Concentration dependence of the morphology of electrodeposits and a criterion for the morphological change of copper electrodeposits

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The morphology of copper electrodeposits from acidic copper sulphate solution was studied at various copper sulphate concentrations and at relatively low overpotentials. The morphology at the various concentrations was not affected much by the current density, but rather by the overpotential. The evolution of 3–D nuclei was found to be a possible cause of the morphological change, since the critical overpotential for the evolution had a nearly constant value despite the concentration change. Unfortunately, a quantitative explanation of the data are not yet possible.

1. Introduction

The morphology of electrodeposits is determined by the selection of plating bath conditions and the current density or applied potential. The mechanism by which morphology appears at very high current density (under limiting current conditions) has been actively studied by Ibl [1, 2]). However, we could not find similar studies at lower overpotentials. Moreoever, there is uncertainty about the criterion for morphological change in this region. For example, Damjanovic, Setty and Bockris [3] mentioned briefly that the morphology of copper electrodeposits from acidic solution did not change with the variation of copper sulphate concentration at the same current density. This has not been generally accepted. The confusion seems to be caused by the lack of a common cause for the morphological change.

We considered the possible cause could be the evolution of nucleus. The nucleus can be distinguished by two types: 2–D nuclei and 3–D nuclei. The mechanism of nucleation has been studied extensively using a theoretical approach [4–10]. Moreoever, 2–D nucleation was experimentally surveyed by Budewski *et al.*'s elegant technique, in which they studied silver electrodeposition on dislocation-free or -controlled silver single crystal [11]. The 3–D nucleation is commonly observed on electrodeposition under diffusion controlled current density conditions. However, 3–D nucleation has been observed by a few workers even at relatively low current (or overpotential) in the early stage of the deposition [12–14]. Here, we have studied whether the evolution of the 3–D nucleus could be a cause for the morphological change, and also the factors which would control the type of nucleation.

2. Experimental procedure

A polycrystalline copper disc of purity 99.9% was used as a working electrode. The electrode was mechanically polished with alumina powder, and rinsed with acetone then triply distilled water. After these treatments, the electrode was electropolished in 50 vol% phosphoric acid solution at a current density of $0.6\,A\,cm^{-2}$ for four minutes. Then it was rinsed again with triply distilled water. The electrode was used as the working electrode. The counter electrode was a copper plate, whose surface area was much greater than the working electrode's in order to avoid the concentration

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change of cupric ion during the measurement. A copper plated copper rod embedded in Teflon was employed as the reference electrode. The potential was sometimes monitored by a Hg_2SO_4/Hg electrode. The potential of the copper reference electrode remained very stable throughout the measurements.

The solutions employed were x mol dm^{-3} ($x = 5 \times 10^{-3}$ to 5×10^{-1}) copper sulphate + 1.0 mol dm^{-3} sulphuric acid solutions. They were prepared by using special grade reagents and triply distilled water. The cell was manufactured with acrylate resin. After the electrodes were set up, about 150 cm^3 of solution was introduced into the cell. Argon was bubbled through the solution and the solution was stirred by a magnetic stirrer. All the measurements were performed potentiostatically and at ambient temperature. The electrode deposits were observed by a scanning electron microscope (Japan Electron Optics Laboratory Co. JSM-20).

3. Results and discussion

3.1. Morphological changes with the variation of overpotential and of the charge passed

The morphology of copper electrodeposits from acidic baths on poly or single crystal copper electrodes has been widely studied and our results were essentially similar. The characteristics of the deposits are shown in Table 1. At lower overpotentials than -0.060 V, the morphology was principally epitaxial. The grain size was about the same as the substrate's up to c. 20 C cm^{-2} of electrodeposition, then the size increased gradually and the surface of the deposits became smooth.

The shapes observed at the overpotentials higher than -0.150 V were very different from the ones at the lower overpotentials. In the early stage of deposition, powder-like 3–D nuclei appeared, then grew in size. On exceeding 10 C cm^{-2} of deposition, the shape of the deposits changed to an irregular aggregate of small crystallites. Further electrodeposition led to the appearance of pyramidal and/or block shapes with smooth surface and grape-like aggregates which were formed from small crystallites, in the irregular structure mentioned above. The overpotential range between these seemed to be a transition region. The shapes resemble those at low overpotentials, but the 3–D nuclei also appeared in the early stage of electrodeposition. The 3–D nuclei were incorporated in the growth mode of the layer type and disappeared as the deposition progressed. The typical features are shown in Fig. 1.

