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STUDY ON SELF-FORMED REGULAR COPPER AND ALUMINUM PARTICLES ON THE SURFACE OF ANNEALED Cu (Al)-Zr ALLOYED FILMS

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Abstract. In this paper, regular Copper (Cu) and Aluminum (Al) particles and rods in submicron and nano-scale were prepared by annealing Cu-Zr, Cu-Al-Zr or Al-Zr alloyed thin films on polyimide substrates. XRD, FESEM, AFM, and EDS were used to characterize their microstructures and composition. Results show that faceted Cu particles are very regular and pure Cu element. Furthermore, it was interesting to find that Cu rods might appear on the surface of the annealed Cu-Al-Zr composite thin films. Compared with Cu particles, faceted Al particles are slightly irregular. According to the experimental result and analysis, it were speculated that these Cu and Al particles are single crystals. The particle sizes are closely related to the content of Zr as well as annealing temperature. Mechanism was put forward to elucidate the formation of Cu and Al particles according to the morphological characterization and residual stress analysis. This work may provide a new approach to prepare metal particles and rods on the surface of films bonded on polyimide substrates.

1. INTRODUCTION

Recently, zero and one dimensional submicron-scale metal particles and nanowires have been the subject of intense research due to their significantly unique properties and potential applications in the fields of electronics, optics, and biochemical sensing, and so on [1-5]. Of all metal particles, Cu particles and its two stable semiconductor oxides (CuO and Cu_2O) have attracted a great attention on research and technological applications. CuO can be used as high-temperature superconductors, lithium-copper oxide electrochemical cell materials and giant magneto resistance materials [6]. Cu_2O plays an important role in solar energy conversion, electronics, magnetic storage and catalysis [7]. Al and its oxides particles present some unique properties and have been used as electronic materials and lubricants as well additives [8-10]. In a previous work [11], we fabricated micron-scale regular Cu particles with different shapes by annealing Cu-7.29at.%Zr composite thin films on polyimide substrates, and a corresponding mechanism was put forward taking into accounts the distinct residual stress, atomic diffusivity and deformability of polyimide substrates.

In this work, we tried to adjust the particle sizes by changing the Zr content in the composite Cu-Zr thin films, the film thicknesses and the annealing temperatures. Additionally, the Cu-Al-Zr and Al-Zr composite thin films were prepared for comparison. X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), and Energy Dispersive Spectroscopy (EDS) were used to

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characterize the microstructures and surface morphology of these samples. Based on the detailed characterization, the formation mechanism of Cu/Al particles and Cu nanorods as well as the dominant factors of this process were further discussed.

2. EXPERIMENTAL MATERIAL AND METHOD

Cu-Zr, Cu-Al-Zr, and Al-Zr composite thin films were prepared on polyimide (PI) substrates by co-sputtering deposition using Cu and Al targets (99.99%, purity) overlaid with Zr and Al plates (99.9%, purity), respectively, in a vacuum chamber with base pressure of 2×10^{-4} Pa. The substrates, ultrasonically cleaned with absolute ethyl alcohol, were placed on a substrate holder located 70 mm above the target. Prior to deposition, the substrates were cleaned for 15 minutes using Ar ion bombardment. The composite thin films were deposited at a dc power of 200 W and a working gas (Ar) pressure of 0.3 Pa. The deposition rate was approximately 0.6 nm/s. For one set of specimens, in-situ anneal (vacuum $<2\times10^{-4}$Pa) was carried out at 180 and 330 °C for an hour to induce the nucleation and growth of Cu and Al particles on the surface of films.

