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Influence of ultrasonic irradiation on the microstructure of Cu/Al_2O_3, CeO_2 nanocomposite thin films during electrocodeposition

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Abstract

The agglomeration of nanoparticles during electrocodeposition of nanocomposite thin films is an unresolved issue. In this paper, the effects of ultrasonic irradiation on agglomeration during electrocodeposition of Cu–Al_2O_3 and Cu–CeO_2 nanocomposite thin films on a silicon substrate are investigated. In addition, the effect of electrolyte concentration on agglomeration of nanoparticles is investigated. Irradiation by ultrasound during electrocodeposition yields smaller grain size, improved surface conditions, decreased agglomeration and higher volume fraction of nanosized inert particles within the nanocomposite thin films.

Keywords: Electrocodeposition; Ultrasonic irradiation; Nanocomposite thin film

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1. Introduction

For the last few decades, electroplating has been employed for refining metals, deposition of decorative coatings and protective films for corrosion control, improving electrical conductivity, and modifying surface properties [1]. Recently, this technique has received more interest in part because of the ability to fabricate high aspect ratio and net-shape structures at reduced cost which are suitable for microelectromechanical systems (MEMS) [2,3]. However, because pure metals suitable for electrodeposition, such as copper and nickel, often have relatively poor mechanical properties in the as-deposited condition, a technique known as electrocodeposition has been developed for fabricating durable thin films enhanced with ceramic reinforcements. With this method, nanosized inert particles or whiskers, such as Al_2O_3 [2,4–9], colloidal silica [10], SiC [11], and TiO_2 [12] suspended in electrolyte, are co-deposited along with pure metals (especially, Cu and Ni) or in a polymer matrix [13] to increase the strength of thin films. This in situ process to fabricate nanocomposite thin films is attractive because it is a relatively simple, effective and inexpensive technique [3].

Even though electrocodeposition of nanoparticles in thin metal films has many advantages, agglomeration of nanoparticles remains an unresolved issue. Several strategies have been pursued to try to reduce agglomeration, including varying pH [14], dilution of electrolyte [6], ultrasonic irradiation [6,14], etc. In this paper, we focused on the use of ultrasonic irradiation during electrocodeposition with the goal of reducing agglomeration. It is assumed that the extremely high variation in pressure and the cavitation associated with ultrasonic irradiation may help to disperse the agglomerated nanoparticles in the electrolyte and also on the surface of the deposited film [15]. Previous studies show that applying ultrasonic energy to electrodeposition of pure metals and alloys has many advantages: higher current efficiencies [15], harder, more compact, and better adherent deposits [16–18] which corresponds to improved wear resistance, as well as improved smoothness and brightness [17,19]. Few studies, however, have been performed employing ultrasonic irradiation during electrocodeposition to fabricate composite thin films. Moreover, relatively fewer studies have been achieved applying ultrasonic energy to fabricate composite thin films with nanosized ceramic particles on silicon wafers for applications

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in MEMS devices. The work that has been performed has found that ultrasound irradiation both before and during electrodeposition produces more uniform dispersion and less agglomeration of inert particles or whiskers [6,7,10] than composite thin films electrodeposited without ultrasonic irradiation.

In this study, we focus on how ultrasonic irradiation affects the microstructures and distribution of nanoparticles of electrocodeposited Cu/Al_2O_3, and Cu/CeO_2 nanocomposite thin films on a silicon substrate as well as pure Cu film for comparison. Additionally, dilution of electrolyte concentration was attempted to reduce agglomeration of nanoparticles under a certain power density of ultrasonic irradiation.

2. Experimental procedures

The copper metal matrix nanocomposite thin films employed in this study were deposited on a silicon wafer via electrocodeposition using a set of deposition parameters developed in a previous study [4]. A 76 mm diameter (1 0 0) silicon wafer with 300 μm thickness was used as a substrate for the nanocomposite thin films. It had a surface roughness of less than 3 nm and was cleaved to a size of 12.5 mm × 37.5 mm. A 5 nm Cr (for adhesion of conductive Au film) film followed by a 50 nm thick Au film (as a conductive layer) were deposited by thermal evaporation (Auto 306, BOC Edwards Inc.). The nanocomposite thin film was then deposited on the conductive Au layer with electrocodeposition. Since the micromorphologies of the thin films by electrodeposition are very sensitive to the deposition parameters such as current density, temperatures, energy of ultrasonic irradiation, etc., all parameters were carefully controlled. An electrolyte mixture of copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) with A.C.S. standard purity and sulfuric acid with Certified A.C.S. Plus grade were employed. Inert particles employed in this study are Al_2O_3 (γ-phase, Buehler) and CeO_2 (*n*Gimat Co.) with an average diameter of approximately 50 and 20 nm, respectively. The anode was a pure copper plate (99.999%) with a width of 12 mm and the silicon wafer with chromium and gold coatings was taken as the cathode. The configuration of the cathode and anode was such that they were facing each other in a parallel manner at a distance of 20 mm. At the bottom of the cylindrical beaker, an electromagnetic stirring rod encapsulated in Teflon coating was rotating at the rate of 500 rpm so that dynamic agitation of the solution was obtained to keep the inert nanoparticles suspended in the solution during electrocodeposition process. The plating parameters such as temperature, voltage and current density were tested through a series experiments and subsequently optimized by factorial analysis. The electrolyte and the optimized electrochemical conditions are given in Table 1. It should be noted that the deposition experiments were performed at a prescribed current, so that the applied electrical potential depended upon the dilution of the electrolyte. However, typically the applied potential was about 2 V.

