รายงานวิจัยฉบับสมบูรณ์

โครงการ

การศึกษาผลของคลอไรด์และผลของอันตรกิริยาของคลอไรด์กับสารเติมแต่งชนิดอื่นระหว่างกระบวนการชุบทองแดงโดยวิธีไฟฟ้าเคมีในสารละลายซัลเฟต

โดย

อ.ดร.นิสิต ตัณฑวิเชฐ
ภาควิชาเคมีเทคนิค คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

รศ.ดร.อรวรรณ ชัยลภากุล
ภาควิชาเคมี คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ธันวาคม 2552

สัญญาเลขที่ MRG4980074

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รศ.ดร.อรวรรณ ชัยลภากุล
ภาควิชาเคมี คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

สนับสนุนโดยสำนักงานคณะกรรมการอุดมศึกษา และสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกอ. และ สกว.ไม่จำเป็นต้องเห็นด้วยเสมอไป)

กิตติกรรมประกาศ

ขอขอบคุณสำนักงานคณะกรรมการอุดมศึกษา และสำนักงานกองทุนสนับสนุนการวิจัย ที่มอบทุนเพื่อใช้ในการดำเนินงานโครงงานวิจัยนี้ให้สำเร็จไปได้ด้วยดี และขอขอบพระคุณผู้อำนวยการ ฝ่ายวิชาการ สำนักงานกองทุนสนับสนุนการวิจัยที่เข้าใจถึงปัญหาที่เกิดขึ้นระหว่างการดำเนินโครงงานวิจัยนี้ โดยอนุญาตให้ขยายระยะเวลาดำเนินงานวิจัยจากเวลาสิ้นสุดโครงงานเดิม จนสามารถทำโครงงานวิจัยนี้ได้สำเร็จตามเป้าหมายที่วางไว้ และขอขอบคุณภาควิชาเคมีเทคนิค คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย ที่เอื้ออำนวยสถานที่และเครื่องมือเพื่อใช้ในโครงงานนี้

บทคัดย่อ

รหัสโครงการ : MRG4980074

ชื่อโครงการ : การศึกษาผลของคลอไรด์และผลของอันตรกิริยาของคลอไรด์กับสารเติมแต่งชนิดอื่นระหว่างกระบวนการชุบทองแดงโดยวิธีไฟฟ้าเคมีในสารละลายซัลเฟต

ชื่อนักวิจัย : ดร.นิสิต ตัณฑวิเชฐ
ภาควิชาเคมีเทคนิค คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

E-mail Address : **nisit.t@chula.ac.th**

ระยะเวลาโครงการ : **1 ก.ค. 2549 – 31 ธ.ค. 2552**

งานวิจัยนี้เป็นการศึกษาอันตรกริยาระหว่างคลอไรด์ และไทอเรีย(thiourea)เพื่อความเข้าใจถึงกลไกการเกิดปฏิกิริยาไฟฟ้าเคมีของการฟอกฟูนทองแดง โดยพบว่า คลอไรด์มีผลต่อการทำงานของไทอเรียระหว่างการฟอกฟูนทองแดงโดยวิธีไฟฟ้าเคมี ซึ่งปกติไทอเรียเป็นสารเติมแต่งที่ใช้อยู่ทั่วไปเพื่อให้ผิวทองแดงที่ฟอกฟูนได้มีความเป็นมันเงาขึ้นเมื่อเทียบกันการการฟอกฟูนทองแดงที่ไม่ใช้สารติมแต่ง โดยไทอเรียทำให้โครงสร้างของทองแดงที่ฟอกฟูนได้มีความละเอียดขึ้นส่งผลให้ผิวมีความเป็นมันเงา แต่จะมีปุ่มขนาดเล็กระดับจุลภาคโผล่ขึ้นจากผิวซึ่งกระจายทั่วผิวส่งผลให้ผิวมีความมันเงาที่ไม่คมชัด ในทางตรงข้ามเมื่อใช้คลอไรด์เป็นสารเติมแต่งผิวทองแดงที่ฟอกฟูนได้จะด้านและไม่มีความเป็นมันเงาเมื่อเทียบกันการไม่ใช้สารติมแต่ง แต่เมื่อใช้คลอไรด์ร่วมกับไทอเรียผิวของทองแดงที่ฟอกฟูนได้จะมีความมันเงาที่คมชัดมากขึ้น โดยปุ่มขนาดเล็กระดับจุลภาคที่พบกระจายทั่วผิวเมื่อใช้เพียงไทอเรียเป็นสารเติมแต่งได้หายไป และผิวทองแดงที่ฟอกฟูนได้มีความเป็นมันเงาที่คมชัดมากขึ้น แต่จะส่งผลกระทบต่อโครงสร้างทองแดงที่ชุบระดับมหภาคซึ่งสามารถเห็นได้ด้วยตาเปล่าว่าผิวทองแดงที่ชุบได้จะมีความขรุขระ เป็นหลุม และไม่สม่ำเสมอ

งานวิจัยนี้จึงมุ่งเน้นไปที่การตอบปัญหาและพยายามหากลไกที่ว่าเหตุใดคลอไรด์จึงมีผลต่อการทำงานของไทอเรียระหว่างการชุบทองแดงโดยวิธีไฟฟ้าเคมี โดยใช้กล้องจุลทรรศน์แบบส่องกราด กล้องจุลทรรศน์แรงอะตอม และเทคนิคทางเคมีไฟฟ้า ซึ่งพบว่าพื้นผิวที่ขรุขระเมื่อใช้ไทอเรียและคลอไรด์เป็นสารเติมแต่งเกิดจากการที่ชั้นฟิล์มของสารเชิงซ้อนทองแดงไอออน-ไทอเรีย-คลอ

ไรด์ที่เกาะบนผิวระหว่างการฟอกฟูนโดยไฟฟ้ามีความไม่สม่ำเสมอกัน ส่งผลให้การฟอกฟูนทองแดงที่ปริเวณต่าง ๆบนพื้นผิวผ่านกลไกที่แตกต่างกัน ทำให้พื้นผิวที่ฟอกฟูนได้ขรุขระ ไม่สม่ำเสมอ และพบว่าความหนาแน่นกระแสที่ใช้ในการฟอกฟูนมีผลต่อการสร้างชั้นฟิล์มของสารเชิงซ้อนทองแดงไอออน-ไทอเรีย-คลอไรด์ที่เกาะบนผิวชิ้นงาน โดยที่หากใช้ความหนาแน่นกระแสที่สูงพอชั้นฟิล์มของสารเชิงซ้อนทองแดงไอออน-ไทอเรีย-คลอไรด์ที่เกาะบนผิวชิ้นงานจะสลายตัวอย่างสม่ำเสมอกันทั้งผิวชิ้นงานระหว่างการฟอกฟูน ส่งผลให้ทองแดงที่ฟอกฟูนได้มีโครงสร้างที่ละเอียดและผิวมีความเป็นมันเงา โดยผิวมีความเรียบทั้งระดับมหภาคและจุลภาค ซึ่งสามารถใช้เป็นแนวทางเพื่อนำไปประยุกต์ใช้จริงในอุตสาหกรรมทั่วไป รวมทั้งอุตสาหกรรมผลิตวงจรไฟฟ้า

คำหลัก : กระบวนการชุบทองแดงโดยวิธีไฟฟ้าเคมี; ไทอเรีย; คลอไรด์; อันตรกิริยา; ลักษณะโครงสร้าง

Abstract

Project Code : MRG4980074

Project Title : The study of influence of copper and its interaction with other additive on copper electrodeposition in sulphate plating solution

Investigator : Dr. Nisit Tantavichet
Department of Chemical Technology, Faculty of Science,
Chulalongkorn University

E-mail Address : nisit.t@chula.ac.th

Project Period : July 1, 2006 – 30 December, 2009

The interaction between chloride and thiourea in copper electrodeposition in a sulfate-plating bath was investigated. The sole addition of thiourea to the bath increased the polarization of the electrode potential during copper deposition, leading to very fine and smoothly structured deposit but with microscopic nodules distributed over the surface. When chloride was added to a plating solution containing thiourea, the copper deposition mechanism was changed, showing a depolarization of the electrode potential, and the copper deposits were found to have a relatively rougher microstructure, but without the formation of microscopic nodules. However, rough deposit surfaces having no distinct pattern were formed at the macroscopic scale. Observations of roughening evolution show that the rough surface was initiated from small holes formed across the deposit surface during the initial stage of deposition that eventually developed into visibly rough deposits. The copper deposition inside these holes and at other areas was expected to undergo different deposition mechanisms. Copper deposition in the areas that ultimately developed into holes was almost totally inhibited by the thiourea-Cu(I)-chloride complex film, not just in the grain growth process, but over practically the entire electrodeposition process. Conversely, copper deposition occurred in other areas under conditions where nucleation

proceeded, but grain growth was inhibited to produce a fine, homogeneous microstructure. An uneven deposit surface that had different microscopic structures in different areas was then formed. The structure of the thiourea-Cu(I)-chloride film was strongly affected by the current density and appeared to break down completely if sufficiently high current density was applied to yield a fine and homogeneous microstructure that was also macroscopically smooth.

Keywords : copper electrodeposition; thiourea; chloride; synergetic effect; morphology

Exclusive Summary

การศึกษาผลของคลอไรด์และ ผลของอันตรกิริยาของคลอไรด์กับสารเติมแต่งชนิดอื่น ระหว่างกระบวนการชุบทองแดงโดยวิธีไฟฟ้าเคมี ในสารละลายซัลเฟต

The study of influence of copper and its interaction with other additive on copper electrodeposition in sulphate plating solution

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1. ความสำคัญของปัญหา และที่มาของปัญหาที่ทำการวิจัย

เนื่องจากงานวิจัยในอดีตพบว่า คลอไรด์มีผลต่อการทำงานของไทอเรีย(thiourea) ในการชุบทองแดงโดยวิธีไฟฟ้าเคมีโดยที่เมื่อใช้คลอไรด์ร่วมกับไทอเรีย ผิวของทองแดงที่ชุบได้จะมีความมันเงาที่คมชัดมากขึ้น ดังนั้นในงานวิจัยนี้จะมุ่งเน้นไปที่การตอบปัญหาและพยายามหากลไกที่ว่าคลอไรด์จึงมีผลต่อการทำงานของไทอเรียอย่างไร นอกจากนี้จะทำการศึกษาสภาวะที่ดีที่สุดในการชุบทองแดงโดยมีคลอไรด์และไทอเรียเป็นสารเติมแต่งที่ เพื่อให้ได้มาซึ่งทองแดงชุบได้มีความมันเงาที่คมชัดและมีความสม่ำเสมอของผิว เพื่อนำไปประยุกต์ใช้จริงในอุตสาหกรรมทั่วไป รวมทั้งอุตสาหกรรมผลิตวงจรไฟฟ้า

2. วัตถุประสงค์ของโครงการ

2.1. เพื่อศึกษาและเข้าใจถึงบทบาทของคลอไรด์ และอันตรกริยาของคลอไรด์และไทอเรียต่อการเกิดปฏิกิริยาไฟฟ้าเคมีของทองแดงโดยใช้ กล้องจุลทรรศน์แบบส่องกราด (SEM) กล้องจุลทรรศน์แรงอะตอม (AFM) ประกอบกับเทคนิคทางเคมีไฟฟ้า (electrochemical technique)

2.2. เพื่อศึกษากลไกของของการฟอกฟูนทองแดงโดยวิธีไฟฟ้าเคมีโดยมีคลอไรด์และไทอเรียเป็นสารเติมแต่ง

2.3. เพื่อหาสภาวะที่เหมาะสมในการชุบทองแดงโดยไฟฟ้าเคมีจากสารละลายซัลเฟตโดยมีสารเติมแต่งที่ประกอบด้วยคลอไรด์และไทอเรีย เพื่อสามารถนำไปประยุกต์ใช้ในอุตสาหกรรมต่าง ๆ เช่น อุตสาหกรรมที่เกี่ยวกับการผลิตวงจรไฟฟ้า

3. ระเบียบวิธีวิจัย

3.1. preliminary study (4 เดือน) เพื่อศึกษาสภาวะที่เหมาะสมของการชุบทองแดงในสภาวะสารละลายหยุดนิ่ง (stagnant plating solution) โดยจะศึกษา

- ความเข้มข้นของทองแดง และ ความหนาแน่นกระแสที่ใช้
- ความเข้มข้นของไทอเรีย
- การเพิ่มคลอไรด์ไอออนลงไปร่วมกับไทอเรีย

3.2. เรียนรู้การใช้เครื่อง AFM และ set up AFM เพื่อการใช้งานจริง (2 เดือน)

3.3. ศึกษาผลของสารเติมแต่งต่าง ๆต่อลักษณะทางกายภาพของโครงสร้างของทองแดงที่ฟอกฟูนได้ โดยใช้ AFM ภายใต้สภาวะที่สารละลายมีการเลื่อนไหวโดยใช้อิเลคโทรดแบบจานหมุน (rotating disc electrode) (8 เดือน)

- ไม่มีสารเติมแต่ง
- เมื่อมีสารเติมแต่งชนิดเดียวอยู่ในสารละลาย (ไทอเรีย)
- เมื่อมีคลอไรด์อยู่ในระบบกับไทอเรีย

3.4 ศึกษาผลของสารเติมแต่งต่าง ๆต่อการฟอกฟูนทองแดงโดยใช้ Electrochemical surface plasmon resonance (ESPR) (8 เดือน)

3.5. ศึกษาผลของคลอไรด์ที่มีต่อลักษณะที่ไม่สม่ำเสมอของทองแดงที่ฟอกฟูนได้โดยใช้ AFM และ SEM (6 เดือน)

3.6. ศึกษากลไกการเกิดปฏิกิริยาไฟฟ้าเคมีของการฟอกฟูนทองแดงโดยมีคลอไรด์และไทอเรียเป็นสารเติมแต่งโดยใช้ AFM SEM และ เทคนิคทางเคมีไฟฟ้าSEM (8 เดือน)

3.7. ศึกษาผลของความหนาแน่นกระแส และการไหลเวียนของสารละลายระหว่างการชุบทองแดงต่ออันตรกริยาของคลอไรด์และไทอเรียของเกิดปฏิกิริยาไฟฟ้าเคมีของการฟอกฟูนทองแดง (8 เดือน)

Introduction

In electrodeposition, it is well known that the addition of small amounts of certain substances into the plating bath results in significant changes in the properties and throwing power of the deposit. The added substances are expected to modify the deposition mechanism depending on their functions during the electrodeposition process. In copper electrodeposition in a sulfate-plating bath, various additives such as gelatin [1,2], benzotriazole [3-9] and thiourea [2,7,8,10-21] have been widely used to improve the surface finish of metal deposits.

Besides these additives, chloride has also been found to play a significant role during the electrodeposition of copper in a sulfate-plating bath. The presence of chloride as the sole additive has been reported to have inconsistent results in influencing copper deposition, where some researchers find improvements in copper deposition properties [22,23] while others find the opposite [24-26]. Moreover, the presence of chloride in plating baths containing other additives such as polyethylene glycol (PEG), bis(3-sulfopropyl) disulfide (SPS) or 3-mercapto-1-propanesulfonate (MPSA) and their combinations has been found to alter deposit properties relative to those in the absence of chloride, and a number of extensive studies on the interactions of chloride and those additives have been reported [23,25,27-29]. On the other hand, although thiourea has been commonly used as a brightening agent for copper electrodeposition [7,14,18,19,30,31], to date very few studies on electrodeposition in a solution containing thiourea and chloride have been conducted [15,32,33].

Previously, we reported the tendency of the combination of thiourea and chloride to improve the copper deposit structure [26]. In this study, we extensively investigate the synergetic effects of thiourea and chloride on the morphology of the copper deposit during direct current (DC) electrodeposition. The experiments were initially conducted on copper disc electrodes rotating at 500 rpm using DC electrodeposition at 0.04 A cm^{-2}. The influences of the fluid-flow conditions and the applied current density were also studied. The deposit morphologies were characterized by scanning electron microscopy (SEM) and *ex situ* atomic force microscopy (AFM). Cyclic voltammetry was used for Cu^{2+} reduction, and electrode potentials were monitored during electrodeposition to provide better insight

into the synergy between the effects of thiourea and chloride during copper electrodeposition.