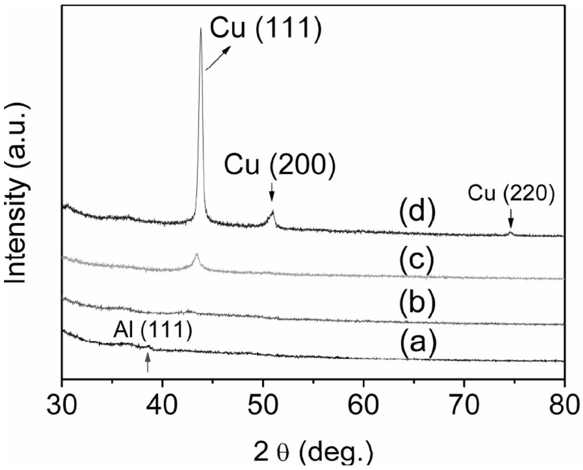

Fig. 1. XRD patterns of the annealed composite films at different temperatures. (a) Al-8.1%Zr/PI at 400 °C, (b) Cu-13.9%Al-7.3%Zr/PI at 420 °C, (c) and (d) Cu-17.1Zr% anneal at 180 and 330 °C, respectively.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the annealed Cu-17.1Zr%, Cu-13.98%Al-7.34%Zr/PI, and Al-8.03%Zr/PI composite thin films at different temperatures. As shown in Fig.1, only a weak diffraction peak can be observed at about 38° and 43° in the XRD patterns of the annealed Cu-13.98%Al-7.34%Zr/PI at 420 °C,

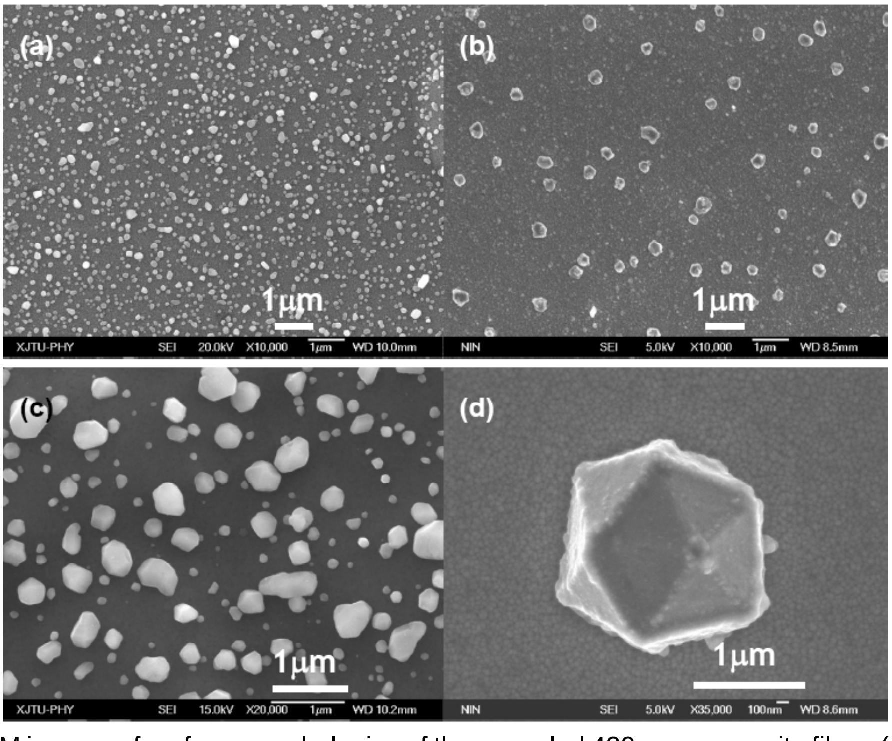

Fig. 2. FESEM images of surface morphologies of the annealed 420 nm composite films. (a) The surface morphology of Cu-12.28% Zr composite films on PI substrates annealed at 300 °C. (b) The surface morphology of Cu-7.29% Zr composite films onPI substrates annealed at 200 °C. (c) The surface morphology of the Cu-17.1% Zr composite films on PI substrates annealed at 300 °C. (d) the typical morphology of the regular particles.

