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Orientation-controlled nanotwinned copper prepared by electrodeposition

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ABSTRACT

Highly-textured nanotwinned Cu (nt-Cu) films with different twin orientations were prepared by pulse electrodeposition in an acidic Cu sulfate bath containing a combination of conventional bath additives. We found that the orientation of nanotwins is dependent on the deposition potential. Copper deposits with horizontally oriented nanotwins were formed at an on-potential of -0.2 V vs. saturated calomel electrode (SCE), while deposits with vertically oriented nanotwins are obtained at -0.6 V vs. SCE. For horizontally oriented nt-Cu, the twin spacing was found to decrease with an increase of pulse-off time, accompanied by a decrease in the number of stacking faults that are vertical or inclined to the horizontal direction. The findings offer the possibility of more flexible engineering of nanotwin structure in Cu electrodeposits.

1. Introduction

Mechanical properties of metals are highly dependent on their microstructure such as grain size, crystal texture, crystal imperfections, and impurities. On the one hand, the designing and engineering of the grain size has been a main strategy for a long time. Many studies of nanocrystalline metals showed that the grain boundaries which impede the glide of dislocation, leading to a strengthening of material [1–5]. Alloying of metal with solid solution elements also offers the strengthening of metals [6–9]. However, these solutions unfortunately increase the electrical resistivity. On the other hand, nanotwins, which are often observed in metals and alloys of low and medium stacking-fault-energy elements, are considered to be one of the most promising strengthening methods without losing a good electrical resistivity. It has been shown that nanoscale twin boundaries restrict the dislocation motion during plastic deformation and thereby nanotwins in metals improve the strength analogous to the grain refinement strengthening [10,11]. Importantly, unlike the grain boundaries, nanoscale twins do not significantly deteriorate the electrical conductivity because the electron scattering of twin boundary is about one order of magnitude less than that of incoherent high-angle grain boundaries, [12] which is highly desirable especially for applications in electronic devices.

Nanotwinned Cu (nt-Cu) has been investigated intensively by many researchers mainly due to the interests for the application to interconnects in advanced electronics [13]. The experimental and theoretical studies [14–17] have shown that well-ordered twin boundaries with their spacing of 100 nm or less act as a perfect interface for strengthening of materials. It has been shown that the twin spacing determines the strength of nt-Cu, following a Hall-Petch-type relationship [11,18,19]. The anisotropy in mechanical properties of highly-oriented nanotwins has been discussed by some researchers [20–22]. The previous studies also revealed the outstanding properties of nt-Cu: not only for mechanical and electrical properties but also electromigration resistance, [23] which is extremely important for sub-micrometer scale interconnects application. Recently, highly (111) textured nt-Cu, where dense nanotwins are preferentially oriented in the horizontal direction within columnar grains, has attracted many researchers' attention as a model material to investigate the deformation mechanism of twinned metals [11,13,18,20,24–27]. Highly-textured nt-Cu has been synthesized either by electrodeposition [13,14,27] or by sputtering [24,28,29]. By employing electrodeposition techniques, nt-Cu with various dimensions including thin films [13,20,27] and nanopillars [14,17] and nanowires, [26,30] has

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been reported so far. These nt-Cu films and structures were achieved by employing different electroplating parameters as well as plating baths. Liu and co-workers, [27] who reported the nt-Cu prepared by DC electrodeposition in a copper sulfate bath containing some additives, claimed that highly (111)-textured nanotwin formation is highly dependent on the agitation speed of the plating bath and the current density. Pulse electrodeposition is another choice to produce (111)-textured nt-Cu electrodeposits [13,14,17,26,31]. Jang and coworkers, [14] who studied the mechanical properties of nt-Cu nanopillars fabricated by pulse plating, reported that twin spacing can be adjusted by the length of on-time, although the detailed information was not provided. Chan and coworkers [30] reported that the density of nanotwins increases when pulse plating is carried out at a low current density and at a low temperature. As described above, highly textured nt-Cu films and nanostructures have been fabricated using various electrodeposition methods and conditions by many different groups. However, the very limited information is available in terms of the mechanism of the well-oriented nanotwin formation, despite the intensive studies of their mechanics.

The growth twins formed in randomly oriented grains have been classically observed in many electrodeposits, especially produced by pulse electrodeposition techniques. The twinning in electrodeposits have been believed to be related to the relaxation of the internal stress, which is generated due to film growth phenomena such as nucleation, coalescence of nuclei and thickening of the film. Xu and coworkers [32,33] measured the stress evolution in Cu during pulse electrodeposition in order to explain the twinning in Cu electrodeposits. Their in-situ stress measurements revealed that the stress rapidly increases during pulse-on times, while it is relaxed during the pulse-off times. The stress relaxation is attributed to the rearrangement of Cu atoms in the film to form a more energetically favored structure. Nano-twinning is considered to occur during this relaxation step.

