Effect of superimposed square wave alternating current during electrowax- 

tallization of copper on copper single crystal planes

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The morphology of copper electrodeposits on copper single crystal planes is affected by superimposing a square wave alternating current (ac) on a direct current (dc). The effects of 'ac' are discussed from the morphological point of view and from the cathodic polarization studies. In the presence of superimposed 'ac' on the (111) plane, hexagonal and triangular pyramids observed in purified acid copper sulphate bath truncate and change to layers, then to a truncated triangular block and finally to polycrystalline type of deposit. Layer type of deposit observed on (100) plane transforms to truncated square pyramidal blocks and finally to polycrystalline deposit. On the (110) plane, ridges break up and give rise to a polycrystalline deposit. It was found that a superimposed 'ac' has a depolarising effect. The mechanism of the deposition process is discussed.

Alternating current is widely used for its signifi-
cant influence on many electrode processes and in electronal investigations such as the double layer studies, the rates of formation and dissolution of oxide films, electrodeposition and dissolution of metals and alloys. Reports indicate that 'ac' can affect the grain size, brightness and porosity of electrodeposited metals. It is also reported that internal stresses in the electrodeposited nickel are reduced by superimposition of 'ac' on 'dc'. Superimposed 'ac' have been used on 'dc' in electrodeposition of Ni-Fe alloys and it has been shown that the alloy composition can be suitably altered by a known amount of 'ac' superimposed on 'dc'. However, the mechanism of the effect of 'ac' in electrodeposition of metals and alloys has so far not been adequately explained. Moreover, there are very few data on the structure of the deposits obtained under these conditions.

It is known that the physical properties of electrodeposits which are generally crystalline depend on the type of crystals that are grown at the cathode. Hence it is of interest to investigate the effect of 'ac' during electrowaxellation on single crystal planes of metals. Various current forms obtained through a simultaneous use of 'dc' on 'ac' voltages in electrolysis may have significant effects on the morphology of electrodeposited metals on single crystal substrates.

Superimposing sinusoidal 'ac' on 'dc' has also shown to produce levelling effect during electrowaxellation of metals at low dc densities and also enhances the degree of epitaxy during growth of metals like lead and zinc on copper single crystal planes. In view of the above, the present work has been carried out in order to deposit copper on copper single crystal planes in the presence of superimposed square wave 'ac' of various frequencies on low dc densities.

Experimental Procedure

A 90 V battery was used as a constant 'dc' source. Alternating current (10-50 Hz) stabilized to maintain a galvanostatic conditions was superimposed on dc by means of a circuit described earlier. The ac densities (peak to peak) were always higher than the dc, so that only the effect of 'current with an anodic component' (asymmetric square wave ac) was studied.

Single crystal copper cathodes were fixed in Tygon tubing so that only the desired face of the crystal was exposed, namely (111), (100) and (110). Each single crystal plane was first mechanically polished together with the Tygon tubing using emery 4/0 paper with ethanol as lubricant. After mechanical polishing the crystal was electropolished in 50% orthophosphoric acid at 1.2 V for 30 min. The crystal after electropolishing was washed with 10% phosphoric acid then with triple distilled water and was immediately transferred to the deposition cell. A polycrystalline copper foil (AR) was used as a cathode. A freshly prepared copper electrode was used as a reference electrode.

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As the superimposed 'ac' density was increased to 12.5 mNcm², a large number of triangular blocks were noticed in the layer background (Fig. 1c). At 5 mNcm² ac, it was found that the deposit was smooth and bright polycrystalline type (Fig. 1d).

The effect of 'ae' frequency on the deposit morphology at the corresponding 'ac' densities superimposed on 5 mNcm² was investigated. It was found that at higher frequencies the effect of superimposed 'ac' on 'dc' in bringing about the changes in deposit morphology was less pronounced.

Effect of 10 Hz square wave 'ac on (100) plane—A layer type of deposit (Fig. 2a) (along [100] directions and [010] is diagonal to [100] directions) was obtained when copper was deposited from a highly purified acid copper sulphate bath at a 'dc' density of 5 mA/cm² as observed by earlier workers. There was no appreciable change in the morphology of copper deposit when the 'ac' density of 5 mA/cm² was superimposed. At 5 mA/cm² dc + 7.5 mA/cm² ac, most of the hexagonal pyramids became truncated (Fig. 1b) and grew sideways producing macrotips. As the superimposed 'ac' density was increased to 12.5 mA/cm², large number of triangular blocks were noticed in the layer background (Fig. 1c). At 5 mA/cm² dc + 25 mA/cm² ac, it was found that the deposit was smooth and bright polycrystalline type (Fig. 1d).

