SHORT COMMUNICATION

Observations of inclusions of polymeric additives in copper electrodeposits by transmission electron microscopy

G. A. HOPE, G. M. BROWN

Faculty of Science and Technology, Griffith University, Nathan, Brisbane 4111, Australia

D. P. SCHWEINSBERG

School of Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane 4001, Australia

K. SHIMIZU, K. KOBAYASHI

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama 223, Japan

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1. Introduction

The use of organic reagents as additives in metal electrodeposition processes is common practice. Typically, additives are employed in plating baths in the parts per million (ppm) concentration range and serve to enhance the quality of electrodeposited metal by deposit smoothing, deposit brightening and grain refinement. Such effects on deposit morphology are attributed in part to adsorption of reagent molecules at the electrode surface during deposition [1, 2].

The consumption of additives during the course of deposition can be accounted for by a number of processes. Gelatin, an additive commonly used as a smoothing agent in copper and zinc electrodeposition undergoes acid-catalysed hydrolysis in electrolytes and may also be adsorbed onto anode slimes which accumulate over long periods of plating [3, 4]. Thiourea, widely used as a grain refining agent, is known to adsorb at the surface of copper electrodes and additionally forms stable complexes with copper(I) species in solution [5]. Decomposition of thiourea in acid electrolytes has also been proposed [6].

The incorporation or inclusion of reagent molecules into the metal matrix during deposition is a process which is believed to further account for additive consumption. Typical inclusions may be in the form of individual molecules, as aggregates of reagent molecules, or as species derived from decomposition of the reagent forming secondary impurities which then undergo incorporation (eg., CuS from the decomposition of thiourea). Gamburg has suggested [7] for example, that reagents such as *o*-phenanthroline are weakly adsorbed on the surface of electrodes; the molecules are sufficiently mobile and are swept ahead of growing atom layers of a deposit. The reagent molecules are incorporated into the deposit when layers of atoms growing from opposite directions approach each other leading to 'entrapment'. Evidence for the inclusion of organic reagents in electrodeposits was first reported by Steinemann and Hintermann [8], and has been reviewed in more detail by Nakahara [9] using a transmission electron microscope technique for various inclusions in a range of metallic deposits.

To observe inclusions of organic reagents in electrodeposits, the inclusions must be sufficiently large to be resolvable by TEM. Furthermore, direct incorporation of reagent molecules into deposits without significant decomposition at the cathode is advantageous [9].

High molecular weight polymeric reagents such as polyethylene glycol (PEG), polyvinyl alcohol (PVA) and polyethylene imine (PEI) have been used as additives in the deposition of copper from acid sulfate electrolytes. PEG has been found to suppress copper deposition in plating baths containing greater than 20 ppm of the additive [10]. On the other hand, PVA has been observed to influence the grain orientation of copper deposits to a preferred (2 2 0) orientation, in addition to exhibiting a grain refining effect on the microstructure of copper deposits [11]. These polymeric reagents display greater stability in acid sulfate electrolytes than gelatin and are resistant to decomposition in the acid environment over long periods of plating. Thus, observation of inclusions of stable, well characterized molecules such as PEG, PEI and PVA should be possible if the additives are incorporated during deposition.

In this paper, inclusions of PEI and PEG in polycrystalline copper electrodeposits produced in an acid sulfate electrolyte containing 10 ppm of the additive have been examined by transmission electron microscopy of ultramicrotomed sections of the deposited metal. The technique of ultramicrotomy, whereby ultra thin slices of specimens, less than 10 nm in thickness, are mechanically prepared by sectioning, and which in turn are suitable for examination in a transmission electron microscope has been extensively applied to studies of surface films and coatings of various kinds on a range of metals and alloys [12]. Additionally, thin sections of bulk metal and alloy specimens containing second phase material have also been successfully prepared [13].

2. Experimental details

Stainless steel foil (316 grade) of dimensions 50 mm × 10 mm × 0.1 mm were used as substrates for

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copper electrodeposition. The foils were lightly abraded with 1200 grade silicon carbide paper, washed with acetone and distilled water and dried in a cool air stream prior to use. The anode was machined from a high purity (99.99%), commercially available copper block.

Analytical reagent grade sulfuric acid and copper sulfate pentahydrate were supplied by Ajax Chemicals. Polyethylene glycol (MW: 8000) and polyethylene imine (MW: 30 000–40 000) were supplied by Fluka. All solutions were prepared with distilled deionised water.