Ultrasonic irradiations with various acoustic power densities ranging from 70 to 120 W/cm^2 were applied to the salt bath for electrodeposition of the nanocomposite films and also the Cu control film. A schematic diagram in Fig. 1 shows the electrodeposition cell with ultrasonic processor (model UP50H, Hielscher Inc.) equipped with a 3 mm diameter titanium alloy tip. The tip of ultrasonic probe and the anode and cathode form an equilateral triangle with sides of 20 mm, when viewed from the top of the beaker containing the salt bath. The bottom tip of ultrasonic probe displaces in the vertical direction, so the resulting waves propagate down in the shape of an expanding cone. Additionally, the salt bath was diluted (with concentration of [Cu^{2+}] from 1 to 0.45 M), and codeposition of Al_2O_3 nanoparticles was performed under various acoustic power densities up to 120 W/cm^2. The power density was estimated by the total power from the ultrasonic probe normalized by the area of the region of ultrasonic agitation. The film thickness of all samples was in the range of 3–5 μm. The microstructure of the as-deposited specimens was observed by scanning electron microscope (SEM, Hitachi 4700) with energy dispersive X-ray spectroscopy (EDX). All pictures of microstructures are taken in as-deposited condition. The volume fraction of nanoparticles in the thin films is measured by a standard metallographic method [20]. Electron backscatter diffraction (EBSD, HKL channel 5 system on an SEM, JEOL 5600) was used to analyze crystal orientation of the thin films. The crystallographic texture was studied only for Cu/CeO_2 composite film because texture analysis of Cu/Al_2O_3 composite films was presented in an earlier work [4].

Table 1
Process parameters for electrocodeposition of Cu/Al_2O_3 and Cu/CeO_2 nanocomposite

Process parameters	Values
$CuSO_4 \cdot 5H_2O$	112, 150, 250 g/l
H_2SO_4 (98%)	100 g/l
Temperature	≈50 °C
Current density	≈200 A/m^2
Mechanical stirring rate	≈500 rpm
Ultrasonic irradiation	70–120 W/cm^2
Inert particles (Al_2O_3, CeO_2)	20 g/l
pH	∼1 (Cu/Al_2O_3), 3.5–4 (Cu/CeO_2)

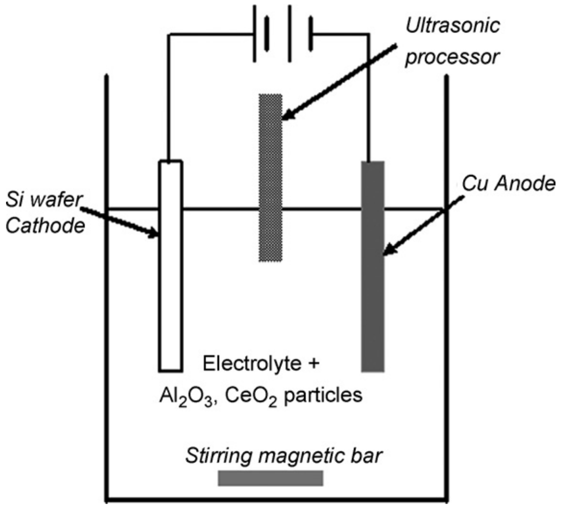

Fig. 1. A schematic diagram of experimental arrangements with ultrasonic processor.

3. Results and discussion

3.1. Pure Cu film

Fig. 2a and b represent the microstructure of a pure Cu control thin film without and with (120 W/cm^2) ultrasonic irradiation during electrodeposition, respectively. As can be seen in Fig. 2b, smaller grain size is achieved when ultrasonic energy is applied during electroplating. Average grain size of the pure Cu film with no irradiation of ultrasound is about 2.1 μm while much smaller and uniform sized grains about 0.9 μm are obtained with ultrasonic agitation. It was also observed that the brightness and smoothness of the film improved after applying ultrasonic irradiation which is in agreement with the results from other studies [17,19]. Ultrasonic irradiation induces the formation and sudden collapse of bubbles in the electrolyte near the solid surface. Kristof and Pritzker [17] postulated that as bubble collapse occurs near the solid surface, a drag force created on the portion of the void nearest the surface will cause the bubble to move toward the surface. This asymmetric force results in an effective microjet oriented toward the surface which produces intense mixing at the cathode surface and significantly improves mass transfer. In addition, ultrasonic irradiation decreases the electrical double layer near the cathode surface [17,21–23], which also helps to enhance the mass transfer. Moreover, the ultrasonic irradiation may inhibit out-of-plane growth of the films thus promoting lateral growth rather than three-dimensional growth which may explain the improved brightness and smoothness [19].