Experimental

The electrodeposition experiments were conducted using a rotating disc electrode (RDE) (MetroOhm) immersed in a cylindrical electrolytic cell containing 50 cm^3 of a plating solution. DC electrodeposition and voltammetry experiments were carried out using a μAUTOLAB II Potentiostat (Eco Chemie) with a three-electrode system. The working electrode was a 0.43-cm diameter (0.1452 cm^2 area) copper disc polished with SiC-type abrasive paper (1200 grade), followed by silicon carbide grinding paper (P4000) (Buehler) and 0.3 and 0.05 μm Al_2O_3 powder (Buehler), to a mirror finish. A copper disc, placed at the bottom of the cell about 2 cm from the working electrode, was used as the counter electrode. A mercury/mercurous sulfate electrode (MSE, Radiometer analytical) was used as the reference electrode. All potentials reported herein correspond to the MSE scale.

An acidic sulfate-plating bath containing 0.1 M $CuSO_4$ and 1 M H_2SO_4 was used for all experiments. The concentrations of HCl (Aldrich Chemical) and thiourea (Aldrich Chemical) used to study the effect of additives on copper deposition were 10^3 μM and 20 μM, respectively. Stock thiourea solutions were prepared freshly before the electrodeposition experiments. The presence of these additives in the concentration ranges used in this work did not have a noticeable effect on the open circuit potential.

DC electrodeposition experiments were conducted at a current density of 0.04 A cm^{-2} on copper disc electrodes rotating at 500 rpm to achieve a charge density of 6 C cm^{-2}. However, later in the study, the rotational speed and the applied current density were varied in order to investigate the correlation between those parameters and deposit topographies during the copper electrodeposition in the presence of thiourea and chloride. Experiments were conducted several times under identical conditions to assess repeatability and consistent results were obtained from run to run. Deposit morphology was characterized using *ex situ* atomic force microscopy (AFM) (Veeco, NanoScope IV) and

scanning electron microscopy (SEM) (JOEL, JSM-5410LV). AFM studies were carried out in contact mode using a Si_3N_4 tip to acquire images of different sizes. The root mean square (RMS) microroughness of the deposited surfaces was also obtained by AFM. Measurement of the RMS microroughness was intended to complement the information provided by the AFM images to determine the topography of the copper deposits produced under different conditions. To obtain the cross-sectional images, the deposited copper disc was mounted in Bakelite and cut through the disc center using a diamond wafering blade on a low-speed saw. The cross-sectional deposited copper disc was then polished using SiC-type abrasive paper (1200 grade) followed by 0.3 and 0.05 μm Al_2O_3 powder and was etched in a solution of NH_4OH and H_2O_2 in water [28]. The cross-sectional images showing the deposit profiles were obtained by SEM.

Results and discussion

1. Cyclic voltammetry – To investigate the synergetic effect of the combination of thiourea and HCl for copper electrodeposition, a series of cyclic voltammetry experiments for Cu^{2+} reduction were carried out in the absence and presence of additives. The voltammograms for the rotational speeds of 500 and 2,000 rpm are shown in Fig. 1a and b, respectively. As shown in Fig. 1a and b, the voltammograms obtained in the same plating solution indicate similar trends for different rotational speeds, except that the voltammograms for Cu^{2+} reduction obtained at 2,000 rpm reach a higher level of limiting current density for the forward scans (i.e., 0.12 A cm^{-2}) than those obtained at 500 rpm (i.e., 0.06 A cm^{-2}). The forward scans in Fig. 1 confirm the findings from previous studies showing that Cu^{2+} reduction is accelerated in the presence of HCl alone [25-27,34,35]. Conversely, the voltammograms obtained in the presence of thiourea alone confirm that copper deposition is strongly suppressed at lower overpotentials before being abruptly activated at a critical potential (approximately –0.77 V MSE) [18,26,36]. Detailed discussions of the voltammograms in the presence of HCl alone and in the presence of thiourea alone can be found in the previous work [26] and in the literature [18,25,27,34-37].

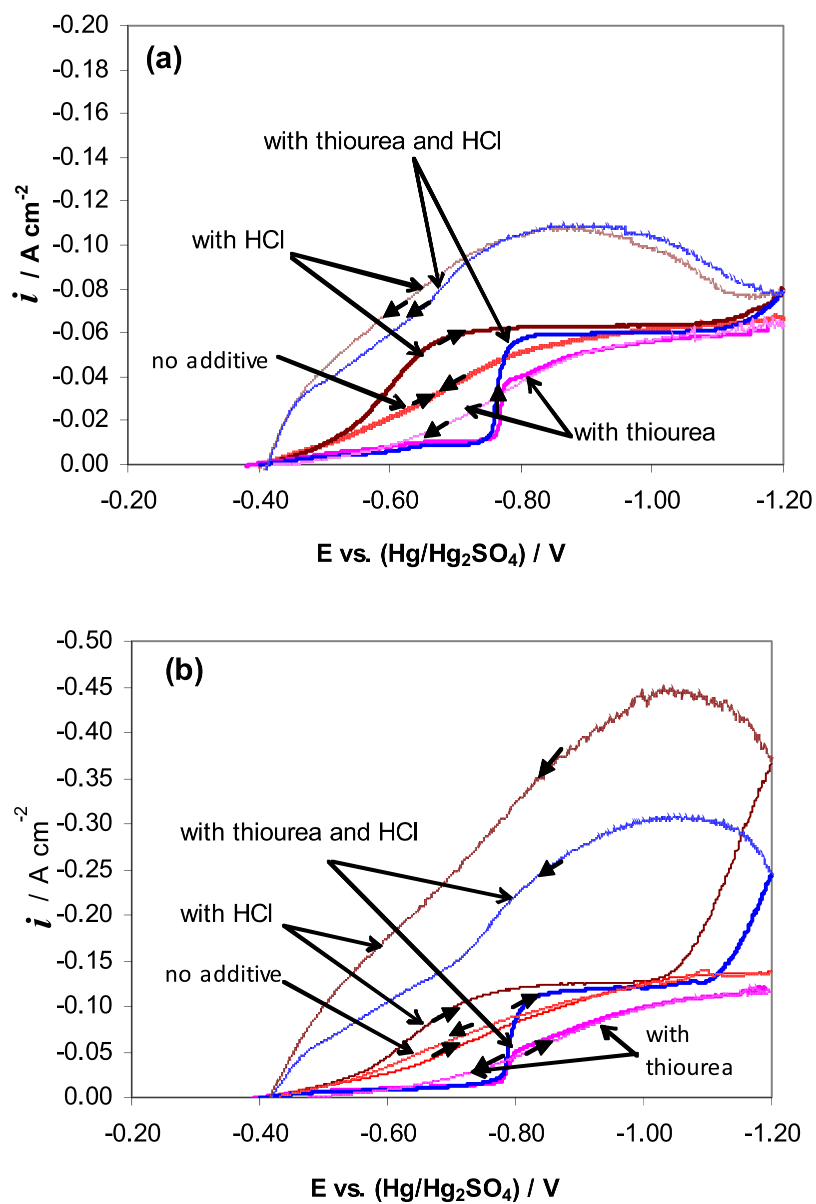


Fig. 1 Cyclic voltammograms for Cu^{2+} reduction on rotating disc electrodes immersed in various 0.1 M $CuSO_4$—1M H_2SO_4 solutions at rotational speeds of (a) 500 rpm and (b) 2,000 rpm using a scan rate of 10 mV s^{-1}

When both HCl and thiourea are present in the solution, the forward scans are polarized relative to those observed in the absence of additives, whereas the reverse scans are depolarized with respect to those obtained in their absence. In fact, the forward scans almost follow those obtained in the solution containing thiourea alone, except that they establish a more well-defined limiting current density plateau. The reverse scans show the opposite results. In the presence of thiourea alone, the reverse scans still indicate an inhibition of Cu^{2+} reduction over the entire scan. They closely follow the corresponding forward scans until reaching the critical potential (below –0.77 V) where they do not show the almost complete inhibition of Cu^{2+} reduction. The inhibiting film formed during the forward scan for Cu^{2+} reduction in the presence of thiourea alone partially breaks down at high potentials or completely breaks down, but is gradually restored during the reverse scan (from the critical potential to approximately –0.6 V) and is completely restored when the potential reaches –0.6 V. In contrast, the reverse scans in the presence of thiourea and chloride indicate the acceleration of Cu^{2+} reduction; here they tend to follow those obtained in the solution containing HCl alone, despite the substantial discrepancy shown for the case of 2,000 rpm. The significantly higher current density of the reverse scan at 2,000 rpm when HCl alone is present compared to that when both thiourea and HCl are present is likely due to the considerably rougher deposit formed at this rotational speed when HCl is the only additive. The inhibiting film formed during the forward scan in the presence of thiourea and chloride is mostly destroyed at high potentials and is not restored quickly enough to cover the copper substrate. Since the reverse scans show acceleration similar to that in the presence of HCl alone, it is possible that only thiourea detaches from the inhibiting film, leaving chloride alone on the copper surface during the reverse scan. The reverse scan results suggest that, in the presence of thiourea and chloride, thiourea should attach on the copper surface through chloride to form the inhibiting complex, whereas, in the absence of chloride, thiourea attaches directly onto the copper surface to form the inhibiting complex. The voltammogram results indicate that the addition of HCl in the plating solution containing thiourea changes the structure of the inhibiting complex adsorbed on the copper surface and hence the mechanism of copper electrodeposition.

2. Microscopic study – To study the synergetic effect of the combination of thiourea and HCl on the deposit morphology, electrodeposition experiments were carried out in the absence and presence of additives using a current density of 0.04 A cm^{-2} on copper disc electrodes rotating at 500 rpm as the standard conditions. The current density of 0.04 A cm^{-2} was chosen based on the response in Fig.1a, showing that it is sufficiently high to maintain a high nucleation rate without causing electrodeposition to be mass transfer limited. The electrodeposition of copper at the rotational speed of 2,000 rpm is discussed in section 3.4. The AFM images of the copper deposits obtained in the absence and presence of additives after passing a charge density of 6 C cm^{-2} are shown in Fig. 2. The AFM image of the bare copper substrate is included (Fig. 2a) for comparison. Each AFM image was obtained *ex situ* of a deposit produced from a separate deposition experiment. The electrode potentials monitored during the electrodeposition are shown in Fig. 3.

Similar to the results reported previously [26], the copper deposit structure produced in the presence of HCl alone (Fig. 2c) contains bigger grains and becomes coarser and rougher (roughness = 79.37 nm) compared to that obtained in the absence of additives (Fig. 2b) (roughness = 60.55 nm), whereas the copper deposit structure produced in the presence of thiourea alone (Fig. 2d) consists of very fine grains and a mostly very smooth surface. The deposit surface produced in the solution containing thiourea alone appears brighter than that produced in the absence of additives or in the presence of HCl alone. However, the surface is not as reflective as the polished uncoated copper surface since it appears to already have a very thin cloudy film overlay when a charge density of 1 C cm^{-2} has been passed. The thin cloudy film is expected to be due to microscopic nodules protruding from the flat deposit surfaces, which are locally found on the deposit structures when a charge density of 1 C cm^{-2} has been passed (data not shown) and become larger and denser as the electrodeposition proceeds, eventually merging altogether to form an entirely rough deposit structure [38]. The influence of chloride alone and thiourea alone on the electrodeposition of copper has been discussed in our previous work [26,38] and in the literature [8,16,17,25,26,29,31,38-41].

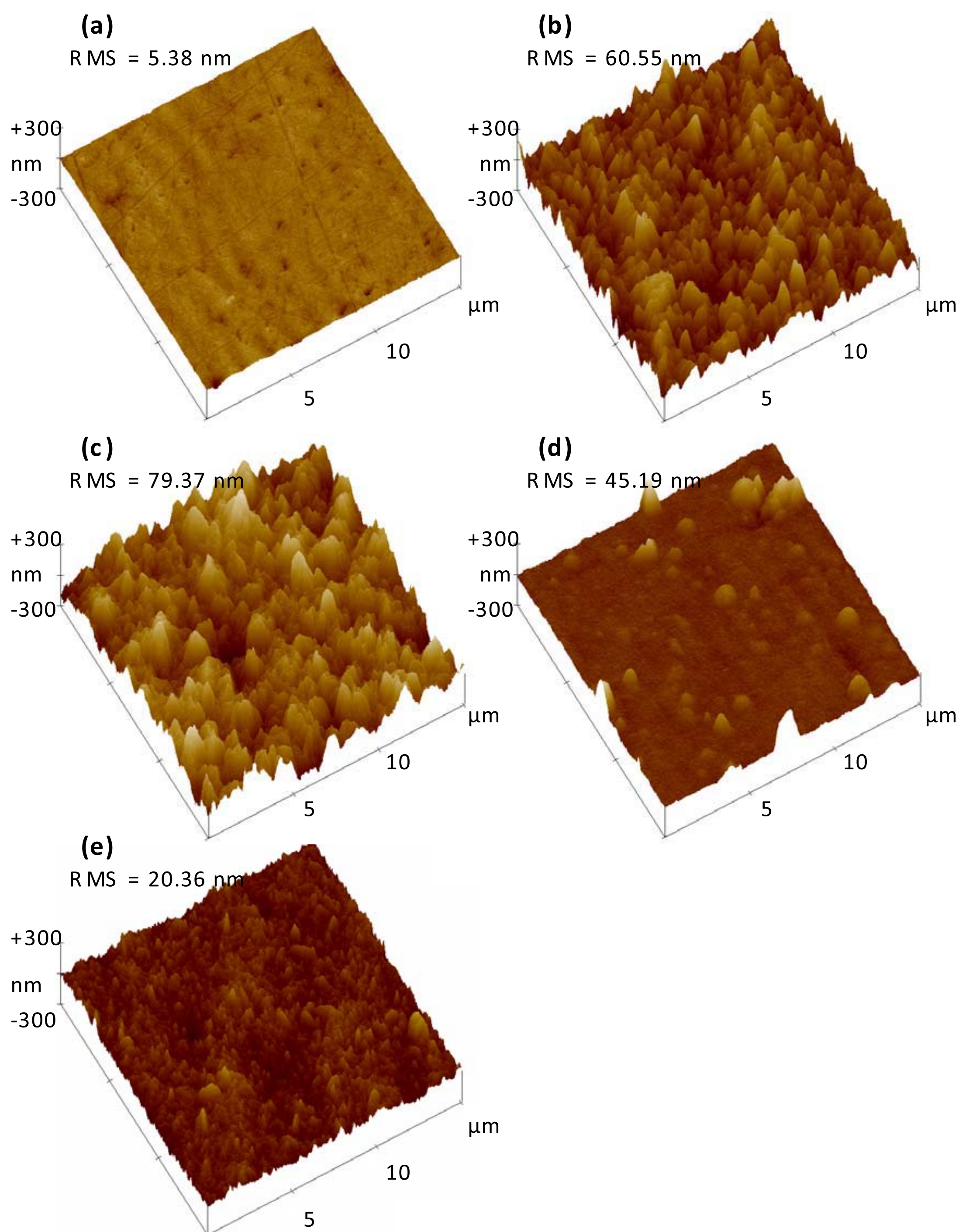


Fig. 2 AFM images (15 mm × 15 mm) of (a) bare copper surface, and copper deposits obtained from the 0.1 M $CuSO_4$-1M H_2SO_4 solution containing (b) no additive, (c) 1×10^3 µM HCl, (d) 20 µM thiourea, (e) 20 µM thiourea and 1×10^3 µM HCl at a current density of 0.04 A cm^{-2} and a rotational speed of 500 rpm after passing a charge density of 6 C cm^{-2}

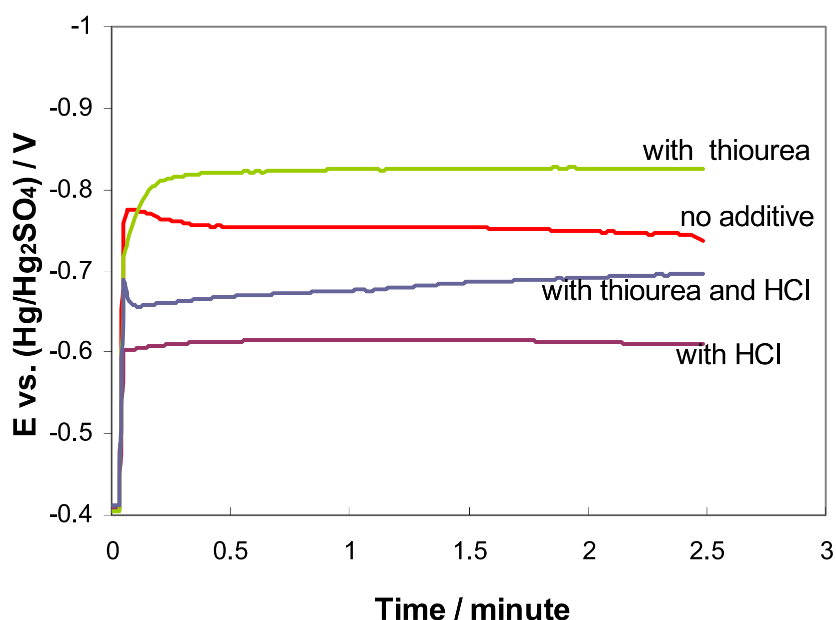


Fig. 3 Electrode potentials monitored during DC electrodeposition in 0.1 M $CuSO_4$–1 M H_2SO_4 solutions in the absence and presence of different additives until a charge density of 6 C cm^{-2} is passed

The microroughness of the deposit obtained in the presence of thiourea is found to be lower (45.19 nm) than that in the absence of additives (60.55 nm), but it strongly depends on the location of the image taken since the surface of the deposit obtained in the presence of thiourea consists of a very smooth and fine structure, with nodules distributed randomly across the surface (Fig. 2d). It should be noted that although the nodule formation was observed in the 3-D images using AFM, the deposit surface still appears to be very smooth macroscopically since no rough surface features were observed by SEM at a magnification of 50X.

