Effects of sputtering power on mechanical properties of Cr films deposited by magnetron sputtering

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Chromium (Cr) films were deposited on plain carbon steel sheets by dc and rf magnetron sputtering as well as by electroplating. Effects of dc or rf sputtering power on the deposition rate and properties such as, hardness, adhesion strength, surface roughness and corrosion resistance of the Cr films were investigated. X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microcopy (SEM) analyses were performed to investigate the crystal structure, surface roughness, thickness of the Cr films. Salt fog tests were used to evaluate the corrosion resistance of the samples. The deposition rate, hardness and surface roughness of the Cr film deposited by either dc or rf sputtering increase with the increase in sputtering power but the adhesion strength is nearly independent of the sputtering power. The deposition rate, hardness and adhesion strength of the Cr film deposited by dc sputtering are higher than those of the Cr film deposited by rf sputtering, but rf sputtering offers smoother surface and higher corrosion resistance. The sputter deposited Cr film is harder and has a smoother surface than the electroplated one. The sputter deposited Cr film also has higher corrosion resistance than the electroplated one, which may be attributed to the smoother surface of the sputter deposited film.

Keywords: Chromium, Sputtering, Deposition rate, Hardness, Adhesion strength

Introduction

Since the use of hexavalent chromium in chromium electroplating was found to cause cancer in human body,[1] alternative deposition techniques have been widely investigated. These techniques include spray,[2] ion plating,[3] sputtering,[4] ion implantation[5] and trivalent chromium plating.[6] Among these techniques spray has been most widely investigated. The spray technique is attractive in that its deposition rate is high and process cost is low enabling this technique to compete with the electroplating technique. However, it is not suitable for depositing films on the surface of a component with a complex geometry, for instance, the inside of a cylinder, because of its extremely narrow range of vision. In comparison with spray, sputtering offers a much better step coverage if the specimen holder is designed to be rotatable and tiltable.

The present paper reports some basic research results on the sputter deposition of Cr as an alternative to Cr electroplating. The Cr films were deposited by magnetron sputtering either dc or rf. Effects of sputtering power on the deposition rate, hardness, adhesion strength, surface roughness and corrosion resistance of the Cr films deposited by dc and rf sputtering were investigated. Also the hardness, surface roughness and corrosion resistance of the sputter deposited Cr films were compared with those of the electroplated ones.

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Experimental

Cr films were deposited by using a dc/rf magnetron sputtering system and a Cr target with a purity of 99·98%. Before the deposition plain carbon steel sheets with a dimension of $21\times21\times1$ mm were mirror polished, cleaned in an ultrasonic cleaner with a mixture solution of acetone, methyl–alcohol and deionised (DI) water for 15 min, and dried by a nitrogen blower. Sputtering process was conducted at a chamber pressure of 8 mTorr. The substrate temperature used was room temperature, 20°C. Both the dc and rf powers for the Cr target were varied in a range from 100 to 350 W. The prepared samples were characterised using a field emission scanning electron microscope (FESEM, Hitachi S4200) and a thin film X-ray diffractometer (XRD, Phillips X'pert MPD). Hardness tests were performed using a nanoindenter XP system (MTS, USA). Also the thicknesses of the Cr films were measured using a DEKTAK3 profilometer (Veeco, UK). In addition, accelerated atmospheric corrosion tests were conducted in a salt spray cabinet (ASTM B 117-73) to investigate the corrosion resistances of the Cr