Copper deposits of between 5 and 10 μm in thickness were formed at a current density of $3\,mA\,dm^{-2}$ in a 2 M H_2SO_4/0.7 M $CuSO_4.5H_2O$ electrolyte at 298 K, containing the appropriate additive. The appropriate quantity of additive stock solution was introduced to the electrolyte prior to deposition to provide a solution concentration of 10 ppm (10^{-7} M, PEI; 10^{-6} M, PEG). After deposition the specimens were removed from the electrolyte, washed with distilled water and dried in a cool air stream. Deposits formed on the stainless steel were carefully removed by gently bending the foil, which resulted in the deposit lifting off the substrate.

Ultramicrotomed sections of the copper deposits were prepared according to the procedure of Furneaux *et al.* [14] using a RMC 6000XL ultramicrotome. Briefly, the resin (Epon 812, DDSA and DMP-30; 20:30:1) encapsulated specimens were trimmed initially with a diamond knife, and sections as thin as 10 nm or less were prepared by sectioning in a direction approximately parallel or perpendicular to the deposit–substrate interface with a diamond knife. The ultramicrotomed sections were collected on copper grids and examined in a JEM 2000 FX II analytical transmission electron microscope at an accelerating voltage of 200 kV.

3. Results

A transmission electron micrograph of an ultramicrotomed section of a copper electrodeposit grown on a stainless steel substrate in the presence of PEI is presented in Fig. 1. The deposit–resin interface can be observed at the top one fifth of the micrograph, while the deposit bulk is observed in the lower portion. A grain boundary is observed in the middle of the micrograph and is highlighted by the discontinuity in extinction contours associated with the electron beam incident upon the specimen. The grain boundary extends from the upper left hand portion of the deposit diagonally downwards to the right, approximately 300 nm below the deposit surface. Regions of lighter contrast, approximately 20–50 nm long and which appear to be free of deposit are occasionally evident along the grain boundary within the deposit bulk. An electron diffraction pattern of a local area of the deposit shown in Fig. 1 demonstrates that structural damage to the copper specimen during sectioning is minimal.

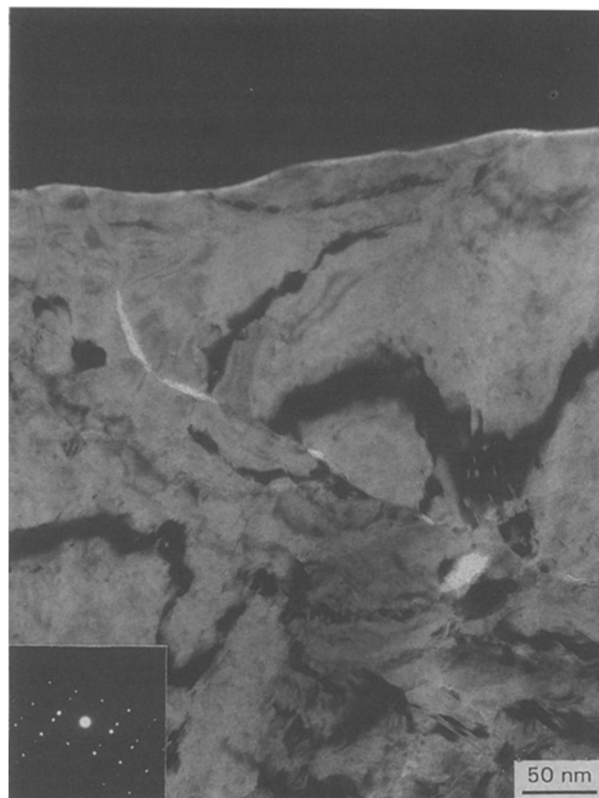

Fig. 1. Transmission electron micrograph of an ultramicrotomed section of a copper deposit formed in the presence of PEI.

The local regions of lighter contrast are revealed in greater detail in transmission electron micrographs of ultramicrotomed sections of copper deposits at higher magnifications, Fig. 2(a) and (b). Here cross sections of the deposit bulk are presented in which several grain boundaries are observed. In Fig. 2(a) a trapezoidal shaped region, of dimensions approximately 75 nm × 50 nm is observed at a grain boundary, in the middle of the micrograph. Other similar regions of varying dimensions are also observed in this cross section. An important feature of these local regions is that they exhibit a light, granular texture. Regions of similar texture and size are observed in the micrograph presented in Fig. 2(b), which represents a cross section of a different area of the deposit bulk. Again, the textured region is observed along a grain boundary, which extends horizontally across the middle of the micrograph.

A transmission electron micrograph of an ultramicrotomed section of a copper deposit formed in the presence of PEG is presented in Fig. 3. A large region approximately 250 nm × 100 nm and which exhibits a dark cloudy texture against a lighter background is immediately observed in the middle of the micrograph. Furthermore, this region is located at and extends along the grain boundary. It is apparent that the texture of this region differs significantly from that of similar regions shown in Fig. 2.