When both HCl and thiourea are present in the plating solution, the combination of these two additives shows a synergetic effect. Fig. 2e shows that the deposit structure obtained from a solution containing 20 μM thiourea and 1×10^3 μM HCl is substantially different from that obtained in the presence of thiourea alone (Fig. 2d) or HCl alone (Fig. 2c), as it has a slightly bigger-grained structure than that obtained in the presence of thiourea alone, but

still has much smaller and finer-grained structure than that obtained either in the absence of additives or in the presence of HCl alone. Thiourea and chloride are expected to form a complex and adsorb at the solid-liquid interface and block the surface diffusion process of copper adatoms. However, the inhibition mechanism of the thiourea-Cu(I)-chloride complex should differ from that of the thiourea-Cu(I) complex since the deposit structure obtained in the presence of both additives is obviously not as smooth as the flat regions (i.e., the smooth areas excluding the nodule spots) of the deposit produced in the presence of thiourea alone and more importantly no nodules are formed. No cloudy film is formed on the deposit surface, which leads to more reflective surface. The disappearance of nodules leads to a more uniform structure, lower overall microscopic deposit roughness (roughness = 20.36 nm) and a more reflective surface compared to the deposits obtained in the presence of thiourea alone.

As shown in Fig. 3, the electrode potential for the copper deposition in the presence of thiourea alone, as for the voltammogram results (Fig. 1a), is polarized toward a higher cathodic potential (~ -0.83 V) relative to that in the absence of additives (~ -0.74 V). On the other hand, the electrode response for copper deposition in the presence of thiourea and HCl is depolarized toward a lower cathodic potential (~ -0.69 V) which is closer to the value attained during the reverse scan in Fig. 1a than to that reached during the forward scan at the same current. These indicate the difference in electrocrystallization mechanisms of these two systems, which leads to different deposit structures. The polarization condition for the deposit in the presence of thiourea alone indicates that the Cu^{2+} reduction is strongly inhibited and the nucleation rate is enhanced compared to the surface diffusion rate, resulting in a fine-grained deposit structure (Fig. 2d). The depolarization of the electrode potential indicates an acceleration of Cu^{2+} reduction, which normally results in a coarse-grained deposit structure, like the copper deposition in the presence of HCl alone (~ -0.61 V; Fig. 2c). However, the opposite is observed for copper deposition in the presence of thiourea and HCl, as a fine-grained deposit structure is produced (Fig. 2e), although the electrodeposition proceeds under the depolarization condition (~ -0.69 V). This indicates that the normal influence of the electrode potential on the nucleation rate may not apply in this case, and the electrodeposition in the solution containing thiourea and chloride undergoes a very complicated electrodeposition mechanism that is not well understood.

Compared to the more well-studied system of copper deposition in the presence of PEG and HCl, the thiourea/chloride system possesses different behavior. PEG is considered an inactive or low-activity inhibitor by itself since, when added alone, the deposit morphology and voltammograms change only slightly compared to the additive-free system [29,40,42-46]. When a suitable amount of chloride is added to a solution containing PEG, dramatic changes are then observed in the deposit morphologies and voltammograms [40,44-51]. It is widely accepted that the PEG is bound to the copper surface by chloride to form the inhibiting film [51,52]. In contrast, for the thiourea/chloride system, thiourea exhibits the inhibiting effect by itself and the addition of chloride changes the way the electrodeposition mechanism proceeds. In the absence of chloride, thiourea is bound directly onto the copper surface via its unsaturated sulfur atom to form the complex film. In the presence of chloride, as discussed in section 3.1, thiourea is likely to be bound to the copper surface by chloride and the copper deposition proceeds through a different mechanism.

On a microscopic scale, the AFM results show that the synergetic effect of thiourea and chloride tends to improve the overall microscopic deposit structure since the nodules are eliminated and no thin cloudy film is observed, which leads to more reflective surface. However, similar to what we found in the previous study [26], the deposit surface becomes rough on a macroscopic scale, which can easily be seen under SEM at 50X or with the naked eye when the deposits are thick enough, as discussed in the next section. These results indicate that the addition of chloride to a plating bath containing thiourea improves the morphology of the copper deposit on the microscopic scale, but worsens the copper deposit surface on the macroscopic scale.

3. Macroscopic study – The macroscopic study considers the formation of rough deposits that are easily noticeable with bare eyes or under SEM at a magnification of 50X. Here, we attempted to closely investigate the roughening evolution of the deposit surfaces when the electrodeposition took place in the solution containing thiourea and HCl. SEM was used to monitor a series of deposits to investigate the evolution of roughening of the surfaces over a range of deposition times.

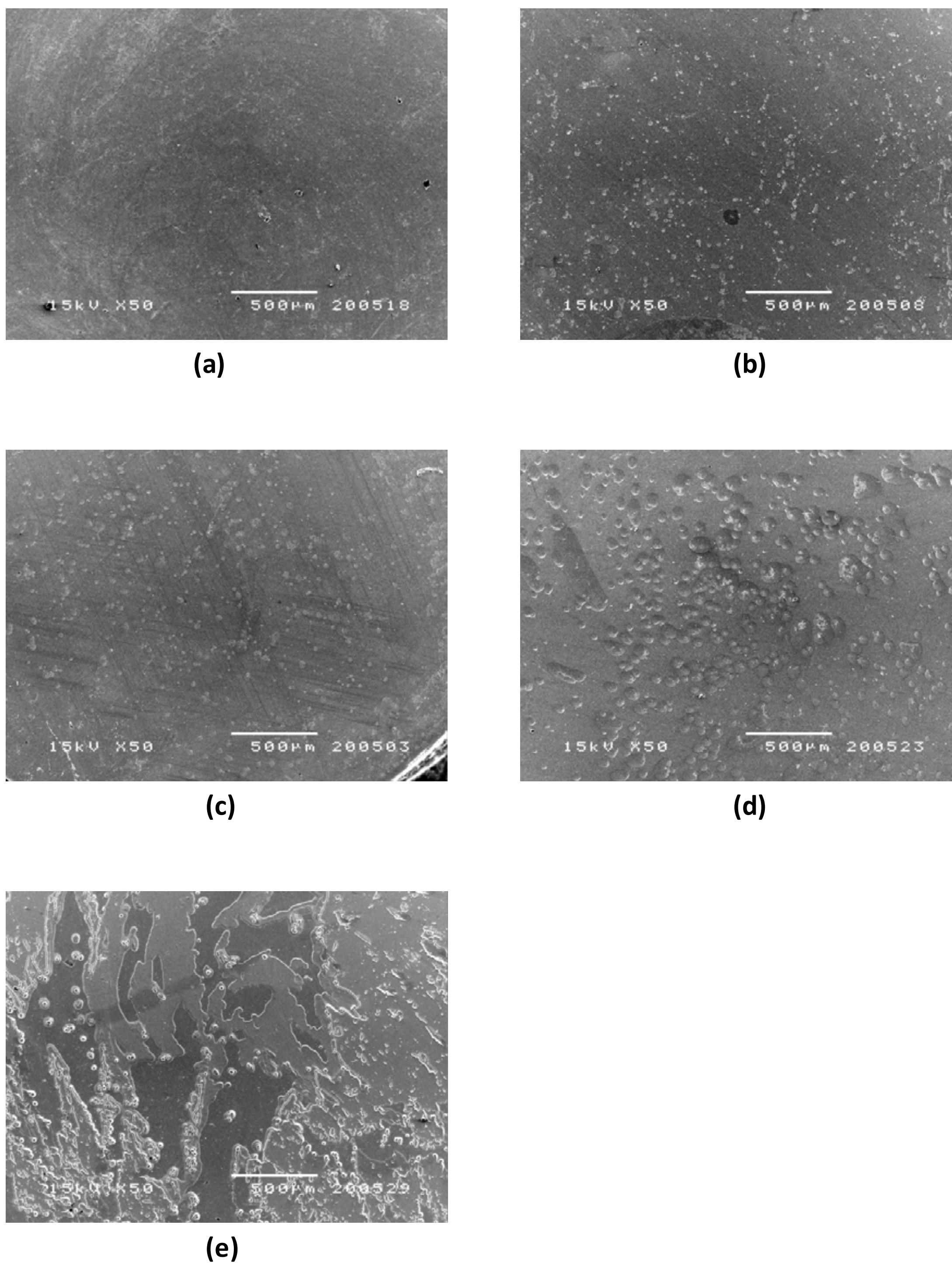


Fig. 4 SEM images (at 50X) of deposit macrostructures obtained from the 0.1 M $CuSO_4$—1M H_2SO_4 solution containing 20 μM thiourea and 1×10^3 μM HCl at a current density of 0.04 A cm^{-2} and rotational speed of 500 rpm for coverages of (a) 1 C cm^{-2}, (b) 2 C cm^{-2}, (c) 3 C cm^{-2}, (d) 6 C cm^{-2}, (e) 12 C cm^{-2}

The macroscopic images (at 50X) of the copper deposits obtained in the solution containing thiourea and HCl at different charge densities are shown in Fig. 4. Fig. 4a shows that after passing 1 C cm^{-2}, no obvious features, except very small white spots distributed on the surface, are observed. After passing higher charge densities, the white spots become bigger and more noticeable, as shown in Fig. 4b and c for 2 C cm^{-2} and 3 C cm^{-2}, respectively. As these white spots are not found on the bare copper substrate prior to the electrodeposition and they are not observed in every deposition condition, as will be shown later, they should be associated with a deposition feature rather than pre-existing defects on the substrate. We hypothesize that the white spots are shallow holes, not nodules, initiated during electrodeposition. The formation of locally irregular spots during the initial stage of electrodeposition could be due to a non-uniformity of the thiourea-Cu(I)-chloride complex film. It is also possible that the thiourea-Cu(I)-chloride complex film could be rather homogeneous, but it may not form uniformly across the entire depositing surface. Thus, the electrodeposition in different areas proceeds via different mechanisms. The electrodeposition taking place on the areas that develop white spots proceeds at a slower rate compared to the rest of the surface. After the deposit is thick enough (after passing a charge density of 6 C cm^{-2}), the white spots appear to develop into holes on the deposit surfaces, as shown in Fig. 4d, and eventually develop into very rough surface, as shown in Fig. 4e (after passing 12 C cm^{-2}). The rough surface, in the form of pits, starts to be noticeable by eye after passing a charge density 6 C cm^{-2}. As the deposition proceeds further, these pits tend to merge together and form an unpatterned-rough surface.

Fig. 5 shows the SEM images, at a higher magnification (5,000X), focused on a white spot (or hole) (Fig. 5a and c) and on the flat area (Fig. 5b and d) of the deposits obtained after passing charge densities of 2 C cm^{-2} (Fig. 5a and b) and 6 C cm^{-2} (Fig. 5c and d). The SEM images show that the deposit structures at these two areas are substantially different. After passing 2 C cm^{-2}, the deposit structure at the flat area consists of uniform, fine-grained crystals (Fig. 5b), whereas the deposit structure at the white spot is made of irregular crystals (Fig. 5a). This indicates that two different electrodeposition mechanisms may occur in these two areas. Alternatively, it may also be possible that a single mechanism occurs in both of these areas, and that the white spots, consisting of irregular crystals, are generated at defects as deposition proceeds. As higher charge density is

passed (6 C cm^{-2}), the difference in the deposit structures of these areas appears to be more pronounced, as shown in Fig. 5c and d.

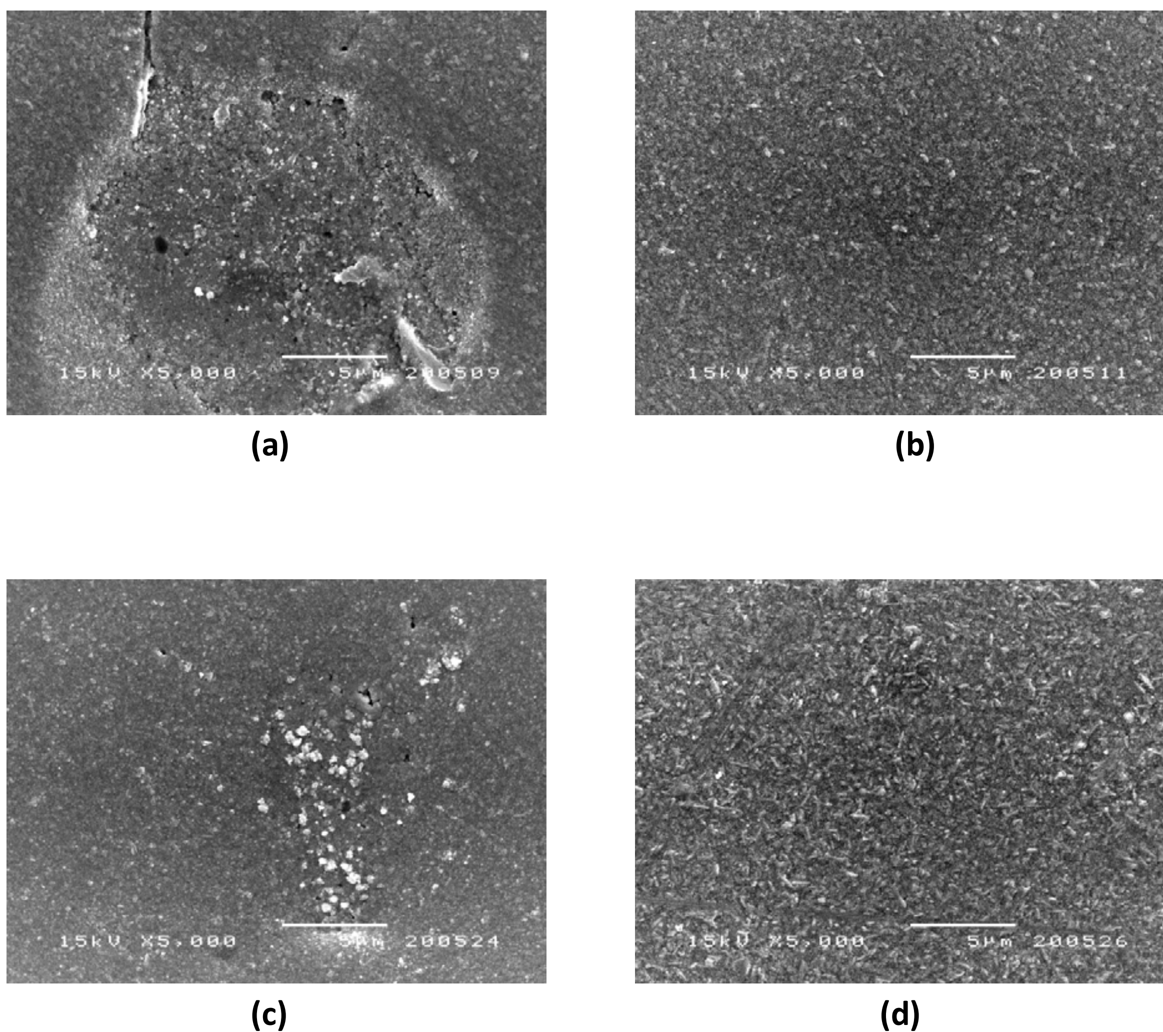


Fig. 5 SEM images at higher magnification (5,000X) of deposits obtained from the 0.1 M $CuSO_4$—1M H_2SO_4 solution containing 20 μM thiourea and 1×10^{3} μM HCl at a current density of 0.04 A cm^{-2} and rotational speed of 500 rpm (Fig. 4b and d): (a) focused on the white spot after passing 2 C cm^{-2}, (b) focused on the flat area outside white spots after passing 2 C cm^{-2}, (c) focused in the hole after passing 6 C cm^{-2}, (d) focused on the flat area outside holes after passing 6 C cm^{-2}

To obtain a new insight into the evolution of roughening, AFM was used to acquire the topographies over an image size of 50 × 50 μm. The AFM was scanned to cover the white

spots revealed in SEM images. Fig. 6 shows the AFM images, including the sectional analysis, of the deposits obtained in the presence of thiourea and HCl after passing charge densities of 1, 2 and 3 C cm^{-2}, corresponding to the deposit thicknesses of 370, 740 and 1100 nm, respectively. The AFM information obtained for thicker electrodeposits is not available since the surfaces are too rough to scan for such a large area (50 × 50 μm). AFM images indicate that the white spots observed in the SEM image as early as 1 C cm^{-2} has been passed (Fig. 4a) are, in fact, holes, as we originally hypothesized. The holes become deeper as the electrodeposition proceeds, as shown in Fig. 6. For a closer look in each figure, the sectional analysis indicates that the depth of the hole is close to the thickness of the copper deposit corresponding to each respective charge density (i.e., the measured depths of 374, 715 and 1018 nm after passing 1, 2 and 3 C cm^{-2}, respectively). The bottom of the holes contains a few layers of irregular-grained deposit (as shown in Fig. 5a and c). The AFM image of the deposit obtained in the solution containing thiourea and HCl presented in Fig. 2e is obtained from the flat area outside the holes.

