Surface & Coatings Technology 214 (2013) 8–18

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

# Effect of thiourea on grain refinement and defect structure of the pulsed electrodeposited nanocrystalline copper

K. Shravan Kumar [1], Krishanu Biswas *

*Department of Materials Science and Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, U.P., India*

ARTICLE INFO

*Article history:*
Received 12 June 2012
Accepted in revised form 5 October 2012
Available online 16 October 2012

*Keywords:*
Pulsed electrodeposition
Nanocrystalline copper
Thiourea
Grain refinement
Twins
Dislocations

ABSTRACT

The present investigation reports an extensive study on the grain refinement and the defect structure in the pulsed electrodeposited nanocrystalline copper. Copper is deposited on the stainless steel substrate using aqueous acidic copper sulfate solution prepared from 0.25 M $CuSO_4.5H_2O$ and 0.5 M $H_2SO_4$ with addition of varying amounts of thiourea. Copper deposits are made using 0, 9, 18, 27 and 36 mg/L addition of thiourea in the electrolyte. The results indicate formation of nanocrystalline copper grains by even small addition of thiourea with three orders of magnitude reduction in the grain size as compared to the sample deposited without thiourea. The defects formed in the copper deposits are found to change predominantly from dislocations to the twins with addition of thiourea. The grain refinement in the thiourea containing samples is deemed to be due to change in the nucleation kinetics, growth as well as the kind of defect structure developed in the samples. The transient studies at the initial stage of deposition using chronoamperometry indicate the change in nucleation mode from instantaneous to progressive by addition of thiourea. EFTEM investigation conclusively proves the preferential segregation of thiourea at the grain boundaries of copper during pulsed electrodeposition. Detailed microscopic analysis reveals the grain refinement affected by the defect structure.



## 1. Introduction

Nanocrystalline materials (nc) or nanostructured materials are a field of vigorous activity in recent times because of their unique mechanical, physical and chemical properties that differ substantially from the coarse grain counterpart [1–4]. The preparation and characterization of these novel materials are very much required to probe the effect of size on different properties of these materials. A number of processes have been developed to synthesize these materials. These processes are categorized either top-down or bottom-up approach. In the top-down category, the micron or submicron-sized microstructure of the bulk material changes to nanostructures by application of energy. On the other hand, the bottom-up approach corresponds to build up of the nanostructures atom-by-atom, layer-by-layer or cluster-by-cluster. The bottom-up processes include inert gas condensation, chemical synthesis, electrodeposition, etc. Among all the methods, electrodeposition has several significant advantages over other routes. This is an inexpensive and versatile technique used to prepare bulk nanostructures of various metals and alloys with few size and shape limitations [5]. Therefore, this technique has been extensively used to prepare nc materials.

Electrodeposition of copper has received attention because of the fact that it finds applications as the interconnect material for the printed circuit boards and the integrated chips replacing the materials like aluminum and tungsten [6,7], multilayer sandwiches of giant magneto resistive hard disk read heads, and protective and decorative coatings [8,9]. As compared to conventional Al technology, damascene structures are used for Cu technology in which Cu fills the trenches that are patterned over dielectric films [7]. Electroplating is widely used in the industries as a standard deposition method to prepare the damascene interconnects. This is mainly due to the fact that it is possible to deposit nanocrystalline copper with excellent filling of the small features with the help of different additives in the electrolyte during electrodeposition.

Extensive literature survey indicates the usage of different organic additives in the electrodeposition of copper, such as polyethylene glycol and chloride ions [7], polyvinyl pyrrolidone [10], nicotinic acid, benzotrizole, sulphonic acids [11] and thiourea [12]. Among these, thiourea is the most widely used additive to fill small features without voids and as the leveling and brightening agent to get a high degree of mirror reflection in copper deposits [11–16]. There are few reports in the literature showing thiourea playing an important role in controlling the grain size of the copper electrodeposits [15,17,18]. Thiourea is reported to adsorb and block the active sites for copper

* Corresponding author. Tel.: +91 512 259 6184; fax: +91 512 259 7505.
*E-mail addresses:* shra.one1986@gmail.com (K.S. Kumar), kbiswas@iitk.ac.in (K. Biswas).
[1] Presently at Corrosion and Surface Engineering Division, CSIR-National Metallurgical Laboratory, Jamshedpur, 831007, Jharkhand, India.

0257-8972/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.surfcoat.2012.10.018

electrodeposition and thus inhibits the crystal growth processes, resulting in a fine grained structure [15,19–22].

In our previous study, we have reported the mechanisms of the microstructure evolution and the leveling of the copper film electrodeposited with the addition of thiourea [23]. In the present paper, the influence of thiourea on the mechanisms of grain refinement and the formation of defect structure in the electrodeposited copper will be described and discussed. We made an attempt to propose plausible mechanisms of the grain refinement with emphasis on the formation of defect structure in electrodeposited copper with addition of thiourea. The formation mechanism of nanocrystalline copper grains during electrodeposition is not fully understood so far. The nanocrystal formation is always thought to be due to the process of bottom-up way. There are very few studies concentrating on the issue of grain refinement and defect structure formation during copper deposition in presence of additive [24]. The present study targets at systematically understanding the evolution of microstructure in a series of electrodeposits prepared with different concentrations of thiourea using transmission electron microscopic observations. It will be shown that the formation of the nanocrystalline copper grains by addition of small amount of thiourea is due to three different aspects, change in the nucleation kinetics of copper, the grain growth and the defect structure formation.

