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A novel preparation of gold films by electrodeposition at the interface between a $Na(AuCl_4)$–$CuSO_4$ aqueous phase and an immiscible hexyl acetate organic phase

T. MITSUI, H. KANEKO

Department of Materials Engineering and Applied Chemistry, Mining College, Akita University, Tegata-Gakuencho 1-1, Akita 010, Japan

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Electrolysis at the interface between a $Na(AuCl_4)$–$CuSO_4$ aqueous phase and an immiscible hexyl acetate phase resulted in continuous growth of gold films along the interface. To maintain filmy growth of gold, it was effective to stimulate displacement of predeposited copper with gold by applying a rectangular or triangular potential in a given range. Two types of electrodes were applied: from a point electrode the film grew concentrically like a blooming flower, and from a line electrode the film grew unidirectionally toward the counter electrode as a spreading wave. A long time electrolysis could be performed by circulating and filtering the aqueous solution. The film contained no trace of copper and was very thin ($<1\ \mu m$).

1. Introduction

In the conventional electrodeposition of metals on solid electrode substrates from aqueous solutions, electrodeposits grow perpendicularly on the substrates. However, it is known that electrodeposits grow two-dimensionally under specialized experimental conditions. The Hele–Shaw cell is a well-known example, in which metal deposits grow in planar dense-branching morphology [1]. As another example, Mylius and Fromm [2] found that a metal deposit in the morphology of a leaf grew on the surface of an aqueous solution which had been contaminated with an oily substance. This phenomenon at the interface, between an aqueous phase and an immiscible organic phase, was reinvestigated, and two growth patterns were found: filmy and branched growth [3]. Subsequently, films of metals, such as zinc [3], copper [4] and cobalt [5], were successfully prepared in appropriate conditions, and a new technique to produce metal films unidirectionally and continuously along the interface was developed [6]. In the case of gold, however, it was difficult to obtain filmy deposits with good reproducibility [7]. Recently, the authors obtained gold films at the interface by addition of Cu^{2+} in the aqueous phase; copper was deposited as a precursor for the deposition of gold. Here we report the experimental conditions for the filmy growth of gold at the interface between a $Na(AuCl_4)$–$CuSO_4$ aqueous phase and a hexyl acetate phase and the morphology of the films obtained.

2. Experimental details

Two kinds of apparatus were used. Figure 1 shows the apparatus for the point electrode method which resulted in the concentric growth of gold films. The electrolytic cell was a glass beaker (6 cm dia., 5 cm high) with a water jacket to circulate thermostated water. The working electrode (WE) was a gold wire (1 mm dia.), polished with emery paper (no. 1200) and washed with deionized distilled water prior to each electrolysis run. The counter electrode (CE) was a cylindrical gold plate (0.1 mm thick, 1 cm high, 5 cm dia.). An Ag/AgCl (sat. KCl) electrode was used as the reference (RE). Each experiment was performed according to the following procedure. A small amount (20 ml) of hexyl acetate was added carefully to an aqueous solution (100 ml) containing metal salts and a supporting electrolyte in the cell. The cylindrical counter electrode was placed concentrically with respect to the point working electrode in the aqueous solution. The tip of the Luggin capillary connected to the reference electrode was set up just beneath the working electrode. The tip of the working electrode had been positioned precisely at the interface by a micromanipulator, and then the electrolysis was carried out using a potentiostat and a function generator.

Figure 2 shows the apparatus for the line electrode method which resulted in the unidirectional growth of gold along the aqueous–organic interface. The basic procedure was similar to that mentioned above. The glass electrolytic cell was rectangular (10 cm wide, 20 cm long, 5 cm high) and was placed in a thermostated bath. A gold wire working electrode (0.2 mm dia., 9.5 cm long) and a gold plate counter electrode (0.1 mm thick, 9.5 cm wide, 1 cm long) were positioned as follows: the arm of the wire and the plane of the counter electrode were horizontal and coincided with the aqueous–organic interface. The volumes of the aqueous and organic phases were

