face), the growth rate of (200)face which has the highest surface energy would be larger than (111) face. As a result, the area possession of (111)face on film surface will increase. Therefore the film shows (111) orientation. When the argon gas pressure increased, as the argon atoms are easier to be adsorbed on the (200) surface than on the (111) surface the growth rate of (200) face will become lower by the argon adsorption. In this case, the area possession of (200) face on the film surface will be larger than the (111) face. The film therefore will show (200) preferred orientation. When the alumi-num film is deposited at high gas pressure, the crystal growth will be disturbed by argon atoms adsorption. Eventually, the growth rate of all crystal faces will decrease. The presence of occluded argon atoms can also restrict atom diffusion across grain boundaries, disturbing grain growth. It can be seen that the films which exhibited granular structure with (200) preferred orientation can be obtained by ion plating at higher argon gas pressure relatively. Increasing bias voltage will enhance both adatom diffusivities and ion bombardment. The ion bombardment will decrease the amount of adsorbed argon ato-ms on the growing crystal surface. The enhanced adatom mobilities could also make it easy to create the nuclei orientation with low surface energy face. Consequently the effect of increasing bias voltage will be similar to that of decreasing argon gas pressure.

CONCLUSIONS

The results of this investigation are summarized as follows :

1) The deposited aluminum film which had fine granular structure with (200) preferred orientation showed good corrosion-resistance.

2) The deposited aluminum films exhibited a columnar structure at low argon gas pressure, but at high argon gas pressure it exhibited granular structure with (200) preferred orientation due to the adsorption or occulusion of argon gas.

3) The crystal orientation and morphology of films depended not only on gas pressure but also bias voltage. i.e., the effect of increasing bias voltage was similar to that of decreasing gas pressure.

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