Influence of Pulse Plating on the Crystal Structure and Orientation of Chromium

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ABSTRACT

Chromium deposits with various structures and orientations were prepared by pulse plating from a sulfate-catalyzed chromic acid solution with and without formic acid addition. The influences of the pulse duration, off-time, current density, formic acid concentration, and plating time on the structure and orientation were studied by x-ray diffraction and transmission electron microscopy. Results suggest that the β -Cr obtained by either direct current or pulse plating is converted from α -Cr by hydrogen charging, a reaction opposite to the well-known β -to α -Cr transition. A simple model involving the incubation time, t_c , of α - to β -Cr transition is proposed to explain the formation of β -Cr. The preferred orientation of α -Cr obtained by either direct current or pulse plating is [110], independent of the pulse parameters. However, the preferred orientation of β -Cr obtained by pulse plating is influenced by the codeposited phases and their relative proportions.

It has been reported that, depending on the electrolysis conditions, chromium may crystallize in several structures: body-centered cubic (α -Cr), hexagonal (β -Cr), face-centered cubic (δ -Cr), and amorphous structure (1-8). Both β - and δ -Cr are chromium hydride (CrH_x) with different hydrogen contents. Deposition of β - and δ -Cr from the sulfate-catalyzed chromic acid bath is favored under the following conditions: (*i*) high concentration of chromic acid, (*ii*) low temperature, (*iii*) high current density, (*iv*) addition of reducing agents, and (*v*) pulsing of current (4).

In pulse plating (PC plating), the pulse current density (j_p) , the on-time (t_{on}) and the off-time (t_{off}) can be varied independently over a very broad range. This results in two important features of pulse plating. First, very high instantaneous current densities and hence very negative potentials can be attained. The high overpotential causes a shift in the ratio of the rates of reactions with different kinetics. It also greatly influences the nucleation rate because of the availability of high energy for the formation of new nuclei. The second characteristic feature of pulse plating is the influence of t_{off} during which important adsorption and desorption phenomena as well as recrystallization of the deposit may occur (9).

In previous publications (6, 10), it was shown that amorphous chromium films could be deposited from a chromic acid solution containing a small amount of formic acid by direct current (DC) plating. It was also discovered that if the concentration of formic acid was too low, a crystalline β -Cr film was obtained instead. Therefore, the structures of Cr deposits are strongly influenced by the formic acid concentration.

The microstructure of a material is important in determining many of its properties. It has been shown that the basic factor which accounts for the brightness of chromium is a nearly perfect crystal orientation and fine crystal size (11). The preferred orientation of the deposits depends mainly upon two factors: (*i*) the crystal structure of the base metal and (*ii*) the bath conditions (12). Using x-ray and electron diffraction methods it has been clearly demonstrated that there are several stages in the growth of electrodeposits, each stage being characterized by a definite type of crystal orientation (11-13).

In this paper, we report the influence of pulse plating parameters (t_{on} , t_{off} , and j_p), formic acid concentration, and plating time on the structure and orientation of the chromium deposits using x-ray diffraction (XRD) and transmission electron microscopy (TEM). We propose an incubation time t_c for the conversion of α - to β -Cr by hydrogen charging. This is a reaction opposite to the well-known β to α -Cr transition. Understanding the mechanism of the Cr

¹ Present address: Department of Materials Science and Metallurgy, University of Cambridge, CB2 3QZ, England. phase formation may help control the structure of the Cr deposits.

Experimental

Chromium was deposited from an electrolyte containing 100 g/liter of chromic acid, 1 g/liter of sulfuric acid, and 0-30 ml/liter of an 85% solution of formic acid. The plating was carried out at room temperature (25°C) with constant j_p of 40 A/dm² for an hour. The plating cell was a beaker containing 200 ml electrolyte. The anodes were two facing Pb-5% Sb alloy plates of dimensions $80 \times 50 \times 6$ mm. They were situated vertically at the ends of the beaker. The cathode was a polycrystalline copper foil with <110> preferred orientation of dimensions $40 \times 20 \times 0.02$ mm.

After the removal of the copper foils with concentrated nitric acid, the films were subjected to XRD analysis within an hour after plating to identify the crystal structures. Peaks were indexed using published values for the lattice parameters (14). For ease of comparison, the XRD data were normalized with respect to the maximum peak height for each pattern.

