

Effects of Gelatin on Electroplated Copper Through the Use of a Modified-Hydrodynamic Electroplating Test Cell

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Received: 3 October 2020 / Accepted: 11 December 2020 / Published: 31 December 2020

We demonstrated the effects of gelatin in an electroplating bath on the morphology of electrodeposited copper through the use of a modified-hydrodynamic electroplating test cell (M-HETC). The proposed M-HETC is an electroplating test cell that provides a stable and reproducible flow field and controllable mass transfer. In addition, the M-HETC allows exploration of the variations in the surface appearance of electrodeposits over a wide range of current densities in a single electroplating test. Results indicate that this proposed time-efficient tool can be used to study the key factors that influence the surface morphology and properties of electrodeposited copper.

Keywords: electrochemical deposition; copper electroplating; electroplating test cell; gelatin

1. INTRODUCTION

Copper electrodeposition is an essential technique for forming wires in the electronic devices. To date, copper electrodeposition is a key technology to construct the interconnects of ultralarge-scale integrated circuits and printed circuit boards[1–4]. The control of the electrodeposition processes and the properties of the deposited copper are highly dependent on various process parameters, such as temperature, current density, and the stirring conditions of the electroplating bath[5–7]. In addition, the compositions of electroplating baths and the additives introduced are key factors that greatly affect the behavior of copper electrodeposition and result in differences in the surface morphology, resistivity, and crystal orientation of electrodeposited copper[7,8]. Therefore, the development of a time-efficient tool for studying the influential factors in copper electroplating processes for advanced electronic devices is very important.

In this study, we propose an efficient electroplating cell that can be used to study the surface profile and a series of properties of the deposited copper as a function of current density, plating bath

composition and other electroplating parameters. The surface profile is a very important factor in the properties of deposited copper for interconnects. The resistance, adhesion and reliability of the electronic devices are highly correlated to the surface profile of the composed copper interconnects.

The classical Hull cell is a versatile tool to analyze the performance of electroplating baths[9,10] and is a trapezoidal structure in which the cathode is placed at an oblique angle with respect to the anode. In addition, several modified Hull cells with different structures have been proposed[11,12]. These cells allow studies on the variation in the appearance of an electrodeposit over a wide range of current densities along the cathode. The disadvantage of the Hull cell is its limited and irreproducible solution agitation[13,14]. The Hull cell is normally operated under the conditions of free convection, but in some cases, solution agitation is conducted by gas bubbling near the cathode, by a magnetic stirrer or by a reciprocating paddle.

Numerous studies have been performed to enhance mass transfer in Hull cells or other types of test cells. Designs[15] and numerical simulations[13,16] of and experimental investigations[14,16,17] on Hull cells with improved mass transfer are conducted. A rotating electrode, in the form of a cone or cylinder, is introduced to provide well-defined hydrodynamic conditions. A novel hydrodynamic electroplating test cell (HETC) proposed by Yen, which consists of a rotating cylinder, an annular electrolyte cell, and two electrode plates, has been developed to offer well-defined hydrodynamic conditions[18]. The device structure of the HETC has a fan-shaped geometry, and the outer arc of the sidewall of the cell is an insulating plate. The inner concentric arc of the HETC is an insulated rotating cylinder. The rotation of the central rotating cylinder drives the movement of the electrolyte; thus, the device provides a stable and reproducible flow field and controllable mass transfer conditions. Although HETCs have many advantages, the current density distribution along the cathode is not very wide.

To achieve a wider range of current densities in the test cell, the structure of HETC is further modified into a modified-hydrodynamic electroplating test cell(M-HETC). The configuration of M-HETC is sketched as shown in Figure 1(a). The sidewalls (Face 1, Face 2 and Face 3) and the bottom (Face 6) of the cell are all made of acrylic resin and insulated. The anode and cathode are placed on Face 1 and Face 2 of the cell, respectively. Face 3 represents the sidewall of the cell opposite to the rotating cylinder. Face 4 is the surface of the rotating cylinder. Face 6 represents the bottom of the cell. In this case, the cover at the top of the cell (Face 5), is not used; therefore, a free moving surface of the electrolyte is generated during electroplating.

