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ORIGINAL PAPER

Surface roughness of thin silver films pulse-plated using silver cyanide-thiocyanate electrolyte

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Abstract We investigated the effect of the pulse current density, current-on time and current-off time on the surface roughness of a silver thin film that was pulse-plated using a silver cyanide-thiocyanate electrolyte. The interface width, which is defined by the root mean square of the fluctuations in the height of the surface, is found to decrease rapidly with the current-off time and to increase with current-on time. However, it should be noted that when the value of current-off time is sufficiently large, the interface width decreases with pulse current density. These experimental results indicate that by appropriate selection of the current-on time and current-off time, we can fabricate silver electrodeposits with minimal surface roughness. We have discussed the influence of these three parameters on the interface width from the viewpoint of the cathode potential and adsorption.

Keywords Pulse current electrodeposition · Silver · Surface roughness

1 Introduction

Silver electrodeposits with smooth surfaces have wide application in jewellery, electronic components, electrodes, and antibacterial agents [1, 2]. We have utilized a silver cyanide-thiocyanate electrolyte with a levelling agent to produce silver electrodeposits with smooth surfaces [3]. Although antimony potassium tartrate (APT) [4–6] can be used as a levelling agent and to form patterns in a silver deposit [7, 8], its use is generally avoided due to its toxic nature. It is necessary to use silver electrolytes with low-toxicity to avoid the hazards of cyanide and to comply with environmental regulations [9].

Pulse electrodeposition is known to produce deposits with finer grain sizes than those produced by direct current (DC) electrodeposition. In this study, we have investigated the influences of the current-on time, current-off time and pulse current density on the surface roughness of silver thin films. On the basis of the conclusions of previous studies [10–18], it should be noted that it is difficult to a priori predict the influences of these parameters because each electrochemical system reacts in a different way. For instance, the grain size in Zn electrodeposition [18] decreases with current-on time, while the trend is opposite in Ni electrodeposition [14]. Thus, surface roughness is closely related to the grain size of electrodeposited thin films [18].

Hence, experimental evidence is required to understand the influences of the aforementioned three parameters on the surface roughness of silver electrodeposits. However, there are very few reports on silver thin films produced by pulse electrodeposition using a low-toxicity electrolyte such as silver cyanide-thiocyanate [6].

The aims of this study are to report the influences of these three parameters on the surface roughness of silver electrodeposits produced using silver cyanide-thiocyanate electrolyte and to develop a technique whereby silver thin films with smooth surfaces can be produced.

2 Experimental setup

The experiments were performed using an electrolyte comprising the following components (g l^{-1}): $AgNO_3$, 25.5; $K_4Fe(CN)_6 \cdot 3H_2O$, 72; KSCN, 146; $KNaC_4H_4O_6 \cdot 4H_2O$,

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59.3; K_2CO_3, 31.3. After boiling the solution of $AgNO_3$, K_2CO_3 and $K_4Fe(CN)_6 \cdot 3H_2O$ for 30 min, burnt umber precipitates of iron hydroxides were obtained. After the removal of iron hydroxide, the remaining components, i.e., KSCN and potassium sodium tartrate were added in order to the solution. The pH of the electrolyte was approximately 8.2. Thus, we synthesized a low-toxicity silver cyanide-thiocyanate electrolyte comprising a silver complex agent $\mathrm{Ag(CN)_2CNS}_{\phi}^{-(\phi+1)}$ [19] where φ has a value between 1 and 2.

In this study we used potassium sodium tartrate to stabilize the electrolyte [7, 8]. The concentration of Ag^+ in the electrolyte was very low because most of the silver ions were incorporated into the complexing agent [19], $\mathrm{Ag(CN)_2}CNS_{\phi}^{-(\phi+1)}$. Since the amount of neutral complex formed in the electrolyte by Ag^+ and tartaric monoanions [20–23] is very small, the presence of potassium sodium tartrate in the electrolyte has little influence on the surface roughness. In fact, in our preliminary experiments, it was observed that there was no difference in the surface roughness of the silver deposits of electrolytes with potassium sodium tartrate and those without it.