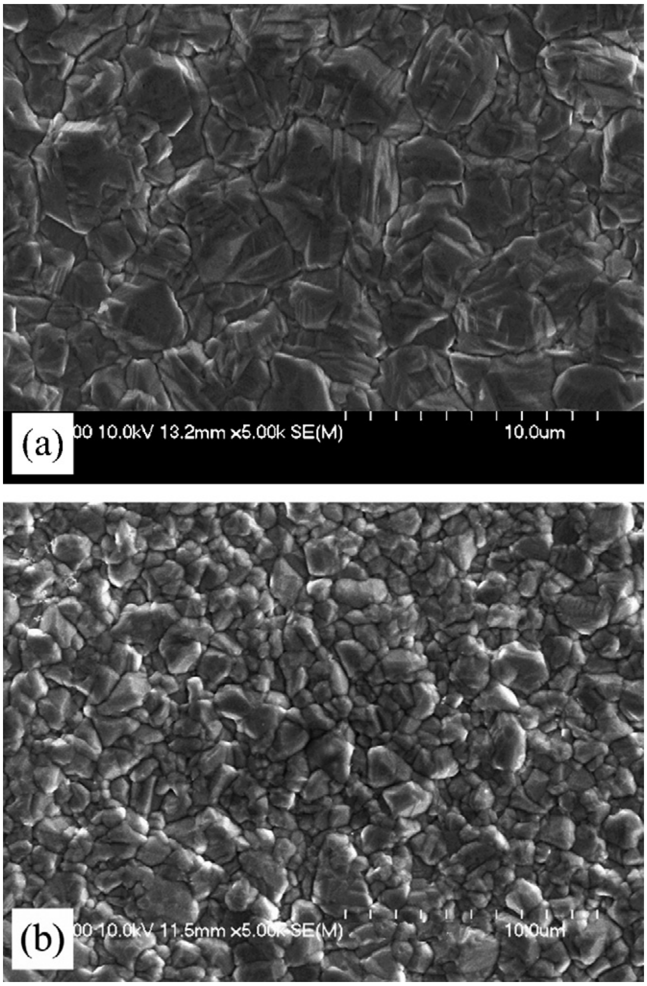

Fig. 2. SEM micrographs of pure Cu thin films by electrodeposition: (a) pure Cu film and (b) pure Cu film in ultrasonic irradiation (120 W/cm^2).

3.2. Cu + Al_2O_3 nanocomposite films

As two charged particles in solution approach one another, forces of various origins between the particles determine whether two particles are separated or agglomerated. According to the Delaguin–Landau–Verwey–Overbeek (DLVO) theory, repulsion between two particles is directly related to the electrochemical double layer charge on the particles [22]. Therefore, agglomeration may be controlled by changing the double layer. One of the ways to control the double layer is to change the ion concentration by dilution of electrolyte. For example, if ion concentration decreases by diluting electrolyte, the electrochemical double layer expands and van der Waals attractions decrease [14]. Kuo et al. [6] reduced particles agglomeration by diluting electrolyte concentration in this way. They reported that the method reduced agglomeration of nanosized particle in nickel matrix. Another way to reduce agglomeration of nanoparticles is to apply ultrasonic irradiation to the electrolyte containing nanoparticles before and/or during electrocodeposition. When ultrasonic waves propagate in the electrolyte, the pressure waves that will be high enough to overcome the forces will lead to less agglomeration. Saterlay et al. [23] reported that ultrasonic energy enhances mass transport and contributes to the uniform dispersions of inert particles (PbO_2) on cathodic electrode (highly boron-doped diamond, BDD). Kuo et al. [6] also reported that agglomeration of nanosized particles in nickel matrix was reduced by applying ultrasonic irradiation to the electrolyte before deposition.

We employed both methods, diluting electrolyte concentration and ultrasonic irradiation, on Cu/Al_2O_3 thin films deposition. Fig. 3 shows SEM micrographs of electrocodeposited Cu/Al_2O_3 nanocomposite thin films with various concentration of electrolyte, from 1 down to 0.45 M. In 1 M solution, agglomeration of nanoparticles is apparent; some of agglomerations are larger than 1 μm (see Fig. 3b). With decreasing concentration of Cu^{2+} in electrolyte, less agglomeration of the nanoparticles is observed, as shown in Fig. 3c–f. In the bath concentration of 0.45 M Cu ions, nanoparticles are much better dispersed [6], which is predicted by DLVO theory [22]. The effects of ultrasonic irradiation on de-agglomeration of the nanoparticles on the nanocomposite thin films were also investigated, which is shown in Fig. 4, for which an ultrasonic density of 120 W/cm^2 was employed. As can be seen in Fig. 4a and b, ultrasonic irradiation does not effectively disperse nanoparticles on the surface when the film is deposited in 1 M solution. However, the nanoparticles are more efficiently dispersed on the surface of the films when the films are deposited in increasingly diluted solutions (see Fig. 4c–f). To summarize, Fig. 5 shows the relationship between the cluster size of nanoparti-