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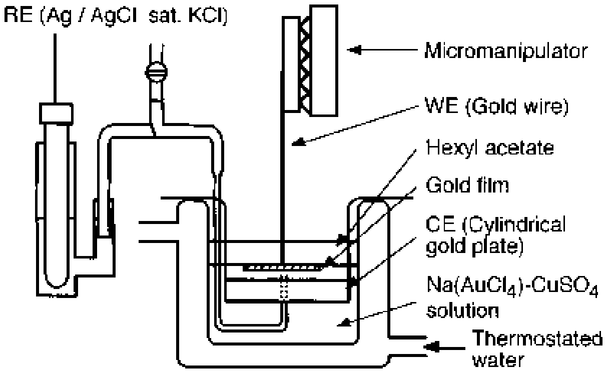

Fig. 1. Schematic diagram of the apparatus for the point electrode method.

200 ml and 50 ml, respectively. A mobile stage and a stepping motor were employed to move the counter electrode horizontally so that the distance to the growing front of the film could be kept constant at 2 cm. The Luggin capillary, connected to an Ag/AgCl (sat. KCl) reference electrode, was also attached to the mobile stage, its tip being maintained just beneath the growing front of the film. During the electrolysis run the solution became contaminated with detached gold particles. To remove the small suspended particles, the aqueous solution was circulated by a pump and filtered through a G4 filter. A low flow rate was necessary to prevent the interface from vibrating. A polyester sheet was positioned vertically between the counter and working electrode, traversing the aqueous and organic layers; this sheet prevented small particles of deposited metal, which had been generated and then become detached from the counter electrode, from contaminating the growing film.

All chemicals were reagent grade and used without further purification. A typical solution was prepared using deionized distilled water with $Na(AuCl_4) \cdot 2H_2O$ (0.01–0.02 M), $CuSO_4 \cdot 5\ H_2O$ (0.1 M) and $NaClO_4 \cdot H_2O$(0.1 M). In some experiments, acetic acid and its sodium salt (0.1 M each) were used as pH buffer reagents instead of $NaClO_4 \cdot H_2O$, but there was no noticeable change in the growth of the films. The above concentrations of the metal salts were preferred for filmy growth [4, 7]. The thermostated water (Fig. 1) or bath (Fig. 2) was maintained at 40 or 50 °C.

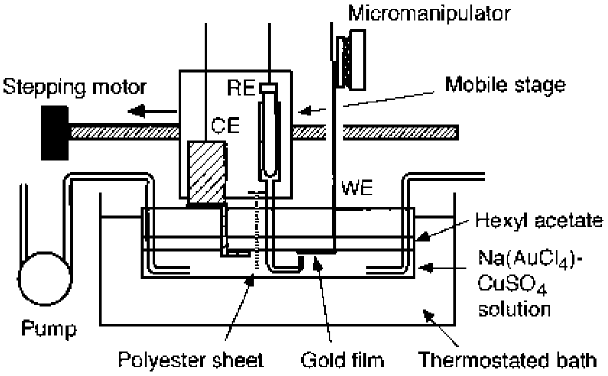

Fig. 2. Schematic diagram of the apparatus for the line electrode method.

3. Results and discussion

3.1. *Displacement reaction of copper with gold*

In a preliminary experiment, a film of gold containing a less noble foreign metal was reproducibly formed at the interface from an aqueous solution containing $Na(AuCl_4)$ and a foreign metal ion, but films were occasionally formed from a solution without the foreign metal ion. Therefore, it is preferable to add the foreign metal ion in the solution. Due to the displacement reaction, the less-noble foreign metal deposited as a precursor was displaced with gold. To investigate effective foreign metals, cobalt, copper, zinc and lead were tested. The result showed copper was the most effective, so that $CuSO_4$ was employed as a foreign metal salt in this study.