The morphology of deposits was not affected very much on decreasing the concentration of copper sulphate (Fig. 2), although the current density–potential curves were different (Fig. 3). In Fig. 3, it must be noted that the ordinate is overpotential not potential because of the reference electrode used. We could not see significant changes between two sets of the experiments with the same overpotentials and number of coulombs but different concentration at least from the viewpoint of the 3–D nuclei.

Damjanovic, Setty and Bockris [3] did comment briefly on the morphological change of copper electrodeposits from acidic solutions and reported that there was no appreciable change in the shapes at the same current densities but with the different concentrations of copper sulphate.

Table 1. Morphology of copper electrodeposits

| η	Charge density (C cm^{-2})					
	1	5	10	20	50	100
$< |-0.06|$ V	Layer growth, ridges			Smooth grains, expansion of grains, disappearance of ridges		
-0.07 to -0.12 V	Layer growth, ridges, 3-D nucleation and growth			Smooth grains, rearrangement and disappearance of 3-D nuclei		
$> |-0.15|$ V	3-D nucleation and spherical growth		Fine crystallites, irregular granules		Fine crystallites, pyramids or blocks, grape-like aggregates	
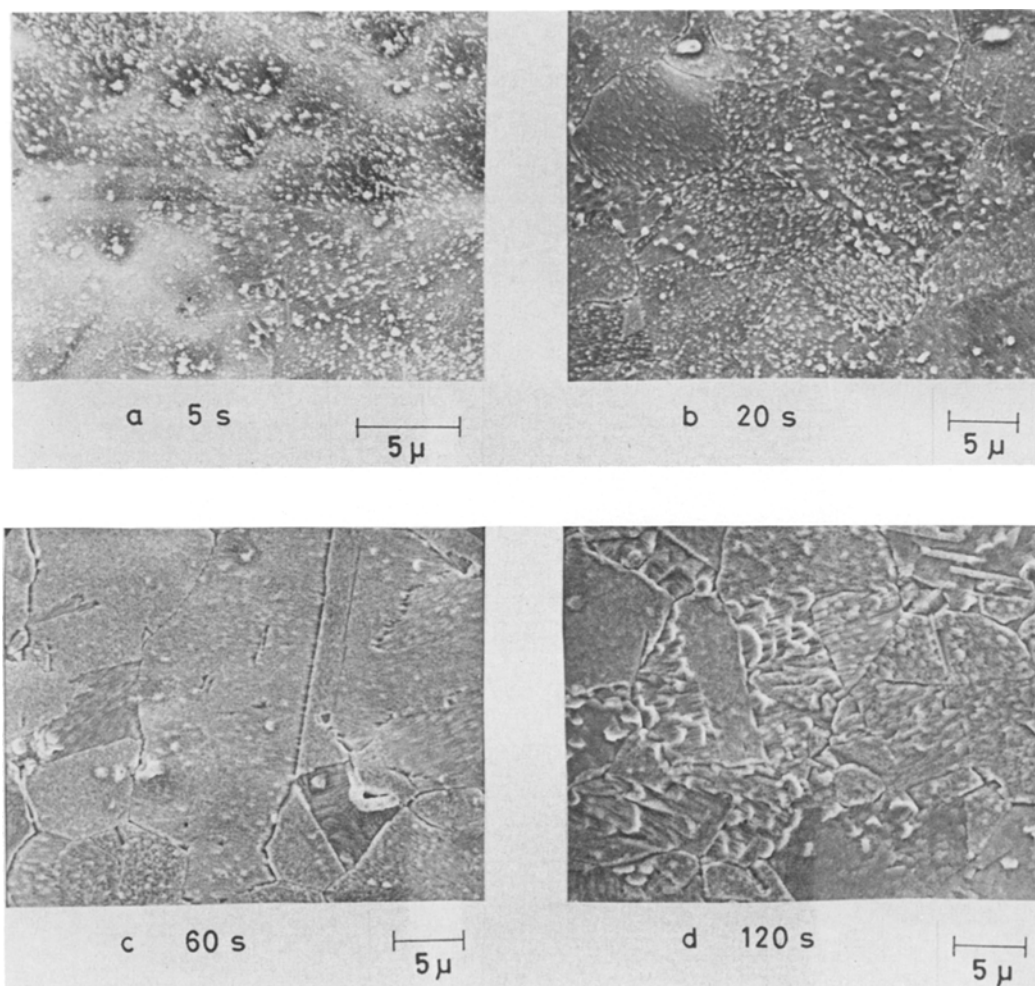
Fig. 1. Evolution and disappearance of 3–D nuclei, $\eta = -0.071$ V.