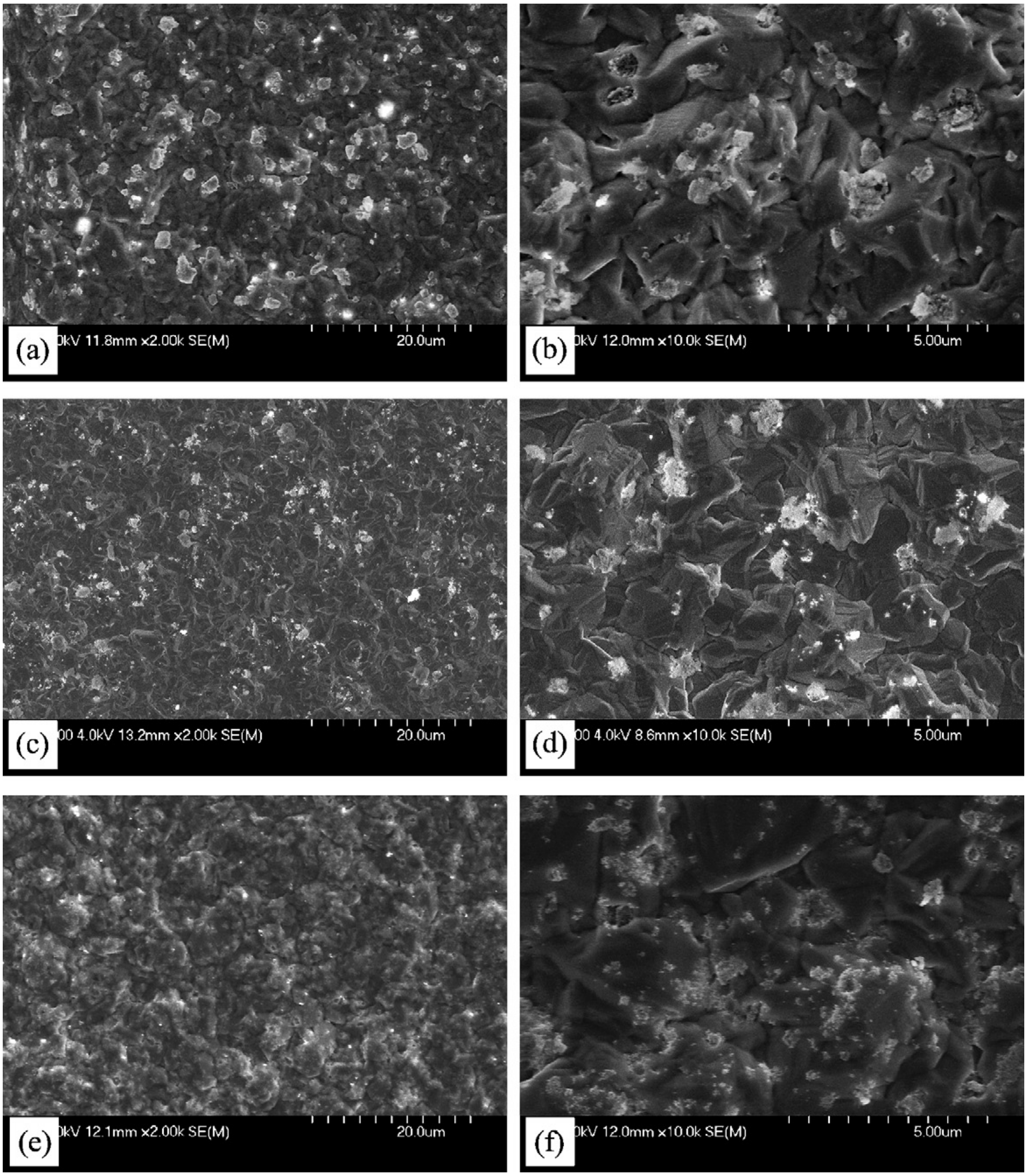

Fig. 3. SEM micrographs of Cu/Al_2O_3 thin films by electrocodeposition with various concentration of electrolyte. No ultrasonic irradiation was applied. (a and b) 1 M; (c and d) 0.6 M; (e and f) 0.45 M.

cles on the films with concentration of electrolyte and ultrasonic energy. Because a cluster size of nanoparticles on the specimen fabricated at 0.6 and 0.45 M with ultrasonic irradiation, 120 W/cm^2 (see Fig. 4d and f), was too small to measure, the average particles size provided by manufacturer was used.

Fig. 6 shows the effects of ultrasonic irradiation of varying power densities on the microstructure of thin composite films with respect to the dispersion of Al_2O_3 particles while maintaining a constant 0.6 M concentration. The results of ultrasonic irradiation apparently demonstrate breaking up of agglomerated particles. As can be seen in Fig. 6b–d, dispersion of nanosized particles depends upon ultrasonic agitation energy. The higher the power density of ultrasound, the better dispersion and the larger the volume fraction of particles are embedded in the films. The volume fraction of nanoparticles on the matrix with ultrasonic energy was roughly measured by a standard metallographic technique [20], which is summarized in Table 2. Interestingly, in the composite film electrocodeposited with a power density of 70 W/cm^2, fewer particles are incorporated into the films than thin films fabricated with no ultrasonic irradiation, even though ultrasonic energy promotes de-agglomeration. Qu et al. [7] reported less agglomeration of Al_2O_3 nanowhiskers with increasing ultrasonic frequency, but fewer nanowhiskers co-deposited in coatings. They assumed that higher ultrasonic frequency may cause collisions between nanowhiskers in the electrolyte or escapement of absorbed nanowhiskers form the