The electrode potentials of gold and copper at the interface between a $Na(AuCl_4)$–$CuSO_4$ aqueous phase and a hexyl acetate phase ([$Na(AuCl_4)$], 0.01 M; [$CuSO_4$], 0.1 M; [$NaClO_4$], 0.1 M; temperature, 50 °C) were +0.91 V and +0.19 V (vs Ag/AgCl sat. KCl), respectively. Cyclic voltammetry of a gold wire electrode at the interface between a $CuSO_4$ aqueous phase and a hexyl acetate phase ([$CuSO_4$]: 0.1 M; temperature: 25 °C; sweep rate: 10 mV s^{-1}) showed that the cathodic current increased from +0.05 V in the negative sweep. These suggest that the following reactions occur at a potential lower than +0.05 V:

$$AuCl_4^- + 3\,e^- \longrightarrow Au + 4\,Cl^- \qquad (1)$$

$$Cu^{2+} + 2\,e^- \longrightarrow Cu \qquad (2)$$

At a potential between +0.05 V and +0.91 V, the electrodissolution of copper (Reaction 3) and the displacement of copper with gold (Reaction 4) occur simultaneously with the electrodeposition of gold (Reaction 1):

$$Cu \longrightarrow Cu^{2+} + 2\,e^- \qquad (3)$$

$$3\,Cu + 2\,AuCl_4^- \longrightarrow 2\,Au + 3\,Cu^{2+} + 8\,Cl^- \qquad (4)$$

In this $Na(AuCl_4)$–$CuSO_4$ electrolyte, Cl^- exists in equilibrium with $AuCl_4^-$, so that Cl^- produces adsorbed CuCl on the electrode in the redox processes described above [8], although a detailed mechanism is beyond the scope of the present discussion.

Electrolysis at a potential lower than +0.05 V, for example at −0.2 V (vs Ag/AgCl sat. KCl), using the point electrode method resulted in a concentric filmy growth of metal with a good reproducibility. Analysis with an electron probe microanalyser (EPMA) showed that the metal film consisted of copper (85 at%) and gold (15 at%). To investigate the effect of mode of applied potential on the filmy growth, the following experiments were carried out. Cathodic potentials (E_c) were applied for 10 s to the working electrode by the point electrode method, and the resultant potential–time curves after switching off were

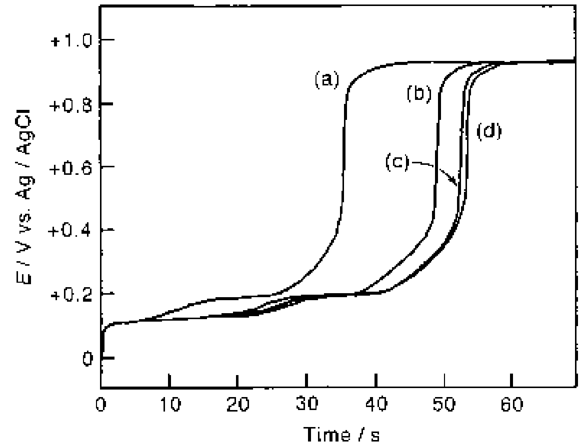

Fig. 3. Potential changes with time after the electrolysis run at E_c for 10 s by the point electrode method. E_c: (a) 0, (b) −0.1, (c) −0.2 and (d) −0.3 V. Conditions: temperature, 50 °C; [Na(AuCl$_4$)], 0.01 M; [CuSO$_4$], 0.1 M; [NaClO$_4$], 0.1 M.

recorded as shown in Fig. 3. Three plateaux were observed; these corresponded with the equilibrium of CuCl/Cu, Cu^{2+}/CuCl and AuCl$_4^-$/Au, respectively, from negative to positive potentials. The lower the value of E_c applied, the longer the displacement reaction of copper with gold continued, but there were few differences between the curves of (c) and (d). These results indicate that the increase in the deposition rate of copper became less at a potential lower than −0.2 V. In addition, the time to reach the equilibrium potential of AuCl$_4^-$/Au, +0.91 V, was almost proportional to the quantity of charge consumed during the cathodic process. Figure 4 shows the similar potential–time curves; some anodic potentials (E_a) were applied for 5 s after the deposition at −0.2 V for 10 s. The higher the value of E_a applied, the more the copper dissolution was accelerated and the more rapidly the displacement reactions of copper with gold terminated. These results indicate that it is possible to obtain gold films with a high purity by controlled potential electrolysis in which two different potentials, one lower than +0.05 V and the other higher than +0.05 V, were applied periodically. For example, Fig. 5 shows the applied rectangular potential (a) and the corresponding current curve (b) by the line electrode method. On changing the potential from −0.2 to +0.6 V, the cathodic current changed rapidly to an anodic value and then decayed toward less than zero (cathodic) due to the total dissolution of copper. To obtain high-purity gold films, it is necessary to adjust the anodic electrolysis time and potential to values sufficient to dissolve the copper completely.