Depending on the application, additives are frequently introduced into the electroplating bath for copper electrodeposition[1,2]. Additives have attracted attention for modulating the film properties of electroplated copper due to their effects on surface morphology, resistivity, and crystal orientation[3,7,8]. Studies on the effects of additives on copper deposits thorough Hull cells and modified Hull cells are limited [19]. In this study, we investigated the effects of gelatin on the morphology of electroplated copper using the M-HETC. In regard to health considerations, gelatin is one of the safest and least toxic additives for industrial copper electrodeposition. Gelatin is widely accepted to act as a leveling agent and grain refiner that modifies electrochemical reactions and the crystal growth of electroplating by its preferred adsorption on surface protrusions.

The electroplating test cells allow exploration of the differences in the appearance of an electrodeposit over a wide range of current densities along the cathode. They are being used for the

development of compositions of plating electrolytes and for monitoring the operation of industrial plating baths. Therefore, we proposed a modified electroplating cell with well-defined hydrodynamic conditions that provides a stable and reproducible flow field and controllable mass transfer conditions over a wider range of current densities. In this study, we evaluated the electroplating bath using the M-HETC. The effects of gelatin in the electrolyte on the morphology of copper deposits were revealed under a variety of current densities. Results showed that the M-HETC was an extremely useful and time-efficient tool for research and development (R&D) and quality control (QC) applications. The effects of gelatin on the morphology of copper deposits over a wide range of current densities could be derived in a single experiment.

2. EXPERIMENTAL

In the electroplating experiment, the configuration of the electroplating test cell is shown in Figure 1(a) with 316 grade stainless steel sheets and pure copper sheets as the cathode and anode, respectively. The size of the cathode and anode was 100 mm × 65 mm × 0.5 mm. The back side of each electrode was evenly coated with insulating paint. A pure copper wire was placed near the cathode as a reference electrode. The electrolyte was a copper sulfate/sulfuric acid aqueous solution (1.1 M H₂SO₄/1 M CuSO₄). The speed of the rotating cylinder was 1400 rpm. The temperature of the electroplating bath during electroplating was kept at 20 °C. The applied current was 1 A, and the samples were electroplated for 10 min.

The surface of the stainless-steel plate was cleaned with detergent, rinsed with deionized (DI) water, immersed in 2 M sulfuric acid solution for 10 min to remove oxides, and then cleaned with DI water. The pure copper electrode sheet for the anode was cleaned with detergent and then rinsed with DI water. After electroplating was completed, the stainless-steel plate coated with copper, was immediately removed from the cell, cleaned with DI water, and then dried with nitrogen. The thickness of the deposition layer was determined by the weight of the deposition layer and copper density. Scanning electron microscopy (SEM) was used to study the surface morphology.

3. RESULTS AND DISCUSSION

To understand the theoretical current distribution of the M-HETC, we used FlexPDE to find the potential distribution of the M-HETC. Assuming that the anode surface potential is 1, the cathode surface is 0, and the other two walls are set to be insulated; thus, the two-dimensional potential is solved by Laplace's equation. As shown in Figure 1(b), the equipotential line distribution of the M-HETC was obtained. Assuming that the current efficiency is 100% and the conductivity is a constant value, the potential gradient on the cathode surface can be regarded as the magnitude of the current. The current and position relationship were then taken as dimensionless, and the primary current distribution was derived. The result is shown in Figure 1(c).