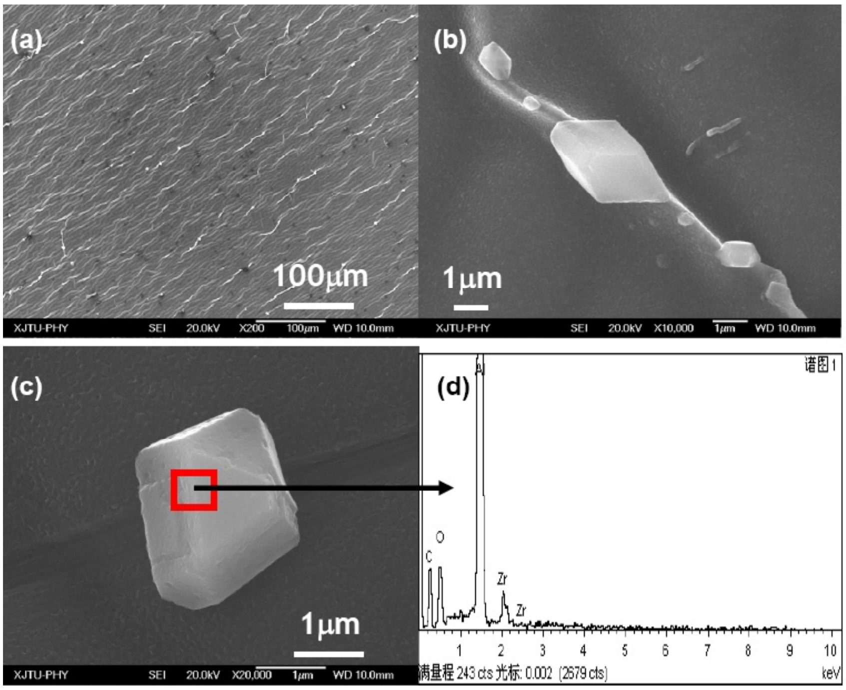

Fig. 3. (a) FESEM images of surface morphologies of annealed 240 nm Al-8.1%Zr composite films anneal at 400 °C, (b) and (c) are the high magnification of some Al particles, (d) EDS patterns of Al particle.

and Al-8.03%Zr/PI at 400 °C, respectively. However, different from the Al-Zr-Cu or Al-Zr thin films, Cu-Zr composite thin films predominately consist of pure Cu phase without any detectable Zr or other phases after annealed at 180 °C, and (111) orientation is preferred, as indicated in the XRD patterns. When the annealing temperature is raised up to 330 °C, two weaker peaks, (200) and (220) appear in the XRD patterns, although (111) texture is still the strongest.

Fig. 2 shows typical FESEM images of the surface morphology of the annealed Cu-Zr composite films and precipitated Cu particles. The particles prepared by this method have feature sizes ranging from several tens of nanometers to several microns, as shown in Figs. 2a, 2b, 2c, and 2d. The average sizes of Cu particles in Figs. 2a, 2b, and 2c are 95, 308, and 205 nm, respectively. Based on the above-mentioned results, it is demonstrated that the sizes of faceted Cu particles can be adjusted by modifying the Zr content, film thickness and annealing temperature. For the composite thin films with the same Zr content and film thickness, the average size of particles increases monotonously with the increasing annealing temperature. This can be explained taking into account the fact that the higher annealing temperature is easier to activate atomic diffusion, and the larger particles appear. On the other hand, the average size of particles decreases monotonously with increasing the Zr content of the composite films. This can be attributed to the fact that larger Zr contents are able to suppress Cu atoms diffusion along grain boundary and surface, and thus lead to smaller Cu particles.

Different from the hillocks commonly observed in other studies [12,13], these Cu particles are very regular, and most of them are polyhedron with clear edges and corners. Among of them, the deformed icosahedron can be observed in Fig. 2d, respectively. EDS data indicates that the compositions of these particles are pure Cu element, as reported in the previous study [11].

Fig. 3 shows typical FESEM images of the surface morphology of the annealed Al-Zr composite thin films and precipitated Al particles. There are many corrugations on the surface of annealed Al-8.03%Zr/PI thin films and some micron-scale faceted particles can be observed at the top of corrugations, as shown in Figs. 3b and 3c. EDS data in Fig. 3d indicates that the compositions of these particles are pure Al element excluding the effect of PI substrate. Obviously, compared with Cu particles, faceted Al particles are slightly irregular.

According to the XRD patterns and morphology of particles as shown in Figs.1, 2, and 3, it were speculated that these Cu and Al particles are single crystals.

From Figs. 2 and 3, it can be seen that many particles and corrugations were observed on the surface of annealed Cu-Zr and Al-Zr composite films,