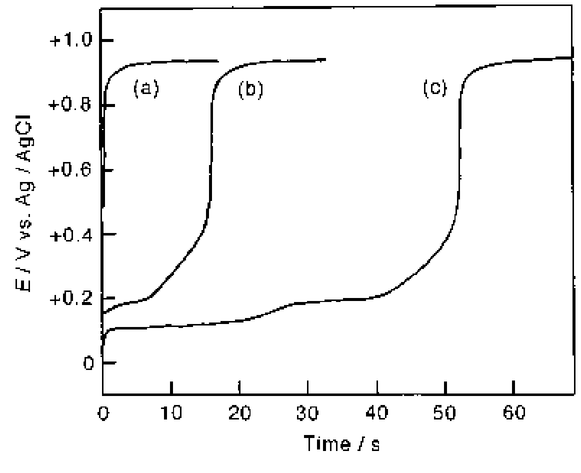

Fig. 4. Sequential potential changes after the electrolysis had proceeded at −0.2 V for 10 s and at E_a for 5 s by the point electrode method. E_a: (a) +0.4 and (b) +0.2 V, (c) no electrodissolution. Conditions: temperature, 50 °C; [Na(AuCl$_4$)], 0.01 M; [CuSO$_4$], 0.1 M; [NaClO$_4$], 0.1 M.

3.2. *Growth of gold film at the interface*

A rectangular potential was applied using the point electrode method, and the corresponding morphological change of a film with time of electrolysis is shown in Fig. 6. The film grew progressively and concentrically from the tip of the electrode with time of electrolysis, its diameter finally being 22 mm at 2 h. The organic liquid side of the film had a gold lustre with radial wrinkles and growth rings, and EPMA analysis showed that the film consisted of gold with no trace of copper. The displacement reaction is generally self-limiting and ceases once the depositing metal completely covers the substrate [9]. In this study, the displacement reaction was forced to continue by repeating the deposition of less noble copper.

It was confirmed that the rectangular potential electrolysis was very effective in the preparation of gold films, so that this electrolysis was applied to the line electrode method; the growth morphology for an electrolysis time of 5 h is shown in Fig. 7. On the right side of the photograph are a working electrode and a deposited gold film, and on the left side is a counter electrode. Although the filmy growth occurred at the interface, it proceeded mainly in the direction of the counter electrode but also, to a certain extent, in the opposite direction. This is because the displacement reaction occurs anywhere independently of current direction. The organic liquid side of the film had fine stripes parallel to the wire working electrode, and the growing front of the film became very wavy after

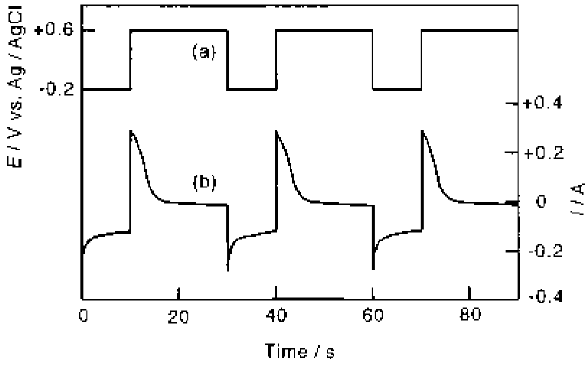

Fig. 5. (a) Applied rectangular potential and (b) corresponding current curve for an electrolysis time of 3 h by the line electrode method. Conditions: temperature, 50 °C; [Na(AuCl$_4$)], 0.02 M; [CuSO$_4$], 0.1 M; [CH$_3$COOH], 0.1 M; [CH$_3$COONa], 0.1 M.