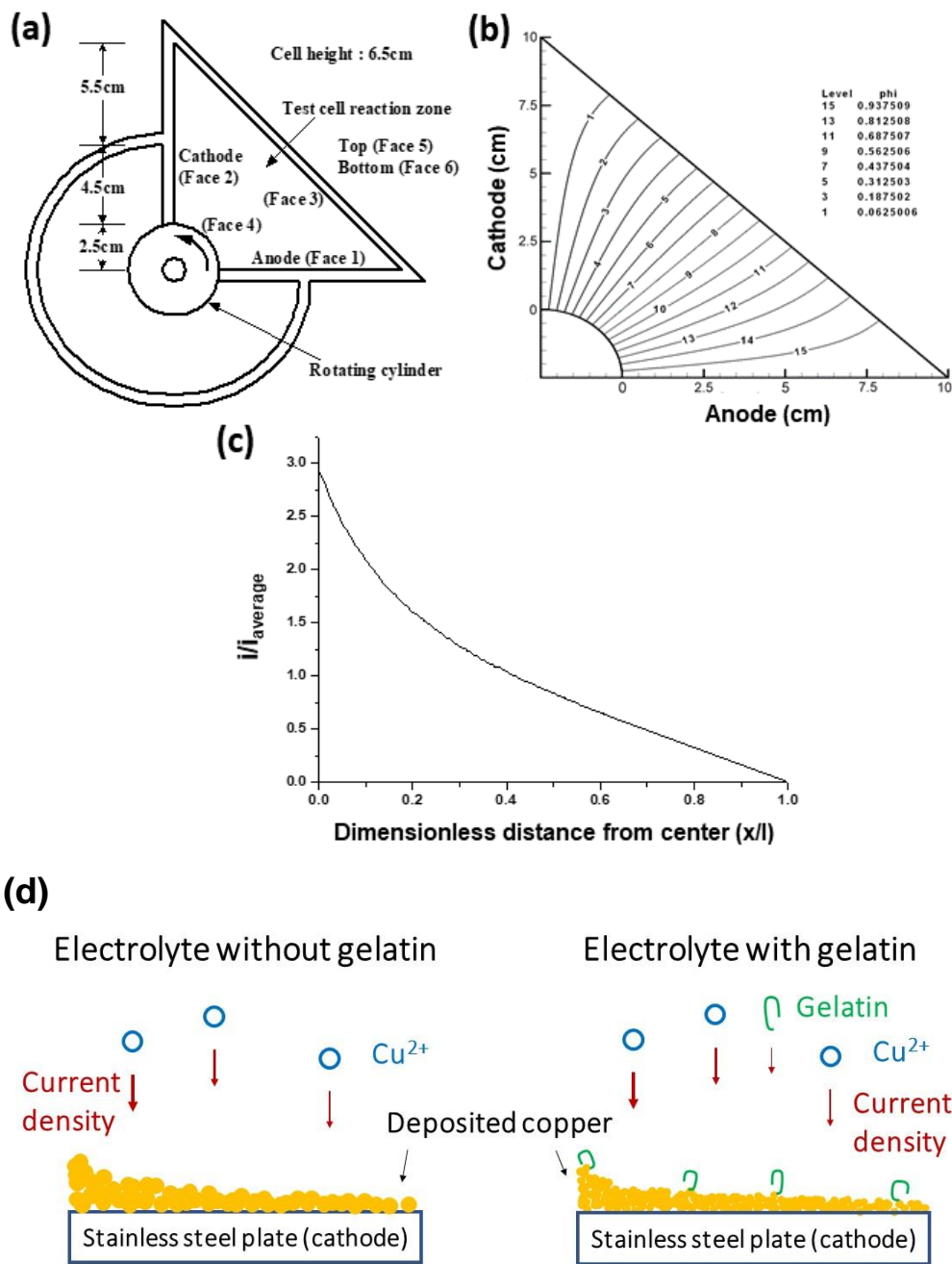


Figure 1. (a) Schematic diagram of the M-HETC (modified-hydrodynamic electroplating test cell). (b) Contour line of the potential distribution in the M-HETC, which was derived by modeling. (c) Primary current distribution of the M-HETC, which was derived by modeling. (d) Schematic diagram of copper electrodeposition on the cathode of the M-HETC.

From the result of Figure 1(c), it can be seen that the M-HETC cathode plate has a wide current density distribution, and the current density gradually approaches zero at the end far from the rotating cylinder. The schematic diagram (Figure 1(d)) shows that through a single electroplating test, copper deposits are obtained on the cathode at different thicknesses as a function of current density. The factors

that influence the electrochemical deposition of copper can be studied by using an electroplating test cell.