The charge transfer reaction of the Ag complexing agent in silver electrodeposition is given by [24]

$$\mathrm{Ag(CN)_2CNS}_{\phi}^{-(\phi+1)} + e^- \rightarrow \mathrm{Ag} + 2\mathrm{CN}^- + \phi\,\mathrm{CNS}^-. \quad (1)$$

A polycrystalline copper plate and a carbon plate, each 30 mm long and 10 mm wide, were used as the working and counter electrode, respectively. One side of the copper electrode was electrically isolated, while the other side had a mirror-like appearance. The electrodes were cleaned by a wet process and placed parallel to each other in a quiescent electrochemical cell at a temperature of 300 K.

A square-wave pulse current having a pulse current density J_p of 2–24 mA cm^{-2}, a current-on time T_{on} of 1–100 ms, and a current-off time T_{off} of 1–900 ms was applied with a power supply. The cathode potential was measured with a Luggin capillary with an Ag/AgCl electrode in a KCl solution and the results were stored in a digital storage oscilloscope.

The surface morphology of the silver electrodeposit was observed with a confocal laser scanning microscope (Keyence VF7500) having a resolution of 0.01 μm in height. The interface width w(t) [25], as defined by Eq. 2, was calculated from the profile comprising 512 pixels of the surface,

$$w(t) = \left(\frac{1}{N}\sum_{i=1}^{N}(h_i - \bar{h})^2\right)^{1/2}, \quad (2)$$

where t is the growth time, N is the number of pixel, h_i is the height of the deposit above substrate position i and $\bar{h}$ is the average height of the profile formed by N points. Eq. 2 denotes the standard deviation of the height of the surface. All the silver deposits grown for the measurement of w(t) had a thickness of approximately 1.0 μm.

3 Results and discussion

Figure 1 shows the images of the surface of a typical silver deposit and the profile of the surface observed with the confocal laser scanning microscope. It is observed that the appearance of the surface is bright white and w(t) is 0.08 μm. All the silver deposits in the study had a thickness of approximately 1.0 μm, which is thick enough for use in printed circuit boards and decorative applications.

3.1 Effect of J_p

Figure 2 shows the plots of w(t) and the cathode potential for varying J_p, a T_{on} value of 1 ms, and a T_{off} value of

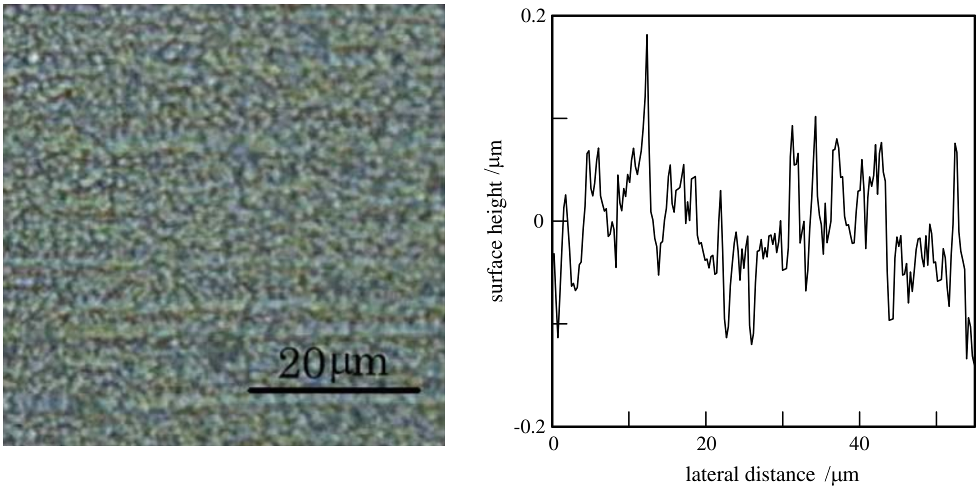

Fig. 1 Microscope image of the silver electrodeposit grown at $J_p = 12$ mA cm^{-2} and the surface profile observed with the confocal laser scanning microscope. The other parameters in pulse electrodeposition are $T_{on} = 9$ ms and $T_{off} = 14$ ms