The effect of 'ac' frequency on the deposit morphology at the corresponding 'ac' densities superimposed on 5 mA/cm² was investigated. It was found that at higher frequencies the effect of superimposed 'ac' on 'dc' in bringing about the changes in deposit morphology was less pronounced.

Effect of 10 Hz square wave 'ac' on (111) plane—Hexagonal and triangular pyramids (Fig. 1a) with steps on their sides were observed on copper (111) substrate from highly purified acid copper sulphate bath at a dc density of 5 mA/cm² as observed by earlier workers. There was no appreciable change in the morphology of copper deposit when the 'ac' density of 5 mA/cm² was superimposed. At 5 mA/cm² dc + 7.5 mA/cm² ac, most of the hexagonal pyramids became truncated (Fig. 1b) and grew sideways producing macrotips.
posed 'ac' density gradually increased. Truncated pyramids and blocks more nearly completely covered the surface and the layers in the background gradually disappeared (Fig. 2c) at 5 mA/cm² dc + 7.5 mA/cm² ac. At 5 mA/cm² dc + 17.5 mA/cm² ac only a polycrystalline type of deposit was noticed (cf. Fig. 1d).

The effect of 'ac' frequency on the deposit morphology at the corresponding 'ac' densities superimposed on 5 mA/cm² dc was examined. The effect of increased 'ac' frequency on the type of deposit produced on (100) plane was less significant compared to those observed at a frequency of 10 Hz.

Effect of 10 Hz square wave 'ac' on (110) plane—A ridge type of deposit (Fig. 3a) was observed when copper was deposited on (110) substrate from a highly purified acid copper sulphate bath at a 'dc' density of 5 mA/cm². These ridges were aligned along [100] direction. There was no appreciable effect of superimposed 'ac' up to 10 mA/cm² on the morphology of the deposit. At 5 mA/cm² dc + 15 mA/cm² ac the ridges gradually broke up (Fig. 3b) and the broken ridges gradually transformed to polycrystalline deposit (cf. Fig. 1d) at a superimposed 'ac' density of 17.5 mA/cm².

The effect of variable frequency at corresponding 'ac' densities on the deposit type on (110) plane was examined. Even though the effect of 'ac' frequency on the deposit morphology was similar, the effect becomes less and less significant when the superimposed 'ac' frequency was increased.

Overpotentials

On copper (111) plane the overpotential during deposition decreases with time and attains a
steady value when copper was deposited from a highly purified acid copper sulphate bath at a ‘dc’ density of 5 mA/cm². When different amounts of ‘ac’ were superimposed at a fixed frequency of 10, 30 and 50 Hz the cathodic overpotentials were always found to be lower compared to the values obtained with ‘dc’ alone. However, the trend in the variation of overpotential with time was unaffected in the presence of superimposed ‘ac’ at all frequencies. The steady state value of overpotential was observed more or less at the same thickness of the deposit. Fig. 4 shows a typical plot of cathodic overpotential with thickness of the deposit on copper (111) plane in the presence of various superimposed ‘ac’ densities at a fixed frequency of 10 Hz on a ‘dc’ density of 5 mA/cm².

On copper (100) plane the cathodic overpotential during deposition increases with time and attains a steady state value when copper was deposited from a highly purified solution. When deposition was carried out in the presence of superimposed ‘ac’ of various current densities and frequencies the overpotential values were always lower than those obtained in pure dc. The steady state attainment of overpotential was more or less the same in the presence of superimposed ac. The variation of cathodic overpotential with thickness in the presence of various amounts of superimposed square wave ‘ac’ at a fixed frequency of 10 Hz on (100) plane at a dc density of 5 mA/cm² is indicated in Fig. 5.

On a (110) plane the cathodic overpotential during deposition increases slightly with time and attains a steady state when copper was deposited from a highly purified acid copper sulphate bath at a dc density of 5 mA/cm². The cathodic overpotential values obtained in the presence of various amounts of the superimposed square wave ac at different frequencies were always lower compared to the pure solutions. However, the trend in the variation of overpotential with time and the attainment of steady state was very much similar to those observed in pure dc. Fig. 6 indicates the variation of cathodic overpotential with thickness on copper (110) plane in the presence of various amounts of superimposed ac density at a fixed frequency of 10 Hz on a dc density of 5 mA/cm².

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**Fig. 4**—Variation of cathodic overpotential with thickness on the (111) plane at (a) 5 mA/cm² dc and in the presence of superimposed ac; (b) 5; (c) 10; (d) 15 and (e) 30 mA/cm².