Figure 2(a) shows the thickness distribution of the copper deposit along the cathode without and with 9 ppm gelatin. This figure shows a slight difference in the thickness distribution between the two conditions. Compared to the thickness distribution of the two conditions with the primary current distribution, the results show that the thickness distribution of the copper deposits is close to the primary current distribution (Figure 2(b)). Under such test conditions, we interpret that the influence of the mass transfer control in the system is not significant and that the current density is dominated by the electric field in the system, which solely relies on the cell structure. Therefore, at a rotating speed of 1400 rpm, the M-HETC can provide good stirring conditions for the electroplating test while minimizing the effects of deficient mass transfer.

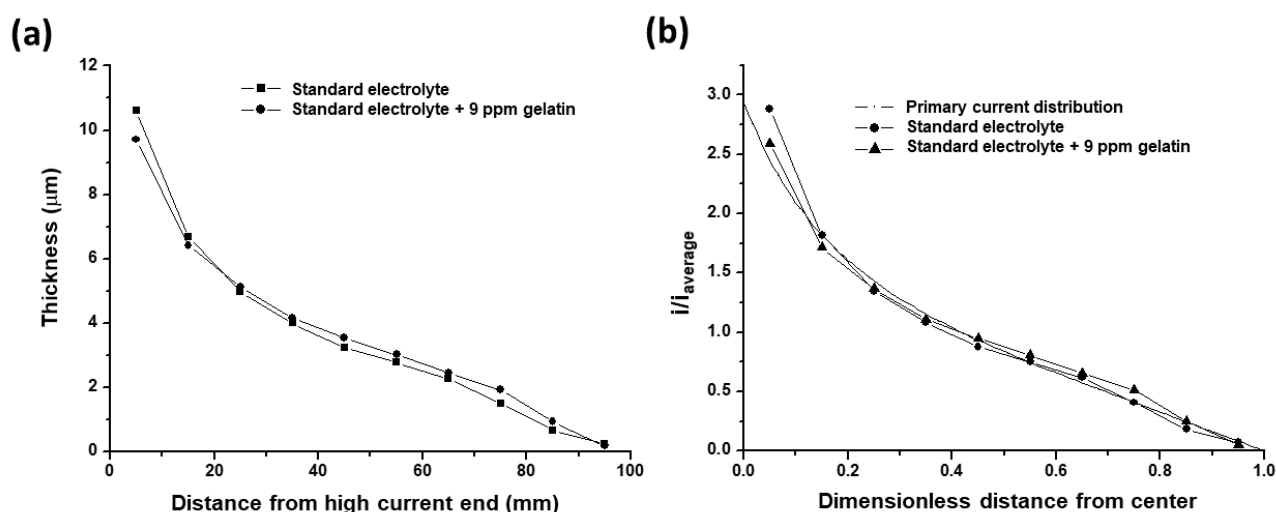


Figure 2. (a) Thickness of the deposited copper layers. (b) Calculated copper electrochemical deposition current density based on the thickness of electroplated copper in comparison with the primary current distribution.

Figure 3 shows SEM micrographs of copper deposits at various positions on the cathode. The images show the surface morphology of the copper deposit obtained on the cathode positioned (a) 0.5 cm; (b) 2.5 cm; (c) 3.5 cm; (d) 5.5 cm; (e) 6.5 cm and (f) 7.5 cm away from the cylinder. The results suggest that the derived film thickness and surface morphology are highly dependent on the current density. The results show that the M-HETC is a useful tool for studying the morphology of copper deposits over a wide range of current densities in a simple, single experiment. The thickness uniformity, resistance and adhesion of deposited copper are highly correlated to the morphology of the deposited copper. Through the electroplating test under various plating conditions along with the efficient selection of proper parameters for the M-HETC, it is possible to effectively derive the desired copper deposit with a proper surface profile and properties.

