TEM observation of two-dimensional growth of lamellar gold electroplated on copper wires

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Abstract
Electroplating is an essential process to produce Cu–Au complex bonding wires. Therefore, mastering the general growth behaviour of gold film plated on copper substrate has an instructive effect on the subsequent processes of pinching-out and annealing in the processing of Cu–Au complex bonding wires. In this paper, plated gold film consisted of an intermediate layer and a gold layer, which were characterised in terms of transmission electron microscope (TEM) observations, especially the techniques of selected area electron diffraction (SAED) and displaced-aperture dark field (DADF). A thin intermediate layer with polycrystalline gold is observed adjacent to the ribbon-like copper substrate, which is due to the competing mechanism between chemical and electrochemical reactions. The gold layer is detected in the outer regions of the intermediate layer, and the formation of the gold layer is dominated by the electrochemical mechanism. Lamellar gold orients randomly in the gold layer, whose outer surface is mainly enclosed by the planes of {111}. The lamellar gold grows in only two dimensions, as the vertical direction is blocked by sulphite near the cathode.

1. Introduction
Bonding wires such as copper, silver, gold and aluminium, have been widely applied in electronic packaging in the semiconductor industry, thus drawing significant attention towards fabricating inexpensive complex bonding wires over the past decades [1–3]. Generally, electroplating, cold-drawing and annealing are the necessary procedures to process complex bonding wires such as Cu–Al, Cu–Pd, Cu–Nb and Ag–Au bonding wires [4–6]. The preparation of Cu–Au complex bonding wires is also an alternative way to process copper-based bonding wires, which greatly decreases their cost and strengthens their antioxidant properties [7]. The electroplating process was focused on in this study to summarise the general growth behaviour of coated gold film on copper wire, which is instructive with regard to the subsequent cold-drawing and annealing processes.

The electroplating process was performed in a sulphite electroplating system with ethylenediaminetetraacetic acid (EDTA) as the other coordinating complex [8, 9]. Citrate is also added to act as a conductive agent and pH buffer. Additionally, the citrate participates in the coordination of gold ions in the inferior inner layer, while EDTA and sulphite serve as strong complexing agents in the innermost layer. During the electroplating reaction, gold should be reduced from the gold ions in the innermost coordination layer. Generally, it is necessary to overcome the inhibitory effect of the innermost and inferior inner layers, thus improving the overvoltage of the gold ion amplification [10]. However, the gold particles obtained from the plating process were too fine, and insufficient structural information could be deduced by optical microscope or scanning electron microscope. In this paper, transmission electron microscopy (TEM) with selective area electron diffraction (SAED) technique is employed to characterize the substrate of copper layer, intermediate layer and gold plating layer.
2. Experiment

2.1. Preparation
Copper wires (Φ 0.8 mm) were supplied by Yantai Kanfort Metal Company Limited, China. At a temperature of 1130 °C, the copper rods (99.99 wt%, Φ 8 mm) were mould-casted, followed by cooling in the same furnace. The plated copper wires were processed by means of continuous cold-drawing performed 12 times. Finally, gold film was electroplated on copper wires by a typical sulphite coating system with a plating solution containing AuCl₃ (46 g l⁻¹), Na₂SO₃ · 7H₂O (135 g l⁻¹), ammonium citrate (80 g l⁻¹), ethylenediaminetetraacetic acid (50 g l⁻¹), and CoSO₄ · 7H₂O (0.75 g l⁻¹). AuCl₃ was prepared by dissolving pure gold into nitrohydrochloric acid at a temperature of 50 °C in a water bath. Later, continuous heating was applied to remove the remaining HCl and HNO₃. The pH of the final solution was controlled between 6.5 and 7 during the electroplating process. Insoluble pure gold was used as the anode. A continuous electroplating method was used to prepare the Cu-Au complex wires with a current density of 0.083 A dm⁻² at a rate of 15 cm min⁻¹.

2.2. Characterisation
The Cu–Au interface TEM specimen was obtained from the surface of the Cu-gold wires with a scanning electron microscope focused by ion beam double beam system (LYRA3 GMU/GMH) at the voltage of 30kV and 10kV, respectively. Structure analysis was carried out with a JEOL-2100F high-resolution TEM at the acceleration voltage of 200 kV. Because the machine is equipped with a low Cs pole piece image and the corresponding dark-field images, projected lens alignment and a shift of the objective aperture were carried out to ensure on-axis images, thus reducing the effect caused by non-parallelism resulting from the setting of the condenser lenses (β). To obtain some comparable structural information from the DADF images, brightness conditions were kept as consistent as possible [11, 12].