In order to understand the initial phase formation, the films were deposited by pulse plating with a total plating time of 7 s. The copper was then removed by soaking in a 50% solution of nitric acid at room temperature. The freestanding films were directly analyzed by TEM within an hour after plating.

Results

Effect of on-time and off-time.—The influence of t_{on} on the structure of chromium deposits with constant j_p (40 A/dm²) and t_{off} (3 ms), and with no formic acid added, is illustrated in Fig. 1. Figure 1 shows that α - and β -Cr were codeposited by pulse plating and an increase in t_{on} resulted in a decrease in β-Cr content. Figure 2 shows the XRD results of chromium deposits with constant j_p (40 A/dm²) and $t_{\rm on}$ (3 ms), and with no formic acid added, but with varying $t_{\rm off}$. When the $t_{\rm off}$ was zero, the deposit was pure α -Cr. No peaks due to β -Cr could be found. When t_{off} was equal to or larger than 1 ms, peaks due to β -Cr appeared. An increase in t_{off} led to an increase of β -Cr content in mixed α - and β-Cr deposits. The results of Fig. 1 and 2 clearly show that codeposition of α - and β -Cr can be obtained by PC plating. The higher the ratio t_{off}/t_{on} is, the higher the β -Cr content of the deposits will be. Since β -Cr has been shown to be a chromium hydride (1, 2), it is reasonable to deduce that chromium deposited by PC plating contains a larger amount of hydrogen than that produced with DC plating. Moreover, the data in Fig. 2 suggest that the hydrogen contents increase with increasing t_{off} .

Effect of pulsed current density.—There are several ways of examining the effect of j_p on the structure of chromium

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Fig. 1. XRD patterns showing the influence of on-time (t_{on}) on the structure of chromium deposits with constant j_p (40 A/dm²) and t_{off} (3 ms). No formic acid was added to the electrolyte.

deposits (15). One way is to increase j_p at a constant pulse charge (*i.e.*, the number of coulombs per pulse is kept constant) and at a constant average current density j_m which is defined as follows

$$j_{\rm m} = j_{\rm p} \frac{t_{\rm on}}{t_{\rm on} + t_{\rm off}}$$
[1]

This method has the advantage that t_{off} is only very slightly changed by increasing j_p , avoiding the ambiguity in interpretation of the results due to the influence of t_{off} . The influence of $j_{\rm p}$ on the structure of chromium deposits while keeping both $j_{\rm m}$ and number of coulombs per pulse constant is illustrated in Fig. 3. An increase in j_p from 20 to 40 A/dm² caused an increase in the α -Cr content of the deposits. However, an increase in the current density implies an increase in the overpotential for the discharge. Therefore, a β-Cr deposit was favored at lower overpotential and α-Cr at higher overpotential. In DC plating from a sulfatecatalyzed chromic acid solution containing formic acid, a similar effect of current density on the chromium deposits was observed (10). A possible explanation is that α -Cr has lower current efficiency than β -Cr at low current density and that the slope of the polarization curve [I = f(E)] increases faster for the deposition of α -Cr than for β -Cr. With these assumptions, the current efficiency for α -Cr would increase with increasing $j_{\rm p}$.

Effect of formic acid concentration.—Figure 4 shows the influence of $t_{\rm off}$ on the structures of chromium deposits with constant $j_{\rm p}$ (40 A/dm²), $t_{\rm on}$ (3 ms), and formic acid concentration (3 ml/liter). A nearly pure β phase was obtained in all deposits and the purity of β -Cr increases with increasing $t_{\rm off}$. Comparison of Fig. 4 with Fig. 2 shows that the fraction of β -Cr in the deposits was greatly increased by the addition of formic acid. When the formic acid concentration was increased to 30 ml/liter, the results shown in Fig. 5 were obtained. When $t_{\rm off}$ was less than 3 ms, the deposits were amorphous. In contrast, when $t_{\rm off}$ was



Fig. 2. XRD patterns showing the influence of off-time (t_{off}) on the structure of chromium deposits with constant j_p (40 A/dm²) and t_{on} (3 ms). No formic acid was added to the electrolyte.



Fig. 3. XRD patterns showing the influence of pulsed current density (j_p) on the structure of chromium deposits with constant average current density (j_m) and constant number of coulombs per pulse. The meaning of P(3/20) is t_{on} : 3 ms, and t_{off} : 20 ms.



