Magnesium Thin Films Possessing New Corrosion Resistance by RF Magnetron Sputtering Method

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Magnesium thin flims were prepared on cold-rolled steel substrates by RF magnetron sputtering technique. The influence of argon gas pressure and substrate bias voltage on their crystal orientation and morphology of the coated films were investigated by scanning electron microscopy (SEM) and X-ray diffraction, respectively. And the effect of crystal orientation and morphology of magnesium films on corrosion behaviors was estimated by measuring anodic polarization curves in deaerated 3%NaCl solution.

From the experimental results, all the sputtered magnesium films showed obviously good corrosion resistance to compare with 99.99% magnesium target of the sputter-evaporation metal. Finally it was shown that the Corrosion-resistance of magnesium films can be improved greatly by controlling the crystal orientation and morphology with effective use of the plasma sputtering technique.

Keywords : *magnesium, corrosion-resistance, RF magnetron sputtering, morphology, crystal orientation, adsorption, occlusion*

1. Introduction

Magnesium metal is 35% lighter than aluminum and has good vibration resistivity. However, magnesium has not been applied as much as aluminum because of its poor corrosion resistivity in all environments. If a new surface coating technique can be developed to improve its corrosion resistivity, magnesium metal will find new applications in various fields. Recent tendency in electronics and mechanical engineering fields aiming for high performance and energy savings requires, the material to be light weight more using coating.[1]

In general, light metal, particularly magnesium, is difficult to plate using conventional coating techniques such as chemical or electrochemical process. This is due to the presence of the easily formed oxide layer. In order to limit oxidization during coating, vacuum deposition techniques can be used as an alternative to conventional techniques operating in wet conditions or in air. It is well known that thin films, particularly those deposited from plasma-assisted vacuum coating technique, are usually quite different from the respective bulk material as to their structure and properties.[2] For this reason, the use of plasma-assisted techinques, e. g., physical vapor deposition such as sputtering technique, has spread into various types of industrial applications.[3-4] However, few studies have been reported dealing with magnesuim metal and using the new techniques.[5-6]

In this work, magnesium films were prepared onto the cold-rolled steel substrates by RF magnetron sputtering technique. Thus, I have found some interesting morphological and orientational effects and the corrosion resistance relation in magnesium films prepared by changing the argon gas pressures and substrate bias voltages. Finally, it was shown that the corrosion resistance of magnesium films can be improved by controlling crystal orientation and morphology.

2. Experimental procedures

Deposition was made in a RF magnetron sputtering system equipped with a 4 inch diameter magnesium target. The experimental apparatus consists of four main parts, i.e. (1) working part ; substrate holder and cathode target, (2) discharging part ; turbo pump and rotary pump, (3) measuring part ; vacuum gauge and gas control system and (4) power supply part ; RF power supply system. The purity of magnesium target used in this experiment was 99.99%. The cold-rolled steel plates used as substrates were progressively polished to a final abrasive size of 0.05 μm Al_2O_3 and then ultrasonically cleaned in a bath of acetone for 30 minutes, prior to mounting in the vacuum chamber. Prior to the sputter-evaporation process, the system was initially evacuated to a pressure in the region

of 5.0 X 10⁻⁶ Torr. The substrate was ion cleaned in an argon glow discharge at a pressure of 1.0 X 10⁻² Torr with a bias voltage of -700 V for about 20 minutes to remove the residual oxides from the surface. And also magnesium target was presputter cleaned in argon gas pressure of 1.0 X 10⁻² Torr at closed shutter. After the argon ion sputter cleaning, the system was pumped down to a base pressure of 5.0 X 10⁻⁶ Torr again. Once the system reached stable condition, the sputter-evaporation lasted typically 30 minutes. Argon gas pressures of 1.0 x 10⁻³, 5.0 X 10⁻⁶ and 1.0 x 10⁻² Torr and bias voltages of 0, -150 and -300V were used in RF magnetron sputtering arrangement. The purity of argon gas used in this experiment was 99.999% . The substrate temperature was measured by a thermocouple attached to the back side of the substrate holder. The substrate temperature during sputter deposition was below 120 °C without any temperature control.

The top surface and cross section of the obtained films were examined by scanning electron microscopy(SEM). X-ray diffractometer with Cu Kα radiation was used to study the crystal structure and the preferred orientation of the films. And anodic polarization measurements of each specimens by masking all 1.0 cm²(1.0 × 1.0 cm²) area without polishing were carried out from the rest potential, at 2 mV/sec in deaerated 3% NaCl solutions at room temperature. Potentials were measured versus SCE(silver chloridel electrode).