3. Results
To clearly reveal the general growth behaviour of gold on the copper wire, TEM was employed to characterise the copper substrate firstly. As shown in figure 1(b), typical ribbon-like copper grains could be observed in the bright-field image of the copper substrate, which is the typical deforming texture that results from the process of cold-drawing. In the elongated copper grains, there exist a large amount of dislocations, generated in the deformation caused by directional rolling [13]. For instance, dislocation walls are observed in region B1 in figure 2(b) as a result of heavy deformation caused by directional rolling (marked by the white arrow). As shown in figure 1(c), the corresponding SAED pattern was used to analyse the dislocation walls. When the [011] pole is on-axis, the diffraction spots extend to higher Brillouin zones in the reciprocal space. The appearance of extra diffraction in the higher Brillouin zones is due to the uniform arrange. Another typical grains can be recorded as shown in figure 2(e). Diffraction contrast is accounted for this phenomenon. The corresponding diffraction pattern is listed and labelled in figure 1(f). When the [233] pole is on-axis, the forbidden planes of m(311) + t(022) ± {111} or (11̅1) appear besides the main spots. Furthermore, a weak diffraction ring is observed in the enlarged diffraction pattern in the inset of figure 1(f), circled by the translucent white circle. Figure 1(d) is a simulated lattice of the face-centred copper with the crystal axis [233]. From the image, it can be deduced that (11̅1) or (11̅1) should not appear in the projected diffraction pattern. The diffraction beams of (022), (311) and (33̅1) are responsible for forming the DADF images in figures 1(g)–(i), respectively. In figure 1(g), many parallel dislocations are approximately perpendicular to the diffraction plane (022). The morphology of the brighter regions in figure 1(e) could be recognised as the sum of the darker regions in the corresponding DADF images (figures 1(g), (h) and (i)), which means that mis-orientation is prevalent in figure 1(e). According to the hypothesis proposed by Liang’s group, the calculated mis-orientation angle (θ) between the regions (G1) and (I1) is only 1.15E-2 rad [14]. In the copper substrate, the mis-orientation stems from the movement of the dislocations.

The characterisation of the intermediate layer and gold layer is demonstrated in figure 2. In figures 2(a) and (b), a thin intermediate layer was observed adjacent to the ribbon-like copper substance. In the outer regions of the intermediate layer, there is a darker gold layer. The contrast between the intermediate layer and the gold layer stemmed from the crystallinity. The polycrystalline materials can be thinned more easily than the crystal, thus rendering the contrast observed in the gold film. The SAED pattern of the intermediate layer is shown in figure 2(c). The diffraction rings could be indexed as nano-sized gold and the corresponding diffraction planes are labelled in figure 2(c). In the outer regions of the intermediate layer in figures 2(a) and (b), different projection diagrams were recorded in the electroplated gold layer. According to the comprehensive analysis of projections in figures 2(a) and (b), the gold layer is composed of round lamellar gold. The enlarged lamellar gold
Figure 1. Schematic diagram (a) of copper wire coated with gold. (b) Typical bright-field (BF) TEM image of Cu substrate and (c) the corresponding SAED pattern obtained from the dotted rectangle in B. The corresponding planes have been labelled in C. (d) Sketch lattice of face-centred Cu (imaging in the software of diamond). The planes of (022) and (311) within the crystal axis [233] are shown in light blue, while the planes of (111) or (T1T) are shown in light green. To clearly reveal the lattice, the crystal axis [233] is offset slightly. (e) Typical BF TEM image of Cu substrate and (f) the corresponding SAED pattern. The diffraction beams of (022), (311) and (313) are used to produce the DADF images in (g), (h) and (i), respectively. G1, H1 and I1 represent the corresponding brighter regions in the images. The letters m and t denote integers.