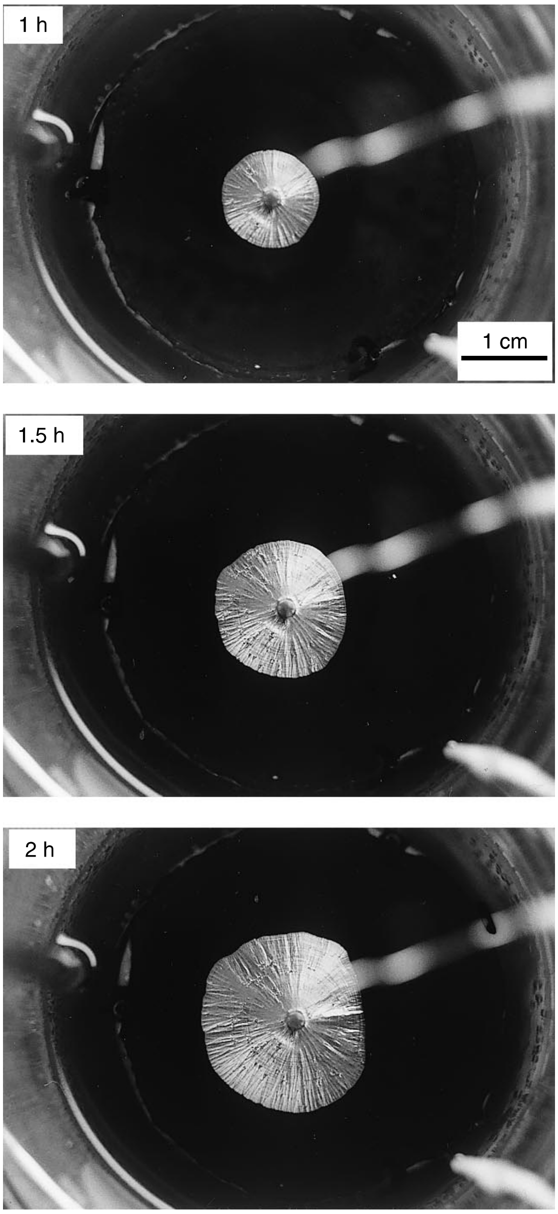

Fig. 6. Growth of a gold film under the rectangular potential electrolysis at −0.2 V for 1 s and at +0.6 V for 2 s by the point electrode method. Conditions: temperature, 50 °C; [Na(AuCl$_4$)], 0.01 M; [CuSO$_4$], 0.1 M; [NaClO$_4$], 0.1 M.

further electrodeposition. The pulse or periodic reverse plating is usually applied to improving physical properties of electrodeposits [10–13]. In this study, the rectangular wave mode was used to accelerate the displacement reaction and prepare high-purity gold films at the interface of two liquid phases.

To investigate the effect of the applied potential on the film morphology, a triangular potential was applied using the line electrode method. Figure 8 shows the applied potential (a) and the corresponding current curve (b) for the following conditions: electrolysis time, 1.5 h; temperature, 50 °C; sweep rate, 10 mV s^{-1}. The abrupt current changes due to applying potential in the rectangular wave mode, shown in Fig. 5, could be avoided by applying a triangular potential mode. The sweep rate had an effect on the composition and growth rate of films; the cyclic voltammograms for a grown gold film at various sweep rates are shown in Fig. 9. As the sweep rate became higher, the dissolution peak shifted to higher potential. At 100 mV s^{-1}, the current was still anodic at +0.6 V, indicating that the dissolution of copper was incomplete. At 1 mV s^{-1}, on the other hand, the growth rate of the film became slower, so that 10 mV s^{-1} was preferable to obtain a high-purity gold film in a short time. The rate of filmy growth decreased with electrolysis time, but the rate was recovered by restarting the electrolysis after interruption of the electrolysis. The sequence of an electrolysis for 2 h and a break for 1 h was repeated so that the small gold particles suspended in the solution could be removed and did not interfere with the film growth. The growth morphology of a gold film for an electrolysis time of 8 h is shown in Fig. 10. The filmy growth of gold proceeded predominantly in the direction of the counter electrode to the extent of about 5 cm, in contrast with the growth of 1.5 cm in the opposite direction. The film retained an even growing front for a longer time of electrolysis than that when undergoing rectangular potential electrolysis (Fig. 7). Judging from these phenomena, controlled potential electrolysis, without abrupt current changes, is con-

Fig. 7. Growth of a gold film under the rectangular potential electrolysis at −0.2 V for 10 s and at +0.6 V for 20 s for an electrolysis time of 5 h by the line electrode method. Conditions: temperature, 50 °C; [Na(AuCl$_4$)], 0.02 M; [CuSO$_4$], 0.1 M; [CH$_3$COOH], 0.1 M; [CH$_3$COONa], 0.1 M.