3. Results

3.1 Crystal orientation and morphology of magnesium films

In order to investigate the influence of argon gas pressure and bias voltage on the crystal orientation and morphology of magnesium films, the specimens were prepared by changing argon gas pressure from 1.0 X 10⁻³ to 1.0 X 10⁻² Torr at bias voltage from 0 to -300V respectively. The X-ray diffraction patterns as a function of argon gas pressure at the different bias voltage for the deposited magnesium films are shown in Fig. 1. First of all, the X-ray diffraction peaks of all the magnesium films coincided well with the one of American Society for Testing and Materials (ASTM) card. The X-ray diffraction patterns of the magnesium films regardless of the negative bias voltage exhibited (002) preferred orientation as the argon gas pressure increased to 1.0 X 10⁻² Torr from 1.0 X 10⁻³ Torr. Here, the diffraction peaks of the film deposited at high argon gas pressure of 1.0 X 10⁻² Torr became less sharp and broadened. And it can be seen that the crystal orientation of the films was influenced not only
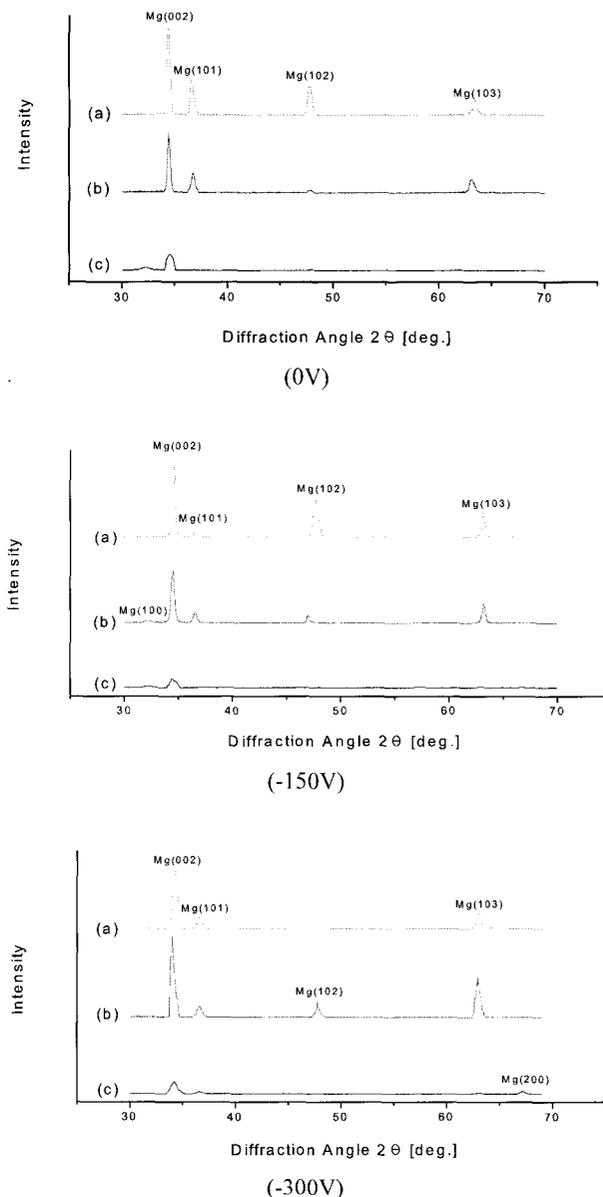

Fig. 1. X-ray diffraction patterns of Mg films deposited at various Ar gas pressures of (a)1.0 × 10⁻³ Torr, (b)5.0 × 10⁻³ Torr and (c)1.0 × 10⁻² Torr

