Microstructural investigation of excimer laser-crystallized metallic thin films

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Abstract

Recent advances in the microstructural modification of metal films using excimer laser projection irradiation and lateral resolidification are discussed. Pure copper films have been directionally resolidified into large sheet-like grains when properly encapsulated for suppression of liquid-phase dewetting. A survey and quantitative assessment of the defects found in these microstructures, typical for rapidly solidified metals, is presented.

1. Introduction

Excimer laser crystallization of thin silicon films on silica (SiO_2) or glass substrates has now achieved wide application in the display industry. From a process perspective, this material system is ideally suited for rapid laser melting and solidification due to the inert nature of the underlying SiO_2, good interfacial adhesion of the Si film in both the liquid and solid states, as well as advantageous thermal expansion characteristics during heating, phase change, and cooling.

A significant challenge today is the extension of excimer laser crystallization processing into other materials systems. Metals, in particular, are an interesting class of materials with a rich array of alloying effects, phase selection, segregation, and microstructural effects. In the thin film configuration they are today employed in microelectronic interconnects[1],[2], magnetic storage[3], photovoltaics[4], optical components[5],[6], and more recently templates for self-assembled nanostructures[7]. In these applications, the microstructural and compositional details of these films are becoming increasingly important. Using the excimer processing infrastructure already in place[8], it is easy to envision further performance gains or entirely new applications using engineered microstructures and laser-induced phase selection.

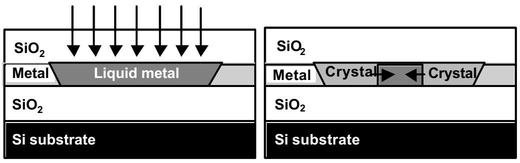

Figure 1. Cross-sectional schematic of the rapid lateral solidification process. Excimer pulse completely melts a region of the film, followed by lateral resolidification initiated from the unmelted side walls.

Until now, laser processing of metallic thin films has been hampered by the tendency of metals to undergo dewetting and agglomeration while molten[9], particularly on inert substrates such as SiO_2. On the other hand, the kinetics of solidification in metals are quite different[10] from Si and can in principle form very large grains on the timescales associated with nanosecond laser processing. We have previously demonstrated that with the addition of a SiO_2 capping layer[11], dewetting can be suppressed and pure FCC metal films of Cu and Au may successfully be laser crystallized. Using a rapid lateral solidification technique, shown in Figure 1, we have been able to produce large sheet-like grains in these materials. Here we report on the microstructural analysis for Cu films crystallized using this technique.

2. Experiment

Copper thin films, 200 nm thick and encapsulated above and below with SiO_2 were prepared via sputtering as described elsewhere[12]. Single shot excimer projection irradiation (248 nm KrF, 28 ns) was used to melt a spatially limited region of the film, typically a line of width 3-60 μm. In this configuration a fluence in the range 400-900 mJ/cm^2 is sufficient to completely melt the metal down to the underlying amorphous SiO_2 substrate. Upon cooling, solidification is initiated from the unmelted regions adjacent to the melt pool, and proceeds laterally toward the center of the pool.

After processing, samples were prepared for transmission electron microscopy (TEM) analysis using a modified acid back-etch technique[13] to obtain free-standing Cu films of uniform (200 nm) thickness. Microstructures were examined in the plan view geometry at 200kV using a JEOL 200CX transmission electron microscope.

3. Results

An example of the resulting microstructure is shown in Figure 2 and consists of directionally solidified grains extending from the edge of the laser-melted region to the center line. These grains are typically 1 µm wide in the transverse direction, and can be several microns in length. Observations reveal several important features of the microstructure:

Planar solidification

Nearly all grains extend through the full thickness of the film, with grain boundaries between adjacent grains largely perpendicular to the plane of the film. The central seam formed where the solidification fronts meet is straight, indicating the solidification proceeded as a planar front with uniform velocity across the front. Notable is the absence of 'thermal' dendrite features, also supporting the assumption of a stable planar front[14]. It is likely that the front is stabilized by the quasi-2D configuration and/or the heat flow geometry, making rapid lateral solidification more like directional solidification than free solidification.