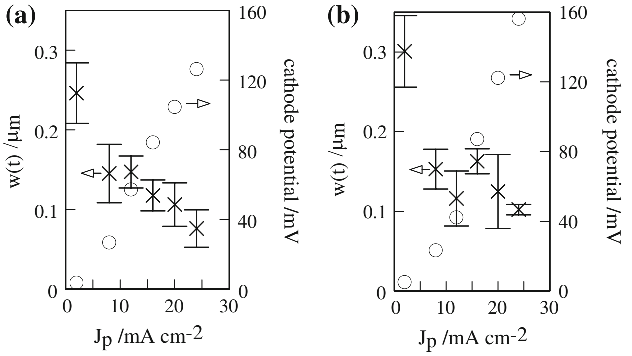

Fig. 2 Plots of w(t) and cathode potential for varying J_p. (**a**) $T_{on} = 1$ ms and $T_{off} = 9$ ms, (**b**) $T_{on} = 100$ ms and $T_{off} = 900$ ms

9 ms. From Fig. 2a w(t) decreases with J_p, while the cathode potential increases with J_p. These experimental results appear to be consistent with those for nickel [17] and zinc electrodeposits [18]: these studies state that the relationship between the fine grain size and high pulse current density is due to the fact that the radius of nucleus of the deposit is inversely proportional to the cathode potential. The high current density yields a finer grain size because the higher electrode potential increases the amount of free energy available for the formation of new nuclei and results in higher nucleation rates. The finer grain size of the deposits results in a smaller w(t) [25].

To confirm the effect of J_p, w(t) was measured for deposits synthesized at a T_{on} value of 100 ms. Figure 2b shows that w(t) decreases with J_p in a manner similar to that shown in Fig. 2a. The values of film thickness and the ratio T_{on}/T_{off} in Fig. 2b are also the same as those in Fig. 2a. Irrespective of J_p, the values of w(t) in Fig. 2b are larger than those in Fig. 2a. This is because of the longer current-on time, which is the period during which grain growth occurs.

However, Fig. 3a, b show that an increase in J_p does not always result in a corresponding decrease in w(t). The values of T_{on} and T_{off} in Fig. 3a are 4 ms and 6 ms, respectively, while those in Fig. 3b are 9 ms and 1 ms, respectively. As expected, an increase in J_p causes an increase in cathode potential. However, on the basis of Fig. 3a, b, it is apparent that an increase in cathode potential does not always cause a decrease in w(t). The ratio T_{on}/T_{off} in Fig. 3 is larger than that in Fig. 2; this implies that the effect of T_{off} on w(t) can occur more explicitly. In our study we show that T_{off} and T_{on} rather than J_p explicitly affect w(t).

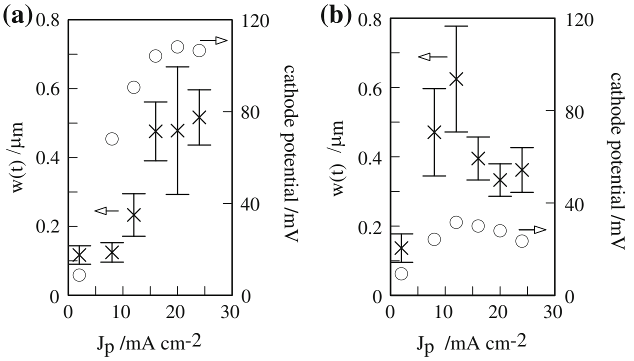

Fig. 3 Plots of w(t) and the cathode potential for varying J_p. (**a**) $T_{on} = 4$ ms and $T_{off} = 6$ ms, (**b**) $T_{on} = 9$ ms and $T_{off} = 1$ ms