The above results reveal that electrodeposition taking place in two areas may have different mechanisms. On the flat area, the thiourea-Cu(I)-chloride complex inhibits the surface diffusion of adatoms and enhances the nucleation process to form the new nuclei so that uniform, fine-grained structures are produced on this region, as shown in Fig. 5b and d and Fig. 2e. On the other hand, electrodeposition in the holes is almost completely inhibited or proceeds at very slow rate. The structure at the bottom of the holes tends to be a few layers of irregular-grained coating, as shown in Fig. 5a and c.

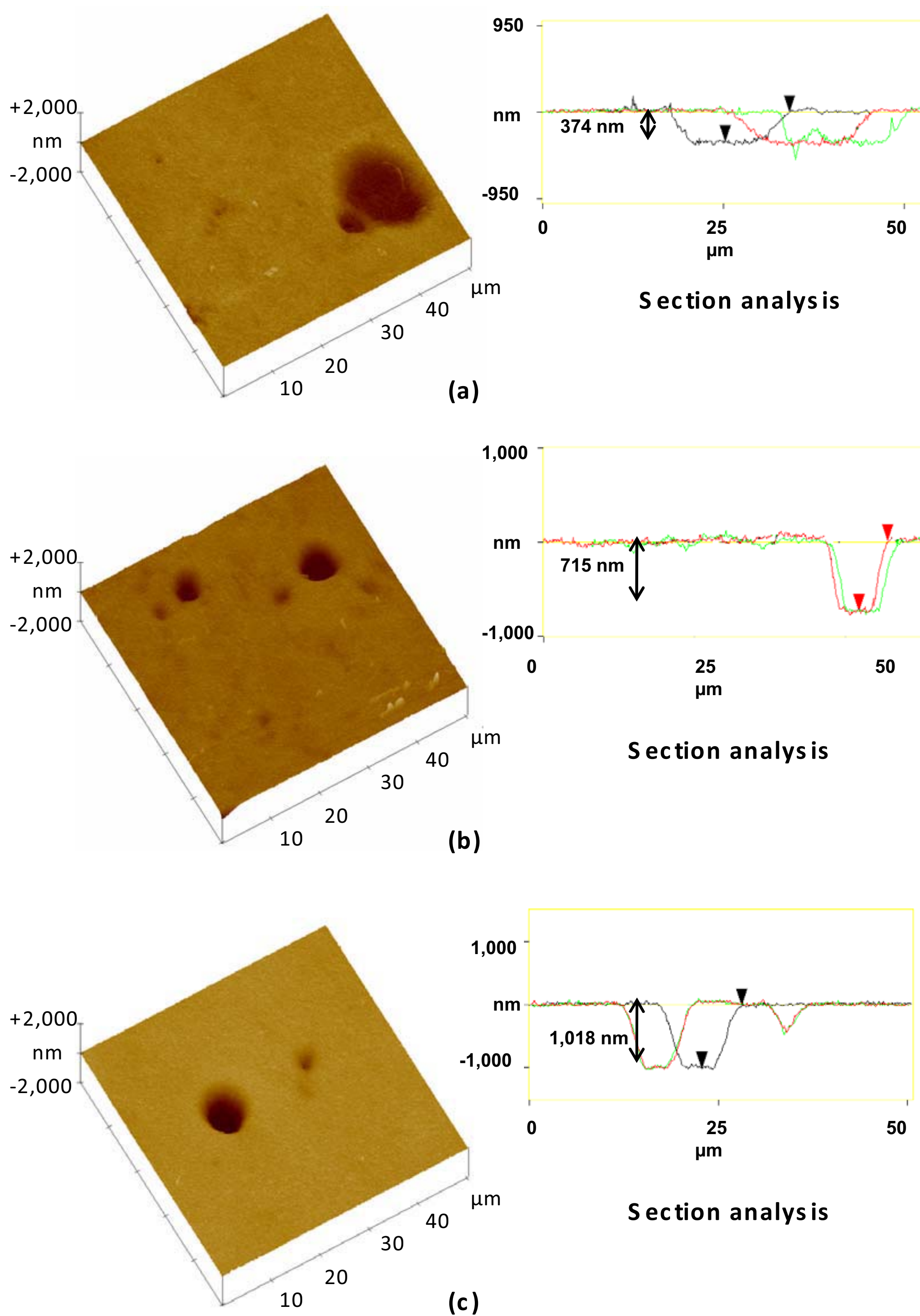
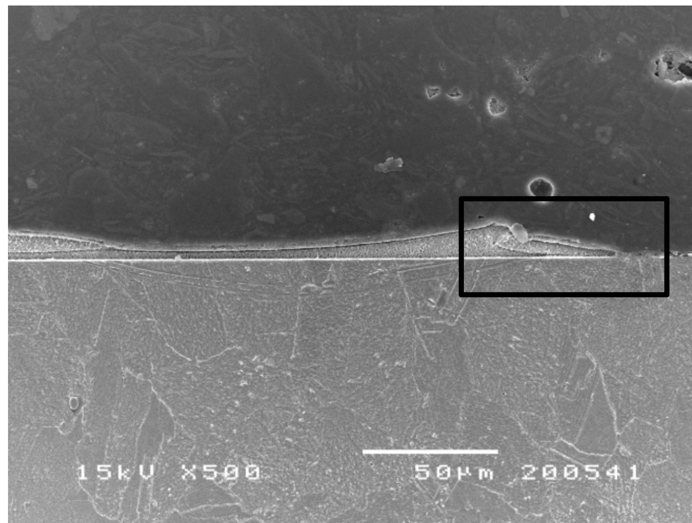
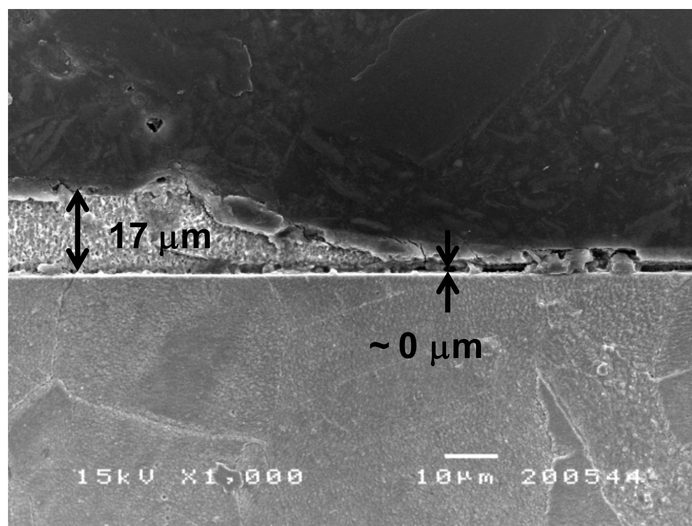


Fig. 6 AFM images (50 μm × 50 μm) and section analysis of copper deposits obtained from the 0.1 M $CuSO_4$—1M H_2SO_4 solution containing 20 μM thiourea and 1×10^3 μM HCl at a current density of 0.04 A cm^{-2} and rotational speed of 500 rpm for coverages of (a) 1 C cm^{-2}, (b) 2 C cm^{-2}, (c) 3 C cm^{-2}

Fig. 7 shows SEM images of a cross-section of the copper-deposited disc produced in the solution containing thiourea and HCl after passing 27.2 C cm^{-2}, which corresponds to an average thickness of 10 μm. Fig. 7a indicates that the copper deposit obviously does not have a uniform thickness. More importantly, some areas almost have no copper or very few copper layers deposited, whereas other regions have copper over-plated (i.e., a thicker deposit than 10 μm), as shown in Fig. 7b. These results indicate that, in the areas having no or very few layers of coating, the adsorbed complex film can completely inhibit the whole electrocrystallization process, where not only surface diffusion of copper adatoms but also the formation of new nuclei is inhibited. Furthermore, while the electrodeposition is almost completely inhibited in some regions, the applied charge is used to deposit copper in other regions where over-plated areas are obtained, as a current efficiency of almost 100% is found in every experiment.



(a)



(b)

Fig. 7 SEM images for the cross-section of copper deposit obtained from the 0.1 M $CuSO_4$—1M H_2SO_4 solution containing 20 μM thiourea and 1×10^3 μM HCl at a current density of 0.04 A cm^{-2} and rotational speed of 500 rpm for coverage of 27.2 C cm^{-2} : (a) 500X, (b) 1,000X

4. Effect of operating parameters – In this section, the effect of operating parameters – the rotational speed of RDE and the current density – on the copper deposits in the presence of thiourea and HCl were studied. First, the effect of the rotational speed was investigated by increasing it from 500 rpm to 2,000 rpm in incremental steps of 500 rpm. All deposition experiments were still conducted at the current density of 0.04 A cm^{-2}. The deposits obtained at higher rotational speeds after passing the charge density 6 C cm^{-2} (data not shown) were basically similar to that obtained at 500 rpm. The microscopically fine structures with macroscopic rough deposits were still produced. This indicates that the stronger hydrodynamic environment of the solution does not affect the complex thiourea-chloride film formation or its properties.

Next, the effect of current density was investigated over a range from 0.004 to 0.08 A cm^{-2} at the rotational speed of 500 rpm. Fig. 8 shows the SEM images of the deposits obtained at various current densities after passing the charge density of 6 C cm^{-2}. Unlike the deposit produced at 0.04 A cm^{-2}, the copper deposit produced at 0.004 A cm^{-2} appears to be relatively smooth, without rough spots or holes distributed on the surface (at 50X), as shown in Fig. 8a. This observation indicates that the thiourea-Cu(I)-chloride complex film formed on the surface is affected by the applied current density. The thiourea-Cu(I)-chloride complex film does not show a local effect on the electrodeposition when the low current density of 0.004 A cm^{-2} is used. However, the overall deposit surface appears dull compared to that produced at 0.04 A cm^{-2}. The deposit consists of a fine structure, but has irregular-grained crystals distributed across the surface, as shown in Fig. 8b (at 5,000X), which is similar to the deposit structure at the bottom of the holes when the current density of 0.04 A cm^{-2} is used (Fig. 5a and c). This implies that the deposition mechanism taking place at the lower or bottom parts of the deposit when the current density 0.04 A cm^{-2} is used is similar to the overall deposition mechanism when the low current density of 0.004 A cm^{-2} is used.

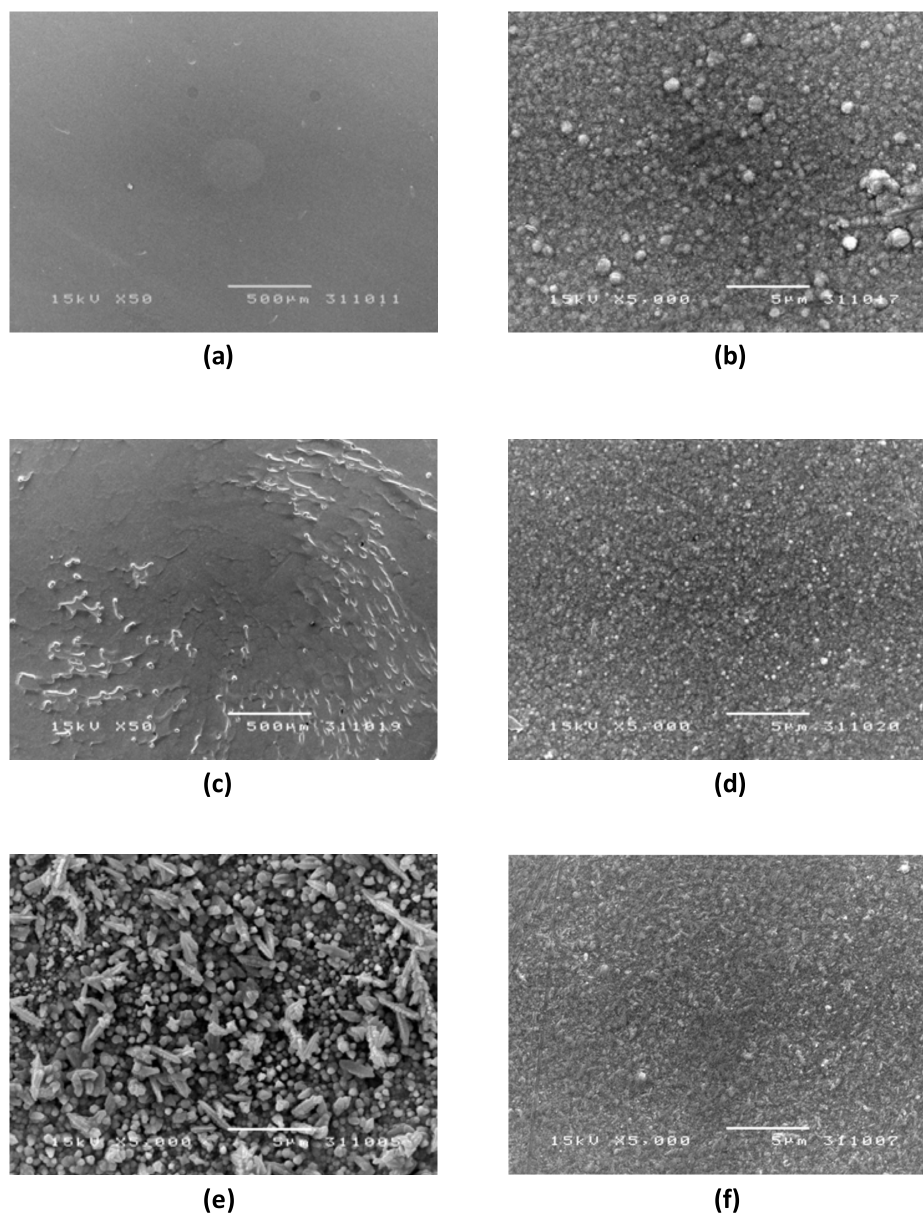


Fig. 8 SEM images of copper deposits obtained from the 0.1 M $CuSO_4$—1M H_2SO_4 solution containing 20 µM thiourea and 1×10^3 µM HCl for coverage of 6 C cm^{-2} at (a) a current density of 0.004 A cm^{-2} and rotational speed of 500 rpm (50X), (b) a current density of 0.004 A cm^{-2} and rotational speed of 500 rpm (5,000X), (c) a current density of 0.02 A cm^{-2} and rotational speed of 500 rpm (50X), (d) a current density of 0.02 A cm^{-2} and rotational speed of 500 rpm (5,000X), (e) a current density of 0.08 A cm^{-2} and rotational speed of 500 rpm (5,000X), (f) a current density of 0.12 A cm^{-2} and rotational speed of 2,000 rpm (5,000X)

When the current density is increased to 0.02 A cm^{-2}, a rough surface is produced (at 50X), as shown in Fig. 8c. Like the rough surface obtained at 0.04 A cm^{-2}, the lower flat part constructs of fine grains with small irregular particles distributed across the surface (at 5,000X), as shown in Fig. 8d. When the current density is increased to 0.05 A cm^{-2}, a rough surface having the same deposit structure as those produced at 0.02 and 0.04 A cm^{-2} is obtained (data not shown). When the current density is increased further to 0.06 A cm^{-2}, relatively inconsistent results are obtained. For the most part, smooth deposits that do not appear rough at 50X magnification, but are also not highly reflective, are obtained at this current density. However, in some experiments, rough surfaces are obtained, but to a lesser degree compared to those produced at 0.02 and 0.04 A cm^{-2}. It is possible that the current density may be high enough to allow the thiourea-Cu(I)-chloride complex adsorbed on the surface to be reduced or break down completely, so that the relatively smooth surface is produced. However, under this high current density the mass transfer limitation is expected to play the major role. When the current density is increased beyond the limiting current density to 0.08 A cm^{-2}, the rough surface is no longer obtained, but the brick-red deposit having the structure shown in Fig. 8e is produced.

