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Orientation-dependent mechanical behavior of electrodeposited Cu with nanoscale twins

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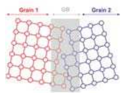
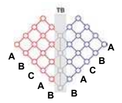
Introduction

The electrodeposition of copper is an important technology for the fabrication of micro-components and the interconnect industry. Nanocrystalline copper, in comparison to coarse grained copper, offers improved yield strength and hardness but poor conductivity and ductility. Unlike nanocrystalline copper, nanotwinned Cu combines remarkable strength, ductility and electrical conductivity[1]. This unique properties combination results from the perfect interface provided by a twin boundary. Understanding the origin of that strengthening and how it varies with the twin orientation is essential to modern applications. In this poster, we report the synthesis of Cu films with highly-oriented nanoscale twins by pulse electrodeposition[2] and their orientation-dependent mechanical behavior under micropillar compression test.

Grain boundary



Twin boundary



Electrodeposition of highly-oriented twins

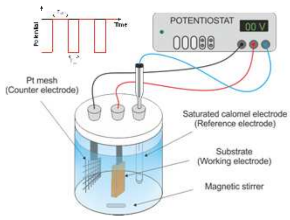
➢ Thin film preparation

Electrochemical pulse deposition of Cu films with nanoscale twins.

Systematic study of two plating parameters to the tune the microstructure:

1. the applied potential E;
2. the duration of the pulse off-time, T_{off}.

Microstructural analysis was performed with XRD, TEM and FIB micrographs.



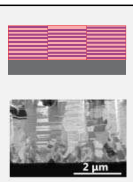
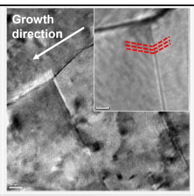
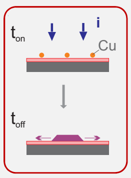
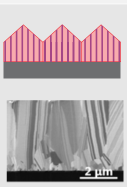
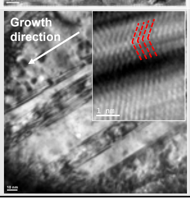
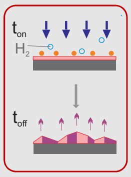
Electrochemical setup

➢ Control of the nanotwin orientation with the applied potential

Effect of the applied potential was assessed for T_{on} = 20 ms and T_{off} = 2 s.

Columnar grains with highly oriented (111)[11$\bar{2}$] nanoscale twins were obtained.

When the potential is increased, twin orientation switches from horizontal to vertical as a result of a different growth mechanism.

	Microstructure	TEM	Growth mechanism
E = -0.2 V			
E = -0.6 V			

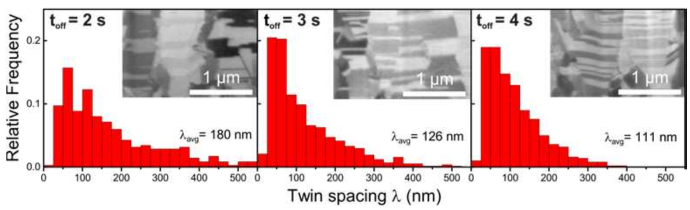
➢ Control of the twin density with the off-time T_{off}

Effect of the off-time duration was investigated at E = -0.2V vs. SCE. Off-time is varied from 2 to 4 seconds.

Nanotwins were generated when T_{off} was longer than 2 s, and the twin spacing decreased with the increase of T_{off}.

The formation of nanotwins during electrodeposition results from the diffusion of Cu adatoms during T_{off}. This mechanism is driven by stress relaxation of the Cu lattice[3].

