

Cold Sample Preparation for Cross-sectional Transmission Electron Microscopy: Cu Nanocrystals Embedded in 2 μm SiO_2 Films

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Cu nanocrystals (1-10 nm diameter) embedded in a dielectric material, e.g. silica (SiO_2), are receiving increased attention in recent years as a consequence of their non-linear optical properties [1], which in turn is caused by their perturbed face-centered cubic (f.c.c.) structure. The structural perturbations, as compared to the bulk material, are typically measured by synchrotron-based x-ray techniques [2], complimented by cross-sectional transmission electron microscopy (XTEM). XTEM offers invaluable information with respect to shape and morphology of the nanocrystals. For the present work, Cu nanocrystals were synthesized within a 2 μm SiO_2 matrix on a 520 μm Si support by ion implantation and thermal annealing following a procedure presented elsewhere [2]. In order to study the influence that ion irradiation has on the nanocrystals, the sample was then irradiated with 1×10^{15} ions / cm^2 high-energy (5 MeV) Sn^+ ions. Subsequent XTEM sample preparation required a low temperature technique to be implemented in order to inhibit Cu atomic diffusion, Cu nanocrystal formation and / or Cu nanocrystal recrystallization.

Cross-sectional samples of both the unirradiated and irradiated nanocrystals were prepared. For the latter, the nanocrystal-rich 2 μm SiO_2 film had been removed from the Si support (to facilitate efficient synchrotron radiation measurements [2], which preceded the XTEM for this sample). For the unirradiated sample, the SiO_2 film was intact and supported by 520 μm of Si. The irradiated sample was glued as a thin film between two diamond buffed $\sim 1 \text{ cm}^2$ glass microscopy slides ($\sim 960 \mu\text{m}$ thick), whereas the unirradiated sample was glued to one buffed microscopy slide covering the SiO_2 surface. Thus, each sample assembly was $\sim 1.5 - 2.0$ mm tall, including the Loctite 363 glue (resistant to acetone) used. The choice of glue enabled room temperature curing within 30 minutes while the sample assemblies were held under mechanical pressure using Teflon coated jig and exposed to UV light. Subsequently, a conventional diamond saw blade was used to cut 2.9×1 mm sections, which were then turned on the side and mechanically ground and polished on both sides to a final thickness of $\sim 80 \mu\text{m}$ while glued (Loctite 460, not resistant to acetone) to a TEM Pyrex-stub. Following mechanical dimpling at the interface (using a Gatan 656 Dimple Grinder) to a final thickness of $\sim 10 - 15 \mu\text{m}$, a 3 mm (outer) diameter stainless steel O-ring was fixed onto each sample as a support using high strength Araldite (resistant to acetone). The O-ring was made from a stainless steel cylinder in order to prevent Cu contamination in the event of sputtering during ion milling. The samples were subsequently lifted off their stubs in acetone.

Finally, the samples were milled from one side (opposite the O-ring) in a Gatan 600 DuoMill™ with Ar^+ ions operated at 0.5 mA / 4.0 kV while the sample was rotating at 10 rpm. The sample stage was in thermal contact with a liquid nitrogen reservoir and the temperature of the sample during milling was estimated to be $\sim -10^\circ\text{C}$. Milling times are listed in Table 1. In general, we note that perforation took in excess of 10 hours for each sample at an angle of $15 - 20^\circ$. Following perforation at the interface in question, the incoming ion beam angle was decreased to 9° while milling continued for 10 – 75 minutes. Prior to TEM investigation both samples were coated with a thin film of C for

better conductivity and imaging stability at 300 kV. Fig. 1 (a) and (b) are the unirradiated and irradiated interfaces, respectively, as seen by an optical microscope at 20x magnification. We notice some amount of sputtering, most likely from the steel sample holder, which partially encapsulates the sample during milling. Inset in each figure is an image of the whole TEM sample at 1.25x magnification including the O-ring.

Samples were analysed using a Philips CM300 microscope operating at 300 kV. Fig. 2 shows a digital micrograph of the unirradiated sample displaying close-to-spherical nanocrystals of 2 – 3 nm diameter. Electron diffraction confirmed the nanocrystals to consist of Cu with the f.c.c. structure. The inset of Fig. 2 shows a micrograph for the irradiated sample taken under similar conditions. The presence of Cu, albeit not in nanocrystal form, was confirmed by an energy-dispersive x-ray probe. We conclude that the Cu nanocrystals are dissolved into the SiO₂ matrix under the irradiation conditions presented here, while proposing that for an intermediate ion irradiation dose Cu nanocrystals are still present, however in an amorphous phase [3].

References

- [1] A. Meldrum et. al., *Nucl. Instr. Meth.* B178 (2001) 7.
- [2] B. Johannessen et. al., *J. Appl. Phys.* 98 (2005) 024307.
- [3] B. Johannessen et. al., submitted to *Nano Letters* (2006).
- [4] We thank the Australian Research Council (ARC) for financial support.

TABLE 1. Milling times for XTEM sample preparation.

Sample	Angle	Time	Comments
Unirradiated (Si / glass)	18°	9h10min	
	15°	7h10min	Perforation occurred ~ 200 μm from interface
	15°	1h10min	
	9°	1h15min	Perforation at interface
Irradiated (glass / glass)	20°	2h25min	
	15°	9h40min	Perforation occurred at interface
	9°	10min	

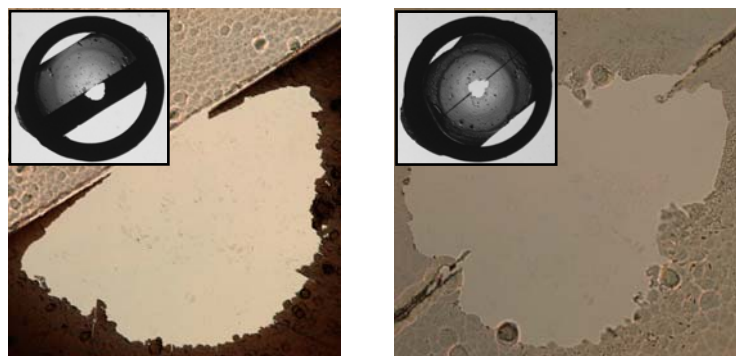


FIG. 1. Optical images of (left) the unirradiated sample interface where the dark region is Si, and (right) the irradiated sample interface. The milled holes are ~ 250 μm wide. Inset are the TEM samples with steel O-rings.

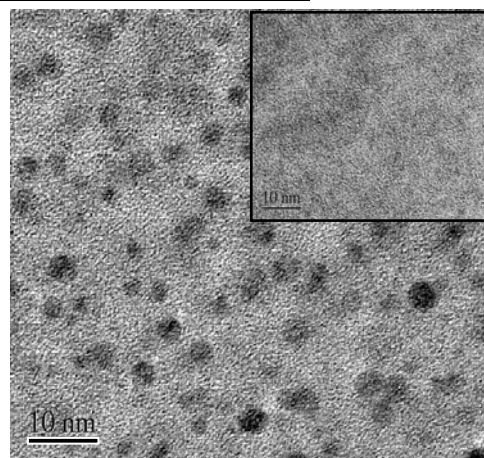


FIG. 2. Digital micrograph of the unirradiated and (inset) irradiated sample.