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Cold Temperature Preparation of XTEM Specimens of Embedded Metallic Nanoparticles

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Nanoparticles (1 – 10 nm in diameter) are particularly susceptible to disorder, amorphization, deformation and/or dissolution upon ion irradiation as compared to their bulk counterparts, which is a consequence of the enhanced surface area to volume ratio of the former (structural disorder is often observed to be preferentially located at the surface [1]). Synchrotron-radiation-based analytical techniques are ideally suited for the elucidation of structural perturbations as compared to the bulk material [2]. Such techniques are commonly complemented by cross-sectional transmission electron microscopy (XTEM). XTEM offers invaluable information with respect to shape and morphology of the nanoparticles.

For the present work, Cu nanoparticles were synthesized within a 2 µm amorphous SiO_2 matrix on a 520 µm Si support by ion implantation and thermal annealing following a procedure described elsewhere [2]. In order to study the influence that ion irradiation has on the nanoparticles, 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 nanoparticle formation and / or Cu nanoparticle recrystallization.

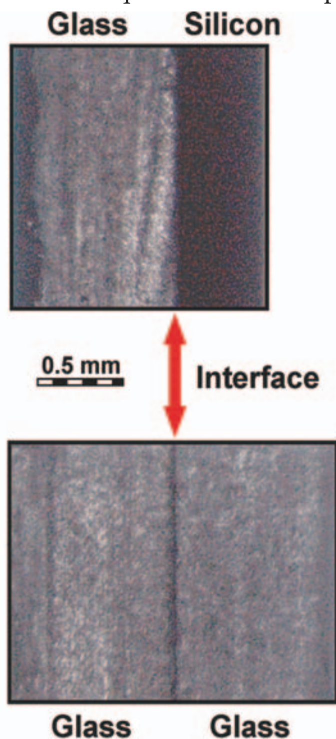

FIG. 1: *Optical images of the unirradiated sample assembly (upper panel) where the darker region is Si, and the irradiated sample assembly (lower panel). The 2 µm SiO_2 film is located at the interface as indicated by the arrow.*

Cross-sectional samples of both the unirradiated and irradiated nanoparticles were prepared. For the latter, the nanoparticle-rich 2 µm SiO_2 film had been removed from the Si support (to facilitate efficient synchrotron radiation measurements, 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 ~ 1x1 cm^2 glass microscopy slides (~ 960 µm thick), whereas the unirradiated sample was glued to one buffed microscopy slide covering the SiO_2 surface. Fig. 1 shows the two sample assemblies in cross-section prior to processing. Each sample assembly was ~ 1.5 – 2.0 mm thick, 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 a Teflon coated jig and exposed to UV light. Subsequently, a conventional diamond saw blade was used to cut 2.9×1 mm^2 sections, which were then turned on the side and mechanically ground and polished on both sides to a final thickness of ~ 80 µm 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 ~ 10 – 15 µm, a 3 mm (outer) diameter stainless steel O-ring, instead of a single-hole Cu grid, was fixed onto each sample as a support using high strength Araldite (resistant to acetone). The O-ring was made from a non-magnetic 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.

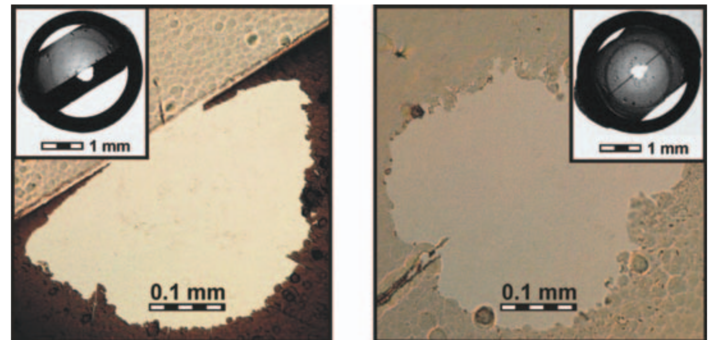

FIG. 2: *Optical images of (left panel) the unirradiated sample interface where the dark region is Si, and (right panel) the irradiated sample interface. The milled holes are ~ 250 µm wide. Inset are the respective XTEM samples with stainless steel O-rings.*

