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Influence of ultrasonication on the mechanical properties of Cu/Al_2O_3 nanocomposite thin films during electrocodeposition

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ABSTRACT

To overcome the poor mechanical properties of pure Cu thin films, we performed electrocodeposition to make nanocomposite thin films by incorporating inert Al_2O_3 nanoparticles (50 nm and 300 nm in diameter). In addition, to reduce agglomeration due to their high surface energy, we used ultrasonication during the electrocodeposition. In this paper, we examined the effects of the ultrasonication on the mechanical properties of nanocomposite films with different ultrasonic energy density up to 225 W/cm^2. Ultrasonication during electrocodeposition efficiently reduced the agglomeration of nanoparticles and reduced the grain size of the Cu matrix. Smaller nanoparticles were more efficiently de-agglomerated by ultrasonication, which resulted in more enhanced mechanical properties in the 50 nm Al_2O_3 nanoparticle-enhanced specimens. Although the addition of nanoparticles in the Cu matrices significantly increased the hardness of the specimens, as observed in nanoindentation tests, we did not observe such an increase in tensile tests. Reducing the grain size by ultrasonication seems to be an important parameter in enhancing the overall mechanical properties of nanocomposites. Ultrasonication provided a significant increase in all mechanical properties, including elastic modulus, yield stress, ultimate tensile stress, and elongation, of all controlled Cu films.

1. Introduction

Electrodeposition has been used primarily to produce metallic films. These films provide decorative coatings, protective coatings against corrosion, or improved electrical conductivity in printed circuit boards. They can also be used to modify the surface properties of matrix materials [1–4]. Additionally, because of its ability to fabricate high-aspect-ratio structures, electrodeposition has been adopted to construct nanowires using templates [5–10]. Despite such advantages of electrodeposition method, they often have relatively poor mechanical properties in the as-deposited state because the electrodeposited metallic films are mostly pure metal, such as copper and nickel. A popular technique used to enhance the mechanical properties of pure metal films is of fabricating nanocomposites embedding inert nanoparticles during electrodeposition, called *electrocodeposition*. Electrocodeposition has long been used; it was developed in the 1920 s for self-lubricating surfaces in car engines [11]. An *in-situ* process (electrocodeposition) to fabricate nanocomposite thin films is attractive because it is a relatively simple, effective, and inexpensive technique [12].

The agglomeration of nanoparticles is an unresolved issue when using electrocodeposition to improve the mechanical properties of pure metal films. In previous study [1], ultrasonication during electrocodeposition was suggested to significantly reduce the agglomeration of 50 nm Al_2O_3 nanoparticles. In addition, dilution of the electrolyte concentration under ultrasonication at an energy of 120 W/cm^2 significantly affected the de-agglomeration and deposition rate of the nanoparticles. Furthermore, ultrasonication during electrocodeposition improved the brightness and smoothness of the films and significantly reduced the grain size of the matrix Cu control films. Qu *et al.* [13] and Shen *et al.* [14] demonstrated that they obtained well-dispersed nanoparticles with fine microstructures with *indirect* ultrasonication, i.e. ultrasonic energy was supplied to the electrolyte including nanoparticles before the deposition process.

To date, most studies have been focused on how ultrasonication affects the microstructures and distribution of nanoparticles in electrocodeposited nanocomposite thin films, as well as pure Cu films for comparison. Few studies have considered the effects of ultrasonication on the mechanical properties of pure metal or nanocomposite films [15,16]. Thus, in this paper, we examine the effects of ultrasonication during electrocodeposition on the mechanical properties of both pure and nanocomposite films.

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Table 1
Process parameters for electrocodeposition of Cu/Al_2O_3 nanocomposites.

Process Parameters	Values
$CuSO_4 \cdot 5H_2O$	150 *g/l*
H_2SO_4 (98%)	100 *g/l*
Temperature	$\approx 50^0 C$
Current density	$\approx 200\ A/m^2$
Mechanical stirring rate	≈ 300 *rpm*
Ultrasonication	up to 225 W/cm^2
Inert nanoparticles (Al_2O_3)	5 *g /l*
pH	1

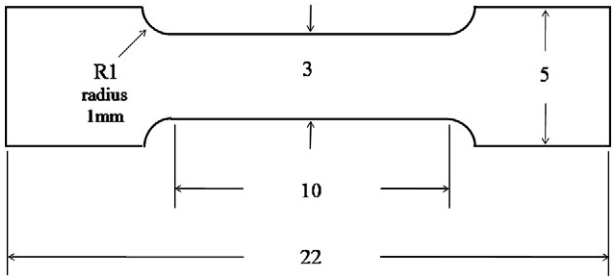

Fig. 1. Schematic diagram of the "dog-bone" shaped tensile test specimens.

2. Experimental procedures

We used the same reagents and process parameters for electrocodeposition of inert particles as earlier works did: *i.e.*, γ-Al_2O_3, $\phi =$ 50 nm; and α-Al_2O_3, $\phi = 300$ nm (Buehler) on a silicon wafer [1,17]. One side of the polished silicon wafer with a surface roughness of less than 3 nm was used as the substrate for the nanocomposite thin films, and was cut into pieces that were 12.5×37.5 mm. Then, 5 nm thick Cr (for adhesion of a conductive Au films) and 50 nm thick Au films (as a conductive layer) were coated using a three-channel thermal evaporation system (Georimtech Co., Ltd., Korea). Since the micromorphologies of electrodeposited thin films are sensitive to the deposition parameters, such as the current density, temperature, and energy of ultrasonication, we used high-resolution potentiostat/galvanostat, a refrigerating/heating circulator, and accurate power controllable ultrasonic processor for precise controlling parameters.