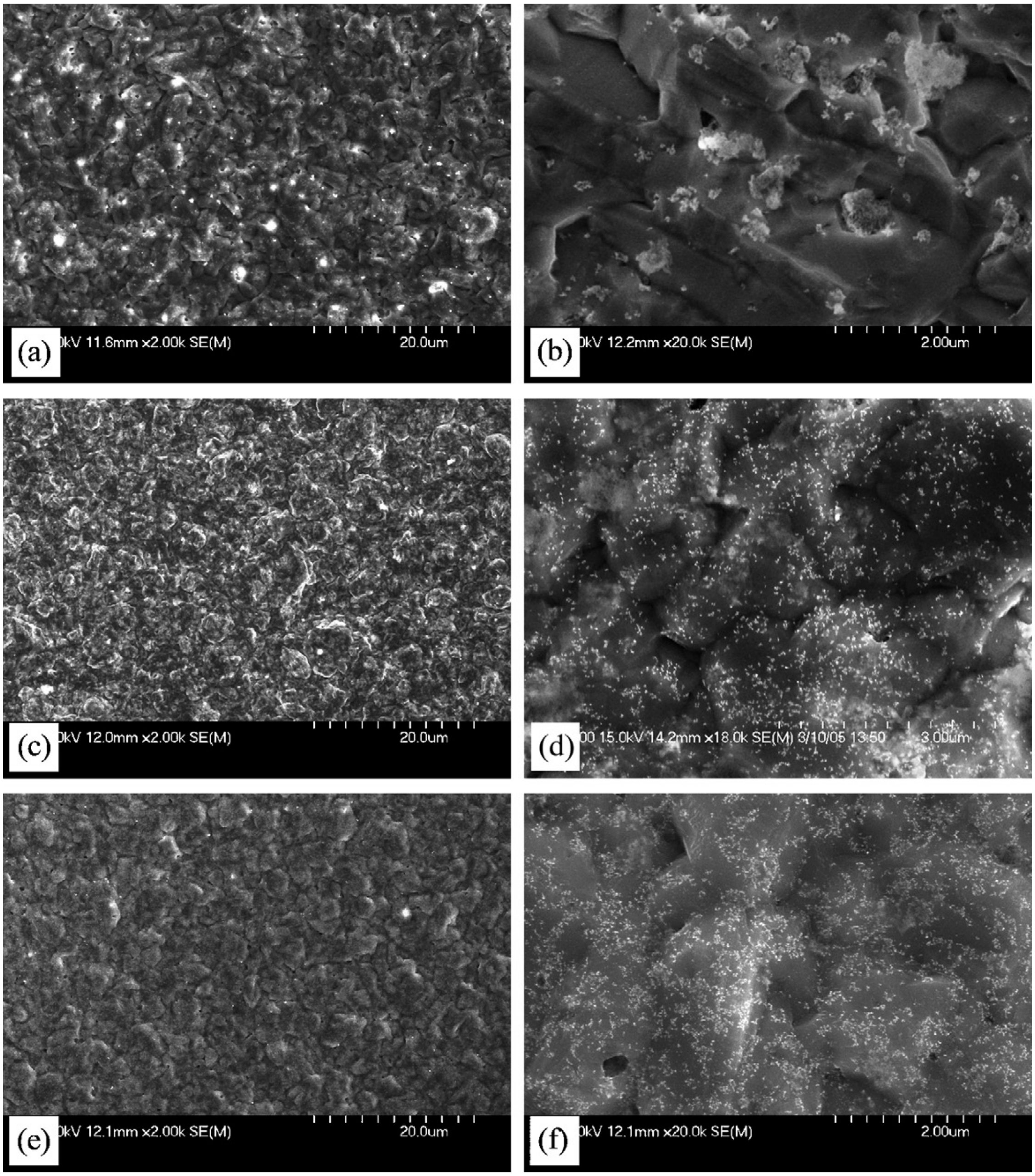

Fig. 4. SEM micrographs of Cu/Al_2O_3 thin films by electrocodeposition with various concentration of electrolyte under ultrasonic irradiation, 120 W/cm^2. (a and b) 1 M; (c and d) 0.6 M; (e and f) 0.45 M.

films. This may occur in our case under certain ultrasonic irradiation intensities. Fig. 7a shows the SEM micrograph of Fig. 6d at higher magnification; an EDX result on the white particles clearly shows an Al peak confirming Al_2O_3 particles in Fig. 7b.

Table 2
Volume fraction of nanoparticles on the Cu matrix with ultrasonic energy

Ultrasonic energy density (W/cm^2)	Volume fraction of nanoparticles (vol.%)
0	2.4
70	1.5
100	4.1
120	6.2

Consequently, ultrasonic irradiation and dilution of electrolyte do help de-agglomeration and incorporation of nanoparticles in Cu/Al_2O_3 nanocomposite thin films.

3.3. Cu + CeO_2 nanocomposite films

Fig. 8 presents microstructures and CeO_2 nanoparticle distributions in Cu/CeO_2 nanocomposite films by electrocodeposition. In earlier work [4], it was revealed that there is no crystallographic texture of pure Cu and Cu/Al_2O_3 film investigated by EBSD. The same results are obtained in Cu/CeO_2 composite film (see Fig. 9). As can be seen in Fig. 8, the degree of agglomeration of CeO_2 nanoparticles is higher than Al_2O_3