The above results indicate that the current density used has a strong influence on the thiourea-Cu(I)-chloride complex film formed on the surface during electrodeposition, which leads to different deposition mechanisms. It is possible that applied current density affects the thiourea-Cu(I)-chloride complex film adsorbed on the substrate and eventually affects the nucleation process. The almost complete suppression of the current in the low potential range of the voltammogram, shown in Fig. 1a, indicates the inhibitory effect of the thiourea-Cu(I)-chloride complex film. Within this region, the current density is limited to lower than 0.01 A cm^{-2}, followed by a steep rise in the current density, from 0.01 to 0.05 A cm^{-2}. Most complex film formed in the low current density range is still intact on the surface, resulting in strong suppression of the surface diffusion process and the production of a deposit with relatively small-grained crystals. The complex film formed in the critical potential range can be reduced or break down, but not uniformly. Thus, the electrodeposition proceeds at different rates in various areas leading to a macroscopically uneven surface, as shown previously. When the current density is increased, the deposit surfaces tend to become more even. However, when the current densities are too high (i.e., 0.06 A cm^{-2} or higher),

the mass transfer limitation starts to affect the electrodeposition process and dominates the effect of additives (0.08 A cm^{-2}).

In order to investigate the effect of a higher current density on the copper electrodeposition in the presence of thiourea and HCl, the rotational speed must be increased to avoid the mass transfer limitation effect. Based on the voltammograms shown in Fig. 1b, we carried out the copper deposition experiment using a current density of 0.08 A cm^{-2} and a rotational speed of 2,000 rpm.

The deposits produced under these conditions appear to be very smooth and featureless (at 50X), similar to Fig. 8a. No rough spots are observed for a copper deposit as thick as 10 μm (charge density of 27.2 C cm^{-2}). As discussed previously, when the applied current density is increased, the thiourea-Cu(I)-chloride complex film tends to have a more uniform property or to break down, allowing the Cu^{2+} from the solution to be reduced. This experiment shows that if the applied current density is high enough, all the complex film on the surface may form evenly across the surface or may break down completely. The electrodeposition then proceeds at the same rate for the entire surface and a smooth deposit is obtained.

While the macroscopic structures show a significant improvement, the microscopic structures do not show a substantial change. AFM (Fig. 9a) and SEM (Fig. 8f) images indicate that the deposit morphologies are similar to those of the upper-flat areas of the deposits obtained at the current density of 0.04 A cm^{-2} (Fig. 2e and Fig. 5b and d) where compact and fine-grained crystals with no irregular grains are produced. In addition, the deposit structure still retains very uniform and fine-grained structures, even after passing the charge density of 27.2 C cm^{-2}, as shown in Fig. 9b. However, it should be pointed out that although the macroscopic analysis suggests the complete breakdown of the complex film and, as observed in Fig. 1, the reverse voltammograms in the presence of thiourea and chloride after the complete breakdown of the complex film tend to follow the reverse voltammogram in the presence of chloride alone, the deposit structures in the presence of thiourea and chloride are totally different from, in fact much better than, that obtained in the presence of HCl alone or in the absence of additives. These results suggest that the state

of the surface after the complex film breaks down during the copper deposition_differs from that prevailing just before the reverse scans in the voltammogram study. The complex film adsorbed on the surface during the copper deposition may still contain intact thiourea within its structure, which helps improve the deposit morphology, but, during the reverse scans in the voltammogram study, thiourea is expected to detach from the complex film leaving only chloride on the copper surface (Fig. 1). However, the information obtained from a surface analytical technique such as XPS or SIMS would be needed to support this statement.

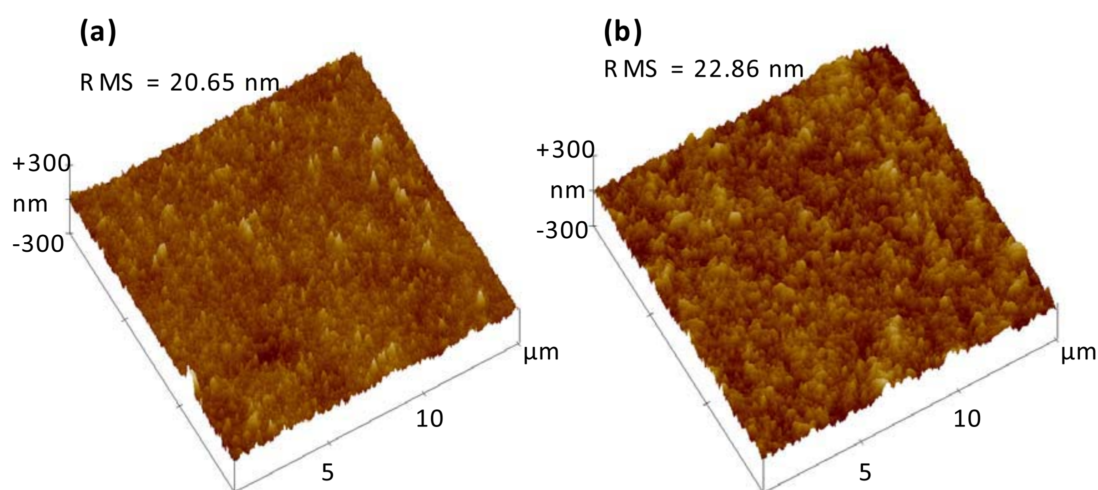


Fig. 9 AFM images (15 mm × 15 mm) of copper deposits obtained from the 0.1 M $CuSO_4$-1M H_2SO_4 solution containing 20 μM thiourea and $1×10^3$ μM HCl at a current density of 0.08 A cm^{-2} and a rotational speed of 2,000 rpm for coverages of (a) 6 C cm^{-2}, (b) 27.2 C cm^{-2}

Conclusions

The results of examination by AFM, SEM and electrochemical methods indicate the synergetic effects of chloride and thiourea during copper electrodeposition in a sulfate-plating bath. The copper deposition mechanism in the presence of thiourea and chloride was found to be different from that in the present of thiourea alone. Copper deposition in the presence of thiourea alone requires increased polarization relative to that in an additive-free solution, whereas deposition in the presence of thiourea and chloride requires less polarization, similar to the situation when chloride alone is added. On the microscopic level, the addition of chloride to a plating bath containing thiourea makes the deposit morphology a little rougher, but nodules disappear from the structure. The disappearance of nodules makes the overall structure of the deposit smoother and more homogeneous, which results in a more reflective surface. However, the presence of chloride leads to a macroscopically rough surface with no distinct pattern since the thiourea-Cu(I)-chloride complex film adsorbed on the surface does not respond to the applied current evenly. Then, copper deposition in different areas proceeds at different rates and an uneven surface is produced. Those areas are found to undergo different deposition mechanisms. In the lower parts or holes of the rough deposit, the thiourea-Cu(I)-chloride complex inhibits both the grain growth and nucleation processes, and the deposition mechanism similar to that using a very low current density (0.004 mA cm^{-2}) is expected since the deposit structures are similar. In the flat areas, the thiourea-Cu(I)-chloride complex inhibits only the grain growth process, while nucleation is enhanced, leading to the formation of thicker deposit with a uniform, fine-grained structure. The roughening effect due to the complex film is minimized at high applied current densities since a high enough applied current density can break up the complex film completely across the entire surface. As a result, the smooth deposit on both microscopic and macroscopic levels is obtained.

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ผลลัพธ์จากโครงการวิจัย

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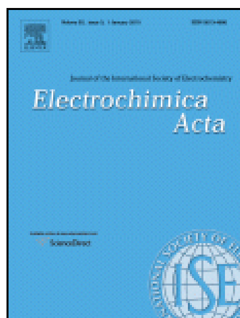

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Influence of the interaction between chloride and thiourea on copper electrodeposition

Nisit Tantavichet [a,*], Somsak Damronglerd [a], Orawan Chailapakul [b]

[a] Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[b] Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

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ABSTRACT

The interaction between chloride and thiourea in copper electrodeposition in a sulfate-plating bath was investigated. The sole addition of thiourea to the bath increased the polarization of the electrode potential during copper deposition, leading to very fine and smoothly structured deposit but with microscopic nodules distributed over the surface. When chloride was added to a plating solution containing thiourea, the copper deposition mechanism was changed, showing a depolarization of the electrode potential, and the copper deposits were found to have a relatively rougher microstructure, but without the formation of microscopic nodules. However, rough deposit surfaces having no distinct pattern were formed at the macroscopic scale. Observations of roughening evolution show that the rough surface was initiated from small holes formed across the deposit surface during the initial stage of deposition that eventually developed into visibly rough deposits. The copper deposition inside these holes and at other areas was expected to undergo different deposition mechanisms. Copper deposition in the areas that ultimately developed into holes was almost totally inhibited by the thiourea–Cu(I)–chloride complex film, not just in the grain growth process, but over practically the entire electrodeposition process. Conversely, copper deposition occurred in other areas under conditions where nucleation proceeded, but grain growth was inhibited to produce a fine, homogeneous microstructure. An uneven deposit surface that had different microscopic structures in different areas was then formed. The structure of the thiourea–Cu(I)–chloride film was strongly affected by the current density and appeared to break down completely if sufficiently high current density was applied to yield a fine and homogeneous microstructure that was also macroscopically smooth.

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1. Introduction

In electrodeposition, it is well known that the addition of small amounts of certain substances into the plating bath results in significant changes in the properties and throwing power of the deposit. The added substances are expected to modify the deposition mechanism depending on their functions during the electrodeposition process. In copper electrodeposition in a sulfate-plating bath, various additives such as gelatin [1,2], benzotriazole [3–9] and thiourea [2,7,8,10–21] have been widely used to improve the surface finish of metal deposits.

Besides these additives, chloride has also been found to play a significant role during the electrodeposition of copper in a sulfate-plating bath. The presence of chloride as the sole additive has been reported to have inconsistent results in influencing copper deposition, where some researchers find improvements in copper deposition properties [22,23] while others find the opposite [24–26]. Moreover, the presence of chloride in plating baths containing other additives such as polyethylene glycol (PEG), bis(3-sulfopropyl) disulfide (SPS) or 3-mercapto-1-propanesulfonate (MPSA) and their combinations has been found to alter deposit properties relative to those in the absence of chloride, and a number of extensive studies on the interactions of chloride and those additives have been reported [23,25,27–29]. On the other hand, although thiourea has been commonly used as a brightening agent for copper electrodeposition [7,14,18,19,30,31], to date very few studies on electrodeposition in a solution containing thiourea and chloride have been conducted [15,32,33].

Previously, we reported the tendency of the combination of thiourea and chloride to improve the copper deposit structure [26]. In this study, we extensively investigate the synergetic effects of thiourea and chloride on the morphology of the copper deposit during direct current (DC) electrodeposition. The experiments were initially conducted on copper disc electrodes rotating at 500 rpm using DC electrodeposition at 0.04 A cm^{-2}. The influences of the fluid-flow conditions and the applied current density were also

* Corresponding author. Tel.: +66 2 218 7677; fax: +66 2 255 5831.
E-mail address: Nisit.T@chula.ac.th (N. Tantavichet).

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studied. The deposit morphologies were characterized by scanning electron microscopy (SEM) and *ex situ* atomic force microscopy (AFM). Cyclic voltammetry was used for Cu^{2+} reduction, and electrode potentials were monitored during electrodeposition to provide better insight into the synergy between the effects of thiourea and chloride during copper electrodeposition.

2. Experimental

The electrodeposition experiments were conducted using a rotating disc electrode (RDE) (MetroOhm) immersed in a cylindrical electrolytic cell containing 50 cm^3 of a plating solution. DC electrodeposition and voltammetry experiments were carried out using a μAUTOLAB II Potentiostat (Eco Chemie) with a three-electrode system. The working electrode was a 0.43 cm diameter (0.1452 cm^2 area) copper disc polished with SiC-type abrasive paper (1200 grade), followed by silicon carbide grinding paper (P4000) (Buehler) and 0.3 and 0.05 μm Al_2O_3 powder (Buehler), to a mirror finish. A copper disc, placed at the bottom of the cell about 2 cm from the working electrode, was used as the counter electrode. A mercury/mercurous sulfate electrode (MSE, Radiometer analytical) was used as the reference electrode. All potentials reported herein correspond to the MSE scale, which has a standard potential of +0.679 V vs. SHE.

An acidic sulfate-plating bath containing 0.1 M $CuSO_4$ and 1 M H_2SO_4 was used for all experiments. The concentrations of HCl (Aldrich Chemical) and thiourea (Aldrich Chemical) used to study the effect of additives on copper deposition were 10^3 and 20 μM, respectively. Stock thiourea solutions were prepared freshly before the electrodeposition experiments. The presence of these additives in the concentration ranges used in this work did not have a noticeable effect on the open circuit potential.

DC electrodeposition experiments were conducted at a current density of 0.04 A cm^{-2} on copper disc electrodes rotating at 500 rpm to achieve a charge density of 6 C cm^{-2}. However, later in the study, the rotational speed and the applied current density were varied in order to investigate the correlation between those parameters and deposit topographies during the copper electrodeposition in the presence of thiourea and chloride. Experiments were conducted several times under identical conditions to assess repeatability and consistent results were obtained from run to run. Deposit morphology was characterized using *ex situ* atomic force microscopy (AFM) (Veeco, NanoScope IV) and scanning electron microscopy (SEM) (JOEL, JSM-5410LV). AFM studies were carried out in contact mode using a Si_3N_4 tip to acquire images of different sizes. The root mean square (RMS) microroughness of the deposited surfaces was also obtained by AFM. Measurement of the RMS microroughness was intended to complement the information provided by the AFM images to determine the topography of the copper deposits produced under different conditions. To obtain the cross-sectional images, the deposited copper disc was mounted in Bakelite and cut through the disc center using a diamond wafering blade on a low-speed saw. The cross-sectional deposited copper disc was then polished using SiC-type abrasive paper (1200 grade) followed by 0.3 and 0.05 μm Al_2O_3 powder and was etched in a solution of NH_4OH and H_2O_2 in water [28]. The cross-sectional images showing the deposit profiles were obtained by SEM.

3. Results and discussion

3.1. Cyclic voltammetry

To investigate the synergetic effect of the combination of thiourea and HCl for copper electrodeposition, a series of cyclic voltammetry experiments for Cu^{2+} reduction were carried out in

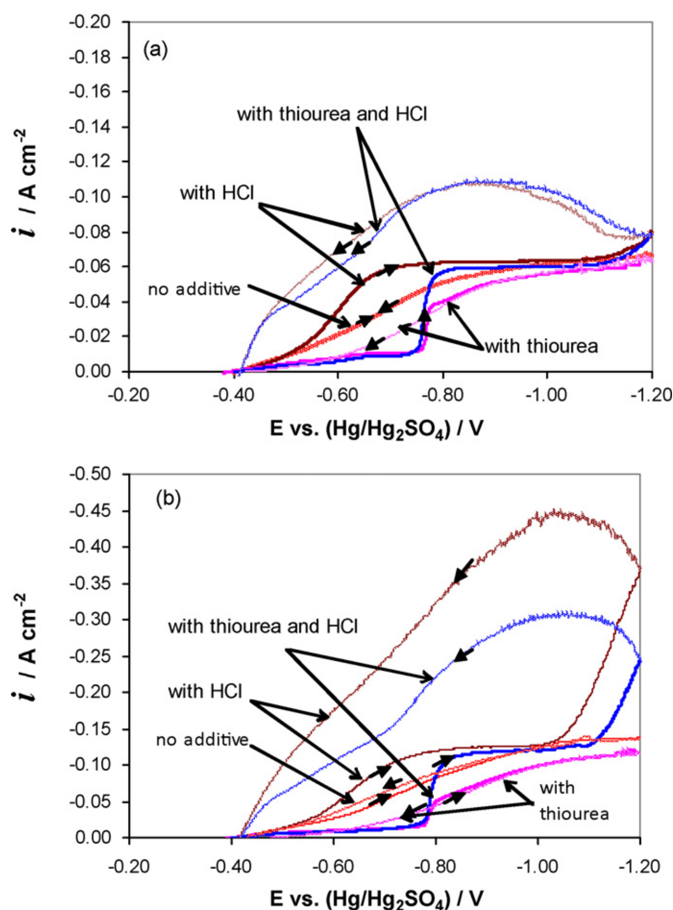

Fig. 1. Cyclic voltammograms for Cu^{2+} reduction on rotating disc electrodes immersed in various 0.1 M $CuSO_4$ – 1 M H_2SO_4 solutions at rotational speeds of (a) 500 rpm and (b) 2000 rpm using a scan rate of 10 mV s^{-1}.

the absence and presence of additives. The voltammograms for the rotational speeds of 500 and 2000 rpm are shown in Fig. 1a and b, respectively. As shown in Fig. 1a and b, the voltammograms obtained in the same plating solution indicate similar trends for different rotational speeds, except that the voltammograms for Cu^{2+} reduction obtained at 2000 rpm reach a higher level of limiting current density for the forward scans (i.e., 0.12 A cm^{-2}) than those obtained at 500 rpm (i.e., 0.06 A cm^{-2}). The forward scans in Fig. 1 confirm the findings from previous studies showing that Cu^{2+} reduction is accelerated in the presence of HCl alone [25–27,34,35]. Conversely, the voltammograms obtained in the presence of thiourea alone confirm that copper deposition is strongly suppressed at lower overpotentials before being abruptly activated at a critical potential (approximately −0.77 V MSE) [18,26,36]. Detailed discussions of the voltammograms in the presence of HCl alone and in the presence of thiourea alone can be found in the previous work [26] and in the literature [18,25,27,34–37].