We think the difference occurs because of a difference in the thickness of the deposited layer. As mentioned above, we also observed that the appearance of deposits became similar when the deposition was continued long enough.

3.2. Overpotential dependence of 3–D nuclei formation

Here, we redefine the term '3–D nucleus', which has been already used in this paper, as a small granule which can be observed by means of scanning electron microscope at the magnification of 500. So, it may be noted that the 3–D may have a different meaning from the 2–D or the 3–D which were treated theoretically and experimentally by several workers [4–14]. Many of these studies used the microscopic view point.

The densities of the 3–D nuclei from the three copper sulphate solutions of different concentrations varied with the variation of overpotentials as shown in Fig. 4. A significant concentration dependence could not be observed and all the data showed the disappearance of the 3–D nuclei around -0.070 V. The critical overpotentials are plotted versus concentration in Fig. 5. The charge for the electrodeposition was $1\,\mathrm{C\,cm^{-2}}$ or $0.1\,\mathrm{C}$ $\mathrm{cm^{-2}}$. The current densities varied greatly, but the critical overpotentials did not vary with the concentration. This behaviour implies that the 3–D nucleus formation is controlled not by current density, but by overpotential.
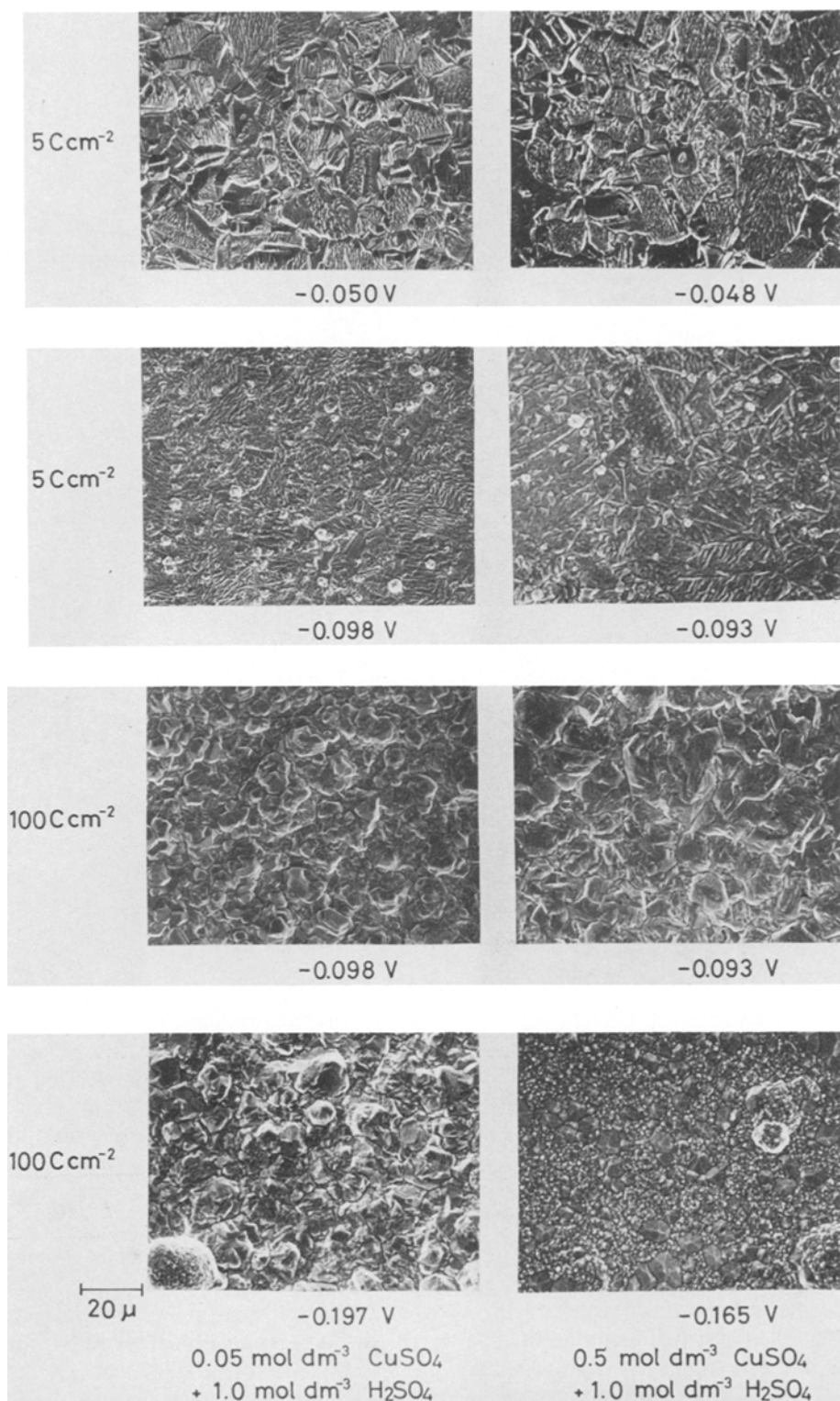
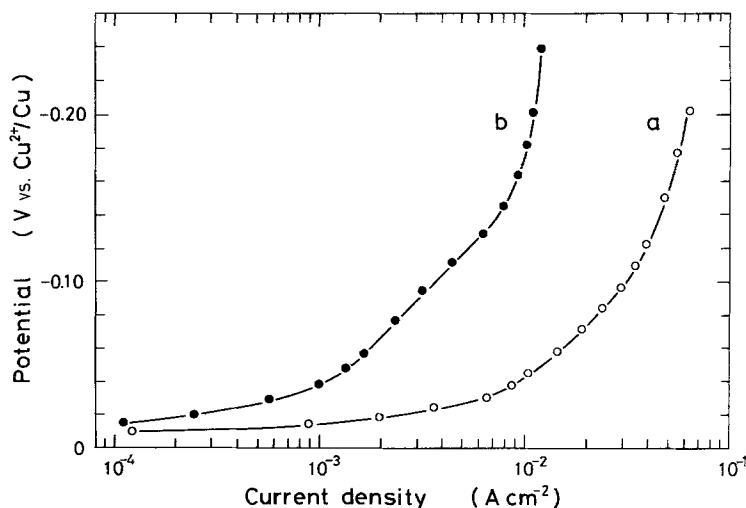Fig. 2. Morphologies of copper electrodeposits from two different concentrations of $CuSO_4$.