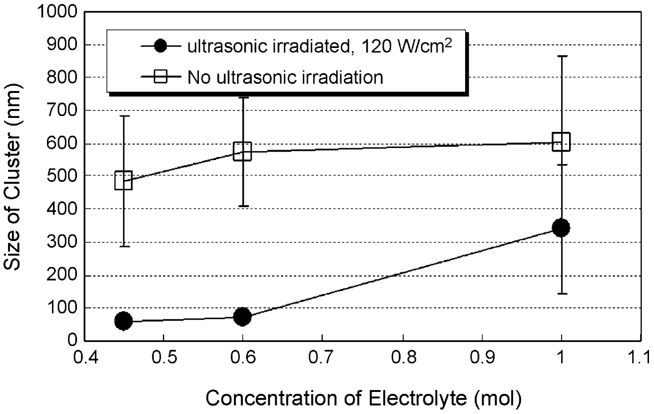

Fig. 5. A plot of the relationship between the cluster size of nanoparticles on the films with concentration of electrolyte and ultrasonic energy.

particles compared with Fig. 6. It is interesting that the volume fraction of CeO_2 particles in Cu matrix with no ultrasonic irradiation and also with 70 W/cm^2 energy density of ultrasound is much less than with the same deposition conditions of Al_2O_3 particles in Cu film (1.17 vol.% with no ultrasonic irradiation, 2.1 vol.% at 100 W/cm^2). However, upon increasing ultrasonic power to 120 W/cm^2, a higher volume fraction of CeO_2 nanoparticles in Cu film is observed (about 20.5 vol.%). This suggests that ultrasonic irradiation during electrocodeposition promotes mass transfer; however, ultrasonic irradiation did not help de-agglomeration of CeO_2 nanoparticles. It is possible that reactivity of CeO_2 with the sulfate bath may contribute to agglomeration of nanoparticles, and the energy of ultrasonic irradiation that was applied in this study is not sufficient to break the agglomeration.

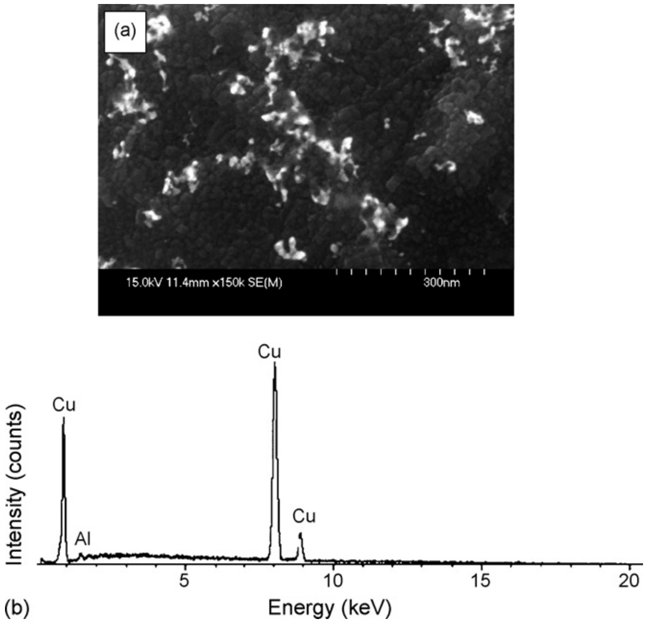

Fig. 7. SEM micrographs: (a) an enlarged micrograph of Fig. 5d, and EDX result on particles and (b) on Cu/Al_2O_3 thin films by electrocodeposition in 0.6 M concentration of electrolyte under ultrasonic irradiation, 120 W/cm^2.