When both HCl and thiourea are present in the solution, the forward scans are polarized relative to those observed in the absence of additives, whereas the reverse scans are depolarized with respect to those obtained in their absence. In fact, the forward scans almost follow those obtained in the solution containing thiourea alone, except that they establish a more well-defined limiting current density plateau. The reverse scans show the opposite results. In the presence of thiourea alone, the reverse scans still indicate an inhibition of Cu^{2+} reduction over the entire scan. They closely follow the corresponding forward scans until reaching the critical potential (below −0.77 V) where they do not show the almost

complete inhibition of Cu^{2+} reduction. The inhibiting film formed during the forward scan for Cu^{2+} reduction in the presence of thiourea alone partially breaks down at high potentials or completely breaks down, but is gradually restored during the reverse scan (from the critical potential to approximately −0.6 V) and is completely restored when the potential reaches −0.6 V. In contrast, the reverse scans in the presence of thiourea and chloride indicate the acceleration of Cu^{2+} reduction; here they tend to follow those obtained in the solution containing HCl alone, despite the substantial discrepancy shown for the case of 2000 rpm. The significantly higher current density of the reverse scan at 2000 rpm when HCl alone is present compared to that when both thiourea and HCl are present is likely due to the considerably rougher deposit formed at this rotational speed when HCl is the only additive. The inhibiting film formed during the forward scan in the presence of thiourea and chloride is mostly destroyed at high potentials and is not restored quickly enough to cover the copper substrate. Since the reverse scans show acceleration similar to that in the presence of HCl alone, it is possible that only thiourea detaches from the inhibiting film, leaving chloride alone on the copper surface during the reverse scan. The reverse scan results suggest that, in the presence of thiourea and chloride, thiourea should attach on the copper surface through chloride to form the inhibiting complex, whereas, in the absence of chloride, thiourea attaches directly onto the copper surface to form the inhibiting complex. The voltammogram results indicate that the addition of HCl in the plating solution containing thiourea changes the structure of the inhibiting complex adsorbed on the copper surface and hence the mechanism of copper electrodeposition.

3.2. Microscopic study

To study the synergetic effect of the combination of thiourea and HCl on the deposit morphology, electrodeposition experiments were carried out in the absence and presence of additives using a current density of 0.04 A cm^{-2} on copper disc electrodes rotating at 500 rpm as the standard conditions. The current density of 0.04 A cm^{-2} was chosen based on the response in Fig. 1a, showing that it is sufficiently high to maintain a high nucleation rate without causing electrodeposition to be mass transfer limited. The electrodeposition of copper at the rotational speed of 2000 rpm is discussed in Section 3.4. The AFM images of the copper deposits obtained in the absence and presence of additives after passing a charge density of 6 C cm^{-2} are shown in Fig. 2. The AFM image of the bare copper substrate is included (Fig. 2a) for comparison. Each AFM image was obtained *ex situ* of a deposit produced from a sep-

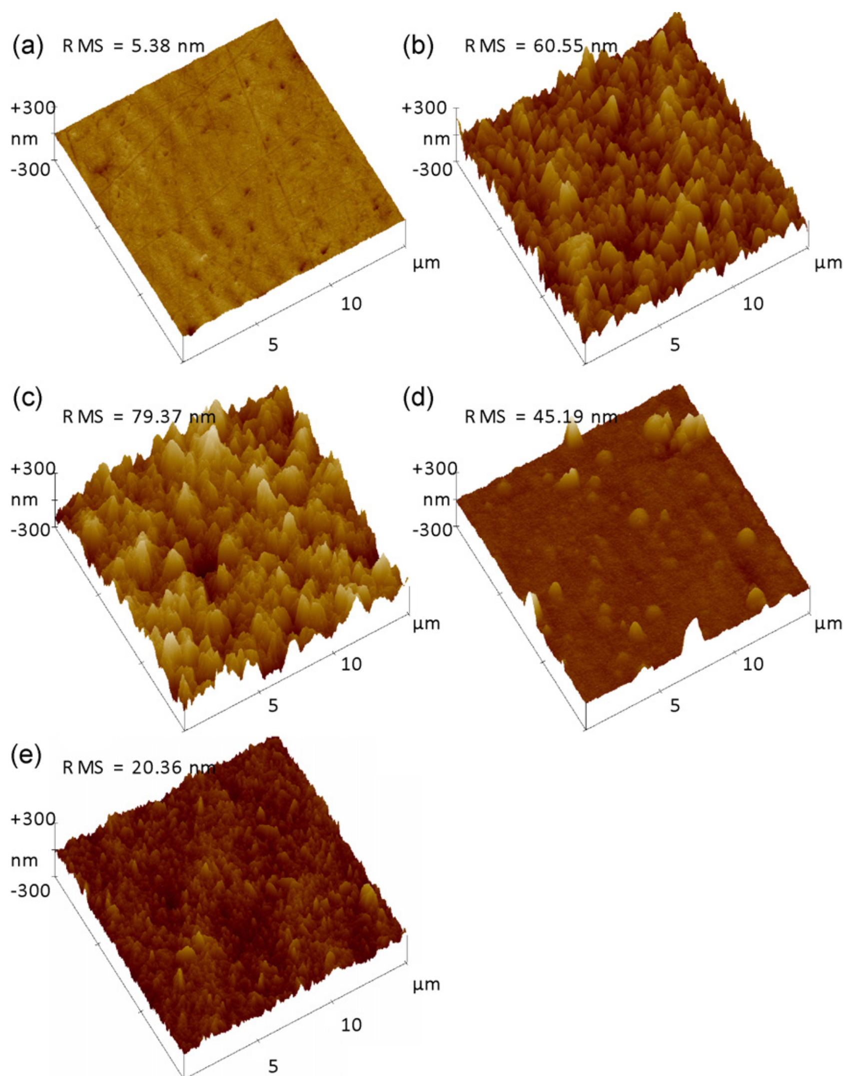

Fig. 2. AFM images (15 μm × 15 μm) of (a) bare copper surface, and copper deposits obtained from the 0.1 M $CuSO_4$ – 1 M H_2SO_4 solution containing (b) no additive, (c) 1×10^3 μM HCl, (d) 20 μM thiourea, (e) 20 μM thiourea and 1×10^3 μM HCl at a current density of 0.04 A cm^{-2} and a rotational speed of 500 rpm after passing a charge density of 6 C cm^{-2}.

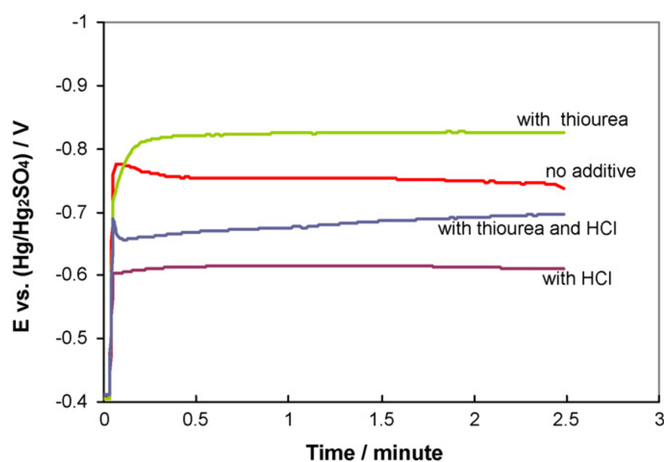

Fig. 3. Electrode potentials monitored during DC electrodeposition in 0.1 M $CuSO_4 - 1$ M H_2SO_4 solutions in the absence and presence of different additives until a charge density of 6 C cm^{-2} is passed.

arate deposition experiment. The electrode potentials monitored during the electrodeposition are shown in Fig. 3.

Similar to the results reported previously [26], the copper deposit structure produced in the presence of HCl alone (Fig. 2c) contains bigger grains and becomes coarser and rougher (roughness = 79.37 nm) compared to that obtained in the absence of additives (Fig. 2b) (roughness = 60.55 nm), whereas the copper deposit structure produced in the presence of thiourea alone (Fig. 2d) consists of very fine grains and a mostly very smooth surface. The deposit surface produced in the solution containing thiourea alone appears brighter than that produced in the absence of additives or in the presence of HCl alone. However, the surface is not as reflective as the polished uncoated copper surface since it appears to already have a very thin cloudy film overlay when a charge density of 1 C cm^{-2} has been passed. The thin cloudy film is expected to be due to microscopic nodules protruding from the flat deposit surfaces, which are locally found on the deposit structures when a charge density of 1 C cm^{-2} has been passed (data not shown) and become larger and denser as the electrodeposition proceeds, eventually merging altogether to form an entirely rough deposit structure [38]. The influence of chloride alone and thiourea alone on the electrodeposition of copper has been discussed in our previous work [26,38] and in the literature [8,16,17,25,26,29,31,38–41].

The microroughness of the deposit obtained in the presence of thiourea is found to be lower (45.19 nm) than that in the absence of additives (60.55 nm), but it strongly depends on the location of the image taken since the surface of the deposit obtained in the presence of thiourea consists of a very smooth and fine structure, with nodules distributed randomly across the surface (Fig. 2d). It should be noted that although the nodule formation was observed in the 3D images using AFM, the deposit surface still appears to be very smooth macroscopically since no rough surface features were observed by SEM at a magnification of 50×.

When both HCl and thiourea are present in the plating solution, the combination of these two additives shows a synergetic effect. Fig. 2e shows that the deposit structure obtained from a solution containing 20 μM thiourea and 1×10^3 μM HCl is substantially different from that obtained in the presence of thiourea alone (Fig. 2d) or HCl alone (Fig. 2c), as it has a slightly bigger-grained structure than that obtained in the presence of thiourea alone, but still has much smaller and finer-grained structure than that obtained either in the absence of additives or in the presence of HCl alone. Thiourea and chloride are expected to form a complex and adsorb at the solid–liquid interface and block the surface diffusion process of copper adatoms. However, the inhibition mechanism of the thiourea–Cu(I)–chloride complex should differ from that of the thiourea–Cu(I) complex since the deposit structure obtained in the presence of both additives is obviously not as smooth as the flat regions (i.e., the smooth areas excluding the nodule spots) of the deposit produced in the presence of thiourea alone and more importantly no nodules are formed. No cloudy film is formed on the deposit surface, which leads to more reflective surface. The disappearance of nodules leads to a more uniform structure, lower overall microscopic deposit roughness (roughness = 20.36 nm) and a more reflective surface compared to the deposits obtained in the presence of thiourea alone.

As shown in Fig. 3, the electrode potential for the copper deposition in the presence of thiourea alone, as for the voltammogram results (Fig. 1a), is polarized toward a higher cathodic potential (∼−0.83 V) relative to that in the absence of additives (∼−0.74 V). On the other hand, the electrode response for copper deposition in the presence of thiourea and HCl is depolarized toward a lower cathodic potential (∼−0.69 V) which is closer to the value attained during the reverse scan in Fig. 1a than to that reached during the forward scan at the same current. These indicate the difference in electrocrystallization mechanisms of these two systems, which leads to different deposit structures. The polarization condition for the deposit in the presence of thiourea alone indicates that the Cu^{2+} reduction is strongly inhibited and the nucleation rate is enhanced compared to the surface diffusion rate, resulting in a fine-grained deposit structure (Fig. 2d). The depolarization of the electrode potential indicates an acceleration of Cu^{2+} reduction, which normally results in a coarse-grained deposit structure, like the copper deposition in the presence of HCl alone (∼−0.61 V; Fig. 2c). However, the opposite is observed for copper deposition in the presence of thiourea and HCl, as a fine-grained deposit structure is produced (Fig. 2e), although the electrodeposition proceeds under the depolarization condition (∼−0.69 V). This indicates that the normal influence of the electrode potential on the nucleation rate may not apply in this case, and the electrodeposition in the solution containing thiourea and chloride undergoes a very complicated electrodeposition mechanism that is not well understood.

Compared to the more well-studied system of copper deposition in the presence of PEG and HCl, the thiourea/chloride system possesses different behavior. PEG is considered an inactive or low-activity inhibitor by itself since, when added alone, the deposit morphology and voltammograms change only slightly compared to the additive-free system [29,40,42–46]. When a suitable amount of chloride is added to a solution containing PEG, dramatic changes are then observed in the deposit morphologies and voltammograms [40,44–51]. It is widely accepted that the PEG is bound to the copper surface by chloride to form the inhibiting film [51,52]. In contrast, for the thiourea/chloride system, thiourea exhibits the inhibiting effect by itself and the addition of chloride changes the way the electrodeposition mechanism proceeds. In the absence of chloride, thiourea is bound directly onto the copper surface via its unsaturated sulfur atom to form the complex film. In the presence of chloride, as discussed in Section 3.1, thiourea is likely to be bound to the copper surface by chloride and the copper deposition proceeds through a different mechanism.

On a microscopic scale, the AFM results show that the synergetic effect of thiourea and chloride tends to improve the overall microscopic deposit structure since the nodules are eliminated and no thin cloudy film is observed, which leads to more reflective surface. However, similar to what we found in the previous study [26], the deposit surface becomes rough on a macroscopic scale, which can easily be seen under SEM at 50× or with the naked eye when the deposits are thick enough, as discussed in the next section. These results indicate that the addition of chloride to a plating bath containing thiourea improves the morphology of the copper deposit

on the microscopic scale, but worsens the copper deposit surface on the macroscopic scale.

3.3. Macroscopic study

The macroscopic study considers the formation of rough deposits that are easily noticeable with bare eyes or under SEM at a magnification of 50×. Here, we attempted to closely investigate the roughening evolution of the deposit surfaces when the electrodeposition took place in the solution containing thiourea and HCl. SEM was used to monitor a series of deposits to investigate the evolution of roughening of the surfaces over a range of deposition times.

The macroscopic images (at 50×) of the copper deposits obtained in the solution containing thiourea and HCl at different charge densities are shown in Fig. 4. Fig. 4a shows that after passing $1\,C\,cm^{-2}$, no obvious features, except very small white spots distributed on the surface, are observed. After passing higher charge densities, the white spots become bigger and more noticeable, as shown in Fig. 4b and c for 2 and $3\,C\,cm^{-2}$, respectively. As these white spots are not found on the bare copper substrate prior to the electrodeposition and they are not observed in every deposition condition, as will be shown later, they should be associated with a deposition feature rather than pre-existing defects on the substrate. We hypothesize that the white spots are shallow holes, not nodules, initiated during electrodeposition. The formation of locally irregular spots during the initial stage of electrodeposition could be due to a non-uniformity of the thiourea–Cu(I)–chloride complex film. It is also possible that the thiourea–Cu(I)–chloride complex film could be rather homogeneous, but it may not form uniformly across the entire depositing surface. Thus, the electrodeposition in different areas proceeds via different mechanisms. The electrodeposition taking place on the areas that develop white spots proceeds at a slower rate compared to the rest of the surface. After the deposit is thick enough (after passing a charge density of $6\,C\,cm^{-2}$), the white spots appear to develop into holes on the deposit surfaces, as shown in Fig. 4d, and eventually develop into very rough surface, as shown in Fig. 4e (after passing $12\,C\,cm^{-2}$). The rough surface, in the form of pits, starts to be noticeable by eye after passing a charge density $6\,C\,cm^{-2}$. As the deposition proceeds further, these pits tend to merge together and form an unpatterned-rough surface.