## 2. Experimental details

### 2.1. Sample preparation

Pulsed current electrodeposition of copper was carried out using Princeton Applied Research Potentiostat/Galvanostat 263 A, USA. The working electrode used was commercial SS 304 grade of stainless steel of dimensions $1.5\times1.5\times0.1$ cm$^3$. The stainless steel sheets were stress relieved at 623 K (350 °C) for 4 h. These sheets were polished to the surface roughness of 0.1 μm and then further ultrasonically cleaned at room temperature for 15 min to remove polishing residues and dried properly. These were soldered to give a conductive path and neatly covered with Teflon tape so that known area of the substrate was exposed to the electrolyte. The counter-electrode was pure copper, which was used to maintain the copper ion concentration in the solution. The electrolyte chosen was aqueous acidic copper sulfate solution prepared using 0.25 M $CuSO_4.5H_2O$ and 0.5 M $H_2SO_4$. Varying amounts of thiourea (0, 9, 18, 27 and 36 mg/L) were added to the electrolyte. All the chemical reagents used were of analytical grade. The electrolyte was stirred with a magnetic stirrer till the homogeneity of the solution was ensured. Each time a fresh solution was prepared for each experiment and deposition was carried out in a double-walled cell to maintain a constant temperature of $303\pm0.5$ K ($30\pm0.5$ °C). The bath was kept static during the deposition and the distance between working and counter electrode was maintained constant at all times (2 cm) and proper care was taken to keep them parallel facing each other. The pulsed current depositions were carried out galvanostatically for 3 h, by applying unipolar pulses of rectangular wave form of peak current density, $I_p=0.2$ A/cm$^2$ with average current density, $I_{av}=0.04$ A/cm$^2$ and a duty cycle of 20% by keeping $t_{on}=8$ ms and $t_{off}=32$ ms. A typical deposition cycle is shown in Fig. 1.

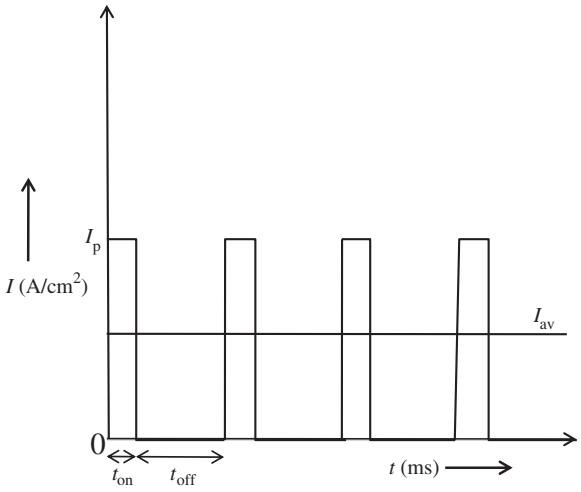


**Fig. 1.** Pulsed electrodeposition cycle of rectangular wave form.

### 2.2. Electrochemical and structural characterization

Chronoamperometry test was conducted without and with thiourea to study nucleation mechanism of copper deposition at constant potential of −0.35 V. The potential has been selected from our extensive measurements using linear sweep voltammetry [23]. These tests were conducted in similar atmosphere where the depositions were carried and the potentials were recorded with reference to saturated calomel electrode (SCE) using luggin capillary. The reference electrode was prepared with great care to ensure there were no gas pockets and inhomogeneity in the electrode.

X-ray diffraction (Seifert, Iso-Debyeflex-2002, USA) was carried out on the copper deposits, thus produced to analyze the phases present without and with thiourea and to estimate the grain size by standard Williamson–Hall method [25]. High resolution transmission electron microscopy observations were carried out using 200 kV (FEI Technai, 20UT, The Netherlands) and 300 kV (FEI Technai, F30, The Netherlands) microscopes. Sample preparation for TEM observations involved mechanical thinning of 3 mm disks, followed by ion-milling to electron transparency in a (Gatan 691, USA) precision ion polishing system. The ion polishing was carried out using beam energy of 4 keV at an incident angle of 4° to minimize heating and sample damage. The sample was then ion milled at 2 keV and 2° incident angle to clean the sample surface from contamination. Energy filtered transmission electron microscope (EFTEM) in Technai F30 with a fine probe (1 nm diameter) was utilized to obtain energy filter maps of different elements present in the copper deposits. The analysis of TEM micrographs was carried out using Metal Power image analyzer software, version 3.0.0.10.

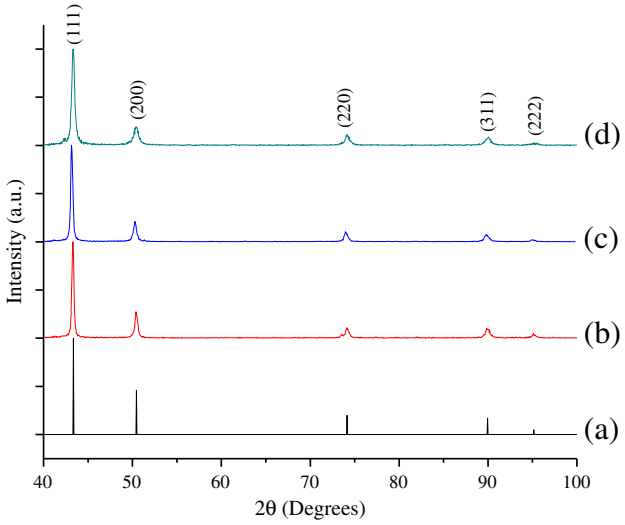


**Fig. 2.** X-ray diffraction peaks of copper electrodeposits: (a) standard copper (ICDD:04-0836), (b) 0, (c)18 and (d) 36 mg/L of thiourea.