3.2 Effect of the current-off time T_{off}

To elucidate the effect of T_{off} on w(t), silver electrodeposits were grown at a fixed T_{on} of 9 ms. Figure 4 shows a plot of w(t) and the cathode potential for varying T_{off}. An increase in T_{off} results in a rapid decrease in w(t), which tends to saturate at 12 ms. The presence of an adsorbed compound formed through electrochemical reactions [10, 11, 14] is believed to act as a levelling agent during the current-off time, even when no levelling agent is added to the electrolyte. When T_{off} increases above 12 ms, w(t) reaches a stable value. Figure 4 indicates that it takes at least 12 ms for the adsorbed compound to cover all the active sites in the cathode. Hence, there exists a limitation period beyond which T_{off} has no influence on the decrease in w(t).

In this study, it is possible that cyanide [26] or thiocyanate ions may have formed adsorption compounds during T_{off}. The presence of an active site implies that a site is available for nucleation. The adsorbed ion suppresses nucleation or growth at the active site and hence the resulting deposit has a smooth surface.

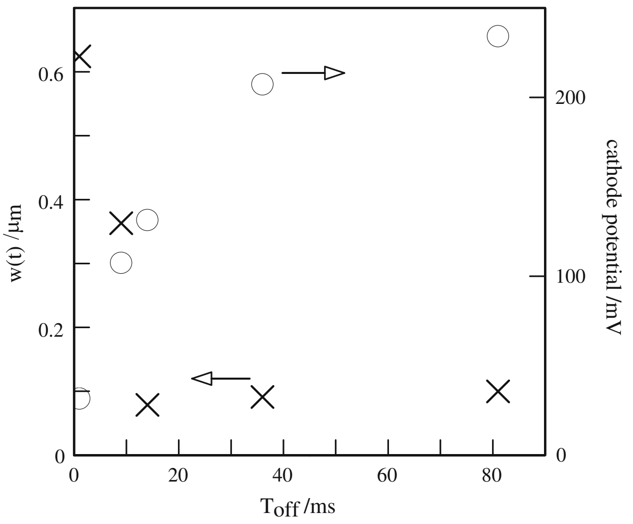

Fig. 4 Dependence of w(t) and cathode potential on T_{off} at a fixed T_{on} of 9 ms and J_p of 12 mA cm^{-2}

Moreover, it is shown that in silver electrodeposition T_{off} has a significant influence on w(t) and on the limitation period of T_{off} above which the value of w(t) decreases to a minimum value.

3.3 Effect of T_{on}

We studied the influence of T_{on} on w(t) for a fixed T_{off} of 9 ms. Figure 5 shows a plot of w(t) and cathode potential for varying T_{on}. Initially, w(t) decreases partially and then increases rapidly with T_{on}. In zinc electrodeposition [18], it is reported that the grain size decreases with T_{on} (hence w(t) also decreases) because an increase in T_{on} causes an increase in the cathode potential.

However, in Fig. 5, the cathode potential increases with T_{on}. The sufficient current-on time may increase the electrical resistance of the charge-transfer reaction of a silver ion owing to the presence of compounds such as thiocyanate ions, which are formed during the electrochemical process. Further, no decrease is observed in w(t) for an increase in cathode potential. It is possible that the value of T_{off} is so small that the formed compound cannot be adsorbed at the active sites. In fact, as seen in Fig. 2b, if the value of T_{off} is sufficient for the compound to adsorb at the active site, w(t) decreases.

3.4 Duty ratio and interface width

The duty ratio, $T_{on}/(T_{on} + T_{off}) = 1/(1 + T_{off}/T_{on})$ can be used to explicitly show the influence of T_{on} and T_{off} on w(t). As seen in Figs. 4 and 5, w(t) remains small for $T_{off}/T_{on} \gg 1$ and increases for $T_{off}/T_{on} < 1.5$.