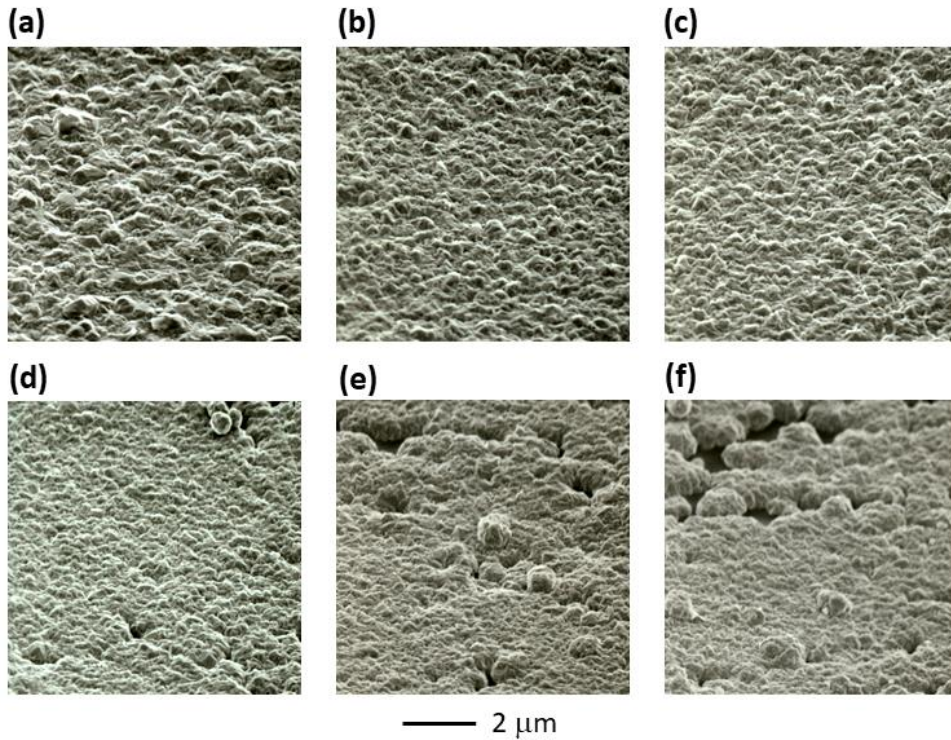


Figure 3. SEM micrographs of copper deposits obtained at various positions on the cathode without an additive in the electroplating bath. (Distance from the cylinder: (a) 0.5 cm; (b) 2.5 cm; (c) 3.5 cm; (d) 5.5 cm; (e) 6.5 cm and (f) 7.5 cm.)