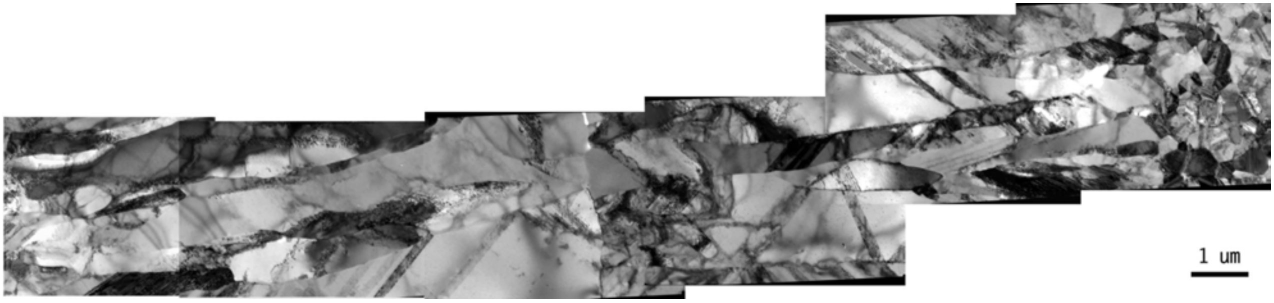

Figure 2. Bright field plan-view TEM micrograph of pure Cu film solidified by rapid lateral solidification with a line width of 16 µm, 696 mJ/cm^2. Columnar grains extend laterally from the right and left sides of the image, terminating in the center of the image.

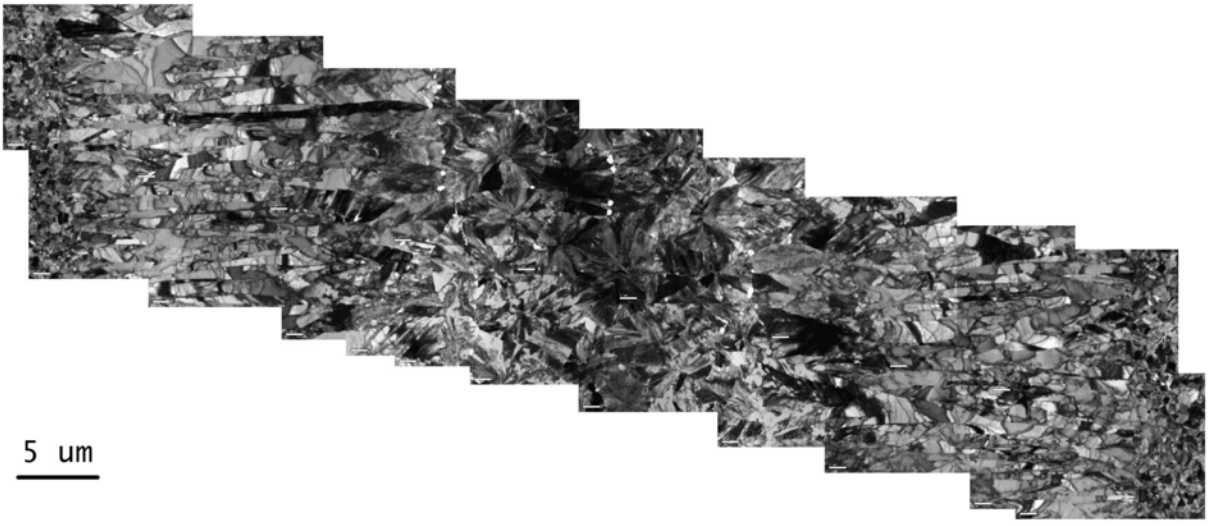

Figure 3. Bright field plan-view TEM micrograph of pure 200 nm thick Cu film solidified by rapid lateral solidification with a line width of 60 µm, 672 mJ/cm^2. substrate initially at ambient temperature.

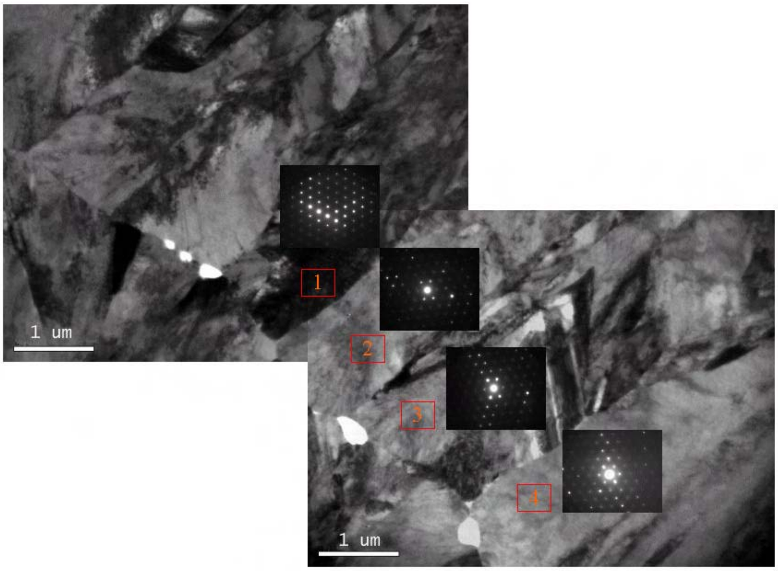

Figure 4. Diffraction analysis of four adjacent grains near the end of solidification in the microstructure of Figure 3, indicates a strong texture with <111> measured 2, 14, 15 and 15 degrees from surface normal in grains 1-4 respectively.