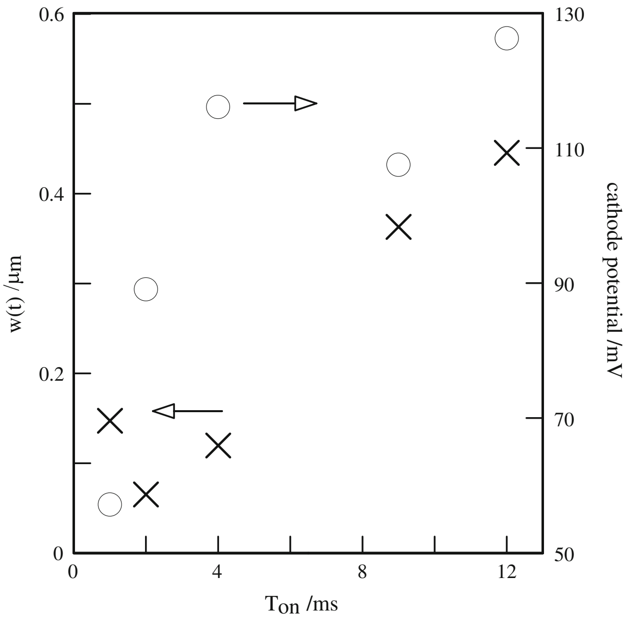

Fig. 5 Dependence of w(t) and cathode potential on T_{on} at a fixed T_{off} of 9 ms and a J_p of 12 mA cm^{-2}

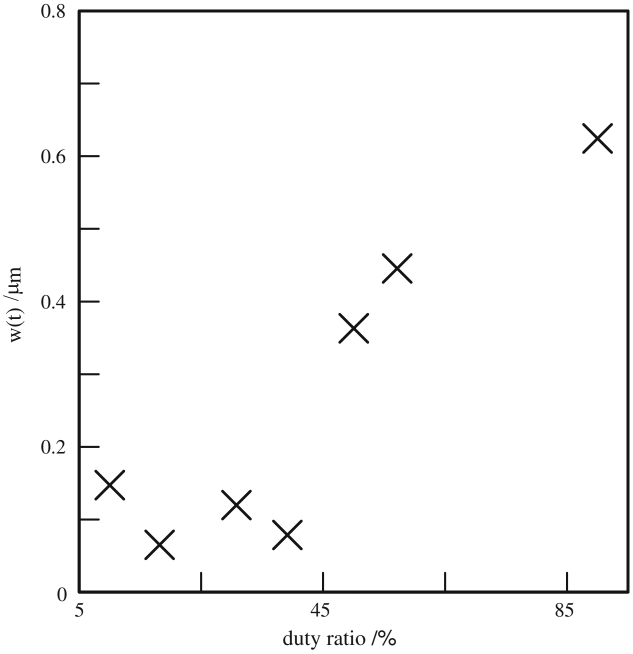

Fig. 6 Plot of w(t) versus duty ratio at J_p of 12 mA cm^{-2}. Duty ratio defined by $T_{on}/(T_{on} + T_{off})$

Figure 6 shows the dependence of w(t) on the duty ratio. Initially, w(t) has a value of 0.1 ± 0.04 µm. An abrupt change in w(t) is observed when the duty ratio is approximately 50%, as seen in Fig. 6. This rapid increase occurs when $T_{on} = T_{off}$.

In summary, the growth conditions, $T_{on} < 10$ ms and $T_{off} > 12$ ms are necessary to obtain silver deposits with minimal surface roughness. From Fig. 1, it is apparent that silver electrodeposits with smooth surfaces can be obtained by appropriate selection of T_{on} and T_{off}.

As stated in the Experimental Setup section, potassium sodium tartrate acts not as a growth inhibitor but as a stabilizer of the electrolyte.

4 Conclusions

The effect of the three parameters, J_p, T_{off}, and T_{on} on the surface roughness of silver thin films was investigated using confocal laser scanning microscopy. The experimental results show that:

(1) w(t) decreases rapidly for larger values of T_{off} rather than T_{on}
(2) a larger value of T_{on} results in an increases in w(t), and
(3) for a sufficiently large T_{off} (in comparison with T_{on}), w(t) decreases with J_p.

In this study, we have shown that silver electrodeposits with minimal surface roughness can be obtained by appropriate selection of T_{on} and T_{off}.

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