Fig. 3. Potential–current density curves, (a) 0.5 mol dm^{-3} CuSO$_4$ + 1.0 mol dm^{-3} H$_2$SO$_4$, (b) 0.05 mol dm^{-3} CuSO$_4$ + 1.0 mol dm^{-3} H$_2$SO$_4$.

In the overpotential region well below the limiting current density region, a few workers have observed this kind of 3–D nucleus in acidic copper sulphate solutions with the relatively high concentrations (e.g., 0.5 mol dm^{-3}) and the current densities around 10 mA cm^{-2}. Most of them did not comment but Vaughan and Pick [14] considered the phenomenon would be caused by the effect of impurities (Cu$_2$O, Cu$_2$S, etc.) on the electrode surface. However, Lacmann and Möller [15] showed that impurities were not important; they performed copper electrodeposition on platinum single crystal electrode from pure solutions. Nucleation was found at low overpotential and the critical overpotential, about $-$ 0.016 V had no concentration dependence.

The supply of atoms by electron transfer exceeding the maximum rate of incorporation into the lattice on the electrode, could be the cause for the 3–D nucleation. The 3–D nucleus is incorporated into the other types of morphological growth and disappears if the overpotential region is not very high. This can be seen in Fig. 6 which shows the densities of the 3–D as a function of deposition time. The decreasing features can be sorted into two types, one is monotonously decreasing with time and the other is decreasing accompanied with a plateau. The former corresponds to the situation where 3–D nucleation occurs but the 3–D centres disappear again by their incorporation into later layers. The latter corresponds to the overpotential at which another type of 3–D nuclei (fine crystallites for the limiting current condition) are formed and it still remains even after further electrodeposition.
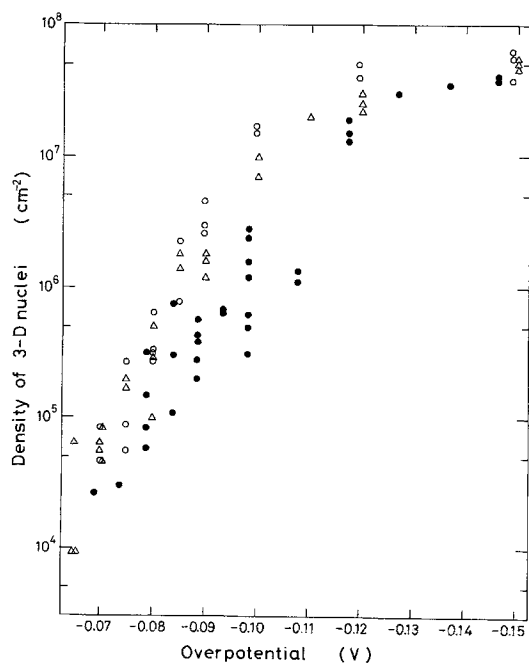
3.3. Characteristics of 3–D nuclei as a function of E–t programme