Twinning of a highly textured nt-Cu is assumed to occur in a similar manner, and the reduction of Cu ions during the pulse-off time as well as the stress-relaxation process during the pulse-off time should play key roles in controlling both the orientation and the density of twins in columnar grains in electrodeposited films. However, as far as the authors are aware, the synthesis of nt-Cu has been carried out empirically, and the roles of pulse-on/off on nanotwinning of electrodeposits have rarely been discussed in the previous reports. Such fundamental knowledge in nanotwinning mechanism is indeed very important for the more precise engineering of microstructure of nanotwinned metals with a desired property. Therefore, in this study, we investigated the effect of pulse electrodeposition on microstructure of nt-Cu in order to obtain insight into the role of the pulse-on/off times on the twinning behavior, namely, the twin orientation and density of highly-textured nt-Cu films.

2. Experimental Section

Cu electrodeposition was performed at room temperature on Si substrate sputter-coated with a 100 nm-thick Au layer on a 10 nm-thick Cr adhesion layer. The plating bath consist of 65 g/L $CuSO_4 \cdot 5H_2O$ (Sigma-Aldrich) and 196 g/L H_2SO_4 (Sigma-Aldrich) as main constituents. The bath also contains some conventional bath additives: 50 mg/L chloride ions (added as HCl, Sigma-Aldrich), 100 mg/L polyethylene glycol (Mw 4000, Sigma-Aldrich) and 10 mg/L 3-Mercapto-1-propanesulfonic acid sodium salt (Sigma-Aldrich). A Pt plated Ti mesh was used as the counter electrode, while a saturated calomel electrode (SCE) was used as the reference electrode. The electroplating cell was connected to a computer-aided potentiostat system (Autolab PGSTAT30, Metrohm) controlled by GPES software. Prior to electrodeposition experiments, substrates were cleaned in Piranha solution (the mixture of H_2O_2 (30%) and H_2SO_4 with a mixing ratio of 1:3) for at least 10 min and then thoroughly rinsed in deionized water (18.2 MΩcm). Subsequently, the conductive surfaces of the cleaned substrates were covered with a masking tape leaving a circular open area of 1 cm diameter for electrodeposition. All electrodeposition experiments were performed at room temperature. Electrodeposition was carried out by a pulse plating technique, which applies the periodical square wave potential pulses. The potential during on-time was set at -0.2 V or -0.6 V vs. SCE while that for off-time was the open circuit potential (+0.055 V vs. SCE). The on-time was fixed at 20 ms whereas the off-time was varied from 1 to 4 s. After the deposition, samples were rinsed in deionized water and dried under clean air flow.

Microstructure of Cu electrodeposits was observed with a focused ion beam (FIB, VELA FIB-SEM, Tescan). Specimens were primarily cleaved and its cross-section was milled by FIB at an acceleration voltage of 30 keV and a probe current of 1000 pA. The cross-sections of samples were observed with a sample tilt angle of 45° with respect to the direction of Ga ion beam. The imaging was carried out with an acceleration voltage of 30 keV and a probe current of 10 pA. Twin spacing was measured from randomly selected around 20 different grains in FIB images of different parts of a sample for each growth condition. Transmission electron microscopy (TEM) was performed for selected samples in order to obtain further insights into the microstructure of Cu deposits. The samples for TEM were prepared by FIB-milling. The TEM samples were prepared by FIB-milling. A JEOL 2200 FX microscope operated at 200 keV was used to perform high-resolution imaging of the samples.

The crystal structure of nt-Cu was analyzed by X-ray diffraction (XRD, Bruker) with a Cu Kα radiation source (40 kV, 40 mA). The texture coefficient [34,35] was defined as

$$TC_{(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{(1/n)\Sigma I_{(hkl)}/I_{0(hkl)}} \quad (1)$$

, where $I_{(hkl)}$ is the relative peak intensity from (hkl) reflection of a Cu electrodeposit, $I_{0(hkl)}$ is that of randomly oriented powder Cu

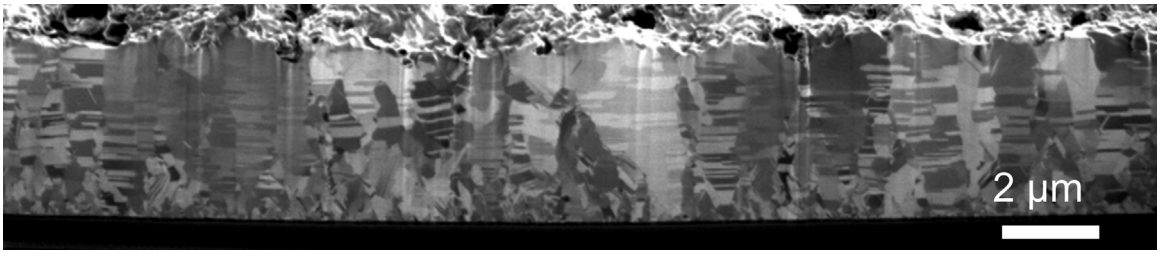

Fig. 1. A FIB image of nt-Cu prepared by pulse plating at an on-potential of -0.2 V vs. SCE (t_{on}: 20 ms, t_{off}: 3 s).