**Fig. 5**—Variation of cathodic overpotential with thickness on the (100) plane at (a) 5 mA/cm² dc and in the presence of superimposed ac; (b) 5; (c) 10; (d) 15; (e) 20 and (f) 25 mA/cm² ac.

**Fig. 6**—Variation of cathodic overpotential with thickness on the (110) plane at (a) 5 mA/cm² dc and in the presence of superimposed ac; (b) 5; (c) 10; (d) 15; (e) 20; (f) 25 and (g) 30 mA/cm².
Table 1—Tafel slopes \( (b) \) and exchange current densities on various crystal planes in the presence of superimposed ac and in pure dc

<table>
<thead>
<tr>
<th>Crystal plane</th>
<th>In the presence of superimposed ‘ac’</th>
<th>In pure dc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \frac{d\eta}{d\log i}, \text{mV} )</td>
<td>( i_0, \text{mA/cm}^2 )</td>
</tr>
<tr>
<td>(100)</td>
<td>110.3</td>
<td>2.0</td>
</tr>
<tr>
<td>(110)</td>
<td>108.9</td>
<td>2.8</td>
</tr>
<tr>
<td>(111)</td>
<td>129.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Tafel plots were constructed for the deposition process of copper on copper (111), (100) and (110) planes in the presence of various superimposed ‘ac’ densities. The steady state overpotentials are utilized to construct the Tafel plots. Table 1 gives the Tafel parameters on various copper single crystal planes in the presence and absence of superimposed ac.

In analysing the effect of superimposed ‘ac’ on ‘dc’ the current flowing in the reverse direction—the anodic component current should be taken into account. The periodic combinations of the current of the ‘anodic component’ and the subsequent ordinary process of electrodeposition (during dc) may account for the observed changes in the morphology.

The effect of base orientation on the surface topography of copper single crystal planes suggests that characteristic growth occurs on the copper single crystal planes during electrodeposition in pure dc. On the (111) plane, formation of hexagonal and triangular and layers and square pyramids on (100) plane can be accounted for by the screw dislocation mechanism of growth. It is known that the pyramids formation is favoured by a mechanism involving a pair of screw dislocations of opposite signs. Macrosteps on the side faces of pyramids form by initial bunching of small, ideally monoatomic steps, which originate at the apex of pyramids. The bunching mechanism is supported by the fact that no visible steps appear close to the apex of the pyramids. On the (110) plane pyramidal growth does not occur, only ridges appear under the current density ranges investigated. It is likely that on a perfect (110) plane any site is a growth site and there is no need for surface diffusion of ions to propagate microsteps. For pyramidal growth, the propagation of microsteps is essential and hence no pyramids would be expected to form on (110) plane.

When the square ‘ac’ of different magnitudes (cd) and frequency was superimposed on dc, on (110) plane the pyramids truncate because during the anodic component of ac the apex of the pyramids dissolves, as these are the active sites and hence no microsteps generate from the apex and the pyramids truncate. During deposition in the cathodic cycle, the truncated pyramids can grow only sideways producing macrosteps which are seen in Fig. 1b. At a higher values of superimposed ‘ac’ on ‘dc’ small triangular pyramids and blocks nucleate along with layers. They completely spread over the surface in the direction of the crystal growth at higher values of superimposed ac. When the critical value of the superimposed ‘ac’ is reached random nucleation leads to the formation of smooth fine grained, levelled polycrystalline deposit.

On the (100) plane, at low superimposed ‘ac’ values the distance between the macrosteps decreases and macrosteps dissolve in the anodic current and in the cathodic cycle cubical layers truncated blocks grow. With increase in the value of superimposed ac density more of such cubical layers and blocks nucleate and completely covers the surface. At a critical superimposed ac density value smooth, levelled and bright polycrystalline deposit is produced similar to that observed on (111) plane.

On the (110) plane on superimposing ac on dc, the ridges dissolve during the anodic current of ac and during cathodic cycle deposits randomly. At a critical ac current density value, bright, levelled smooth deposit is produced.

It is observed that the effect of square wave ac superimposed on dc during electrocrystallisation was very much pronounced at an ac frequency of 10 Hz compared to 50 Hz. This is because at low frequency the effect of anodic current in the anodic cycle is present for a longer period of time and hence one can expect marked influence of current reversal at low frequencies on electrocrystallisation of copper. At higher frequencies of ac (50 Hz) superimposed, the current reversals has less pronounced effect on the electrogrowth of copper during deposition. This is due to the rapid cathodic and anodic cycles at higher frequencies which do not affect either the growth in the cathodic cycle or dissolution in the anodic cycle of ‘ac’ at higher frequencies.
The variation of overpotential with time during electrocrystallisation of copper on various planes have been thoroughly explained\textsuperscript{17,21}. The variation of overpotential with time during electrodeposition of copper on various copper single crystal planes has also been explained and an empirical equation has been proposed:

\[
i = [(1 - A) i_{0(111)} + i_{0(100)}] \exp \left[ -\frac{a \eta F}{RT} \right]
\]

where \(i_{0(111)}\) is exchange current density for the newly formed faces, when pyramids grow on the (111) face and \(A\) is the area of the newly formed face.