Using a wider line, as shown in Figure 3, the maximum lateral solidification is found to extend up to 22 um in the current configuration. Here the solidification front is stopped by nucleation in the central regions of the pool, analogous to silicon[15].

Texture

All grains in the solidification front arriving at the center must have advanced at the same velocity, while inspection of the early stages of solidification (near the edges of the line) indicate an occlusion process had occurred. This suggests that certain grains of favorable orientation must be selected in the first few microns, then proceed as a highly textured microstructure toward the center.

Preliminary confirmation of a strong texture is shown in Figure 4. Here grain 1 exhibits a <111> direction near-normal to the plane of the film, while the other grains analyzed are about 15 degrees from normal. In these latter grains the growth direction is found to be approximately 80 degrees from <111>, corresponding most closely to the <113>, <133> and directions. This appears to be consistent with other experiments[16],[17] showing textures in planar solidification of pure FCC metals transition from <100> to <111> (and <113>,<133>,<024>) along the growth direction as the solidification velocity increases.

Localized and extended defects

Grains in these microstructures are found to have a variety of defects consistent with rapidly solidified FCC pure metals. This can include nanoscale localized defects such as point defect clusters, vacancy clusters, dislocation loops and stacking fault tetrahedra, as well as extended defects, including planar stacking faults, twins, and dislocation tangles. The micrograph in Figure 5 clearly reveals a uniform distribution of dark spots identified as faulted partial or perfect (Frank) dislocation loops. These structures are known to appear via an aggregation of excess vacancies in the solidified material, followed by collapse to stacking faults on the (111) planes bounded by dislocation loops[18]. Preliminary estimates indicate a density of 10^{12} to 10^{13} cm/cc for these features.

Also visible are twin bands or stacking faults are present along (111) planes in Cu, as well as evidence of vacancy supersaturation and clustering to form dislocation loop structures. It is believed these structures were formed during solidification or perhaps by thermal stress effects upon cooling. As the films are prepared via an acid technique to avoid complicating effects of mechanical deformation, and more experiments are underway to characterize these structures.

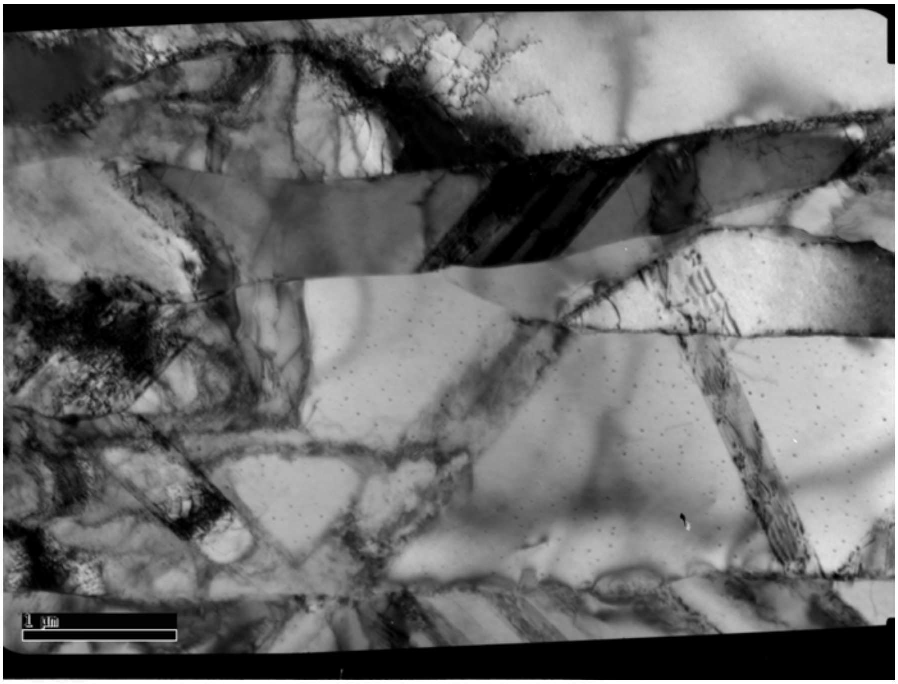

Figure 5. Magnified view of selected grains from microstructure in Figure 2. Dislocation loops visible as dark spots in large grain extending across lower half of image.