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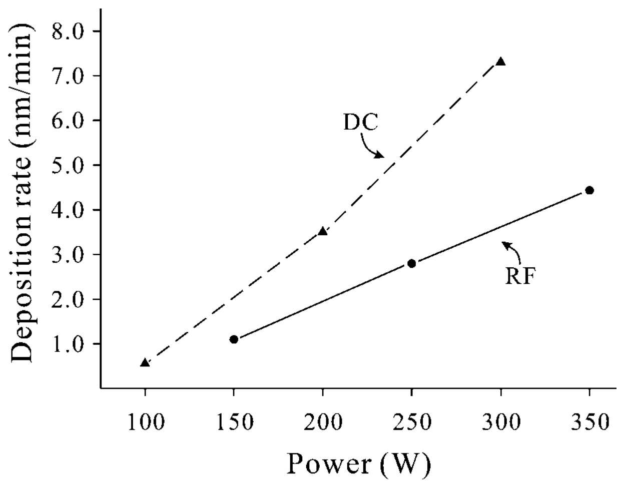
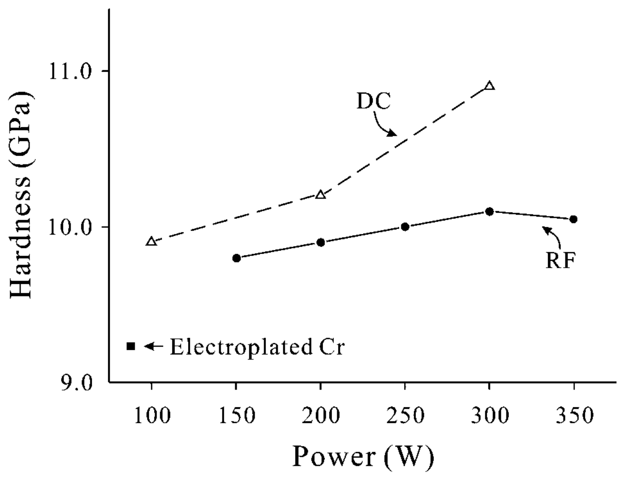


1 Variation of deposition rate of Cr film with sputtering power for rf and dc sputtering at constant pressure and constant substrate temperature



2 Variation of adhesion strength of Cr film with sputtering power for rf and dc sputtering at constant pressure and constant substrate temperature

coatings. A 5%NaCl solution with a pH of 7·0 was used for atomisation, and the temperature of the spray cabinet was maintained at 3·5°C within the exposure zone of the closed cabinet.

Results and discussion

The throughput of the sputtering process is commonly much lower than that of the electroplating process since it takes quite a long time for vacuum pumping in the sputtering process. Therefore, the important factors in developing a sputtering technique as an alternative to electroplating are to increase the pumping speed and deposition rate. However, the pumping speed is generally fixed once a sputtering system is assembled because the vacuum pump is not exchangeable easily. Thus the most important factor is deposition rate. Hence, it should be a good strategy to increase the upper limit of the sputtering power to as high as possible when assembling fabricating a sputtering system and to use a power as high as possible within the hardware limit of the sputtering system when depositing a Cr film without harming the physical and mechanical properties of the film such as hardness, surface roughness and corrosion resistance. Also all other process parameters should be optimised to increase the deposition rate to as high as possible. The important process parameters affecting the deposition rate in depositing a Cr film by sputtering are sputtering power, chamber pressure, substrate temperature, Ar gas flowrate, the distance between the substrate and the target etc. Figure 1 shows dependence of the deposition rate on dc and rf powers. The deposition rate tends to increase remarkably as either dc or rf sputtering power increases and the deposition rate of dc sputtering is almost twice as high as that of rf sputtering for the same power valve. In general Ar ion energy increases as the voltage applied to the sputter target increases and, in turn, the sputtering yield increases as the Ar ion energy increases. On the other hand the number of Cr particles striking the cathode is proportional to current density. Consequently, of the two components of sputtering power, i.e. voltage and current, current makes a much larger effect on the film deposition rate than voltage.