Twin spacing distribution as a function of T_{off}

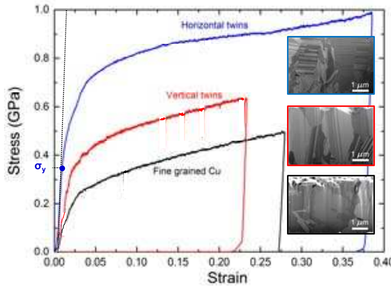


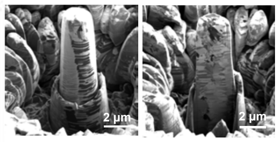
[1] M. Dao, et al., **Acta Mater.**, 54, 5421 (2006)
[2] M. Hasegawa, et al., **Elect. Acta**, 178,458 (2015)
[3] D, Xu, et al., **Appl. Phys. Lett.**, 91 (2007)
[4] J. Wheeler, et al., **Inter. J. Plast.**, 40, 140 (2013)

Micropillar compression tests

Mechanical properties were studied by compressing micropillars prepared with a Focused Ion Beam (FIB) with an *in situ* SEM indenter[4].

Nanotwinned copper showed higher yield strength and 3 times larger strain rate sensitivity than fine grained copper. Large anisotropy in yield strength is observed between vertical and horizontal twins.





	σ_y (MPa)
Fine grained	172 ± 4
Horizontal twins	220 ± 20
Vertical twins	336 ± 16

Representative stress-strain curves of fine-grained Cu and nanotwinned Cu with horizontal and vertical orientations and FIB images of a pillar before and after compression.

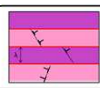
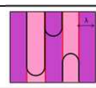
Orientation-dependent mechanical response

In polycrystalline Cu, strengthening is achieved by grain refinement.

Similar dislocation-based mechanism occurs for horizontal twin except that grain boundaries are replaced by twin boundaries.

For vertical twins, dislocations are confined within the twin lamellae resulting in lower strength.

The Schmid factor computed for a fcc {111}<11$\bar{2}$> twinned crystal confirms that the stress required to deform horizontal twins is higher than vertical twins.

	Horizontal twins	Vertical twins
Microstructure		
Texture	[111]	[11$\bar{2}$]
Slip plane	Inclined to TB	Inclined to TB
Slip direction	Inclined to TB	Parallel to TB
Schmid factor	0.314	0.393
σ_y (Mpa)	336±16	220±20
Scaling law	$\sigma \propto \frac{1}{\sqrt{\lambda}}$	$\sigma \propto \frac{1}{\lambda}\ln\left(\frac{\lambda}{b}\right)$

Orientation-dependent elastic properties

The Young's moduli, E, were extracted from the stress-strain curves during unloading and compared to theoretical values. The elastic modulus of fine grained Cu was calculated by using Hill method for polycrystals. The Young's moduli for horizontal and vertical twins were calculated by assuming a Cu single crystal oriented in the [111]- and [11$\bar{2}$]-direction, respectively:

$$\frac{1}{E_{hkl}} = \frac{(C_{11}+C_{12})}{(C_{11}-C_{12})(C_{11}+2C_{12})} - 2\left[\frac{1}{(C_{11}-C_{12})} - \frac{1}{2C_{44}}\right](u^2v^2+v^2w^2+w^2u^2)$$

Potential sources of error include pillar geometry and misalignment. For a metallic pillar of 2 µm diameter yielding at 400 MPa with E=150 GPa, the elastic deformation occurs in the first 20 nm, which is similar to the 17.5 nm error due to a 0.5° misalignment.

	E_{hkl} (GPa)	
	Calculated	Measured
Fine grained	127.3	71.6±2.7
Horizontal twins	125	106.7±2.8
Vertical twins	167	136.7±17

Conclusion

Optimized parameters for the electrodeposition of highly-oriented nanotwinned Cu with control of the twin orientation and twin density.

Nanotwinned Cu exhibited higher yield strength and strain rate sensitivity than fine grained copper.

Anisotropy in the mechanical response with the twin orientation results from the interaction of dislocations with the twin lamellae.

Grain boundary engineering with nanoscale twins is an effective approach to tune the mechanical properties without compromising electrical conductivity or ductility.

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