Fig. 4. XRD patterns showing the influence of t_{off} on the structure of chromium deposits with constant j_p (40 A/dm²), t_{on} (3 ms), and formic acid concentration (3 ml/liter).

greater than 5 ms, the deposits comprised a mixture of β - and amorphous Cr.

Effect of plating time.—The influence of plating time on the structure of Cr deposited from chromic acid solution with constant j_p (40 Å/dm²), t_{on} (3 ms), and t_{off} (10 ms) is shown in Fig. 6. The formic acid concentration was zero. When the plating time was 1 min, the deposit was nearly pure α -Cr, peaks due to β -Cr were few and weak. An increase of the plating time caused a corresponding increase in β -Cr content of the deposits. Hence, the structure of the Cr deposits varied with the plating time and, therefore, the thickness of the film. In order to investigate the structure evolution with the plating time, it was necessary to look into the initial stage of film growth. Using three formic acid concentrations 0, 3, and 30 ml/liter, the plating time was restricted to 7 s while the other plating parameters were kept the same as those in Fig. 6. Free-standing films were obtained by soaking the as-deposited film in a 50% solution of nitric acid. The films were very thin and transparent to the electron-beams and were analyzed by TEM. Since β -Cr is a metastable phase and easily decomposes into the stable α -Cr phase in a few weeks at room temperature, the films were analyzed within 1 h after plating.

Figure 7 shows the bright field (BF) images and corresponding diffraction patterns from the as-deposited films. When the formic acid was absent, the film was α -Cr with the preferred orientation as shown in Fig. 7a and b. No peaks due to B-Cr were found. With addition of 3 ml/liter formic acid, the structure of the film was a mixture of α and β-Cr as shown in Fig. 7c and d. A schematic representation of Fig. 7d is shown in Fig. 8, which identifies the reflections from α - and β -Cr. Figure 7c shows the needleshaped β -phase embedded in the α -phase matrix. The needles were very small with the major axis about 0.3 µm and minor axis about 0.05 µm. When the concentration of formic acid was increased to 30 ml/liter, the film was amorphous. No crystalline phase was detected. This is confirmed by the featureless image and halo ring as shown in Fig. 7e and f, respectively.



Fig. 5. XRD patterns showing the influence of t_{off} on the structure of chromium deposits with constant j_p (40 A/dm²), t_{on} (3 ms), and formic acid concentration (30 ml/liter).

Preferred orientation .-- The XRD results of Fig. 1-6 showed that the preferred orientation of a-Cr was always [110], irrespective of the variation of t_{on} , t_{off} , j_{p} , formic acid concentration, and plating time. The (110) plane is the plane of highest density in the bcc structure. Therefore, the α -Cr deposits tend to grow with the plane of highest density oriented parallel to the substrate surface. In this plane, the surface energy of the film is the lowest as described by the Bravais law (16). In contrast to α -Cr, the preferred orientation of β-Cr changed with the plating conditions. Figures 1 and 2 show that there are no obvious effects of t_{on} and t_{off} on the preferred orientation of β -Cr which is [1011]. It is interesting to note that the XRD patterns of β -Cr in Fig. 1 and 2 are consistent with the powder x-ray diffraction pattern of β -Cr (14). However, the orientation of β -Cr is a function of j_p (Fig. 3), formic acid concentration (Fig. 4 and 5), and plating time (Fig. 6). Figure 3 shows that the preferred orientation of β -Cr shifted from [1011] to [1010] as j_p decreased from 30 to 20 A/dm². This is in contrast to the result obtained by Pangarov (17) who reported that the preferred orientation of thick deposits with hcp structure is [1011] at low overvoltage and [1010] at high overvoltage. Our results suggest, however, that the orientation of β -Cr in the codeposits must correlate with the other phase.

Figure 6 shows that the preferred orientation $[10\overline{1}1]$ of the β -Cr is related to that of the α -Cr during the early stages of growth. This result is also confirmed by the electron diffraction patterns as shown in Fig. 7d. Both α - and β -Cr have the corresponding preferred orientation. With an increase in plating time, the effect of the α -Cr matrix on the orientation of β -Cr is gradually reduced and the development of the β -Cr specific orientation [1120] increased with increased β -Cr content of the deposits. This specific preferred orientation [1120] was shown for pure β -Cr prepared by PC (Fig. 4) and DC plating (14). It has been shown that the organic additive influences the orientation of the deposit (18, 19). However, in β -Cr electroplating, when the β -Cr is the major phase, [1120] is always the preferred orientation, whether the formic acid exists or not as shown in



Fig. 6. XRD patterns showing the influence of plating time on the structure of chromium deposits with constant j_p (40 A/dm²), t_{on} (3 ms) and t_{off} (20 ms). No formic acid was added to the electrolyte.