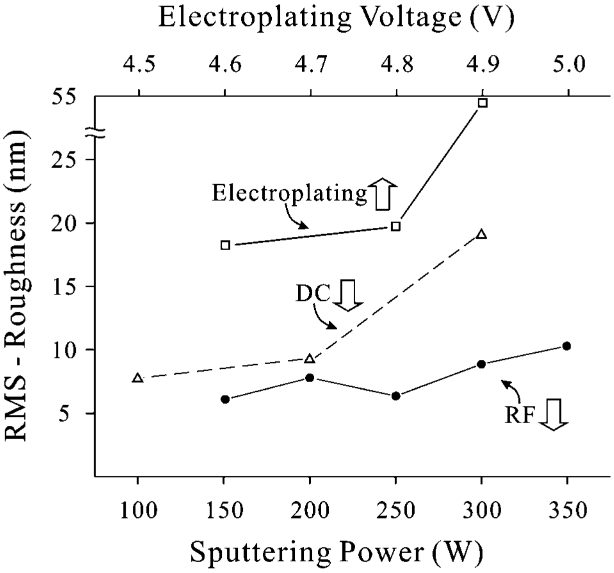
Variation of the hardness of the Cr film with the sputtering power for both rf and dc sputtering at a constant pressure and a constant substrate temperature is shown in Fig. 2. The hardness of the Cr film tends to increase slightly with power for both rf and dc sputtering. This does not seem to be because the hardness changes in reality with power but because the hardness changes with the film thickness which depends upon the sputtering power. If the film thickness is too small, 'size effect' will increase, because the plastic deformation region beneath the indentor will be extended to the substrate. Consequently, the hardness of the substrate material influences the measured hardness. The deposition time was controlled to make the thickness of the Cr film equal for different samples. However, the thickness of the Cr films is in the range from 1·3 to 1·7 μm. According to Paturaud *et al.*'s report,[7] the hardness of the Cr film is proportional to the film deposition rate and the most important process parameter affecting the deposition rate is sputtering power. Figure 2 shows that the Cr film deposited by dc sputtering has higher hardness than that by rf sputtering. Also the hardness of the Cr film deposited by sputtering either rf or dc is higher than that of the electroplated Cr film, which can be explained as follows. The film deposited by sputtering has a much smaller grain size than that by electroplating. Therefore, the former has higher hardness than the latter as expected from the following Hall–Petch equation[8]

$$H = H_0 + \kappa d^{-1/2}$$

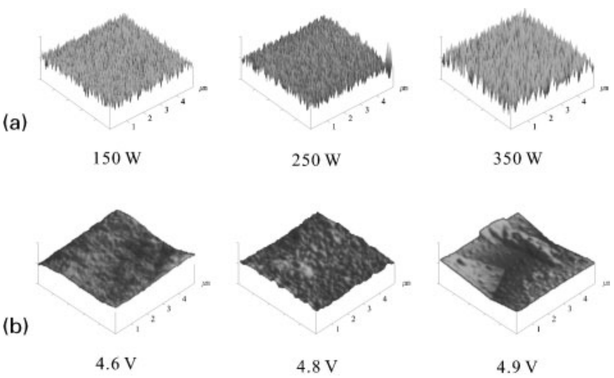
where H, H_0, d and κ are hardness, the intrinsic hardness of the crystal, grain size and a constant depending on the material respectively.

It can also be explained by incorporation of Ar gas into the Cr film. A small amount of Ar gas incorporated into the Cr film may affect the hardness of the film by inducing lattice distortion due to the generation of compressive strain field (solution hardening). The Cr film deposited by sputtering has higher hardness than that by electroplating since Ar ion is usually used in sputtering.

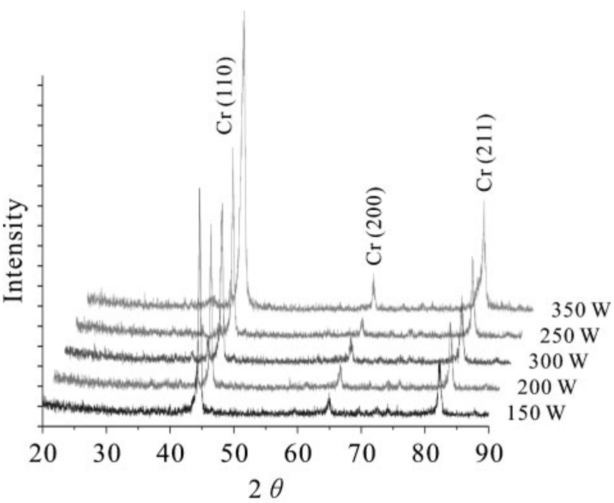
Dependence of the surface roughness of the Cr films on the sputtering power in sputtering and on the applied voltage in electroplating is shown in Fig. 3 and atomic force microscopy (AFM) images for the Cr films