4. Conclusion

The morphology of the films examined here is similar to directionally solidified materials, but is unique in that it is in a thin-film geometry, processed on nanosecond timescales using a flexible non-contact excimer laser irradiation technique. The ability of the rapid lateral solidification process to provide large directionally solidified grains at pre-determined locations opens up the possibility for obtaining single-crystal conducting pathways for microelectronic interconnects. Patterning, as well as electron transport properties and electromigration behavior measurements are future critical steps to determine the suitability of such materials for these applications. It is also notable that large area single crystal regions can be obtained using this process without high-temperature annealing, making this process ideal for integrating self-assembled nanostructures with integrated microelectronic and photonic device structures.

Because this process can produce materials with the microstructures characteristic of rapid solidification processing, it can allows new exploration in this area of fundamental materials science and also promises technical applications. This approach fits well when combined with economical deposition processes such as sputtering, electrochemical, and evaporation deposition techniques. These methods are capable of producing uniform large-area metal films, but with a limited range of microstructural conditions. Excimer laser processing allows a new avenue for microstructural modification after deposition, and can also be economical in this approach. The unique adjustability of parameters and possibilities for microstructure engineering after deposition may allow excimer processing to find other niche areas as well.

As a research tool, excimer laser melting and rapid lateral solidification opens a new window into fundamental studies of rapid solidification and non-equilibrum phase transformations. Although the microstructures produced by this process have characteristics similar to conventional rapid solidification techniques, the solidification occurs laterally in the plane of the film, under conditions that are more easily controlled. Possibilities include: grain refinement for increased homogeneity of films, texture selection, uniform dispersion of fine precipitates, extended solid solubility, and metastable phase formation. Extension of this process to other materials, including magnetic alloy thin films, metal electrodes on active ceramics, and MEMS devices is likely to happen in the near future.

Acknowledgements

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References

[1] K. Wetzig, C.M. Schneider, "Metal Based Thin Films for Electronics", Wiley VCH, (2003).

[2] P. Kapur, J.P. McVittie and K.C. Saraswat , IEEE Trans. Electron Dev. **49**, 590 (2002).

[3] M.F. Doerner and R.L. White, Mater. Res. Bull. **21**, 28 (1996).

[4] J. Kang, J.S. You, C.S. Kang, J.J. Pak and D. Kim, Solar Energy Materials and Solar Cells **74**, 91 (2002).

[5] S. Musikant, "Optical Materials An Introduction to Selection and Application", Marcel-Dekker, Ch. 9 (1985).

[6] D. Attwood, "Soft X-Rays and Extreme Ultraviolet Radiation", Cambridge University Press, Ch. 4 (2000).

[7] M. Kohler, W. Fritzsche, "Nanotechnology - An Introduction to Nanostructuring Techniques", Wiley VCH, (2004).

[8] D. Basting, K. Pippert and U. Stamm, , RIKEN Review **43**, 14 (2002).

[9] J. Bischof, D. Scherer, S. Herminghaus and P. Leiderer, Phys. Rev. Lett. **77**, 1536 (1996).

[10] B.T. Bassler, W.H. Hofmeister and R.J. Bayuzick, Mater. Sci. Eng. A **342**, 80 (2003).

[11] J.E. Kline and J.P. Leonard, Thin Solid Films **488**, 306 (2005).

[12] J.E. Kline and J.P. Leonard, Appl. Phys. Lett. **86**, 201902 (2005).

[13] R.H. Finch, H.J. Queisser, G. Thomas and J. Washburn, J. Appl. Phys. **34**, 406 (1963).

[14] R. Trivedi and W. Kurz, Acta. Metall. **34**, 1663 (1986).

[15] H.J. Kim and J.S. Im, Appl. Phys. Lett. **68**, 1513 (1996).

[16] V.G. Sheplevich, P.A. Siutsova, E.Y. Neumerzhytskaya, E.S. Gutko and K.V. Kuckorecko, J. Alloy Compd. **403**, 267 (2005).

[17] B.S. Mitin, N.V. Edneral, M.M. Serov and V.B. Yakovlev, Physics of Metals and Metallography **87**, 221 (1999).

[18] B.L. Eyre, J. Phys. F **3**, 422 (1973).