by argon gas pressure but also substrate bias voltage. The SEM photographs of top surface and cross section for deposited magnesium 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. The magnesium films which were deposited at no bias voltage exhibited from columnar to a granular structure with porosity and defects as the increase of nitrogen gas pressure. The morphology of the sputtered films deposited at the bias voltage of -0.2 kV changed
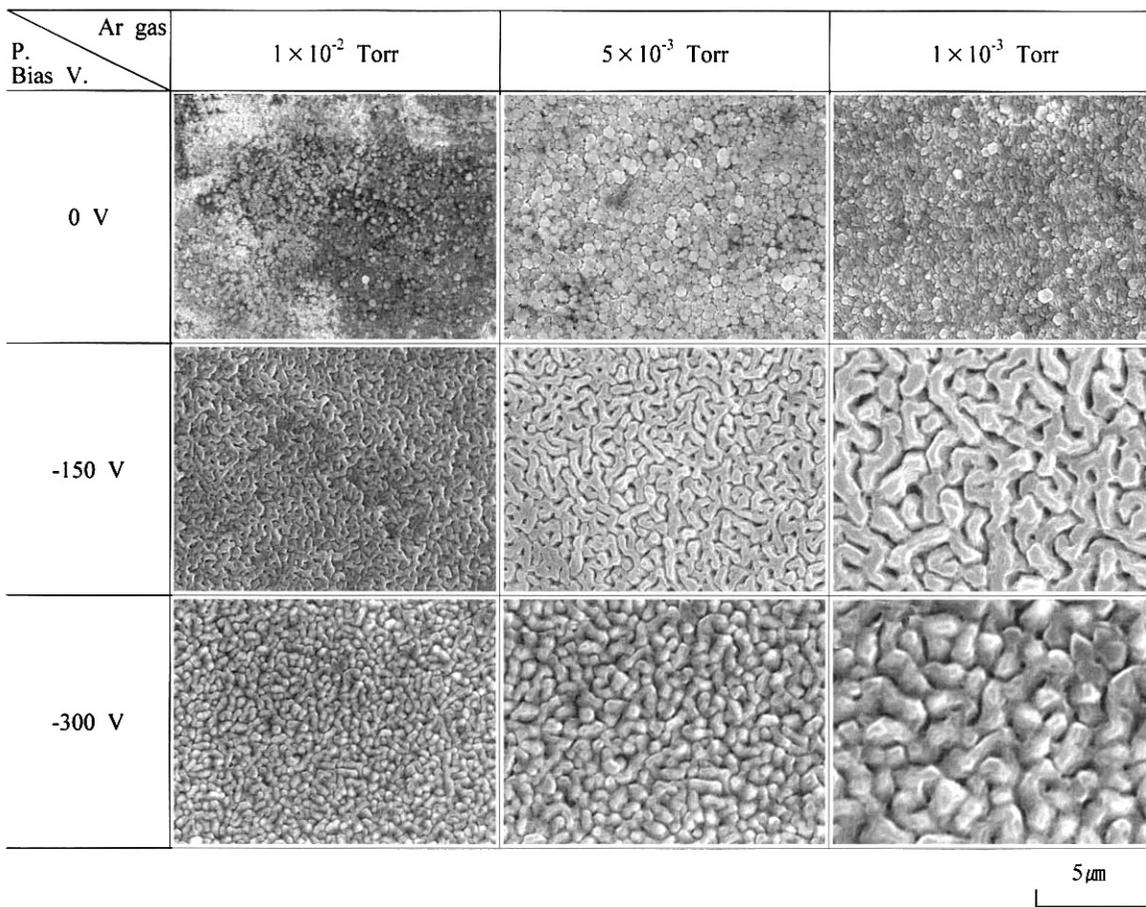
P. Bias V. / Ar gas	1×10^{-2} Torr	5×10^{-3} Torr	1×10^{-3} Torr
0 V			
-150 V			
-300 V			

Fig. 2.(A) SEM photographs of top surface for Mg films prepared by RF magnetron sputtering method.

from a granular structure (without defects or pinholes) with the increase of argon gas pressure as shown Fig. 2 (B). This related to the broadened diffraction peaks of the film shown in Fig. 1. From the bias voltages of -300 V in Fig. 2(B), the film sputtered at low argon gas pressure exhibited clearly columnar structures. However, column width of the films become larger with the argon gas pressure increased up to 1.0×10^{-2} Torr. 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.

3.2 Corrosion test of the deposited magnesium films

The result from corrosion test of the deposited magnesium films as a function of argon gas pressure is shown in Fig. 3. It shows the anodic potentio dynamic polarization curves for the films measured in deaerated 3% NaCl solution. The pure magnesium of 99.99% used in evaporation metal were also measured the anodic potentiodynamic polarization curves to compare with the deposited magnesium films. All the deposited magnesium films

appeared to show the active/passive polarization behaviors. When scanned from the rest potential, most of the films firstly became active and there was a substantial increase in corrosion current (critical current density for passivation) as shown in Fig. 3(A), (B) and (C). The deposited magnesium films nearly tend to show low corrosion current (passive current density) to compare with 99.99% magnesium target of the sputter-evaporation metal. The polarization behavior of these films changed with the gas pressure and bias voltage. The passive current density of all the deposited magnesium films tend to decrease with the increase of argon gas pressure. Eventually, corrosion-resistance of the magnesium films obtained in this experiment exhibited at high argon gas pressure of 1.0×10^{-2} Torr. That is, the magnesium films which had fine granular structure showed good corrosion resistance.