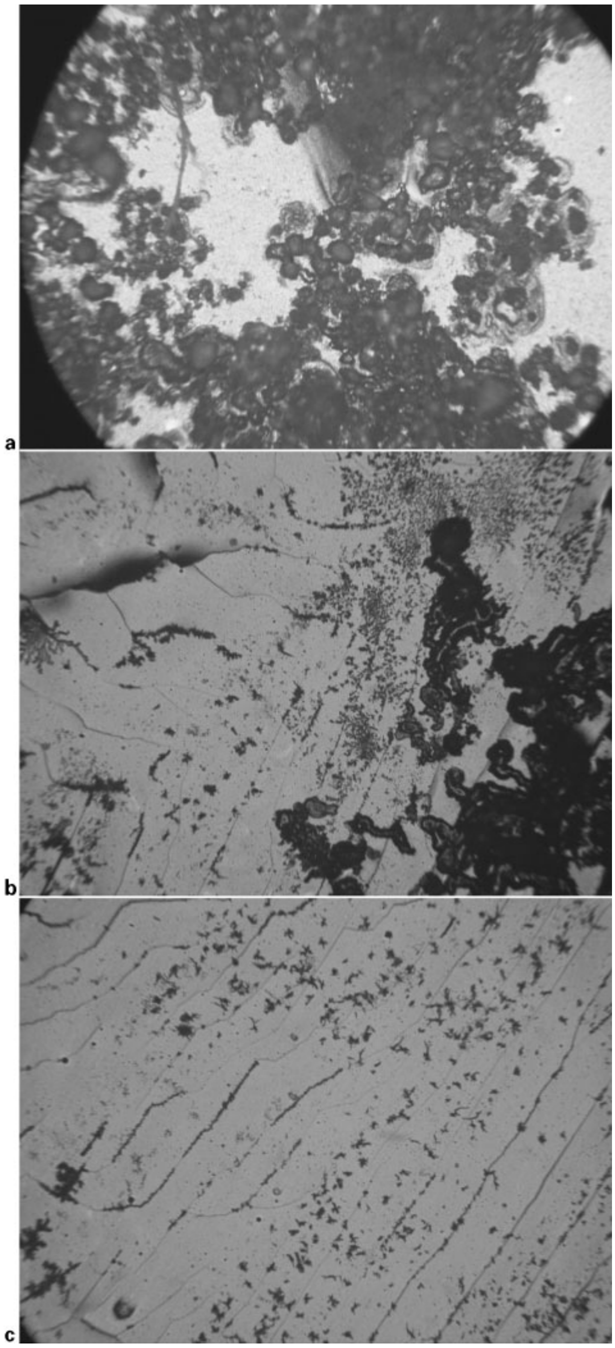
3 Variation of RMS surface roughness of Cr film with sputtering power for rf and dc sputtering at constant pressure and constant substrate temperature



4 Images (AFM) of *a* Cr films deposited by rf magnetron sputtering at different rf powers and *b* electroplated Cr films deposited at different applied voltages



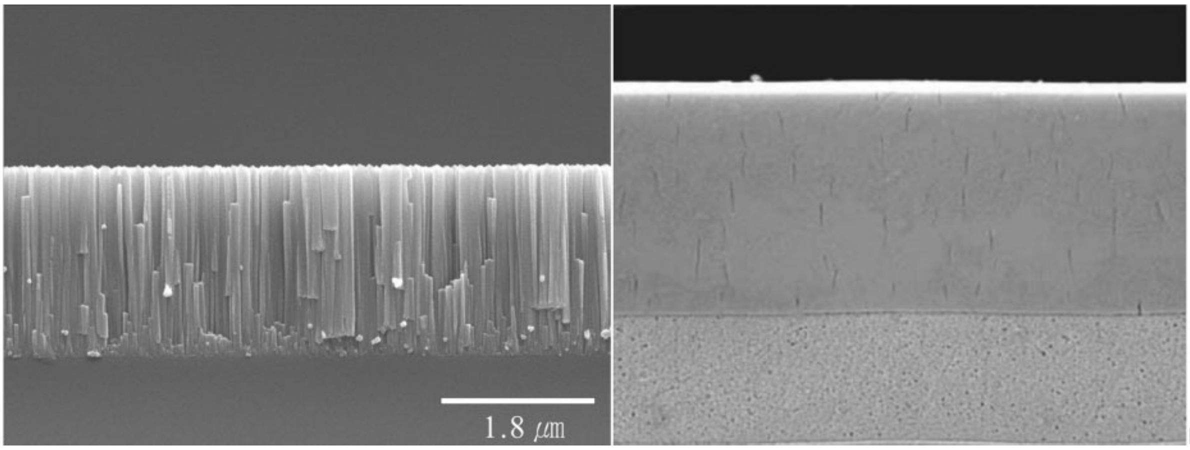
5 X-ray diffraction spectra for Cr films deposited by magnetron sputtering either dc or rf at different sputtering powers



