Microelectronic Engineering 121 (2014) 83–86

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Mechanical properties of Cu electroplated in supercritical CO_2 emulsion evaluated by micro-compression test

Hikaru Kinashi, Takashi Nagoshi, Tso-Fu Mark Chang, Tatsuo Sato, Masato Sone *

Precision and Intelligence Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

ARTICLE INFO

Article history:
Received 18 October 2013
Received in revised form 5 March 2014
Accepted 23 March 2014
Available online 2 April 2014

Keywords:
Micro-compression
Cu
Electroplating
Supercritical CO_2

ABSTRACT

This paper reports mechanical properties of Cu films fabricated by electroplating with supercritical CO_2 emulsion (EP–SCE). Also, mechanical properties of Cu films fabricated by conventional electroplating (CONV) were evaluated to examine the effects of EP–SCE. The films were electroplated in an electrolyte composed of copper sulfate plating bath, supercritical CO_2 and surfactant. Scanning ion microscopy images confirmed the supercritical CO_2 emulsion refined microstructure of the plated Cu from about 1 μm of grain size in CONV to about submicron order of grain size in EP–SCE. Non-tapered micro-sized Cu pillars were prepared by focused ion beam and used in the micro-compression test. Strengths of the Cu films fabricated by EP–SCE were 300 MPa, which is higher than the CONV case. Impurity concentration in the films was evaluated by glow discharge optical emission spectroscopy, and no significant difference between EP–SCE and CONV was observed. The high strength in EP–SCE is believed to be mainly a result of grain refinement strengthening.

1. Introduction

Cu materials are used in various electronic devices because of the superior electric and thermal conductivity. Electroplating is an important technology for fabrication of micro-components used in micro-electro-mechanical system (MEMS) devices [1,2] and related packaging technologies, such as Cu wiring damascene process [3]. Especially for fabrication of three-dimensional (3D) structures, electroplating is an important process for miniaturization and densification of the microelectronics [4]. As shown in International Technology Roadmap for Semiconductors, half pitch of dynamic random access memory will become 15.9 nm in 2018 [5]. However, voids and pinholes can be formed in electrodeposited Cu applied in an integrated device, which would cause malfunction of the device. Several studies have reported that different type of additives can be used to attain defect-free nano-scale Cu filling [6–9]. However, further studies show that usage of additives can increase impurity concentration in the electrodeposited Cu, and impurity can cause serious problems for electric devices, such as increased electric resistance [10].

To solve these problems, a novel electroplating system is propose by our group, which is electroplating with supercritical CO_2 (sc-CO_2) emulsion (EP–SCE) [11,12]. Critical point of CO_2 is relatively low (304 K and 7.39 MPa) when compared with other solvents, which make it a commonly used SCF in the industries and research area. Merits of applying supercritical fluid (SCF) are high diffusivity, solubility and low surface tension. Agitation with surfactant enables the aqueous Cu electrolyte and sc-CO_2 to form emulsions with CO_2-in-water (C/W) type micelles at a certain pressure and temperature. In addition, CO_2 is non-polar, which can promote desorption of H_2 gas bubbles from the surface of cathode. Adsorption of H_2 gas bubbles on the surface of cathode is reported to be one of the causes for defects found in electrodeposited films [13]. In previous studies, we confirmed that these features given in EP–SCE can increase quality of the electrodeposited film, such as film smoothening, and defect- and pinhole-free [14] and demonstrated application of EP–SCE in defect-free Cu filling into nano-scale holes [15].

However, effects of the sc-CO_2 emulsion on the Cu film electroplated by EP–SCE, especially microstructure and mechanical property, have not been well studied. In the case of Cu wiring or applications in MEMS, not only electrical property but also mechanical property is important. Characterizing the small-scaled and scale-specific mechanical properties of materials can provide design guidelines for reliable nano- and micro-electromechanical devices and clarify mechanical behavior of multicomponent structural materials. Therefore, mechanical property of the Cu films fabricated by EP–SCE was evaluated by micro-compression test using a non-tapered micro-sized pillar with square

* Corresponding author. Tel.: +81 45 924 5043; fax: +81 (0)45 924 5044.
E-mail address: msone@m.titech.ac.jp (M. Sone).

http://dx.doi.org/10.1016/j.mee.2014.03.029
0167-9317/

cross-section, which is fabricated from the electrodeposited films by using focused ion beam (FIB). Film texture was also observed, and impurity concentrations in the films were measured by glow discharge optical emission spectrometry (GDOES).

2. Experimental

2.1. Materials

CO_2 with purity of 99.99% purchased from Nippon Tansan Co., Ltd., was used. Cu plate with purity of 99.99% and dimensions of $2.0 \times 1.0\ cm^2$ was used as cathode, and Pt plate with dimensions of $2.0 \times 1.0\ cm^2$ was used as anode. The Cu electrolyte was composted of $CuSO_4$ (0.85 mol/L) and H_2SO_4 (0.55 mol/L) with 4.5 mL/L of Top Lucina α-M, 1.0 mL/L of Top Lucina α-2, 3.0 mL/L of Top Lucina α-3 (Okuno Industry Co., Ltd.), and 1 mmol/L of Cl^- (NaCl, Okuno Industry Co., Ltd.). For conventional electroplating (CONV), only the Cu electrolyte was used. For sc-CO_2 emulsified electrolyte, the Cu electrolyte, CO_2 and a non-ionic surfactant, polyoxyethylene lauryl ether [$C_{12}H_{25}(OCH_2CH_2)_{15}OH$], were used for formation of the emulsion. Concentration of the Cu electrolyte and the surfactant were 60 and 1.0 vol%, respectively.