4. Discussion

The inclusion of organic additives in electrodeposited metal matrices has been of much interest to

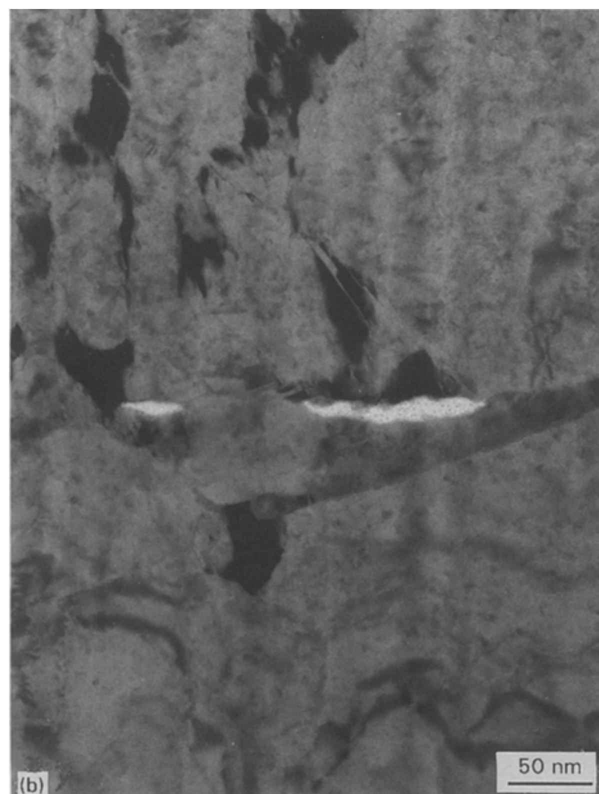

Fig. 2 (a) and (b). Transmission electron micrographs of local areas shown in Fig. 1, at higher magnification. Inclusions are observed at deposit grain boundaries and exhibit a granular texture.

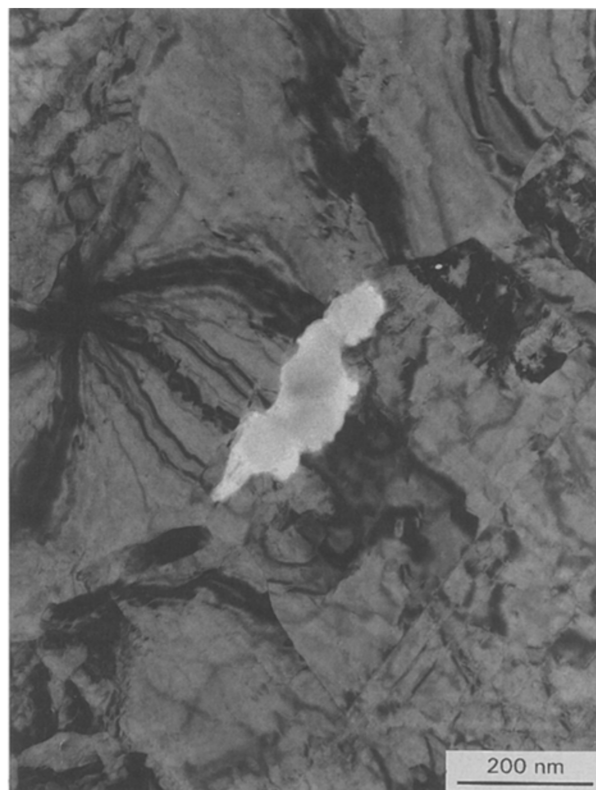

Fig. 3. Transmission electron micrograph of an ultramicrotomed section of a copper deposit formed in the presence of PEG. The inclusion shown here exhibits a cloudy texture, in contrast to those of Fig. 2, where a granular texture is observed.

investigators for many years. Attention has been focused on elucidating the role and activity of addition agents in electrodeposition processes in light of their influence on the microstructure and physical properties of electrodeposits. Nakahara has reviewed [9] many works in this area and has applied an electron microscopic technique to directly and indirectly observe various kinds of additives (organic, metallic, gaseous) in films of electrodeposited metals and alloys. In most cases, electrodeposited films were prepared in solutions containing high additive concentrations. Specimens were then electrochemically or ion beam thinned and the resulting specimens examined using a phase contrast technique to image the inclusions. Important parameters worthy of consideration in the preparation of electrodeposits include current density (which affects the deposition rate), electrolyte composition, electrolyte stirring conditions and solution additive concentration. High current densities or high cathodic overpotentials, accompanied by fast stirring rates can adversely affect electrodeposition processes resulting in brittle deposits which can comprise occlusions of additives and foreign material [15]. In the present work, copper electrodeposits have been formed under standard deposition conditions, in synthetic electrolytes containing normal additive concentrations, in order to prepare typical samples for examination.