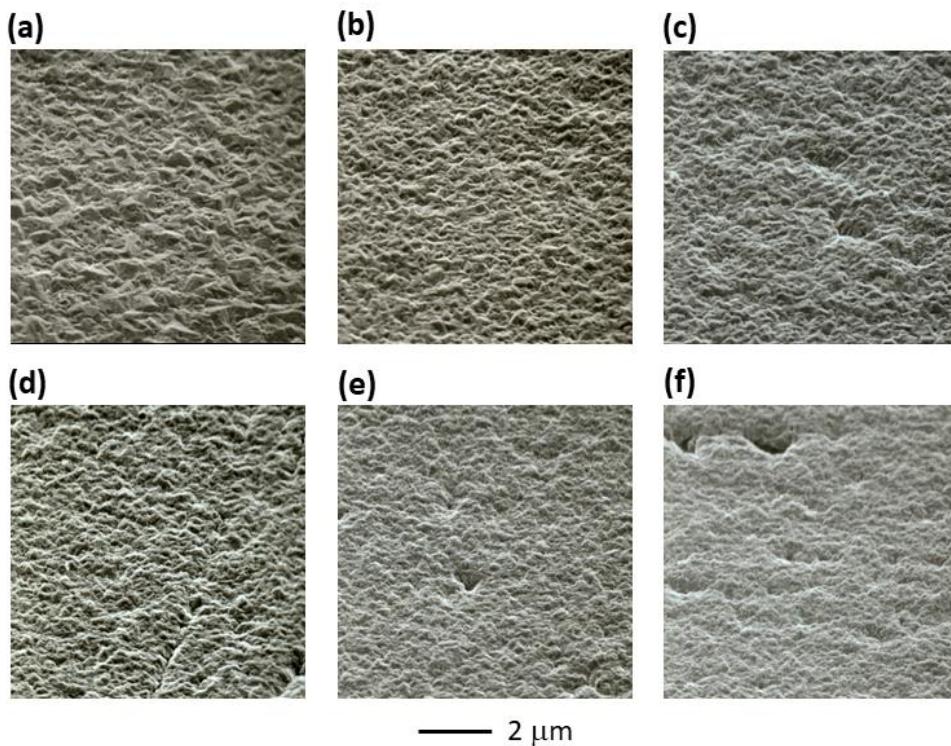


Figure 4. SEM micrographs of copper deposits obtained at various positions on the cathode with 9 ppm gelatin in the electroplating bath. (Distance from the cylinder: (a) 0.5 cm; (b) 2.5 cm; (c) 3.5 cm; (d) 5.5 cm; (e) 6.5 cm and (f) 7.5 cm.)

Figure 4 shows the SEM micrographs of copper deposits at various positions on the cathode obtained from the electroplating bath with 9 ppm gelatin. The images show the surface morphology of the copper deposit obtained at different positions ((a) 0.5 cm; (b) 2.5 cm; (c) 3.5 cm; (d) 5.5 cm; (e) 6.5 cm and (f) 7.5 cm from the cylinder). The results suggest that the derived surface morphology changes due to the addition of gelatin. Compared to Figure 3, the added gelatin acts as a leveling agent, and the refined grain results in a lower surface roughness at different current densities. The electrochemically deposited copper with improved thickness uniformity is obtained at a variety of current densities by the introduction of gelatin in the electroplating bath. In addition, the surface protrusions disappear due to the addition of gelatin, and the surface roughness decreases as a result. The improvement in the film thickness and the decrease in surface protrusions are more pronounced. This result suggests that the M-HETC is a useful tool for studying the effects of additives on the morphology of deposited copper.

Gelatin is widely accepted as an additive in electrolytes for leveling and grain refining during copper electrodeposition. Although the effects of gelatin on copper deposition under certain conditions have been widely studied[7,8], the effects of gelatin at various current densities or temperatures have not been reported and are still unknown. In this paper, the effects of gelatin as a function of current density are revealed with the aid of the proposed electroplating test cell(M-HETC). The effects of gelatin over a wide range of various current densities can be studied in a single experiment. The results show that the effects of gelatin are more pronounced at a low current density, including the decrease in the surface roughness, and number of surface protrusions along with the increase in thickness uniformity.

Figure 5 displays the images of the copper deposited layer on the stainless-steel plate obtained from the electrolyte without an additive (Figure 5(a)) and with 9 ppm gelatin (Figure 5(b)). From the appearance of the deposited layer, it is interpreted that the copper deposit without gelatin has relatively coarse crystal grains. With the incorporation of gelatin in the electrolyte, the appearance of the copper deposit shows enhanced uniformity over the entire region from the end at a high current density toward the end at a low current density.

In prior studies, a rotating cylinder Hull cell (RCHC) has been introduced to improve mass transfer in an electroplating test cell[12–17,20,21]. A numerical simulation of the current distribution along the cathode has been reported[13], while an experimental investigation of the primary and secondary current distributions has been conducted[14]. Additionally, the RCHC has been used to study pulse current electrodeposition[17]. Most research has focused on numerical simulations and experimental investigations of the current distribution of the cathode of the RCHC, and only a few studies have reported or discussed the surface morphology of the deposited layer[17,21]. In this study, we conducted simulations of the primary current distribution along the cathode and experimental investigations on the current distributions of an M-HETC. In addition, the surface morphology of the deposited layer was characterized in this paper.

The studies on RCHC conclude that RCHC is well suited for the study of plating processes. The simulations and experimental investigations on RCHC demonstrate that a wide range of current densities and well-controlled mass transport rates are achievable. In this study, results indicated that the M-HETC cathode has a wide range of primary current density distributions. This result can be attributed to the fact that the primary current density for an acute angle is zero at the edge regardless of the geometry of the rest of the cell[22]. Because the rotating cylinder drives the movement of the electrolyte, the M-HETC

can provide a stable and reproducible flow field and controllable mass transfer conditions. Since the structure of the cathode of the M-HECT is quite different from that of the RCHC, a cathode with a plate structure M-HECT is easier to study than a cathode with a cylindrical structure (RCHC) in terms of the surface appearance and morphology of the deposited layer.