Fig. 5 shows the SEM images, at a higher magnification (5000×), focused on a white spot (or hole) (Fig. 5a and c) and on the flat area

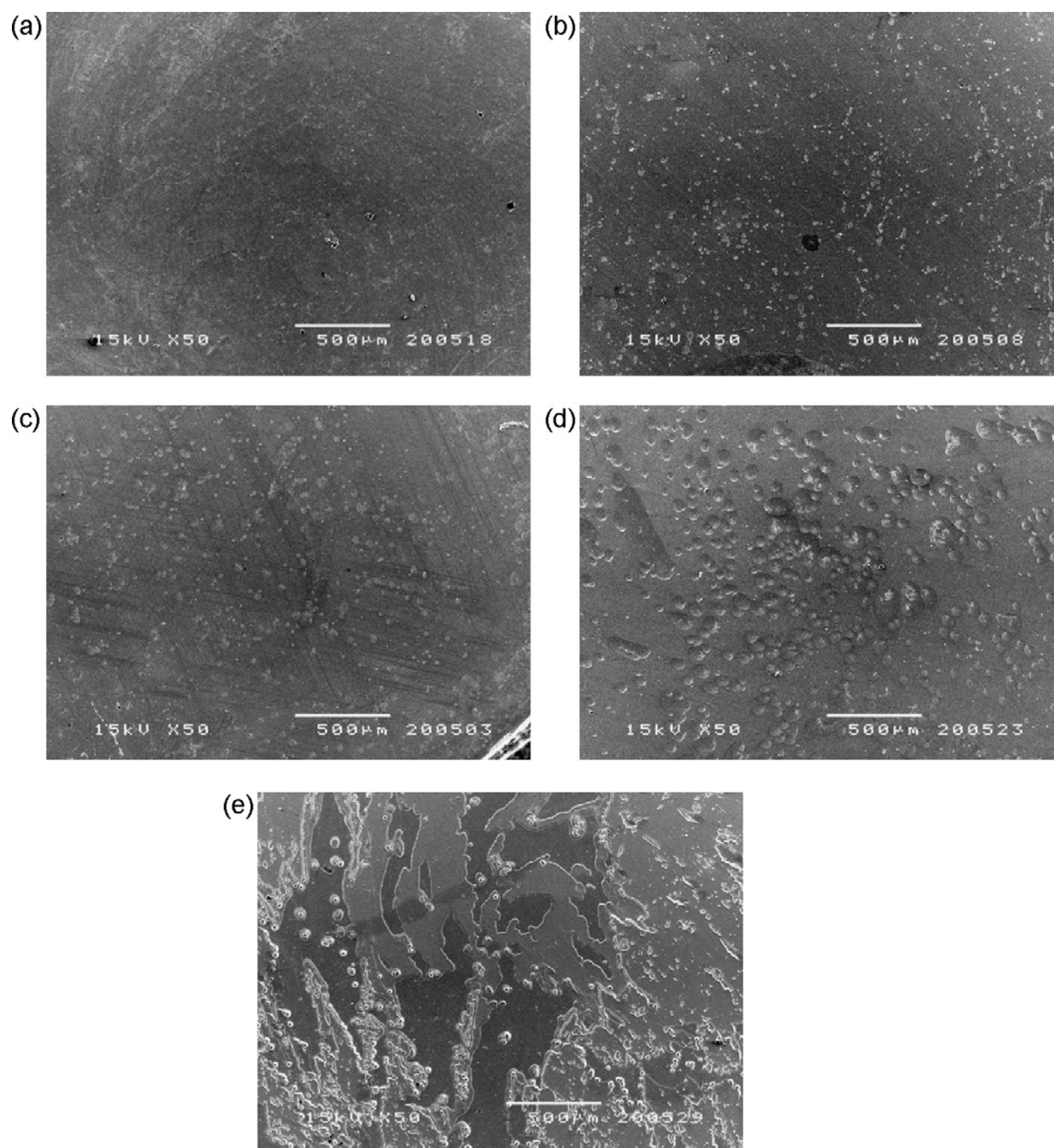

Fig. 4. SEM images (at 50×) of deposit macrostructures obtained from the 0.1 M $CuSO_4$ – 1 M H_2SO_4 solution containing 20 μM thiourea and 1×10^3 μM HCl at a current density of $0.04\,A\,cm^{-2}$ and rotational speed of 500 rpm for coverages of (a) $1\,C\,cm^{-2}$, (b) $2\,C\,cm^{-2}$, (c) $3\,C\,cm^{-2}$, (d) $6\,C\,cm^{-2}$, (e) $12\,C\,cm^{-2}$.

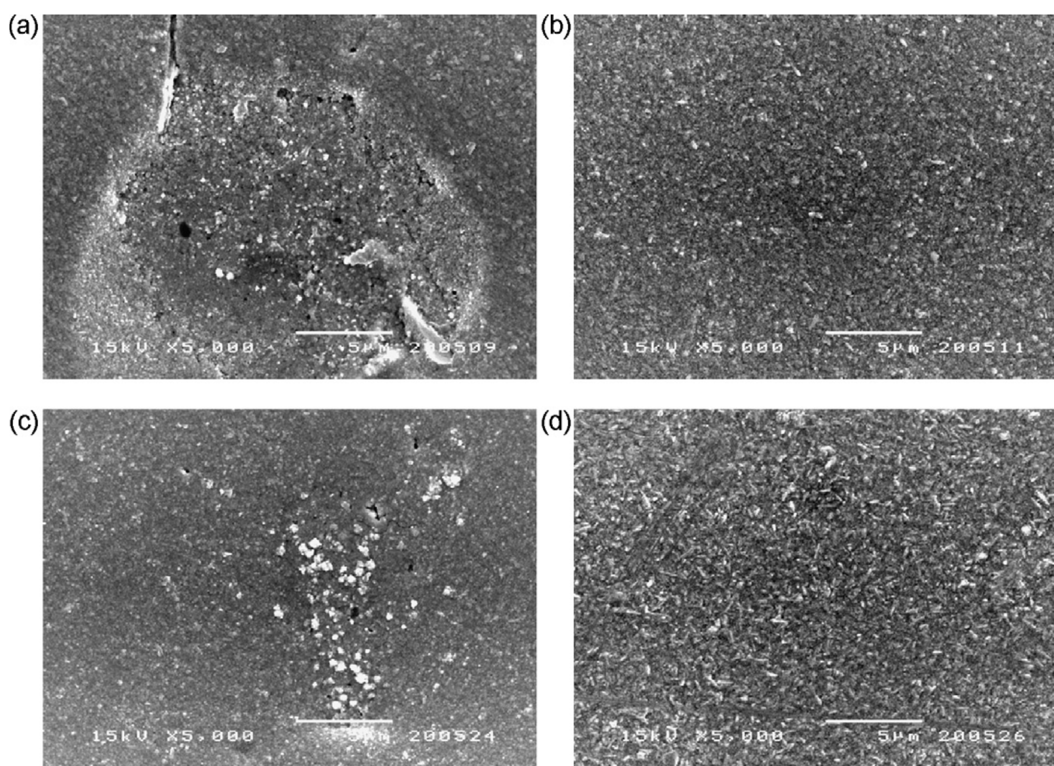

Fig. 5. SEM images at higher magnification (5000×) of deposits obtained from the 0.1 M $CuSO_4$ – 1 M H_2SO_4 solution containing 20 μM thiourea and 1×10^3 μM HCl at a current density of 0.04 A cm^{-2} and rotational speed of 500 rpm (Fig. 4b and d): (a) focused on the white spot after passing 2 C cm^{-2}, (b) focused on the flat area outside white spots after passing 2 C cm^{-2}, (c) focused in the hole after passing 6 C cm^{-2}, (d) focused on the flat area outside holes after passing 6 C cm^{-2}.

(Fig. 5b and d) of the deposits obtained after passing charge densities of 2 C cm^{-2} (Fig. 5a and b) and 6 C cm^{-2} (Fig. 5c and d). The SEM images show that the deposit structures at these two areas are substantially different. After passing 2 C cm^{-2}, the deposit structure at the flat area consists of uniform, fine-grained crystals (Fig. 5b), whereas the deposit structure at the white spot is made of irregular crystals (Fig. 5a). This indicates that two different electrodeposition mechanisms may occur in these two areas. Alternatively, it may also be possible that a single mechanism occurs in both of these areas, and that the white spots, consisting of irregular crystals, are generated at defects as deposition proceeds. As higher charge density is passed (6 C cm^{-2}), the difference in the deposit structures of these areas appears to be more pronounced, as shown in Fig. 5c and d.

To obtain a new insight into the evolution of roughening, AFM was used to acquire the topographies over an image size of 50 μm × 50 μm. The AFM was scanned to cover the white spots revealed in SEM images. Fig. 6 shows the AFM images, including the sectional analysis, of the deposits obtained in the presence of thiourea and HCl after passing charge densities of 1, 2 and 3 C cm^{-2}, corresponding to the deposit thicknesses of 370, 740 and 1100 nm, respectively. The AFM information obtained for thicker electrodeposits is not available since the surfaces are too rough to scan for such a large area (50 μm × 50 μm). AFM images indicate that the white spots observed in the SEM image as early as 1 C cm^{-2} has been passed (Fig. 4a) are, in fact, holes, as we originally hypothesized. The holes become deeper as the electrodeposition proceeds, as shown in Fig. 6. For a closer look in each figure, the sectional analysis indicates that the depth of the hole is close to the thickness of the copper deposit corresponding to each respective charge density (i.e., the measured depths of 374, 715 and 1018 nm after passing 1, 2 and 3 C cm^{-2}, respectively). The bottom of the holes contains a few layers of irregular-grained deposit (as shown in Fig. 5a and c). The AFM image of the deposit obtained in the solution containing thiourea and HCl presented in Fig. 2e is obtained from the flat area outside the holes.

The above results reveal that electrodeposition taking place in two areas may have different mechanisms. On the flat area, the thiourea–Cu(I)–chloride complex inhibits the surface diffusion of adatoms and enhances the nucleation process to form the new nuclei so that uniform, fine-grained structures are produced on this region, as shown in Fig. 5b and d and Fig. 2e. On the other hand, electrodeposition in the holes is almost completely inhibited or proceeds at very slow rate. The structure at the bottom of the holes tends to be a few layers of irregular-grained coating, as shown in Fig. 5a and c.

Fig. 7 shows SEM images of a cross-section of the copper-deposited disc produced in the solution containing thiourea and HCl after passing 27.2 C cm^{-2}, which corresponds to an average thickness of 10 μm. Fig. 7a indicates that the copper deposit obviously does not have a uniform thickness. More importantly, some areas almost have no copper or very few copper layers deposited, whereas other regions have copper over-plated (i.e., a thicker deposit than 10 μm), as shown in Fig. 7b. These results indicate that, in the areas having no or very few layers of coating, the adsorbed complex film can completely inhibit the whole electrocrystallization process, where not only surface diffusion of copper adatoms but also the formation of new nuclei is inhibited. Furthermore, while the electrodeposition is almost completely inhibited in some regions, the applied charge is used to deposit copper in other regions where over-plated areas are obtained, as a current efficiency of almost 100% is found in every experiment.

3.4. Effect of operating parameters

In this section, the effect of operating parameters – the rotational speed of RDE and the current density – on the copper deposits in the presence of thiourea and HCl were studied. First, the effect of

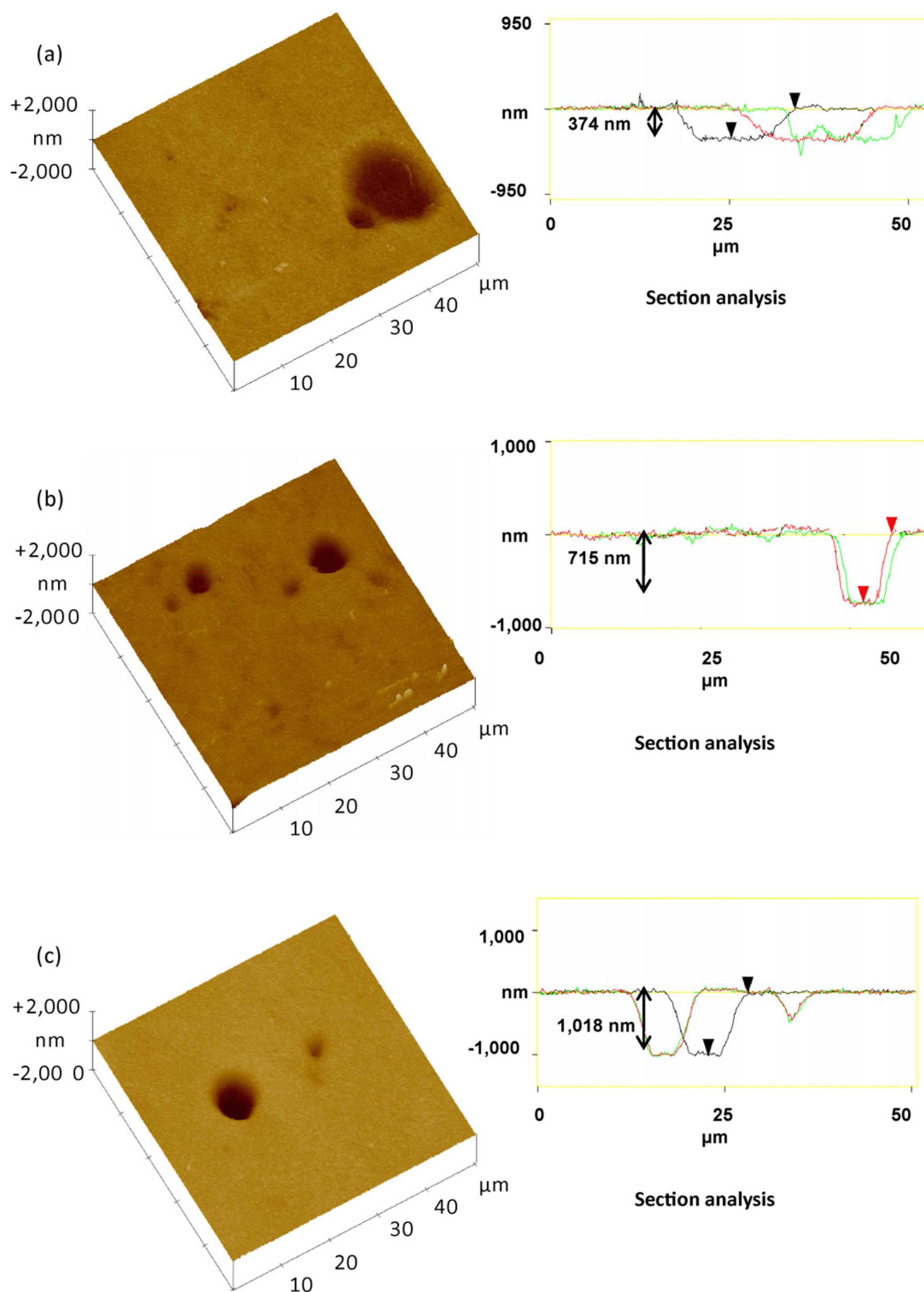

Fig. 6. AFM images (50 µm × 50 µm) and section analysis of copper deposits obtained from the 0.1 M $CuSO_4$ − 1 M H_2SO_4 solution containing 20 µM thiourea and 1×10^3 µM HCl at a current density of 0.04 A cm^{-2} and rotational speed of 500 rpm for coverages of (a) 1 C cm^{-2}, (b) 2 C cm^{-2}, (c) 3 C cm^{-2}.

the rotational speed was investigated by increasing it from 500 to 2000 rpm in incremental steps of 500 rpm. All deposition experiments were still conducted at the current density of 0.04 A cm^{-2}. The deposits obtained at higher rotational speeds after passing the charge density 6 C cm^{-2} (data not shown) were basically similar to that obtained at 500 rpm. The microscopically fine structures with macroscopic rough deposits were still produced. This indicates that the stronger hydrodynamic environment of the solution does not affect the complex thiourea-chloride film formation or its properties.

