Proceedings of the World Congress on Recent Advances in Nanotechnology (RAN'16)
Prague, Czech Republic – April 1 – 2, 2016
Paper No. ICNNFC 119
DOI: 10.11159/icnnfc16.119

Enabling High Aspect Ratio Nano-hole Metal Filling by Employing Supercritical Carbon Dioxide Electrochemical Deposition

Wen-Ta Tsai*, Jun-Jie Yang, Chi-Lin Cheng
Department of Materials Science and Engineering
National Cheng Kung University
Tainan, Taiwan
wttsai@mail.ncku.edu.tw

Extended Abstract

In supporting structural integrity of a miniature component, or for providing electric conduction of a through-silicon via (TSV) in three-dimensional integrated circuits (3D-IC), micro- or nano-hole filling with metallic material becomes increasing important in various micro-electrical mechanical systems (MEMSs) [1-4] and in the advanced semiconductor industry [5]. Although there are several methods available for filling micro- or nano-holes with various types of materials, most of them still suffer incomplete filling and void (or defect) formation. When electrodeposition technique is applied, the lack of wettability of the electrolyte inside via or hole and/or the gas bubble formation are always of great concern. To overcome such problems, the use of an electrolyte incorporating emulsified supercritical carbon dioxide (sc-CO_2) fluid has been proposed. In our previous study, the filling of micro-sized holes (about 50 μm diameter and an aspect-ratio of 8) by electrodeposition of Ni and Ni-P employing sc-CO_2 bath could be achieved [6]. The advantages of using supercritical carbon dioxide containing electrolyte are mainly attributed to its unique characteristics, such as liquid-like density, low surface tension, high diffusivity, low viscosity, and high hydrogen gas solubility, etc.

In this study, an anodic aluminum oxide (AAO) template containing numerous high aspect ratio nano-sized holes (an average diameter of 130 nm and an aspect-ratio about 20) was used as the cathode. The hydrophobicity/hydrophilicity of the AAO template was adjusted before Cu electrodeposition. Electrodeposition of Cu was carried out in an emulsified sc-CO_2 bath containing cupric sulfate aqueous solution as the precursor. Cu deposition into the nano-holes was performed at an apparent constant current density of 2 A/dm^2 for 5 minutes. After electrodeposition, the cross section morphology and chemical composition of the AAO cathode was examined by transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) with the aid of a focused-ion-beam (FIB). The experimental results showed that electrodeposition employing sc-CO_2 bath to fill Cu into nano-sized holes was successful and superior to that of conventional process carried out at ambient pressure, in terms of uniformity and deposition rate. The high solubility of hydrogen gas in sc-CO_2 fluid is the key factor. Moreover, the advantage of sc-CO_2 electrodeposition is more pronounced for the AAO cathode exhibiting hydrophobic nature with respect to aqueous bath.

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