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Cu wiring into nano-scale holes by electrodeposition in supercritical carbon dioxide emulsified electrolyte with a continuous-flow reaction system

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ABSTRACT

In this paper, a continuous-flow reaction system was proposed and examined for filling of Cu into holes with 60 nm in diameter and aspect ratio of 2 and 5 by an electroplating method with supercritical carbon dioxide (sc-CO_2) emulsified electrolyte on a round-type large-area hole test element group (TEG) with diameter of 300 mm, which has an integrated structure of Cu seed layer on TiN barrier layer sputtered on Si substrates. Copper-sulfate-based electrolyte was used and emulsified by sc-CO_2 and a surfactant and Cu particles was added to create a suspension. 313 K and 12 MPa were used with various applied current density (1.41, 2.83 and 4.23 A/dm^2). The TEG was found to be completely covered by electrodeposited Cu when 2.83 A/dm^2 was used. All of the holes were filled by Cu without any voids at 2.83 A/dm^2, while incomplete filling was observed at 1.41 and 4.23 A/dm^2. Moreover, a contamination of carbon was not detected by glow discharge optical emission spectroscopy and the reaction was suggested to be feasible to apply into Cu wiring.

1. Introduction

Supercritical carbon dioxide (sc-CO_2) is generally viewed as a replacement for harmful organic solvents used in extractions, separations, chemical reactions, and many other applications because CO_2 is non-polar and the tunable physical properties between a gas and a liquid [1–3]. Especially for application of dense CO_2 in fine wiring technology, transfer of materials into and out of fine nano-space can be improved to allow proper cleaning and complete filling of the nano-spaces. Dense CO_2 is referring to CO_2 with pressure and temperature close or beyond the critical point. Extremely low surface tension of dense CO_2 can also prevent damage of the nano-space, which is often a problem when aqueous solution is involved. Several studies have been reported recently regarding electroless plating technology using dense CO_2, such as a supercritical fluid deposition (SCD) by Watkins et al. [4] and Kondoh et al. [5].

We have also studied an electroplating method using sc-CO_2 emulsion (EP-SCE) [6,7]. In EP-SCE, electroplating reaction was conducted in an emulsion composed of an aqueous electrolyte, sc-CO_2, and a surfactant. Ni film obtained by this technique was uniform and without pinhole, because sc-CO_2 has low viscosity and compatibility of hydrogen. Thus, we believe EP-SCE could also be applied in fine Cu wiring. However, dissolution of Cu seed layer on hole test element group (TEG) was observed in the sc-CO_2 emulsion (SCE) [8]. Therefore, Cu particles were added to form sc-CO_2 suspension (SCS) to inhibit dissolution of the Cu seed layer. Based on these ideas, we have proposed an electroplating method using SCS (EP-SCS) [8,9]. In previous studies, we have demonstrated complete filling of 70 nm diameter holes with aspect-ratio of 5 on Si substrate by EP-SCS with a batch-type high pressure autoclave system. However, size of the substrate used in the batch-type system is too small for practical application of the technique. A system capable of processing substrate with large diameter is required.

In order to apply EP-SCS into nano-scale wiring with large-area hole TEG, homogenization of the SCS in the high pressure reaction chamber becomes an important problem. Mechanical agitation used in the batch-type system is found to be not sufficient for homogenization of the SCS because of the density difference between the electrolyte, the Cu particles, and sc-CO_2 [6]. Therefore, the aim of this study is to develop a continuous-flow reaction system of EP-SCS to solve the problem. One of the advantages for a continuous-flow reaction system involving supercritical fluid is that additional depressurization step is not required to feed the reactants or recover the products [3,10]. In addition, economically,

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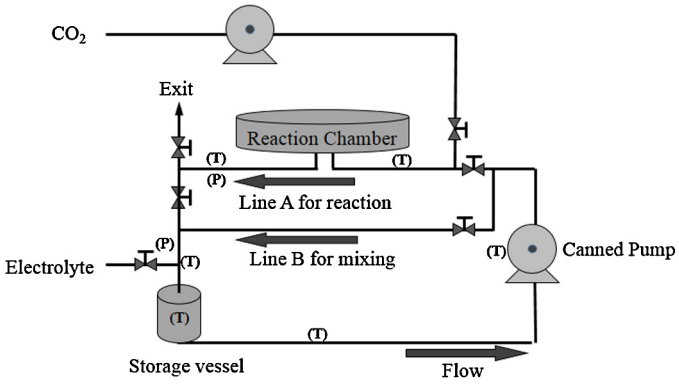

Fig. 1. Experimental apparatus of the continuous-flow reaction system. This reaction system is composed of a reaction chamber, a storage vessel for the aqueous electrolyte, and a canned pump. (T) and (P) mean the points to measure temperature and pressure in system, respectively.

a continuous-flow reaction system is usually preferred than a batch-type reaction system because of the higher efficiency.

In order to demonstrate advantage of the continuous-flow reaction system, a 300 mm diameter round-type hole TEG will be used in this study. Also, size of the nano-scale holes used will be 60 nm with aspect ratio of 2 and 5. In addition, Ni film obtained by EP-SCE was found to contain carbon content higher than the film obtained by conventional electroplating methods [11,12]. The carbon impurities can cause high electric resistance problem in the Cu filled into the nano-holes. Thus, concentration of carbon and oxygen in the electrodeposited Cu film prepared by EP-SCS were also examined by glow discharge optical emission spectroscopy.