Next, the effect of current density was investigated over a range from 0.004 to 0.08 A cm^{-2} at the rotational speed of 500 rpm. Fig. 8 shows the SEM images of the deposits obtained at various current densities after passing the charge density of 6 C cm^{-2}. Unlike the deposit produced at 0.04 A cm^{-2}, the copper deposit produced at 0.004 A cm^{-2} appears to be relatively smooth, without rough spots or holes distributed on the surface (at 50×), as shown in Fig. 8a. This observation indicates that the thiourea–Cu(I)–chloride complex film formed on the surface is affected by the applied current density. The thiourea–Cu(I)–chloride complex film does not show

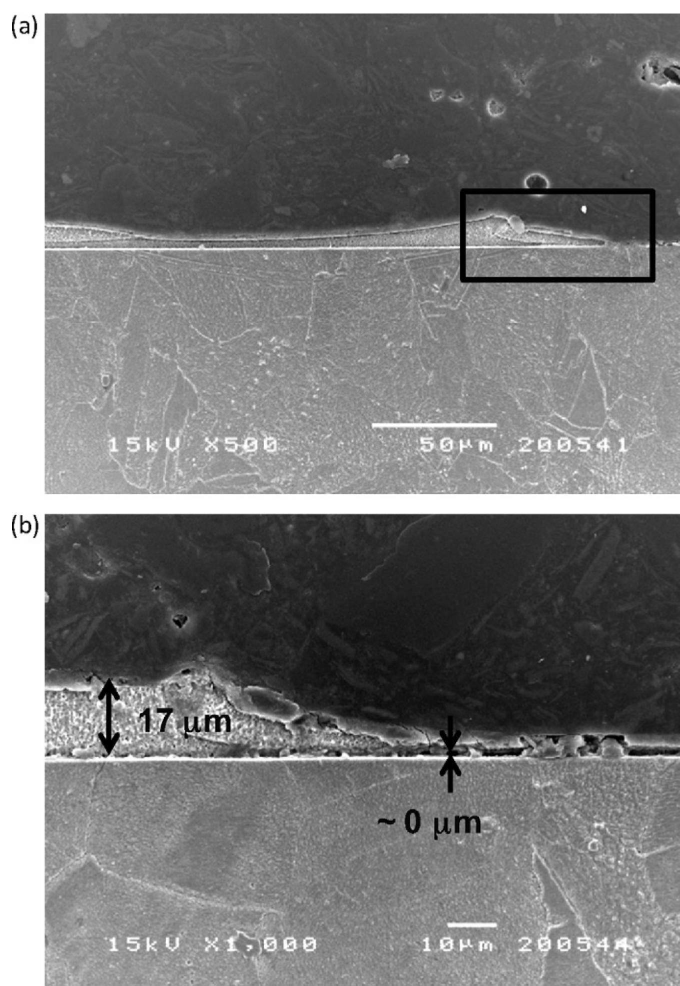

Fig. 7. SEM images for the cross-section of copper deposit obtained from the 0.1 M $CuSO_4$ – 1 M H_2SO_4 solution containing 20 μM thiourea and 1×10^3 μM HCl at a current density of 0.04 A cm^{-2} and rotational speed of 500 rpm for coverage of 27.2 C cm^{-2}: (a) 500×, (b) 1000×.

a local effect on the electrodeposition when the low current density of 0.004 A cm^{-2} is used. However, the overall deposit surface appears dull compared to that produced at 0.04 A cm^{-2}. The deposit consists of a fine structure, but has irregular-grained crystals distributed across the surface, as shown in Fig. 8b (at 5000×), which is similar to the deposit structure at the bottom of the holes when the current density of 0.04 A cm^{-2} is used (Fig. 5a and c). This implies that the deposition mechanism taking place at the lower or bottom parts of the deposit when the current density 0.04 A cm^{-2} is used is similar to the overall deposition mechanism when the low current density of 0.004 A cm^{-2} is used.

When the current density is increased to 0.02 A cm^{-2}, a rough surface is produced (at 50×), as shown in Fig. 8c. Like the rough surface obtained at 0.04 A cm^{-2}, the lower flat part constructs of fine grains with small irregular particles distributed across the surface (at 5000×), as shown in Fig. 8d. When the current density is increased to 0.05 A cm^{-2}, a rough surface having the same deposit structure as those produced at 0.02 and 0.04 A cm^{-2} is obtained (data not shown). When the current density is increased further to 0.06 A cm^{-2}, relatively inconsistent results are obtained. For the most part, smooth deposits that do not appear rough at 50× magnification, but are also not highly reflective, are obtained at this current density. However, in some experiments, rough surfaces are obtained, but to a lesser degree compared to those produced at 0.02 and 0.04 A cm^{-2}. It is possible that the current density may be high enough to allow the thiourea–Cu(I)–chloride complex adsorbed on the surface to be reduced or break down completely, so that the relatively smooth surface is produced. However, under this high current density the mass transfer limitation is expected to play the major role. When the current density is increased beyond the limiting current density to 0.08 A cm^{-2}, the rough surface is no longer obtained, but the brick-red deposit having the structure shown in Fig. 8e is produced.

The above results indicate that the current density used has a strong influence on the thiourea–Cu(I)–chloride complex film formed on the surface during electrodeposition, which leads to different deposition mechanisms. It is possible that applied current density affects the thiourea–Cu(I)–chloride complex film adsorbed on the substrate and eventually affects the nucleation process. The almost complete suppression of the current in the low potential range of the voltammogram, shown in Fig. 1a, indicates the inhibitory effect of the thiourea–Cu(I)–chloride complex film. Within this region, the current density is limited to lower than 0.01 A cm^{-2}, followed by a steep rise in the current density, from 0.01 to 0.05 A cm^{-2}. Most complex film formed in the low current density range is still intact on the surface, resulting in strong suppression of the surface diffusion process and the production of a deposit with relatively small-grained crystals. The complex film formed in the critical potential range can be reduced or break down, but not uniformly. Thus, the electrodeposition proceeds at different rates in various areas leading to a macroscopically uneven surface, as shown previously. When the current density is increased, the deposit surfaces tend to become more even. However, when the current densities are too high (i.e., 0.06 A cm^{-2} or higher), the mass transfer limitation starts to affect the electrodeposition process and dominates the effect of additives (0.08 A cm^{-2}).

In order to investigate the effect of a higher current density on the copper electrodeposition in the presence of thiourea and HCl, the rotational speed must be increased to avoid the mass transfer limitation effect. Based on the voltammograms shown in Fig. 1b, we carried out the copper deposition experiment using a current density of 0.08 A cm^{-2} and a rotational speed of 2000 rpm.

The deposits produced under these conditions appear to be very smooth and featureless (at 50×), similar to Fig. 8a. No rough spots are observed for a copper deposit as thick as 10 μm (charge density of 27.2 C cm^{-2}). As discussed previously, when the applied current density is increased, the thiourea–Cu(I)–chloride complex film tends to have a more uniform property or to break down, allowing the Cu^{2+} from the solution to be reduced. This experiment shows that if the applied current density is high enough, all the complex film on the surface may form evenly across the surface or may break down completely. The electrodeposition then proceeds at the same rate for the entire surface and a smooth deposit is obtained.

While the macroscopic structures show a significant improvement, the microscopic structures do not show a substantial change. AFM (Fig. 9a) and SEM (Fig. 8f) images indicate that the deposit morphologies are similar to those of the upper-flat areas of the deposits obtained at the current density of 0.04 A cm^{-2} (Figs. 2e and 5b, d) where compact and fine-grained crystals with no irregular grains are produced. In addition, the deposit structure still retains very uniform and fine-grained structures, even after passing the charge density of 27.2 C cm^{-2}, as shown in Fig. 9b. However, it should be pointed out that although the macroscopic analysis suggests the complete breakdown of the complex film and, as observed in Fig. 1, the reverse voltammograms in the presence of thiourea and chloride after the complete breakdown of the complex film tend to follow the reverse voltammogram in the presence of chloride alone, the deposit structures in the presence of thiourea and chloride are totally different from, in fact much better than, that obtained in the presence of HCl alone or in the absence of additives. These results suggest that the state of the surface after the complex film

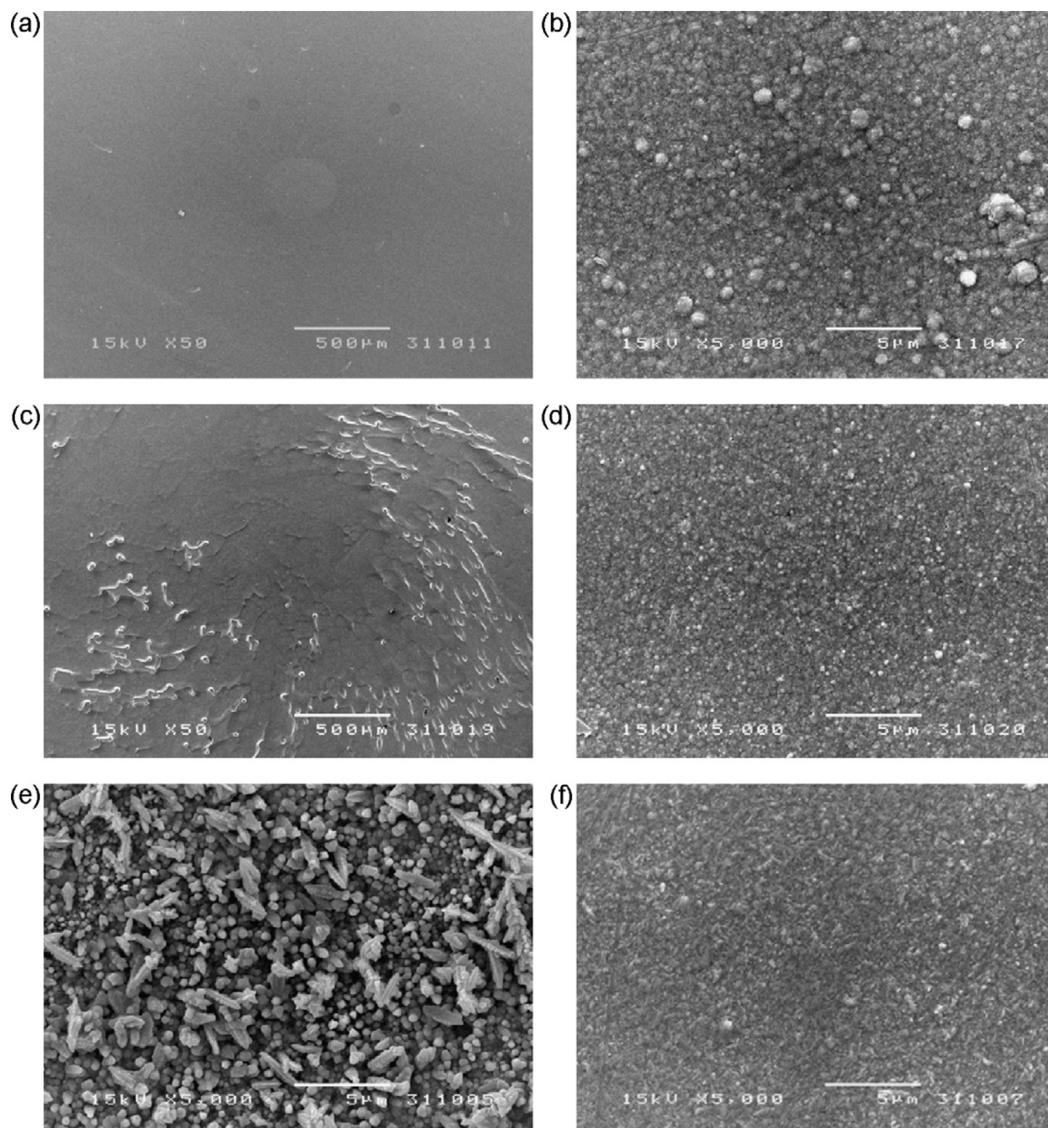

Fig. 8. SEM images of copper deposits obtained from the 0.1 M $CuSO_4$ – 1 M H_2SO_4 solution containing 20 μM thiourea and 1×10^3 μM HCl for coverage of 6 C cm^{-2} at (a) a current density of 0.004 A cm^{-2} and rotational speed of 500 rpm (50×), (b) a current density of 0.004 A cm^{-2} and rotational speed of 500 rpm (5000×), (c) a current density of 0.02 A cm^{-2} and rotational speed of 500 rpm (50×), (d) a current density of 0.02 A cm^{-2} and rotational speed of 500 rpm (5000×), (e) a current density of 0.08 A cm^{-2} and rotational speed of 500 rpm (5000×), (f) a current density of 0.12 A cm^{-2} and rotational speed of 2000 rpm (5000×).

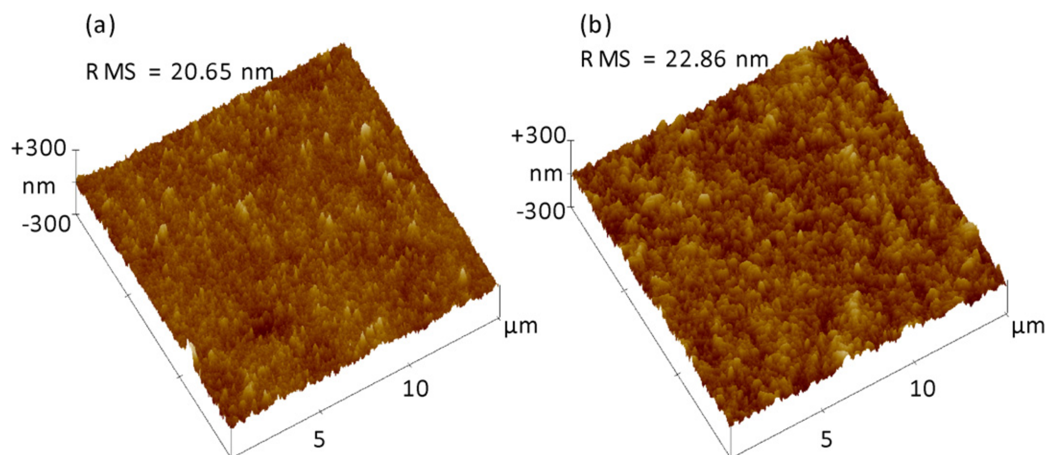

Fig. 9. AFM images (15 μm × 15 μm) of copper deposits obtained from the 0.1 M $CuSO_4$ – 1 M H_2SO_4 solution containing 20 μM thiourea and 1×10^3 μM HCl at a current density of 0.08 A cm^{-2} and a rotational speed of 2000 rpm for coverages of (a) 6 C cm^{-2}, (b) 27.2 C cm^{-2}.

breaks down during the copper deposition differs from that prevailing just before the reverse scans in the voltammogram study. The complex film adsorbed on the surface during the copper deposition may still contain intact thiourea within its structure, which helps improve the deposit morphology, but, during the reverse scans in the voltammogram study, thiourea is expected to detach from the complex film leaving only chloride on the copper surface (Fig. 1). However, the information obtained from a surface analytical technique such as XPS or SIMS would be needed to support this statement.

4. Conclusions

The results of examination by AFM, SEM and electrochemical methods indicate the synergetic effects of chloride and thiourea during copper electrodeposition in a sulfate-plating bath. The copper deposition mechanism in the presence of thiourea and chloride was found to be different from that in the present of thiourea alone. Copper deposition in the presence of thiourea alone requires increased polarization relative to that in an additive-free solution, whereas deposition in the presence of thiourea and chloride requires less polarization, similar to the situation when chloride alone is added. On the microscopic level, the addition of chloride to a plating bath containing thiourea makes the deposit morphology a little rougher, but nodules disappear from the structure. The disappearance of nodules makes the overall structure of the deposit smoother and more homogeneous, which results in a more reflective surface. However, the presence of chloride leads to a macroscopically rough surface with no distinct pattern since the thiourea–Cu(I)–chloride complex film adsorbed on the surface does not respond to the applied current evenly. Then, copper deposition in different areas proceeds at different rates and an uneven surface is produced. Those areas are found to undergo different deposition mechanisms. In the lower parts or holes of the rough deposit, the thiourea–Cu(I)–chloride complex inhibits both the grain growth and nucleation processes, and the deposition mechanism similar to that using a very low current density ($0.004\,\mathrm{mA\,cm^{-2}}$) is expected since the deposit structures are similar. In the flat areas, the thiourea–Cu(I)–chloride complex inhibits only the grain growth process, while nucleation is enhanced, leading to the formation of thicker deposit with a uniform, fine-grained structure. The roughening effect due to the complex film is minimized at high applied current densities since a high enough applied current density can break up the complex film completely across the entire surface. As a result, the smooth deposit on both microscopic and macroscopic levels is obtained.

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