The density of 3–D nulcei was affected by the mode of pulse applied. The typical results are shown in Fig. 7. The following features should be noted:
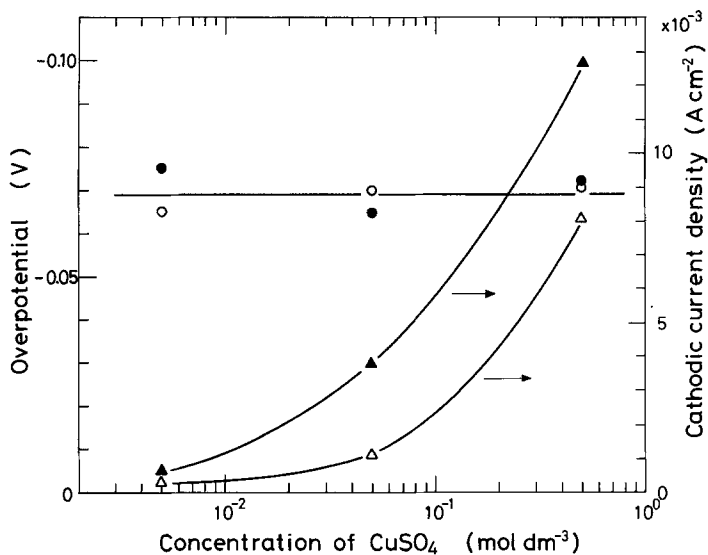

Fig. 4. Overpotential dependence of 3-D nuclei density at 1 C cm^{-2}. CuSO$_4$ concentration; ($\bullet$) 5 $\times$ 10^{-1} mol dm^{-3}, (o) 5 $\times$ 10^{-2} mol dm^{-3}, ($\triangle$) 5 $\times$ 10^{-3} mol dm^{-3}.