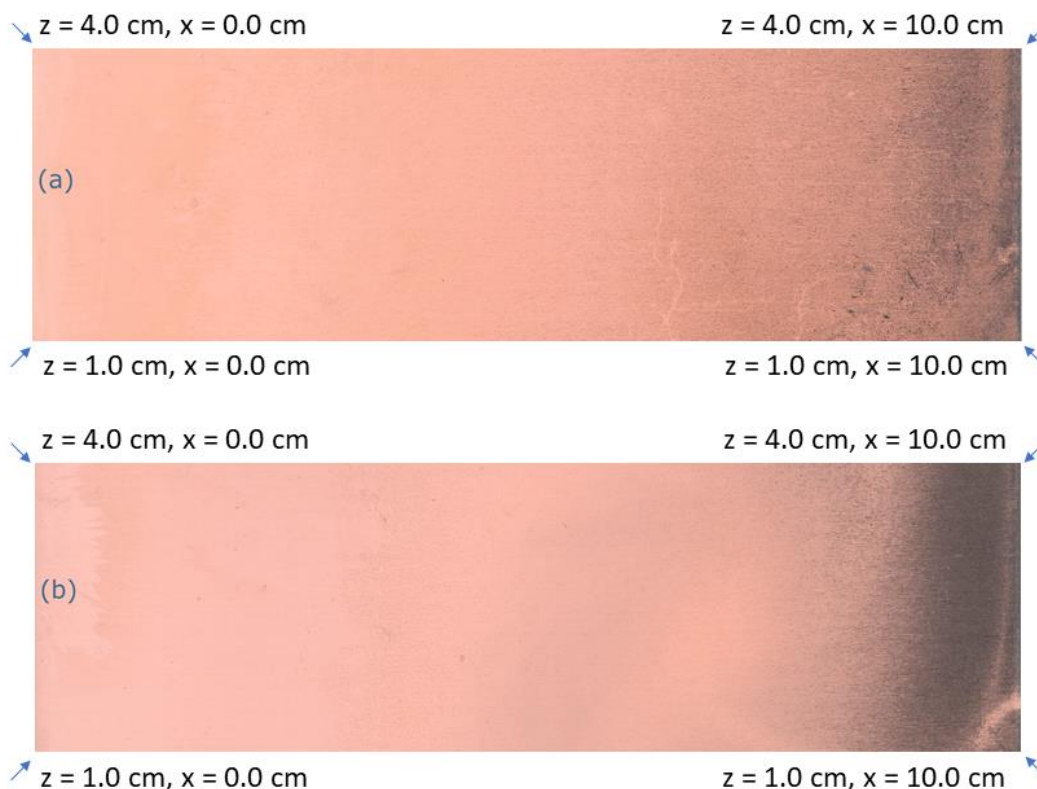


Figure 5. Images of copper deposited on the stainless steel substrate obtained (a) without an additive, and (b) with 9 ppm gelatin in the electroplating bath.

4. CONCLUSIONS

We evaluated the effects of current density and an additive in the electroplating bath on the electrodeposition of copper through the use of an M-HETC. The results suggested that the M-HETC we proposed could provide a stable and reproducible flow field and controllable mass transfer allowing the exploration of electrodeposits over a wide range of current densities in a single electroplating test. The results indicated that the M-HETC was an efficient electroplating cell that could be used to study the surface profile and a series of properties of the deposited copper as a function of the current density, composition of the plating bath and other electroplating parameters.

The electrochemically deposited copper with an improved thickness uniformity was obtained at a variety of current densities along with the introduction of gelatin in the electroplating bath. The results showed that the effects of gelatin were more pronounced at a low current density, including the decrease in the surface roughness, and number of surface protrusions along with the increase in thickness uniformity.

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