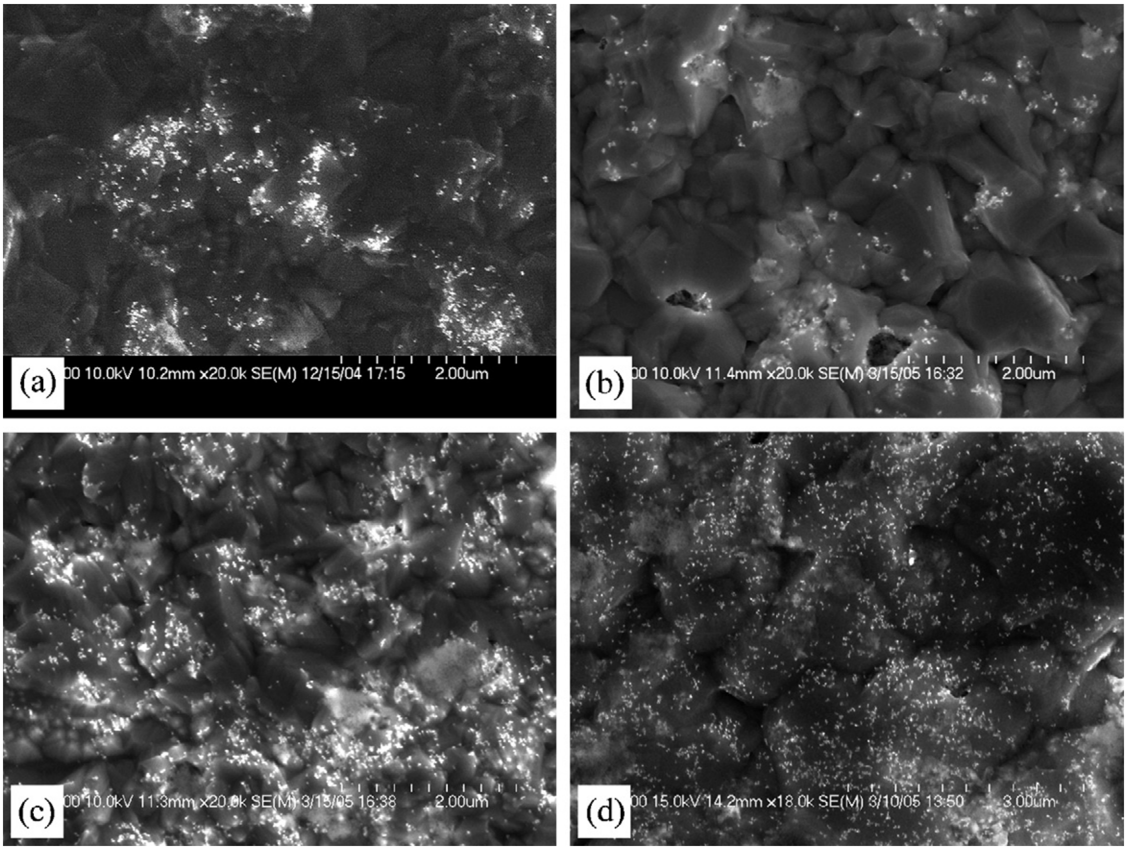

Fig. 6. SEM micrographs of Cu/Al_2O_3 thin films by electrocodeposition in 0.6 M concentration of electrolyte with and without ultrasonic irradiation: (a) no ultrasonic irradiation, (b) 70 W/cm^2, (c) 100 W/cm^2 and (d) 120 W/cm^2.

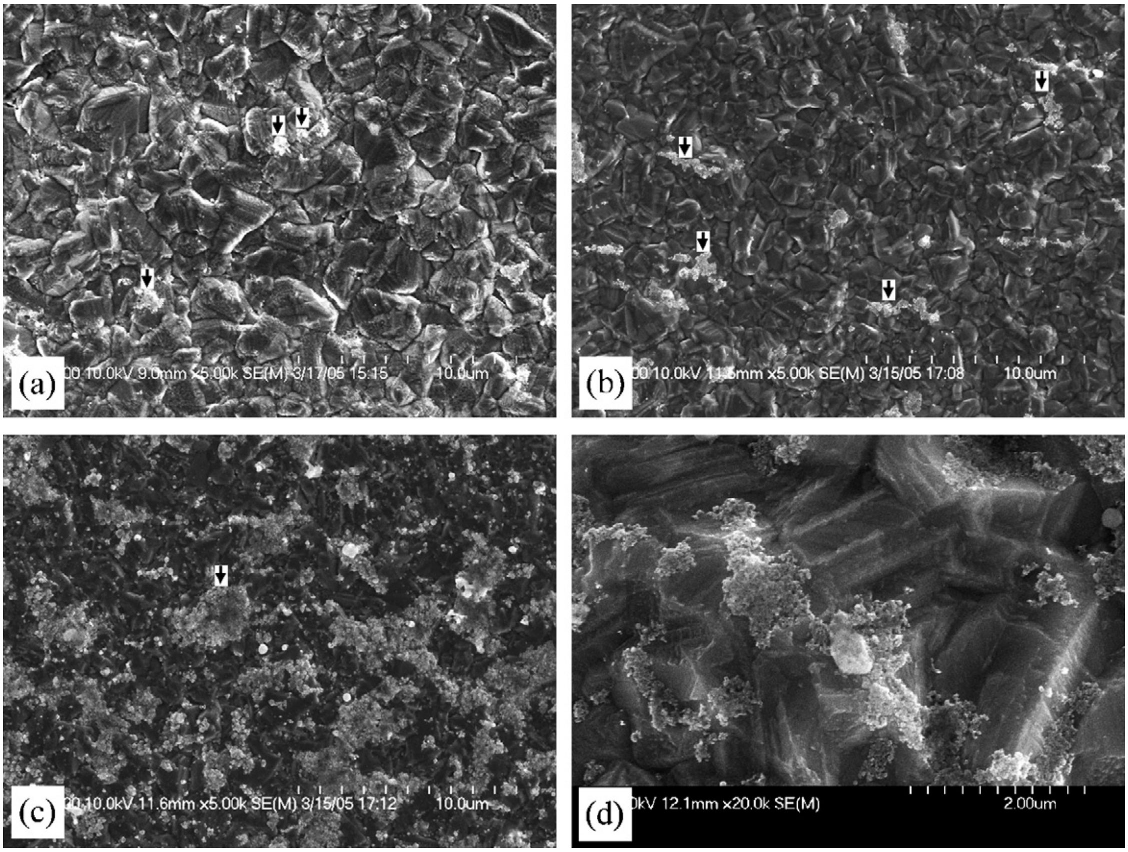

Fig. 8. SEM micrographs of Cu/CeO_2 thin films by electrocodeposition (0.6 M) with and without ultrasonic irradiation: (a) no ultrasonic irradiation, (b) 100 W/cm^2, (c) 120 W/cm^2 and (d) an enlarged micrograph of (c). Arrows indicate agglomerated CeO_2 particles.