Fig. 5. Concentration dependence of critical overpotentials for 3–D nucleation (○, ●) and the current densities (△, ▲). (○, △) $1 \, C \, cm^{-2}$, (●, ▲) $0.1 \, C \, cm^{-2}$.
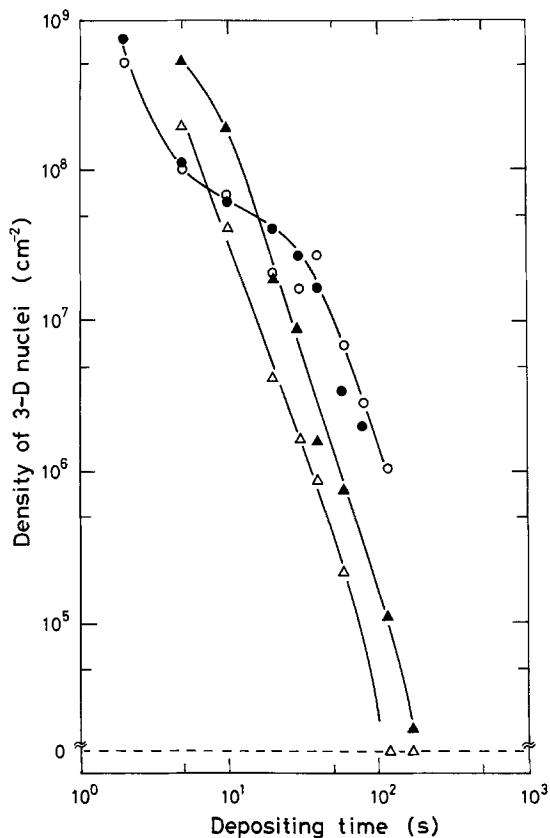
Fig. 6. Decrease of 3–D nucleation density with depositing time in $0.5 \, mol \, dm^{-3} \, CuSO_4 + 1.0 \, mol \, dm^{-3} \, H_2SO_4$. Overpotentials; (△) $-0.071 \, V$, (▲) $-0.087 \, V$, (○) $-0.123 \, V$, (●) $-0.157 \, V$.
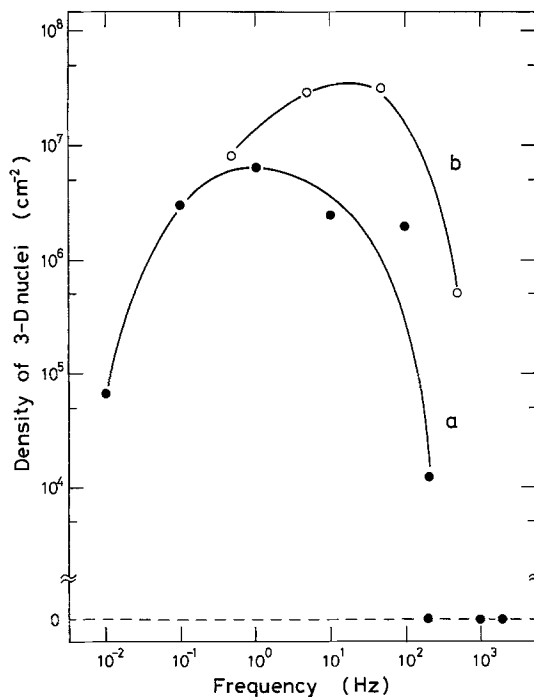
Fig. 7. Frequency dependence of 3–D nucleation density in $0.5 \, mol \, dm^{-3} \, CuSO_4 + 1.0 \, mol \, dm^{-3} \, H_2SO_4$. (a) ON $-0.175 \, V$, OFF $-0.050 \, V$, ON duration 3%, (b) ON $-0.175 \, V$, OFF $0 \, V$, ON duration 50%.

1. The density decreased both at high and at low frequencies and there was a maximum.

2. The value of lower overpotential part of the pulse (called OFF, as opposed to ON.) did not influence the appearance of the 3–D nuclei. However, the density of 3–D nuclei was lowered whether the OFF overpotential was selected to be positive or negative.

The latter may occur because of the decrease in the 3–D nucleation density at the cathodic OFF overpotential promoting the incorporation of the 3–D nuclei into the layer growth. The decrease at the positive OFF overpotential would be caused by the lower probability of the growth since the dissolution reaction takes place at OFF. The dependence on frequency may be explained as follows. The main difference between the different frequencies would be the different durations of the ON part and the effect of charging and discharging of double layer at high frequencies. In Fig. 7, the maxima and the frequencies of disappearing 3–D for (a) and (b) have the same duration as the ON part. The decrease at low frequencies may result from the same cause as for 2.

3.4. Significance of 3–D nucleation

As mentioned in the above sections, the critical overpotential for observing 3–D nucleation was above -0.070 V and this was independent of the concentration. The only exceptions in the present study were the following two conditions where higher overpotentials than the critical value did not bring about the 3–D nucleation. One was the case of a short duration ON pulse, and the other was the case where the electrodes were pre-deposited at overpotentials at which the morphology of the deposit is layer growth type, that is, relatively low overpotential values.

It is obvious that the former case is caused by the effect of double layer charging and discharging. For the latter case, it is true that there was no observable 3–D nucleation, but the morphology was similar to that when 3–D nucleation occurred but was later incorporated to the layer growth. Anyhow, the mechanism of electrodeposition would be expected to change at a critical overpotential which is lower than -0.070 V.

Above the critical overpotential, so-called 'lateral growth' and 'adhesive growth' could co-exist. Here, 'lateral growth' means the growth mode where deposits are formed by fitting to the matrix electrode lattice, i.e., epitaxially, and 'adhesive growth' is when there is a lattice misfit. The ratio of 'adhesive growth' increases with increasing overpotential, as a result, the deposit finally becomes powder like under limiting current density conditions. On the other hand, below the critical overpotential, the only possible mode would be 'lateral growth', and there is no 3–D nucleation.

4. Conclusion

Copper electrodeposition on polycrystalline copper in acidic solutions was studied. The morphology of deposits was determined not by the current density, but by the overpotential. 3–D nucleation in the early stage of electrodeposition was proposed to be a possible cause for the morphological change.

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