Figure 2. Typical TEM images (a and b) of Cu-Au interface. The SAED patterns of the intermediate layer and plated gold layer are shown in (c) and (e), as obtained from the dotted rectangles in (b) and (d), respectively. An enlarged TEM image of the lamellar gold shown in (d) and the simulated image (right-bottom inset). The HRTEM of lamellar gold (f). R1 and R2 represent the regions with larger periodicity, which is consistent with the inner diffraction spots in (e).

is shown in figure 2(d) and its [111] pole diffraction pattern further proves this. In figure 2(d), the surface of the lamellar gold may be dominated by (111), the closest-packed plane in the face-centred materials. In addition to the main diffraction point, other weak diffraction points are also located within the main point. This may be due to the irregular stacking of gold atoms or the dissolution of gold atoms. High-resolution TEM technique is employed to obtain finer structure regarding the lamellar gold. HRTEM is employed to obtain more detailed
information. The formation of the extra stripes (R₁ and R₂) could be considered as the sources of weak spots in figure 2(e). The region between R₁ and R₂ has a large mis-orientation angle. It is possible that the extra inner reciprocal spots in figure 2(e) are the result of the overlaying of different regions with a certain orientation angle, such as the regions of R₁ and R₂. From the view of [111], the lamellar gold in figure 2(d) is the largest projection, which means that the surface of the lamellar gold could be mainly composed of the (111) and other small, low-index planes, such as {220}, {110}, {211} and {422}. Although the planes of {110} and {211} are forbidden for face-centred gold for x-ray diffraction and electron diffraction, these planes should exist in the real lamellar gold. The surface energy with higher Miller indices is so high that the particles are not stable. The lamellar gold is the most stable with the outer surface enclosed mainly by (111) and small round planes, such as {220}, {110}, {211} and {422}. The platinum polyhedrons with higher Miller indices of {730} and {520}, were induced by Wang’s team by means of complex electrochemical methods, which show better catalytic performance [15, 16]. Generally, the lamellar gold is enclosed by the {111} planes with lower Miller indices.

4. Discussion

4.1. Substance of the copper wires

To reveal the general growth behaviour of the lamellar gold clearly, the copper substrate is discussed firstly. For face-centred copper, the main slip planes and directions are {111} and {110} [17]. The axial texture of the original copper shows typical {100} texture as shown in figure S1 is available online at stacks.iop.org/MRX/6/126462/mmedia. With the effect of the directional and the transverse force, the relative rotations between the copper grains are induced to adapt to the easiest slip plane and direction [18]. During the process of cold-drawing, deformation is induced by the movement of movable dislocations. In figure 1(b), the angle between the directional directions and the slip plane (T11) is approximately 60 degrees. A large amount of advantageous dislocations along the (T11) plane are accounted for by the formation of the dislocation walls (B₁ in figure 1(b)). The relative slips make the copper grains rotate to a small degree. However, the column approximation fails to explain the diffraction phenomenon in figure 1(c) owing to the ordered dislocations. The dynamic energy exchange between the n (T11) and the direct spot is strong, thus the diffraction spots extend to higher zones. This phenomenon in figure 1(c) could be explained by launching a single slip plane via (T11), provided that the angle between the elongated direction and the slip plane (T11) is approximately 60 degrees. However, if the real elongated direction has a relatively large angle in comparison with the easiest deforming planes {111}, a single rotation of the copper grain could not accomplish the actual elongated direction. Three of the four {111} planes are composed to satisfy the elongated direction as shown in figure S2. During the deformation, a large amount of dislocations is generated, thus lengthening the inverted rod. The Ewald sphere may intersect more reciprocal lattice points in such as the regions of R₁ and R₂. From the view of 126462 equation fi, the forbidden diffraction spots of (111) could be considered as the sources of weak spots in figure 2(e).

4.2. Two-dimensional growth mechanism of the lamellar gold

The gold film was electroplated in a sulphite coating system with an insoluble anode (thin gold plate). Gold should be replenished in the form of Au(SO₃)₂⁺ because of its consumption in the plating reaction and the oxidation reaction by the oxygen in air. During the entire process, the anode reaction is still the same (equation (3)) [20]. However, the cathode reaction could be divided into two main procedures. At the beginning stage of electroplating, chemical plating (equation (3)) and electroplating compete (equations (2) and (3)) against each other to form the intermediate layer once the surface of the copper wire is immersed into the electroplating solution. Owing to the quicker chemical reaction rate, the obtained gold particles are very fine in the intermediate layer (figures 2(a) and (b)). The following process is dominated by the electrochemical reaction (equation (2)), and the gold atoms stack neatly, so that well-crystallised lamellar gold is formed in the outer region of the intermediate layer.
Anode reaction

\[
\text{SO}_3^{2-} + 2e^- \rightarrow \text{SO}_4^{2-}
\]