Fig. 4 and 6. In our previous report (14), we proposed a model for the development of preferred orientation [1120] during β -Cr electrocrystallization. This model points out the growth of a β -Cr crystallite is slowest along the direction of the c-axis and fastest along the directions <1100>. The anisotropic growth with the β -Cr causes all the crystallites whose c-axis and crystal planes {1120} are not parallel to the substrate surface to be overgrown by other crystallites with {1120} plane parallel to the substrate surface can sustain growth after some critical thickness is reached. This gives rise to the stability of a definite texture under given electrolysis conditions and also explains the lack of texture of the underlying materials.

When β -Cr was codeposited as a minor phase, the preferred orientation was affected by the major phase. This phenomenon was shown in Fig. 5 and 6. When the major phase was α -Cr in the [110] orientation, the orientation of β -Cr was [1011], as shown in Fig. 6. When the major phase was amorphous Cr, the orientation of β -Cr was [0001], as shown in Fig. 5. The morphology of β -Cr was also changed with the matrix. When the matrix was α -Cr, the shape of the β-Cr was needle-like, as shown in Fig. 7c. When the matrix was amorphous Cr, the shapes of $\beta\mbox{-}Cr$ were spherical, rod-like, and dendritic, depending on the carbon content of the deposits, as shown in Fig. 4d, e, and f of Ref. (10). This may be due to the interface thermodynamic equilibrium; the sum of the matrix surface energy, the interface free energy, the β -Cr surface free energy, and the strain energy must be minimized at equilibrium.

Discussion

There are several factors which can affect the phase formation of Cr deposits by DC or PC plating. One is the pH of the cathode film. Snavely (1) found that the structure of the Cr deposits depended on the cathode film pH: α -Cr was formed at the low pH values and β -Cr at high film pH values. The actual pH values were unknown but Snavely suggested that the range covered by the deposits was from



Fig. 7. TEM micrographs showing the bright field image (a, c, and e) and corresponding selected area diffraction pattern (b, d, and f) of chromium deposits obtained with constant j_p (40 A/dm²), t_{on} (3 ms), t_{off} (10 ms), and plating time (7 s). The formic acid concentrations were (a) 0, (c) 3, and (e) 30 ml/liter.

about 3 to 6. The results of Fig. 1 and 2 clearly show that codeposition of α - and β -Cr can be obtained by PC plating and the fraction of β -Cr increases with increasing t_{off} . This is quite different from the results of Faust *et al.* (20) who attributed the reduction in stress of crack-free deposits they obtained with PC plating to the decomposition of hydrides during the t_{off} period. However, our results can be rationalized by the conclusions obtained by Pearson and Dennis (7), who suggested that the codeposition of β -Cr can be explained by desorption of Cr⁺² ions at the cathode film. During the t_{off} , large numbers of Cr⁺² ions can diffuse within the cathode film and react with hydrogen ions or water to form hydrogen gas and Cr⁺³ ions and increase the pH of the cathode film. This could explain the emergence of the hydride inclusions observed in pulse-plated deposits.

Another factor is the presence of interstitial elements, such as C, N, and O. It has been reported (21) in the V-H system, in which the hydrogen solubility increases with increasing contents of C, N, or O, that hydrogen is trapped by other interstitial solutes. In our previous experimental results (10), the adsorption of formic acid increased the carbon content in the deposits, which would facilitate the formation of β -Cr and amorphous Cr, depending on the



Fig. 8. A schematic representation of Fig. 7d identifying the electron diffraction rings from α - and β -Cr.