4. Discussion

In general, the properties of the deposited films depend on the deposition condition and these, in turn depend
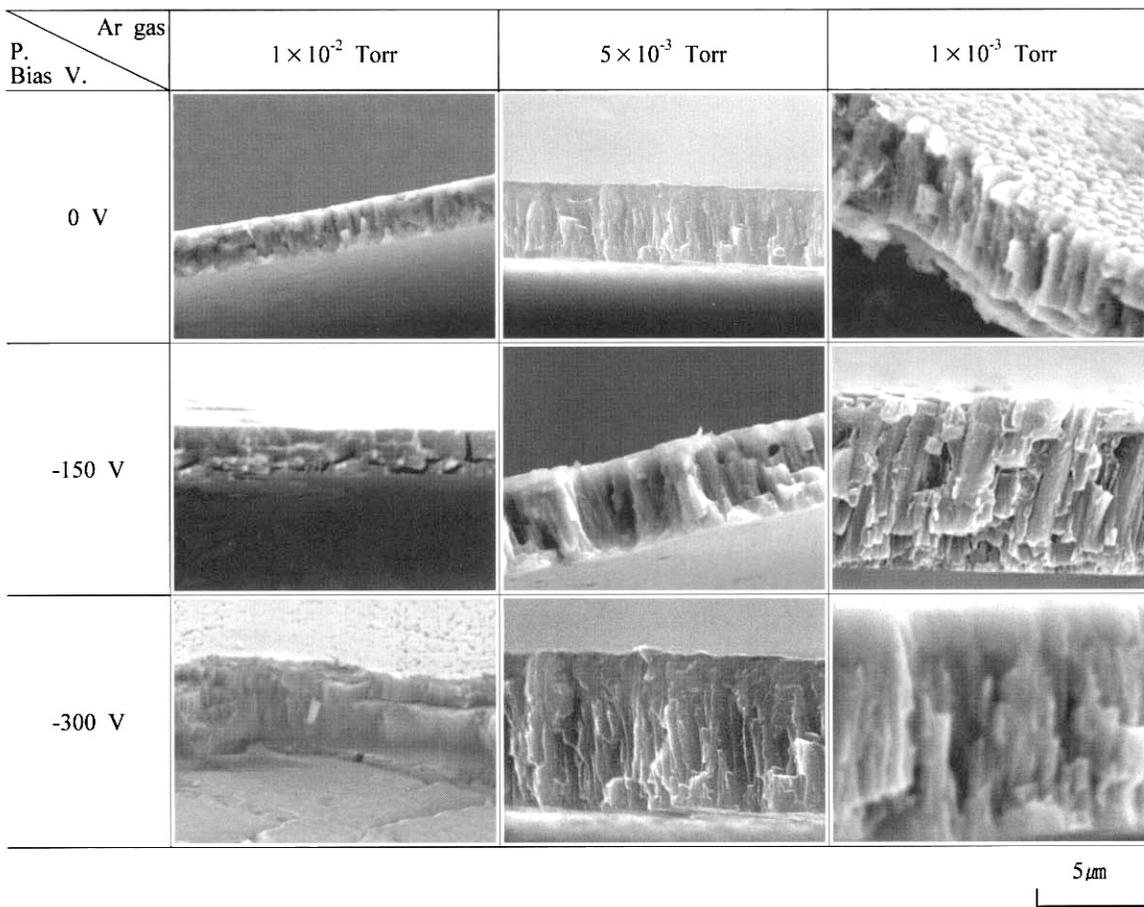
Fig. 2.(B) SEM photographs of cross section for Mg films prepared by RF magnetron sputtering method.

critically on the crystal orientation and morphology of the films.[7)-15)] Therefore, it is important to clarify that the nucleation occurrence and growth stage for the crystal orientation and morphology of the film affected by deposition conditions. In this experimental results, the crystal orientation and morphology of the magnesium film which showed good corrosion resistance tend to have granular structure with (002) preferred orientation or broadened peak. The morphology of magnesium 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 (002) and the diffraction peaks of the films became less sharp and broadened. From the results it is obvious that the argon gas pressure plays a large part in affecting the formation 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.