If \(i_{0(100)} > 10 i_{0(111)}\), the above equation can be written as:

\[
i = [i_{0(111)} + A i_{0(100)}] \exp \left[ -\frac{a \eta F}{RT} \right].
\]

If \(A\) increases by 0.1, then the decrease in overpotential on the (111) plane is substantial. The attainment of the steady state value has also been explained. As the base of the pyramids are also stepped and the macrosteps on the pyramidal faces continue to grow, the surface activity becomes uniform. Hence the overpotential attains a steady state value.

On the (100) plane, in contrast to the (111) plane, the overpotentials generally increase with time of deposition. The extent of increase is, however, far less than the decrease on the (111) plane. This behaviour can be explained in terms of changing the overall activity of the electrode surface.

\(i_{0(100)}\) is larger than \(i_{0(111)}\) and when new faces are formed on (100) plane their effect would be less than the corresponding effect on the (111) planes, were the newly formed faces close to, for instance, the (111) plane, it would be expected that the effect should be the opposite one in that for deposits on the (111) plane, namely the overpotential should increase with time of deposition since more active surface is replaced by less active \{111\} plane. In fact, no large change in overpotential would be expected since the replacement of a small area of active surface by less active surface is far less effective as far as potential change is concerned; than the reverse process. It is possible that initially the electrode surface corresponds to some higher index plane due to misorientation arising, for instance, from electropolishing. Soon, growth results in a smoothing out of the surfaces which become parallel to the (100) plane. Hence overpotential increases with time and then becomes constant.

The exchange current density is higher for the (110) plane than for the other two crystal planes considered. Time dependence of overpotential on the (110) plane is less than the other planes. The overpotential slightly increases on the (110) plane and attains a steady state value. This may be because the faces of the ridges when they grow along [001] direction may correspond to the activity of \{100\} planes. Then the change of overpotential is not significant as the increased surface area is gradually replaced by less active \{100\} plane.

The dependency of overpotential with time has been attributed to the activity of the crystal planes during electrocrystallisation. However, superimposed 'ac' shows a depolarising effect during electrocrystallisation of copper indicating the facilitation of deposition process at lower overpotentials.

The theoretical rate equation for the charge transfer process is

\[
i = i_{0} \exp \left( \frac{a F \eta}{RT} \right) - \exp \left( -\frac{(1 - a) \eta F}{RT} \right)
\]

where \(i\) is the current density, \(i_{0}\) is the exchange current density, \(a\) is the transfer coefficient and \(\eta\) is the activation overpotential. \(R\), \(T\) and \(F\) have their usual significance. At high irreversibilities, i.e., \(\eta > 50\, \text{mV}\) the above equation reduces to

\[
i = i_{0} \exp \left( \frac{a F \eta}{RT} \right)
\]

So, for a cathodic process

\[
\eta = -2.303 \frac{RT}{aF} \log i_{0} + 2.303 \frac{RT}{aF} \log i
\]

Therefore, Tafel equation is

\[
\eta = a + b \log i
\]

where \(a = \pm 2.303 \frac{RT}{aF} \log i_{0}\)

and \(b = 2.303 \frac{RT}{aF}\)

The Tafel parameters deduced from Butler-Volmer equation were evaluated for the deposition process in pure dc as well as in the presence of superimposed ac. Table 1 indicates that the first electron transfer is the rate determining step:

\[
\text{Cu}^{++} + e \rightarrow \text{Cu}^{+}
\]

\[
\text{Cu}^{+} + e \rightarrow \text{Cu}
\]
This is in accordance with the observation of Mattson and Bockris\textsuperscript{22} for the copper deposition process.

**Conclusion**

It has been, therefore, concluded that the superimposed square wave 'ac' shows significant levelling effects at low frequencies on the morphology of copper electrodeposits on copper single crystals as well as cathodic polarisation during electrodeposition of copper. The effect of sine wave ac as observed by earlier works in affecting the morphology of copper deposits on copper single crystal planes is less in magnitude compared to the effect of square wave ac of same frequency and amplitude.

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**References**