carbon content in the deposits. When the carbon content was about 1 weight percent (w/o), the deposit was β -Cr. When the carbon content was higher than 3.3 w/o, the deposit became amorphous. Therefore, the effective formic acid concentration controls the phase formation of the deposits. Furthermore, it has been shown that the higher the concentration of formic acid, the higher the carbon content of the deposits (10). In the present case, when the formic acid concentration was increased from 1 to 3 ml/liter, the fraction of β -Cr in the deposits was greatly increased. Adsorbed carbon atoms located at interstitial sites cause the distortion of the Cr lattice and may increase the trapped-hydrogen concentration of the deposits, thereby inducing the formation of β -Cr. This is consistent with the well-known fact that organic additives encourage hydrogen absorption during chromium plating (1, 2). However, when the formic acid concentration increased to 30 ml/ liter, a larger number of carbon atoms was absorbed and α and β -Cr phases became unstable, resulting in the formation of amorphous Cr. The effective formic acid concentration was also affected by the t_{off} of the PC plating. During the off-time period, the adsorption and desorption of formic acid would change the structure of the deposits. With 30 ml/liter formic acid added and $t_{\rm off}$ shorter than 3 ms, the adsorbed formic acid would be incorporated into the deposits, increasing the carbon content and forming amorphous Cr. However, when toff was larger than 5 ms, desorption of formic acid from the cathode was more extensive, resulting in the codeposition of β - and amorphous Cr as shown in Fig. 5.

A third factor concerns the properties of the cathode. It is evident that once deposition is initiated on a substrate surface, the metal being deposited must, itself, be catalytic in order for deposition to continue. From the XRD (Fig. 6) and TEM (Fig. 7) results, it is clear that the copper substrate has less effect than formic acid concentration on the initial phase formation. The first phase formed at the Cu substrate was α -Cr when formic acid was absent (Fig. 7a and b) and amorphous Cr when the concentration of formic acid was 30 ml/liter (Fig. 7e and f). This is consistent with the previous results as shown in Fig. 2 of Ref. (14), in which the texture is inherent to the film and substrate influence is not significant.

From the above analysis and the results of Fig. 6 and 7, we suggest a model to explain the structural evolution of PC- and DC-plated Cr. Figures 7a and b show that the initial phase formed was α -Cr. With increasing plating time, the β -phase was gradually formed as shown in Fig. 6. Therefore, we propose that α -Cr is converted to β -Cr by hydrogen charging and that there exists an incubation time (t_c) for the α - to β -Cr transition. When the plating time is less than t_c , only the α -Cr forms (Fig. 6, t < 1 min). When the plating time is larger than t_c , codeposition of β -Cr occurs (Fig. 6, t > 5 min). The value of t_c depends on the cathode-film characteristics. With the presence of other interstitial elements and higher pH value, t_c will be decreased. Note that t_c is >1 min in Fig. 6 in the absence of formic acid, but with the addition of formic acid (Fig. 7c) $t_{\rm c} < 7$ s. When $t_{\rm c}$ approaches zero, only β -Cr can be deposited. The cathode film pH can be raised using pulse plating with longer off-time. The carbon interstitial solutes can be increased by adding a reducing agent (e.g., HCOOH). Therefore, β-Cr can be easily obtained by pulse plating or the addition of formic acid. However, too much formic acid causes the formation of amorphous Cr but not β -Cr as shown in Fig. 7e and f and long off-time periods introduce the formation of α -Cr (7, 8).

Conclusion

Chromium deposits with various structures and orientations were prepared by pulse plating from a sulfate-catalyzed chromic acid solution with and without formic acid addition. The influences of the pulse duration, off-time, current density, formic acid concentration, and plating

time on the structure and orientation of the Cr deposits were studied by XRD and TEM. When no formic acid was added to the electrolyte, all the deposits were a mixture of α - and β -Cr. The β -Cr content in the deposits increased with increasing t_{off} and decreased with increasing t_{on} and $j_{\rm p}$, while the other plating parameters were kept constant. When 3 ml/liter formic acid was added, the deposits were nearly pure β -Cr. By further increasing the formic acid concentration to 30 ml/liter, the deposits became amorphous or a mixture of β - and amorphous Cr depending on the off-time period. From the variation of structure of Cr deposits with the plating time, we propose that the β -Cr obtained by either DC or PC plating is converted from α -Cr by hydrogen charging, a reaction opposite to the wellknown β - to α -Cr transition. A simple model involving the incubation time t_c of α - to β -Cr transition is proposed to explain the formation of β-Cr.

The orientation of α-Cr obtained by either DC or PC plating was with the highest density planes (110) parallel to the substrate, and did not change with the plating parameters. However, the orientation of β -Cr depended on the codeposited phases. Pure β-Cr exhibited a preferred orientation [1120]. When α -Cr was codeposited, the orientation of β -Cr shifted gradually from [1120] to [1011], depending on the α -Cr content of the deposits. When amorphous Cr was codeposited as a major phase, the preferred orientation of β-Cr was [0001].

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