Ultrasonication with various acoustic power density ranges up to 225 W/cm^2 was applied to a salt bath, which was diluted to a concentration of 0.6 M [Cu^{2+}], for the potentiostatic electrocodeposition of both pure Cu and two composite films. The power density was estimated by the total power of the ultrasonic probe normalized by the area of the region of ultrasonic agitation. An experimental set-up for the electrocodeposition cell with an ultrasonic processor (Vibra-Cell™, Sonics & Materials, Inc., USA) was similar to previous study [1]. The thickness of the samples was up to 25 μm. Microstructures of the as-deposited specimens were observed by scanning electron microscopy (SEM; Hitachi 4700, Japan) with energy-dispersive X-ray spectroscopy (EDX). We presumed that there was no significant directionality in the composite films based on earlier work [14]. The electrolyte and the optimized electrochemical conditions are given in Table 1.

The mechanical properties of pure Cu films and 50 and 300 nm Al_2O_3 nanoparticle-reinforced nanocomposite films were investigated by a nanoindentation system (Nanoindenter™, Agilent Tech. USA) and a tensile test system (LRX*Plus*, Lloyd Instruments, England). For

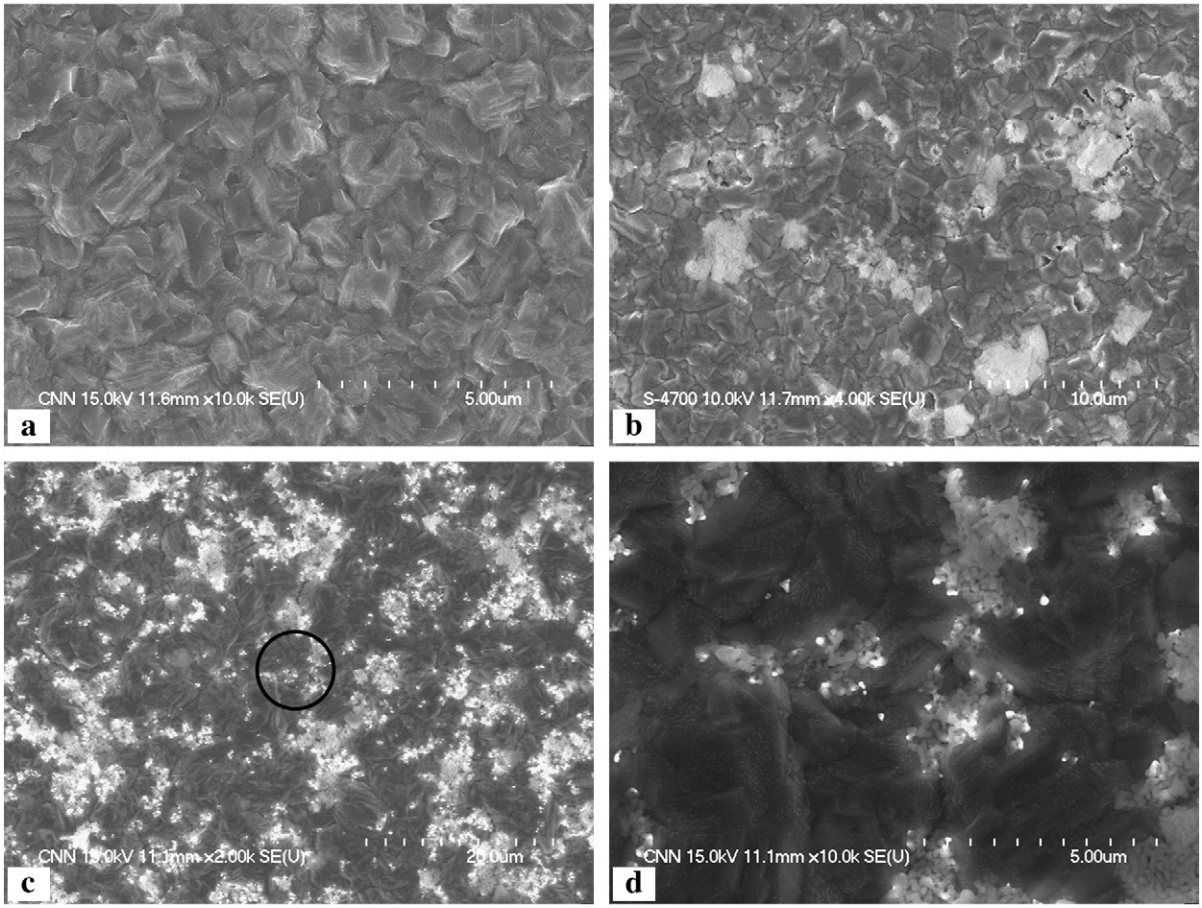

Fig. 2. SEM micrographs of pure Cu and Cu/Al_2O_3 nanocomposite films with no ultrasonication during deposition; (a) pure Cu; (b) Cu/50 nm Al_2O_3; (c) Cu/300 nm Al_2O_3; (d) magnification of an area indicated in (c).