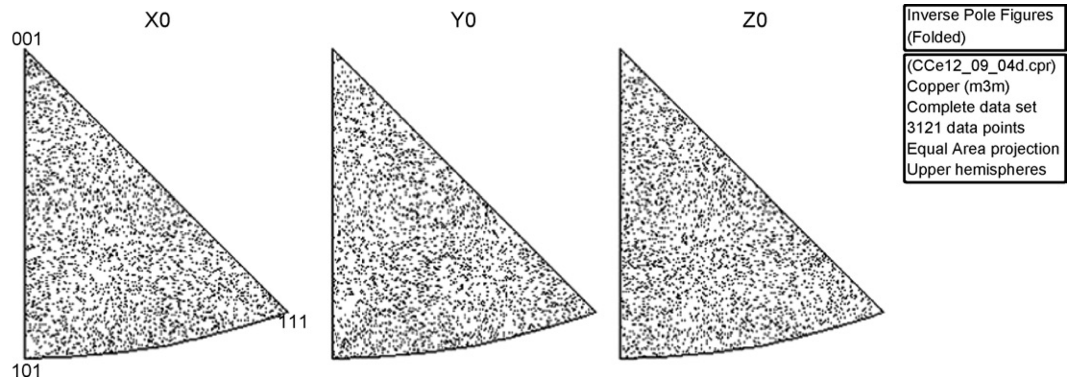

Fig. 9. Inverse pole figures of Cu/CeO_2 thin films with ultrasonic irradiation. No preferred orientation was observed on the thin films by ultrasonic irradiation.

4. Conclusions

The effects of ultrasonic irradiation of various energy densities on the microstructures of pure Cu thin films, Cu/Al_2O_3 and Cu/CeO_2 nanocomposite thin films by electrocodeposition have been investigated. Ultrasonic irradiation during electrocodeposition improved the brightness and smoothness of the films and significantly reduced grain size of the nanocomposite and Cu control films. Al_2O_3 nanoparticles are well dispersed in the Cu film by applying ultrasonic irradiation with density of 120 W/cm^2, but CeO_2 nanoparticles show a strong agglomeration tendency even under ultrasonic irradiation. Dilution of electrolyte concentration under ultrasonic irradiation with density of 120 W/cm^2 significantly affects de-agglomeration and deposition rate of nanoparticles. Future research will focus on how varying nanoparticle volume fractions in the nanocomposite thin films affects the mechanical properties of the films.

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References

[1] F.A. Lowenheim, Electroplating, Part 1, McGraw-Hill, Inc., 1978.
[2] S.H. Goods, T.E. Buchheit, R.P. Janek, J.R. Michael, P.G. Kotula, Metall. Mater. Trans. A 35 (2004) 2351–2360.
[3] M. Schlesinger, M. Paunovic, Modern Electroplating, John Wiley & Sons, Inc., 2000 (Chapter 1).
[4] Y. Gan, D. Lee, X. Chen, J.W. Kysar, J. Eng. Mater. Technol. 127 (4) (2005) 451–456.
[5] J.L. Stojak, J.B. Talbot, J. Electrochem. Soc. 146 (12) (1999) 4504–4513.
[6] S.L. Kuo, Y.C. Chen, M.D. Ger, W.H. Hwu, Mater. Chem. Phys. 86 (2004) 5–10.
[7] N.S. Qu, K.C. Chan, D. Zhu, Scripta Mater. 50 (2004) 1131–1134.
[8] H. Ferkel, B. Muller, W. Riehemann, Mater. Sci. Eng. A234–236 (1997) 474–476.
[9] J.M. Molina, R.A. Saravana, J. Narciso, E. Louis, Mater. Sci. Eng. A383 (2004) 299–306.
[10] P.B.S.N.V. Prasad, R. Vasudevan, S.K. Seshadri, Indian J. Eng. Mater. Sci. 1 (1994) 158–160.
[11] F. Hu, K.C. Chan, Appl. Surf. Sci. 233 (2004) 163–171.
[12] G. Barkleit, A. Grahl, M. Maccagni, M. Olper, P. Scharf, R. Wagner, J. Power Sources 78 (1999) 73–78.
[13] P. Bon, I. Zhitomirsky, J.D. Embury, Mater. Chem. Phys. 86 (2004) 44–50.
[14] G. Vidrich, J.F. Castagnet, H. Ferkel, J. Electrochem. Soc. 152 (5) (2005) C294–C297.
[15] O.V. Abramov, Ultrasound in Liquid and Solid Metals, CRC Press, 1994, p. 354 and 398.
[16] L. Martins, J.I. Martins, A.S. Romeira, M.E. Costa, J. Costa, M. Bazzaoui, Mater. Sci. Forum 455–456 (2004) 844–848.
[17] P. Kristof, M. Pritzker, Plat. Surf. Finish. 85 (11) (1998) 237–240.
[18] P.B.S.N.V. Prasad, R. Vasudevan, S.K. Seshadri, S. Ahila, Bull. Electrochem. 9 (1993) 468–469.
[19] R. Walker, C.T. Walker, Ultrasonics (March) (1975) 79–82.
[20] Metals Handbook, Desk Edition second, J.R. Davis and Davis & Associate, ASM international, 1998, p. 1405.
[21] J.P. Lorimer, B. Pollet, S.S. Phull, T.J. Mason, D.J. Walton, U. Geissler, Electrochem. Acta 41 (17) (1996) 2737–2741.
[22] I. Zhitomirsky, Adv. Colloid Interface 97 (2002) 279–317.
[23] A.J. Saterlay, S.J. Wilkins, K.B. Holt, J.S. Foord, R.G. Compton, F. Marken, J. Electrochem. Soc. 148 (2) (2001) E66–E72.