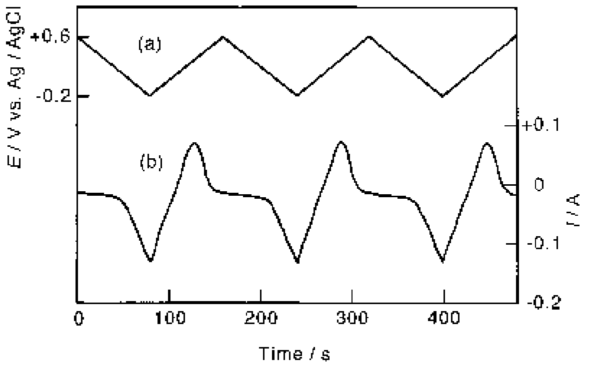

Fig. 8. (a) Applied triangular potential and (b) corresponding current curve for an electrolysis time of 1.5 h by the line electrode method. Conditions: temperature, 50 °C; [Na(AuCl$_4$)], 0.01 M; [CuSO$_4$], 0.1 M; [NaClO$_4$], 0.1 M; sweep rate, 10 mV s^{-1}.

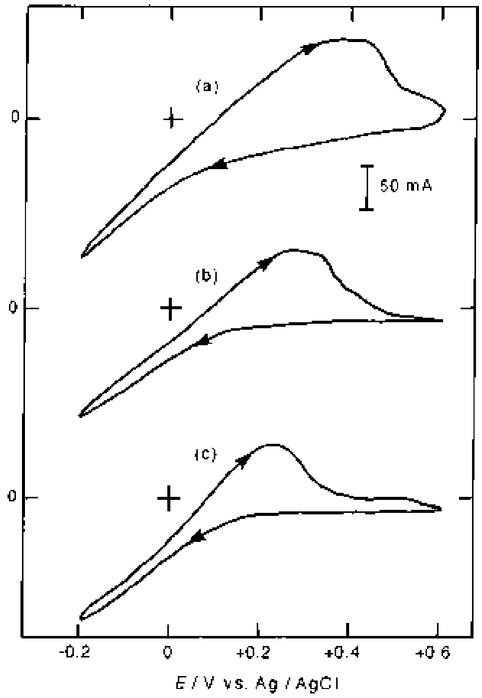

Fig. 9. Cyclic voltammograms for a gold film grown at the interface by the line electrode method. Sweep rate: (a) 100, (b) 10 and (c) 1 mV s^{-1}. Conditions: temperature, 50 °C; [Na(AuCl$_4$)], 0.01 M; [CuSO$_4$], 0.1 M; [NaClO$_4$], 0.1 M.

sidered to be the most appropriate way to prepare gold films at the interface

3.3. *Morphology of gold film*

Figure 11 shows the superficial morphology of the gold film deposited by triangular potential electrolysis as shown in Fig. 10. The organic liquid side (a) had a gold lustre and the aqueous solution side (b) was lustreless reddish brown, just like the circular one obtained by the point electrode method using a Na(AuCl$_4$) solution without CuSO$_4$ [7]. Each side, especially the organic liquid side, had stripes parallel to the wire working electrode.