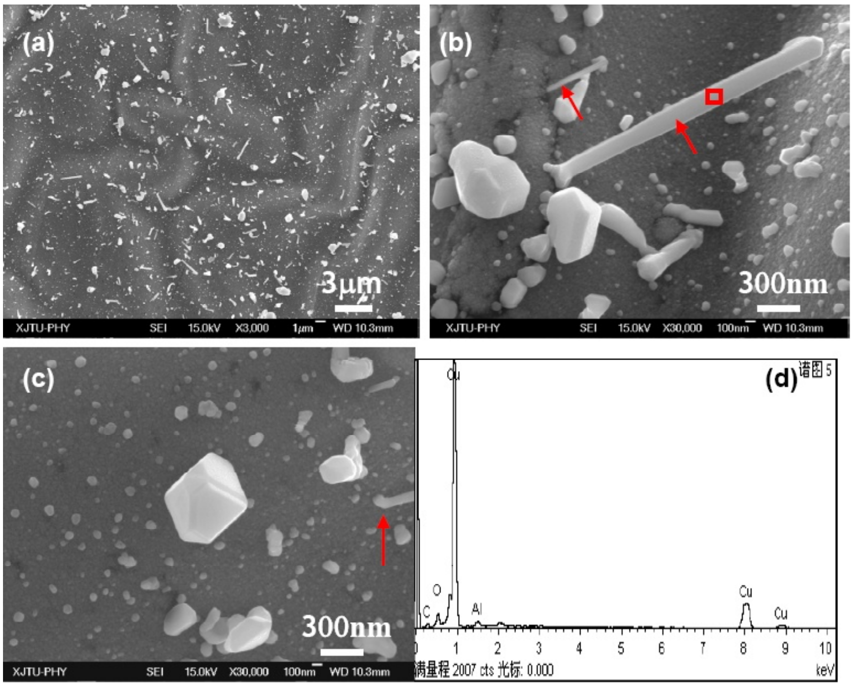

Fig. 4. (a) FESEM images of surface morphologies of annealed 230 nm Cu-13.9%Al-8.1%Zr/PI films anneal at 420 °C, (b) and (c) are the high magnification of some Cu nanorods and particles, respectively, (d) EDS patterns of Cu nanorods.

respectively. In the next part, alloyed (Cu-Al-Zr) thin films will be annealed and investigated.

Fig. 4 shows FESEM images of surface morphology of the annealed Cu-13.9%Al -7.3%Zr composite films. From Fig. 4a, it can be seen that there are many particles and nanorods on the undulate surface of annealed Cu-Al-Zr composite films. EDS data in Fig. 4d indicates that the compositions of these particles and nanorods are pure Cu element excluding the effect of PI substrate, which is consistent with the composition of Cu particles on the surface of Cu–Zr composite.

To clearly identify the microstructures of these faceted Cu particles and nanorods, Figs. 4b and 4c show the high magnification of some typical Cu particles and nanorods. It is interesting to find that some nanorods with the length of one micron were also observed on the surface of annealed Cu-13.9% Al -7.3%Zr composite thin films. However, compared with Cu particles on the surface of Cu–Zr composite thin films, the sizes of Cu particles on the surface of annealed Cu-13.9% Al -7.3%Zr composite thin films are very dispersive. The sizes of some bigger particles are in the magnitude order of one micron, but many smaller particles are less than one hundred of nanometers. Moreover, it can be found from Fig. 4b that nanorods origin from the precipitated Cu particles. Obviously, the formation and growth of these nanorods is the continuation of precipitated Cu particles on the surface of annealed Cu-Al-Zr composite thin films due to the relaxation of compressive stress.

Based on the result of a previous work [11], it was demonstrated that Zr atoms in the annealed Cu-Zr, Cu-Al-Zr and Al-Zr thin films can inhibit the normal growth of Cu grains. As a result, the formation and growth of Cu and Al particles and nanorods dominates to release the stress and energy in thin films. Essentially, both these regular particles and nanorods come into being through atom diffusion along grain boundaries and surfaces driven by the relaxation of a high compressive stress.

4. CONCLUSIONS

Regular Cu and Al particles and nanorods in submicron were obtained on the surface of annealed Cu-Zr, Cu-Al-Zr, and Al-Zr thin films on polyimide substrates. Results show that faceted Cu particles are very regular and consisting of pure Cu element. Furthermore, it was interesting to find that the Cu nanorods could be obtained on the surface of the annealed Cu-Al-Zr composite thin films. Compared with Cu particles, faceted Al particles are slightly irregular. According to the XRD patterns and morphology of particles, it is speculated that these Cu and Al particles are single-crystal. Further analysis demonstrates that the formation of Cu and

Al particles are attributed to atomic diffusion driven by the relaxation of a high compressive stress during annealing. The Cu and Al particles sizes are closely related to the content of Zr as well as annealing temperature. This work may provide a new approach to prepare metal particles and nanorods on polyimide substrates.

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