Structural, Mechanical and Electrical Properties of Highly Textured and Twinned Cu Film Fabricated by Pulsed Electrodeposition

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Abstract

The importance of high strength, high conductive material properties to the design of high field resistive magnets can not be over emphasized. However both properties tend to be inversely related. The purpose of this research is to reverse this relationship by increasing the strength of Cu while maintaining its high conductive properties. This is accomplished by producing the proper alignment of grains and the high density of nanotwins in a sample of Cu film fabricated by pulsed electrodeposition (PED). This work studies the influence of peak current densities (PCDs) on crystallographic textures; twin boundary orientations; micro-voids, hardness and electrical conductivity of the Cu films by the PED on the MP35N substrate.

Introduction

Pure Cu with both high strength and high electrical conductivity was reported to be achievable by the PED [1]. Its structure was characterized by a high density of nanoscale growth twins in irregular-shape Cu grains [1]. In addition, the relationship among deposition substrates, current densities, crystallographic textures, growth twins, electrical and mechanical properties was recently studied for the highly textured and twinned Cu film prepared by PED. Manipulation of pulsed peak current densities during fabrication of Cu film is expected to produce the optimal structural properties of highly textured and twinned Cu thereby increasing strength while maintaining high conductivity. This work studies the influence of peak current densities (PCDs) on crystallographic textures; twin boundary orientations; micro-voids, hardness and electrical conductivity of the Cu films by the PED on the MP35N substrate [2].

Experimental procedure

The PED was carried out galvanostatically at a room temperature of 22°C in an electrolyte of CuSO4 solution with cathodic square wave pulses by turning off the current periodically, with an on-time of 0.02 s and an off-time of 2.00 s. The nominal PCDs were 0.5; 1.0; 0.5/1.0; 0.5/-0.25/1.0/-0.25, for samples 1, 2, 3 and 4, respectively. The schemes of the four different square wave pulses were shown in Fig.1. The $CuSO_4$ concentration was 28 g/L and pH value was 1 by adding sulphuric acid. A copper sheet with purity of 99.99 % was used as the soluble anode without any additives in the solutions. The cathode/deposition substrate was 0.1 mm thick sheet of cold-rolled MP35N alloy [3]. The distance between the anode and cathode was 3.0 cm. The total deposition time was 22 hrs. The electrolyte was continuously stirred mechanically during the PED process. Structure hardness and conductivity of the as-deposited Cu films were examined by X-ray diffraction (XRD), scanning electron microscope (SEM), Vickers micro-hardness tester, and a conventional four-probe technique, respectively.

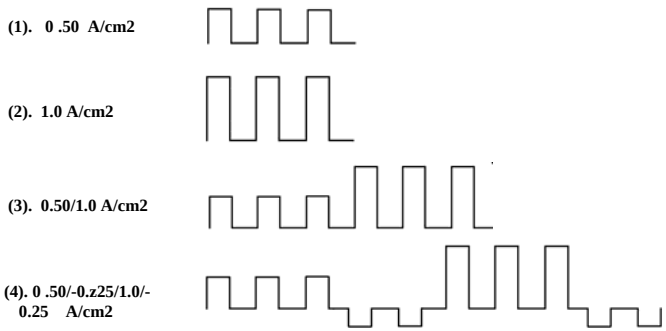

Fig.1 The schemes of the four different square wave pulses.

Results and discussions

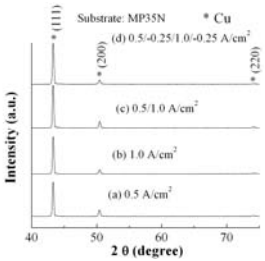

Fig.2 XRD patterns of the Cu films deposited with PCDs of (a) 0.5, (b) 1.0, (c) 0.50/1.0, (d) 0.5/-0.25/1.0/-0.25 A/cm2 .

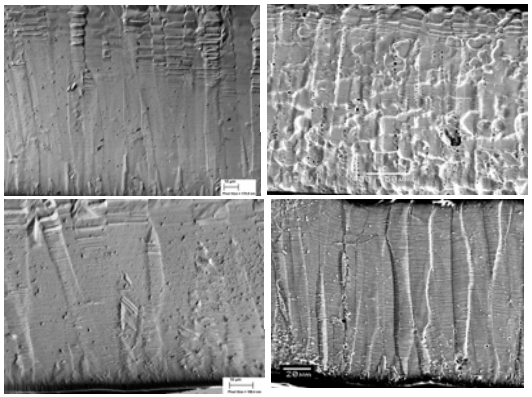

Fig.3 Cross-sectional SEM images of the Cu films of Fig.2 Sample 1 (top left), Sample 2 (top right), Sample 3 (bottom left), Sample 4 (bottom right)

{111} out-of-plane textures were observed in all the samples 1, 2, 3 and 4 (see Fig.2). For samples 1 and 2, a higher PCD resulted in a formation of a higher density of twins with smaller average twin thickness as the deposition/growth rate monotonically increases with increasing the PCD [2]. However, higher current density of sample 2 introduced some micro-voids on the grain boundaries (GBs). The combination of PCD of 0.5 and 1.0 A/cm2 (sample 3) can retain similarly high density of twins with small average twin thickness with those of sample 2. But the micro-voids were successfully removed in sample 3. However, all samples 1, 2 and 3 have a non-uniform structure problem, in which the average twin thickness became much larger close to the solution sides (see Fig.3). This significantly decreases the hardness, strength and also limits growth of thick film for magnet applications. Uniform structure from substrate side to solution side with improved {111} texture intensity was successfully fabricated in the sample 4 by introducing periodic back-polishing (see Fig.3). This results in an increase of hardness and strength of the Cu film. Whereas, the periodic back-polishing also introduced a few micro-voids on the GBs. It is know that the thinner the twin thickness, the higher hardness/strength is while the lower electrical conductivity is [1, 2]. The presence of some micro-voids on the GBs is detrimental to the hardness/strength and electrical conductivity for the deposited Cu films. Due to the above-mentioned trade-off effect, the hardness of 125, 142, 170 and 177 HV and the resistivity of 1.86, 2.00, 1.96 and 1.97 10^{-8} Ωm were obtained for samples 1, 2, 3 and 4, respectively (see Table 1).

Sample No.	PCD (A/cm^2)	Hardness (HV)	Resistivity (10^{-8} Ωm)	Relative conductivity (% IACS)
1	0.50	125	1.86	92.7
2	1.0	142	2.00	86.2
3	0.50/1.0	170	1.96	88.0
4	0.50/-0.25/1.0/-0.25	177	1.97	87.5

Table 1 Summary of hardness, electrical resistivity and relative conductivity of the Cu films deposited on MP35N alloys with several PCDs.

Conclusions

The combination of PCD of 0.5 and 1.0 A/cm2 (sample3) can successfully remove the micro-voids and retain similarly high density of twins with those of sample 2, which increases the hardness. Uniform structure with improved {111} texture intensity and a few micro-voids was successfully fabricated in the sample4 by introducing periodic back-polishing. This sample has the best hardness and retains the high conductivity of Cu.

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References

1. L. Lu et al., "Ultrahigh Strength and High Electrical Conductivity in Copper", Science 304 (2004) 422.
2. B.Z. Cui, et al., "Highly Textured and twinned Cu films fabricated by pulsed electrodeposition", Acta Mater 55(2007) 4429.
3. A. Ishmaku, et al., "Deformation induced Nanostructure and texture in MP35N alloys", J. Mater. Sci. 39 (2004) 5417.