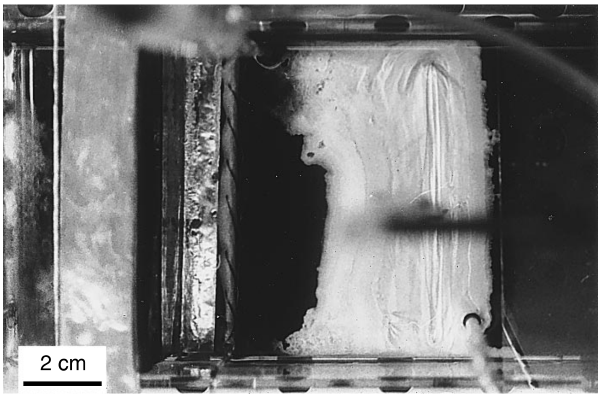

Fig. 10. Growth of a gold film under the triangular potential electrolysis for an electrolysis time of 8 h by the line electrode method; potential was swept from +0.6 to −0.2 V at 10 mV s^{-1}. Conditions: temperature, 40 °C; [Na(AuCl$_4$)], 0.01 M; [CuSO$_4$], 0.1 M; [NaClO$_4$], 0.1 M. (A black, out-of-focus shadow in the centre of the gold film is a holder which hung the working electrode.)

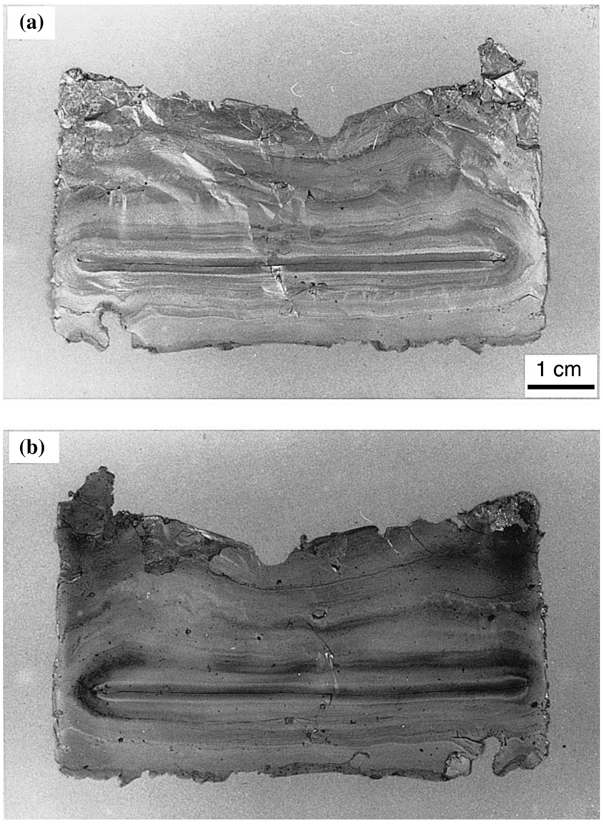

Fig. 11. Morphology of the gold film shown in Fig. 10: (a) organic liquid side, (b) aqueous solution side.

Typical microstructure of the gold film is shown in Fig. 12. The organic liquid side (a) was more even than the aqueous solution side (b) which was covered all over with aggregates of gold particles. The film was slightly porous, especially near the growing front. As shown in Fig. 12(c), the film itself was very thin with a thickness much less than 1 μm, and the small gold particles were deposited on the aqueous solution side of the film. Assuming a dense film, the mean thickness was calculated to be 0.87 μm from its weight and area.

3.4. *Mechanism of filmy growth at the interface*

Electrochemical growth of gold films at the interface between two liquid phases is considered to be unusal and the growth mechanism is not yet understood. However, useful information on the interfacial growth has been obtained from a series of studies in our laboratory.

An appropriate organic liquid is necessary for the reproducible interfacial growth of metals, although surface growth was occasionally observed at the air–aqueous solution interface [14]. Even if the counter electrode was placed at the bottom of the cell, an electrodeposit grew concentrically along the interface from the point electrode. These phenomena show that the existence of an immiscible organic phase has a special role at the interface. In this study, hexyl acetate was chosen as the organic liquid, and other acetic esters and alkanes also led to interfacial