2.2. Electroplating

The Cu plates were treated in 10 wt% degreasing solution purchased from Okuno Industry Co., Ltd., for 1 min follow by rinsing with distilled water. Then, the Cu plates were treated in 10 wt% HCl, purchased from Okuno Industry Co., Ltd., for 10 s. Finally, the Cu plates were again rinsed with distilled water. Before initiation of the electroplating procedures, the emulsion was stirred at 500 rpm for 10 min at 15 MPa to ensure stabilization of the emulsion [15]. Then, the electroplating reaction was conducted at 2.0 A/dm^2.

2.3. Characterization of the Cu films

Impurity content in the film was analyzed using GDOES (GDA750, Rigaku). For GDOES, electric potential and pressure of Ar used were 500 V and 2.8 hPa, respectively. Ar plasma gas sputtering was conducted for 300s to have a depth profiling. The relevant wavelength of C is 156.143 nm. Microstructure of the Cu film was observed by scanning ion microscopy (SIM, FB2100: Hitachi) and a scanning electron microscope (SEM, S-4300SE, Hitachi).

2.4. Micro-compression test

Micro-sized pillars were made by FIB (FB2100: HITACHI). Stress from top to bottom of the pillar would not be uniform when a tapered pillar is used in compression test, since cross-sectional area from top to bottom of the pillar is not uniform. Thus, a non-tapered micro-pillar is crucial in evaluation of mechanical property. FIB induced Ga^+ ion damage on Cu was studied by Kiener et al. [16]. They reported that the ion irradiation can cause an increase of more than 100 MPa in stress for samples with submicron dimensions when solid solution hardening by the penetrated Ga^+ ion and Taylor hardening by introduced dislocations are considered. However, it should be negligible for our samples, because the pillars used in this study were large enough to neglect the influence from the ion irradiation. Fig. 1 shows schematic diagrams of the FIB microfabrication procedures for the micro-sized pillars and SEM image of the fabricated Cu pillar. Detail of fabrication procedures of non-tapered micro-pillar was reported in previous studies [17,18].

The FIB fabricated pillar had square cross-section with 20 μm on a side and 40 μm in height. The compression tests were conducted using a test machine specially designed for micro-sized specimen [19]. Loading directions were parallel to Cu film/substrate interface. Flat-ended diamond indenter equipped to a load cell was used as a compression platen, and controlled at a constant displacement rate of 0.1 μm/s using a piezo-electric actuator. Force and displacement were recorded at every 33 ms.

3. Results and discussion

3.1. 1. Impurity in electrodeposited Cu

Reductions of CO_2 on transition metal surfaces have been reported in several studies [20,21]. In a controlled experimental condition, current efficiency for reduction of CO_2 on Ni and Cu surface could be as high as 100% and 98%, respectively [20]. In fact, concentration of C in the Ni films fabricated by EP–SCE was reported to be higher than the Ni films fabricated by CONV [18,22]. Hence, it is necessary to investigate impurity, especially C, concentration in the Cu film fabricated by EP–SCE. In this study, GDOES was used to evaluate impurity concentration in the films. Fig. 2 shows C concentration in the Cu films. Horizontal axis represents distance from the interface between the electrodeposited film and the electrolyte. Distribution of C was observed with a broad peak near the interface between the substrate and the electrodeposited film. C distribution for the EP–SCE case was very similar to the CONV case. These results indicated that C impurity observed in the EP–SCE case was not derived from reduction reaction of CO_2 but from the additives such as suppresser, accelerator and leveler initially used in the Cu electrolyte. Moreover, the distribution of C concentration shows that most of the C deposited is from early stages of the electroplating reaction. Stangl et al. also reported same results from cyclic voltammetry analysis [23]. When electroplating reaction was initiated, the organic additives adsorbed on cathode could be taken into the electrodeposited Cu. Then the C in the electrodeposited Cu would diffuse away from the interface of the electrodeposited Cu and the substrate to cause the broad peak. Contamination signal of other elements such as H, S, and O was not observed from GDOES. Therefore, the results C distribution in the Cu films confirmed EP–SCE would not cause additional contamination problems in the electrodeposited Cu film.

3.2. Microstructure of Cu film

Grain size of the Cu films can be seen from the SIM images shown in Fig. 3. Grain refinement was observed for EP–SCE, where grain size of the EP–SCE film and the CONV film were about 0.1 and 1.0 μm, respectively. The effect of grain refinement was also observed when EP–SCE is applied in Ni plating [18], and the reasons are considered as follows; agitation of the Cu electrolyte, sc-CO_2 and the surfactant enables formation of sc-CO_2 emulsion with C/W type micelles. The C/W micelles would continuously bounce on the surface of cathode while the electroplating reaction is in process, which would give a phenomenon named periodic-plating-characteristic (PPC). For the PPC, the electroplating reaction is turned off when the surface of cathode is in contact with the micelles and turned on when the micelles detach away from the surface [14]. The PPC would give effects similar to pulse plating, which is believed to be the main cause of grain refinement.

3.3. Mechanical properties evaluated by micro-compression test

Nominal stress–strain (S–S) curve of the Cu pillars is shown in Fig. 4. A significant difference was observed in mechanical strength between the EP–SCE pillar and the CONV pillar, where nominal stress of the EP–SCE pillar was about 300 MPa higher than that