Since 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. In this experiment, it is possible that the growth rate of different crystal planes become different. When the magnesium film was deposited by sputtering at low argon gas pressure, the growth rate of (101)face which has the highest surface energy would be larger than (002) face. As a result, the area possession of (002) on film surface will increase. Therefore the film shows (002) orientation and because fine grain. 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 and fine structure with (002) preferred orientation can be obtained by sputtering method at relatively higher argon gas pressure. Increasing bias voltage will enhance both adatom diffusivities and ion bombardment. The ion bombardment will reduce the amount of adsorbed argon
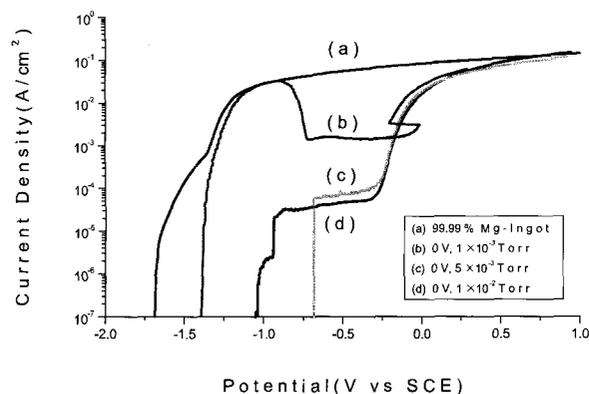
(A)   0V
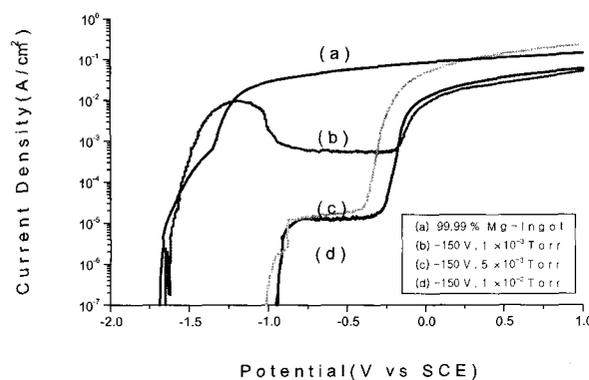
(B)   -150V
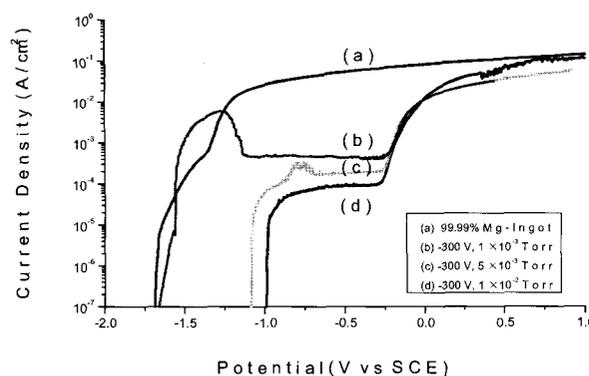
(C)   -300V

Fig. 3. Anodic polarization curves of magnesium films deposited at various bias   voltages (0V ; (A), -150V ; (B), -300V ; (C)) measured in deaerated 3% NaCl solution.

atoms 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 reducing argon gas pressure. The nucleation and growth

mechanism for granular and fine structure of the deposited magnesium films are very complex in a sputtering technique because the morphology and orientation depend not only on the substrate temperature but also on the energy of deposition of the atoms or ions, the kinetic mechanism between metal atoms and nitrogen gas, and even on the presence of impurities. We recognize, by my empirical measurements, that the system is not fully characterized in film growth term but offers an understanding of film growth for reciprocal relation between crystal orientation and morphology of films with added explanation related to the effects of adsorption, occulusion and ion sputter of argon gas.

5. Conclusion

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

2) The fomation mechanism of crystal orientation and morphology can be explained by applying the effects of adsorption, occulusion of argon gas.

3) All the deposited magnesium films showed obviously good corrosion resistance to compare with 99.99% magnesium target of the sputter-evaporation metal. And the magnesium film of fine granular structure which obtained at high argon gas pressure of 1.0×10^{-2} Torr had the highest corrosion resistance.

4) The properties of all the films can be improved greatly by controlling the crystal orientation and morphology with effective use of the plasma sputtering technique.

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