***a* electroplated Cr film; *b* Cr film deposited by dc sputtering; *c* Cr film deposited by rf sputtering**

6 Optical plan view micrographs of Cr films after salt spray test for 7 h

deposited by rf sputtering and electroplating are shown in Fig. 4. The root mean square (RMS) surface roughness values of the electroplated Cr films are 17, 20 and 54 nm for the applied voltage in the electroplating process of 4·6, 4·8 and 4·9 V respectively. In contrast, the RMS surface roughness values of the Cr films deposited by sputtering either dc or rf are <20 nm in the power range below 300 W. The sputter deposited Cr films seem to have much smoother surface than the electroplated Cr film. The Cr films deposited by dc sputtering have smoother surface than those deposited by rf sputtering at the same power. The surface roughness for the film deposited by dc sputtering increases worse rapidly with the increase in power in the power range higher than 200 W, whereas the surface roughness for the films deposited by rf sputtering does not change significantly with power in the entire power



7 Cross-sectional SEM images of *a* sputter deposited and *b* electroplated Cr films

range used in the present study. This difference in the variation of the surface roughness with power between dc and rf sputtering may be attributed to the difference in the growth mode of the film. In the case of rf sputtering the surface roughness does not increase much with an increase in sputtering power since the projecting part of a growing film is removed continuously owing to the frequent periodical switching of the bias voltage. In contrast the projecting part of a growing film keeps on growing preferentially, so that the growth rate is accelerated with an increase in power in the case of dc sputtering.

The XRD spectra for the Cr films deposited at different rf powers are shown in Fig. 5. The XRD patterns indicate that the sputter deposited Cr films have a typical body centred cubic (bcc) lattice structure regardless of the sputtering power suggesting that sputtering power does not affect the crystal structure of the films.

Steels are easily corroded because an iron atom does not have a bond with an iron oxide molecule owing to the difference in size. In contrast chromium oxides form stable surface layers since a chromium atom does have a bond with a chromium oxide molecule because of their similarity in size. The high corrosion resistance of Cr is the most important reason why Cr coatings have been widely used in industry. The plan view optical micrographs of the Cr films after salt spray tests for 7 h are shown in Fig. 6. The Cr film deposited by electroplating was corroded much more severely than those deposited by sputtering. This may be mainly attributed to the higher surface roughness of the former than that of the latter since rough surface offers higher probability for galvanic cell formation. The severe corrosion of the Cr film deposited by dc sputtering compared with that deposited by rf sputtering can also be explained by the higher surface roughness of the former. Figures 7*a* and *b* show the cross-sectional SEM images of the sputter deposited and electroplated Cr films respectively. The main difference between the two kinds of films is that sputter deposited Cr film has a columnar structure, whereas the electroplated one has an equiaxed structure although the resolution of the image is not good enough. This columnar structure seems to be characteristic of sputter deposited thin films. The thin films deposited by other physical vapour deposition technique such as spray or electroless plating have equiaxed structure[9–11] like the electroplated Cr film. The advantages and disadvantages of a columnar structure depend upon the applications of a thin film and whether a thin film material is a unary or a multicomponent system. In the case of alloys or compounds a columnar structure is not desirable because atomic segregation is exacerbated along the columnar structure, but in the case of a unary system such as a sputter deposited Cr thin film, the columnar structure does not seem to make a particularly bad effect. For optical and magnetical applications a columnar structure can be utilised by taking advantage of its anisotropy, but it is not well known whether it makes any particular good or bad effect on the mechanical properties of thin films. It may have a positive effect on the adhesion of the film to the substrate.

Conclusions

The deposition rate and hardness of the Cr films deposited by dc sputtering are higher than those of the Cr films deposited by rf sputtering respectively, but rf sputtering offers smoother surface and higher corrosion resistance. The sputter deposited Cr films are harder and have a smoother surface than the electroplated ones. The sputter deposited Cr film also has higher corrosion resistance than the electroplated one, which may be attributed to the smoother surface of the sputter deposited film. Therefore, if the deposition rate is maximised by increasing the upper limit of the sputtering power when assembling the sputtering system and controlling the process parameters in the sputtering process, Cr sputtering could be an alternative to Cr electroplating.

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