2. Materials and methods

2.1. Materials and experimental conditions

The SCS was composed of copper-sulfate-based electrolyte, Cu particles, CO_2 and a surfactant [$C_{12}H_{25}(OCH_2CH_2)_{15}OH$] as reported in previous report [8,9]. Carbon dioxide with a minimum purity above 99.99% was purchased from Toei Kagaku Co., Ltd. Copper-sulfate-based electrolyte was purchased from Okuno Industry Co., Ltd. with composition of $CuSO_4{\cdot}5H_2O$ (0.85 mol/l) and H_2SO_4 (0.55 mol/l). $C_{12}H_{25}(OCH_2CH_2)_{15}OH$ was supplied by Toshin Yuka Kogyo. Cu particles (Kanto Kagaku, 63 μm, purity 99.5%) were added for formation of the suspension. Current density of electroplating was 1.0 A/dm^2. The additives used were 100 μmol/L of polyethylene glycol with molecular weight of 8000 g/mol, 29.4 μmol/L of Janus Green B, 21 μmol/L of bis(3-sulfopropyl) disulfide and 1.7 mmol/L of Cl^- (NaCl). Regarding the reaction conditions, 23 vol.% of CO_2 at 313 K and 12 MPa were used. Three values of direct current were used, which were 10, 20, and 30 A which correspond to current density (CD) values of 1.41, 2.83 and 4.23 A/dm^2, respectively. TEGs with 300 mm in diameter and cylindrical holes with (I) 60 nm in diameter and 120 nm in depth and (II) 60 nm in diameter and 300 nm in depth were fabricated on Si substrates, where Cu seed layer (12–13 nm thick on inner wall, 50–60 nm on top surface)/TaN barrier layer (3–4 nm thick on inner wall, 15 nm on top surface) were deposited on the Si substrate by sputtering. Anode was gold electroplated Cu plate with 300 mm in diameter.

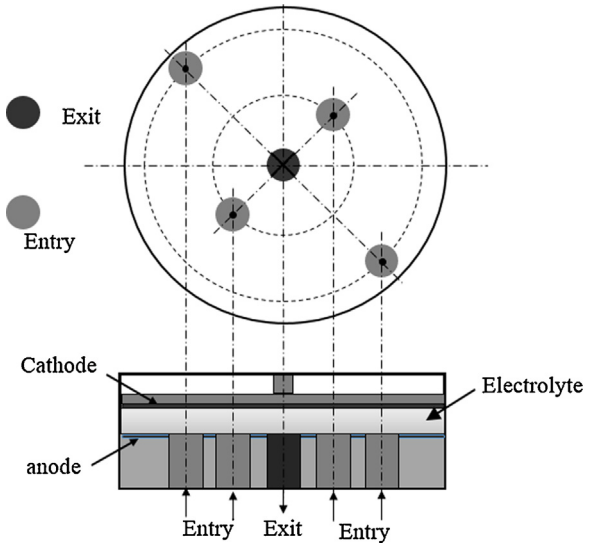

Fig. 2. Detailed structure of the reaction chamber. Upper illustration shows positions of entrees and outlet for circulating the sc-CO_2 suspension; lower illustration is cross-sectional image of the reaction chamber and shows geometry of electrodes, four entrees and outlet. The diameter of reaction area is 300 mm and distance between cathode and anode is 20 mm.

2.2. Design of the continuous-flow reaction apparatus and reaction procedures

Fig. 1 shows the continuous-flow reaction system. This reaction system is composed of a reaction chamber (1.82 L), a storing chamber (3.1 L) for the aqueous electrolyte, and a canned pump

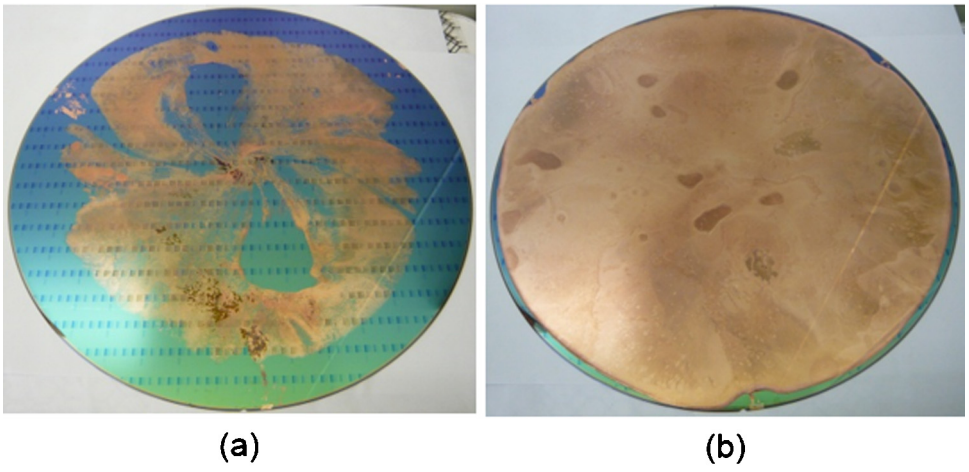

Fig. 3. Photographic images of the 300 mm diameter round-type hole TEG after EP-SCS. The applied currents are (a) 1.41 A/dm^2 and (b) 2.83 A/dm^2.