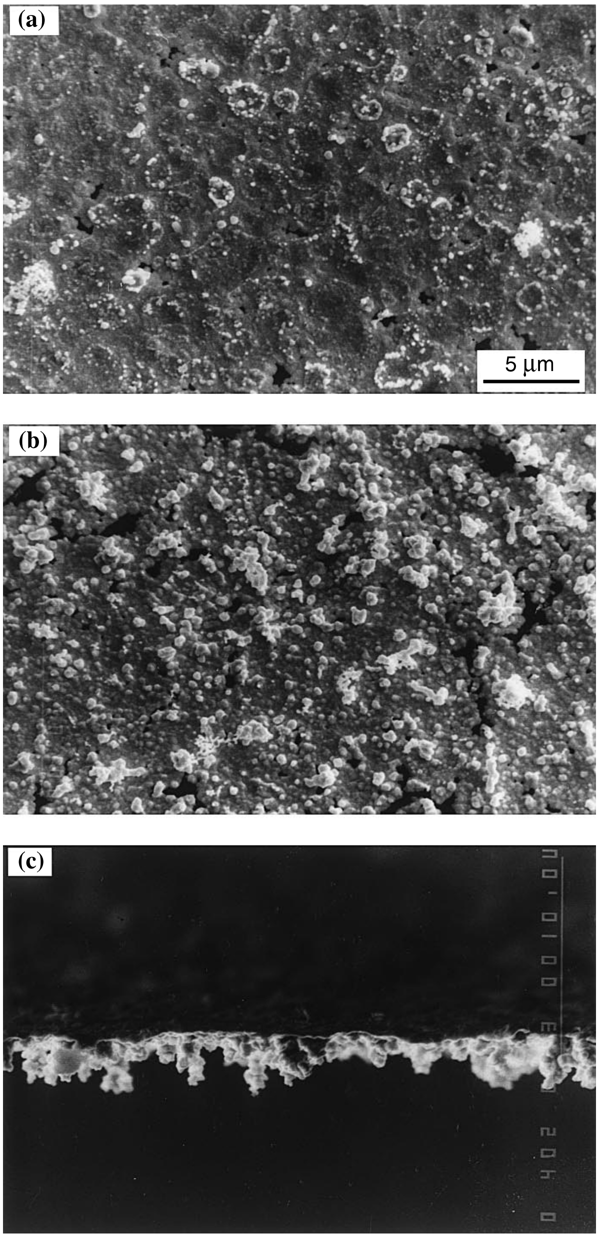

Fig. 12. Microstructure of the gold film shown in Fig. 10: (a) organic liquid side, (b) aqueous solution side (the film grew to the left), (c) cross section (the upper surface of the film faced to the organic liquid).

growth. In the case of zinc [3], it was observed by a low power microscope that a stagnant depleted zone was generated below the growing film during the electrolysis and concentrated solution was supplied to its growing front. A similar phenomenon would occur in the growing process of gold, although it was hardly observable due to slow growth of a thin film. It is considered that a metal is electrodeposited on an organic liquid substrate with a reduced overvoltage due to the adsorption of metal ions at the metal–aqueous solution–organic liquid boundary.

Addition of the organic liquid has another effect. When an electrodeposit is wet with the organic liquid, it is not easily immersed into the aqueous solution. If the growing front of the electrodeposit is immersed into the aqueous solution or the interface is distorted by a mechanical stress of the electrodeposit, the interfacial growth ceases immediately. Similarly, at the start of an electrolysis, it is crucial to maintain the working electrode exactly at the interface. If the electrode is immersed into the aqueous solution, the electrodeposition proceeds into the bulk solution rather than at the interface.

In the Hele–Shaw cell, in which aqueous solution is sandwiched in a thin layer by two glass plates, two-dimensional branched growth due to the geometrical constraint was observed [1]. Even for the interfacial growth, a short depth of aqueous solution was favoured. The growth patterns with branched morphology in the Hele–Shaw cell [15] and at the interface of two liquid phases [16] were explained by the diffusion-limited aggregation model. However, the filmy growth shown in this study is different from the branched growth; there has been no report on filmy growth in the Hele–Shaw cell. The filmy growth is a typical interfacial phenomenon, and appears to be governed by the electrokinetic effect on adsorbed ions at the interface. Further investigation into the mechanism of interfacial growth is now in progress.

4. Conclusions

Gold films were continuously prepared by controlled potential electrolysis at the interface between a $Na(AuCl_4)$–$CuSO_4$ aqueous phase and an immiscible hexyl acetate organic phase. Applying a rectangular or triangular potential resulted in the codeposition reaction of copper and gold followed by the displacement reaction of copper with gold. The growth of high-purity gold films was continued by repetition of this process.

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