Cathode reactions

\[
\{\text{Au}[\text{SO}_3^{2-}][\text{EDTA}]_2\}^{3-}[\text{citric}]_{k_x}^{3-} + e^- \rightarrow \text{Au} + 2\text{SO}_3^{2-} + 2\text{EDTA} + x\text{citric}^{3-}
\]

\[
\{\text{Au}[\text{SO}_3^{2-}][\text{EDTA}]_2\}^{3-}[\text{citric}]_{k_x}^{3-} + 1/2\text{Cu} \rightarrow \text{Cu}[\text{SO}_3^{2-}][\text{EDTA}]_2[\text{citric}]_{6-x-y}^{3-}
\]

\[
\text{Cu}[\text{SO}_3^{2-}][\text{EDTA}]_2[\text{citric}]_{6-x-y}^{3-} + 2e^- \rightarrow \text{Cu} + x\text{SO}_3^{2-} + y\text{EDTA} + (6-x-y)\text{citric}^{3-}
\]

4.3. Two-dimensional growth mechanism of the lamellar gold

On the basis of the theory of Hard-Soft-Acid-Base (HSAB) and Complex, a gold ion, a type of soft acid, tends to form a stable complex with soft alkali, whose electron cloud is easily deformed [21]. Certain nitrogen complexes and sulfur complexes belong to soft alkali, which could be employed to cooperate with gold ions in the aqueous solution. The number of coordination of a gold ion is four. \(\text{SO}_3^{2-}\) and EDTA cooperate with monovalent gold ions in the innermost layer. The detailed coordinating complex has been illustrated in figure 3(a). The inferior inner layer and part of the innermost layer should be overcome to reduce the gold ions, thus allowing a larger overvoltage [7, 8]. When the electric field was introduced, the Au ions moved to the cathode. In the plating procedure dominated by the electrochemical reaction (equation (2)), the outer citrate and the coordinating EDTA are easily driven away, which means that the remaining \(\text{SO}_3^{2-}\) served to block the Z direction in figure 3(a). Owing to the large volume effect in the Z direction, the growth direction of the lamellar gold is restrained to the X-Y plane. Therefore, gold atoms only stack in two dimensions in the plated gold layer. The remaining \(\text{Au}[\text{SO}_3^{2-}]^{3-}\) is arranged beside the coated gold atoms by the electric force. The negative complex (\(\text{SO}_3^{2-}\)) is attracted the positively charged \(\text{(Au}^+)\) until the valence of gold returns to the ground state (0). The arrangement of \(\text{Au}[\text{SO}_3^{2-}]^{3-}\) is shown in figure 3(b). In the lamellar gold, the partial growth direction could conform to be perpendicular to the stripes in figure 2(f) (the white arrows). Thus, the stripes in figure 2(f) and the inner diffraction spots in figure 2(e) appear because of the misalignment in the arrangement of gold atoms. Furthermore, in the plating process, the electrochemical reaction (equation (4)) is inevitable. As the atomic scattering factor \(f_{\text{Au}}-f_{\text{Cu}}\) is not equal to zero, the structure factor \(F(hk0)\) is also usually non-zero, which means that forbidden diffraction spots may be reflected as minor weak spots in the back focal plane of the objective lens. The dissolved copper atom in the lamellar gold may also be responsible for the generation of inner diffraction spots in figure 2(e) [12].

According to the results above, some conclusions can be summarised.

1. In the copper substrate, there are a large number of dislocations in the ribbon-like grains after cold-drawing.

2. The formation of polycrystalline gold in the intermediate layer is due to the competing relationship between the electrochemical and chemical reactions.
(3) In the gold layer, lamellar gold is arranged randomly. Two-dimensional growth accounts for the formation of lamellar gold, which is attributed to the coordinating complex of gold ions.

5. Conclusion

In this study, gold film is successfully plated on copper wires with a sulphite electroplating system. The obtained plating film consists of the gold layer and the intermediate layer. The formation of the intermediate layer is attributed to the competing relationship between the chemical and electrochemical reactions. Lamellar gold is coated in the outer intermediate layer, which is dominated by the electrochemical reaction during the plating process. The special coordinating complex of gold ions is responsible for the formation of the lamellar gold, as the vertical direction is inhibited by sulphite. The fine lamellar gold is obtained owing to the large impedance in the plating solution present during the entire plating process. Thus, Cu–Au complex bonding wires have been successfully prepared by plating, cold-drawing, and annealing.

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