Examination of transmission electron micrographs of ultramicrotomed sections of copper electrodeposits formed in the presence of PEI and PEG has occasionally revealed lightly textured regions along grain boundaries in the deposit cross sections. These regions are not observed near the surface of the deposits, but rather at depths of up to 300 nm in the deposit bulk. Such regions may be attributed to

deposit features such as voids, codeposited foreign material or inclusions of gases or of additives which are present in the plating bath during deposition. Alternatively, the observed regions may be attributed to artifacts introduced to the specimen during sectioning.

The identity of the textured regions revealed in the micrographs has been established taking into account the following. First, the observed regions exhibit a granular or cloudy texture, indicative of material present at these locations. Furthermore, the regions range in size from approximately 20–50 to 200 nm in length. Thus the likelihood that voids account for such observations is minimal and can be discarded.

The possibility of incorporation of foreign material such as hydrogen gas bubbles in the copper deposit is discarded by further consideration of the textured regions. Deposit embrittlement due to the incorporation of hydrogen gas bubbles has previously been observed by Okinaka *et al.* [16]. Such inclusions could be expected in deposits formed at high cathodic overpotentials, where hydrogen evolution and hence incorporation of gas bubbles can occur. However, gas inclusions would not be expected to exhibit any textured appearance if indeed present in the deposit at all. Furthermore, the size of the features observed here discounts the possibility that hydrogen gas bubbles account for such observations. Copper deposits produced in the present study have been formed at sufficiently low cathodic overpotentials where hydrogen evolution is minimized during deposition.

The presence of foreign metallic elements within the copper matrix is also discounted by the texture of the observed regions. Secondary metallic elements could undoubtedly be differentiated from the copper matrix due to a greater electron scattering cross section which would be observed as dark regions of stronger contrast. Additionally, for secondary metallic elements to account for the lightly textured regions observed within the copper deposit, such elements would be required to be present in the plating bath during deposition. The present study has employed synthetic electrolytes and high purity copper anode in order to minimize electrolyte contamination.

Structural damage to the ultramicrotomed section during cutting is possible and can account for tears or shearing of the ultra thin section. Occasionally, chatter bands, associated with the direction of sectioning of the specimen on the diamond knife, are observed in the micrographs of the copper deposits; such features are most readily observed as faint vertical lines in the micrograph of Fig. 2(b). In the micrographs presented here, the structure of the copper sections within the vicinities of the lightly textured regions appears to be fully intact; structural damage of the specimen section is not apparent. Thus, it would appear that the textured regions are genuine features of the deposit cross sections and not artifacts introduced during sectioning.

It therefore appears likely that the light, textured regions observed by transmission electron microscopy of the ultramicrotomed sections of copper electrodeposits are due to inclusions of polymeric additives, PEI or PEG which have been employed during the plating process. Such an explanation appears possible based on considerations of the observed fine, granular or cloudy texture of these regions and their location within the deposit bulk. The presence of regions of differing texture is consistent with the different types of additives, PEI and PEG used during the deposition process. The fact that the textured regions are evident only at the grain boundaries is further support that they are due to inclusions of additives as this behaviour has also been observed by other workers [9, 17].

An interesting feature of the copper cross sections is the size of the organic inclusions within the deposit bulk. Assuming that the polymers exhibit a random coil structure in solution, the radius of gyration of a PEG molecule of molecular weight 10 000 could be expected to be of the order of 2.5 nm. In the present study inclusions up to 250 nm × 100 nm have been observed (Fig. 3). It would thus appear that inclusions observed here are aggregates of additive molecules rather than individual molecules. Furthermore, it appears that the deposit within the local area of the inclusions seems to have grown around and compacted the incorporated molecules during deposition. The inclusion of aggregates of additive molecules may be similar to that described earlier for the case of weakly adsorbed *o*-phenanthroline molecules which are sufficiently mobile and which are entrapped in the deposit by approaching atomic layers, leading to incorporation of aggregates rather than individual molecules [7].

It must be noted that, as suggested by Nakahara [9], the accurate identification of organic inclusions within electrodeposits is not readily possible without appropriate chemical analysis. However, given the present observations, it would appear that under normal conditions of copper electrodeposition in synthetic electrolytes containing PEI or PEG as addition agents, the reagents are consumed in part by inclusion during deposition.

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