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

TABLE 1. Milling times for XTEM sample preparation

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

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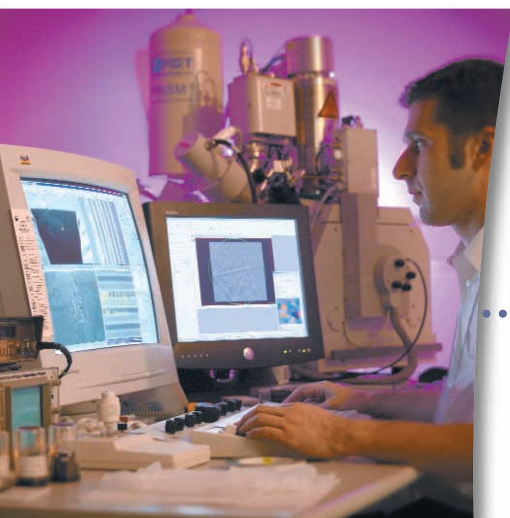

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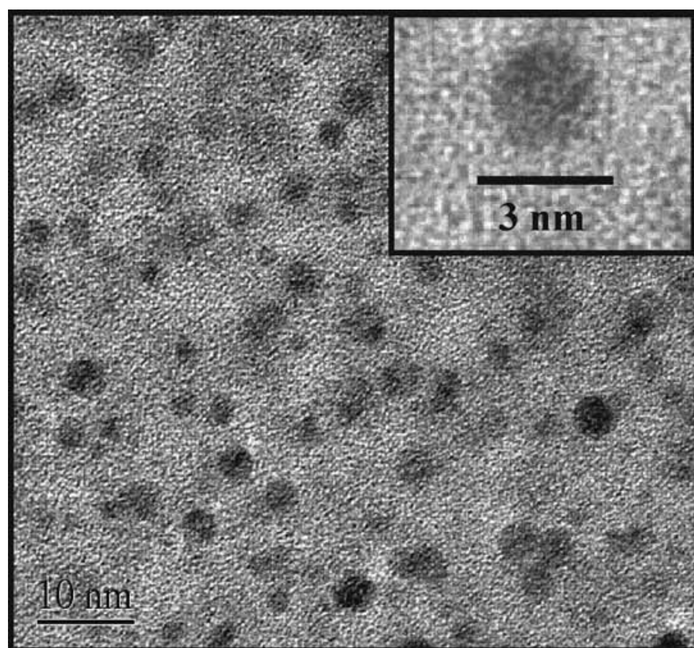

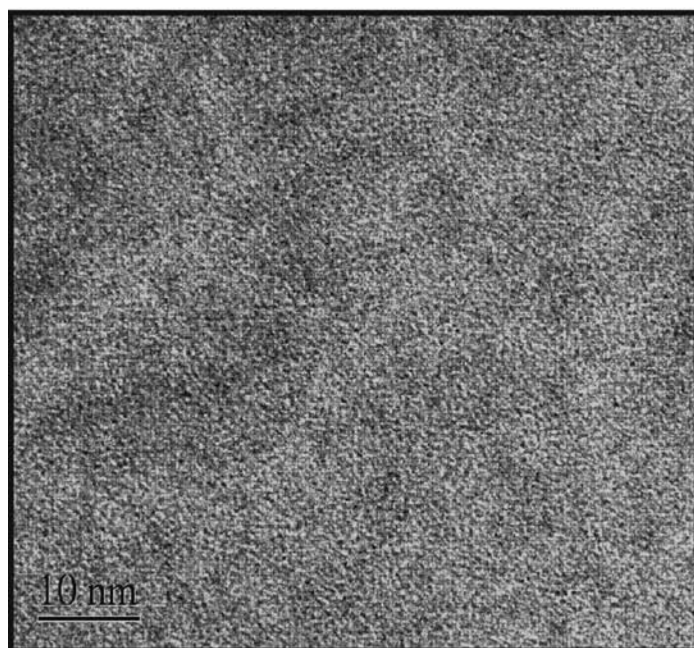

FIG. 3: *(Upper panel) digital micrograph of the unirradiated sample with (inset) high-resolution image of an individual nanoparticle where the (111) planes of the f.c.c. lattice are discernable, and (Lower panel) digital micrograph of the irradiated sample.*

estimated to be ~ - 10°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°. 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. 2 (left and right panels) shows images of 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

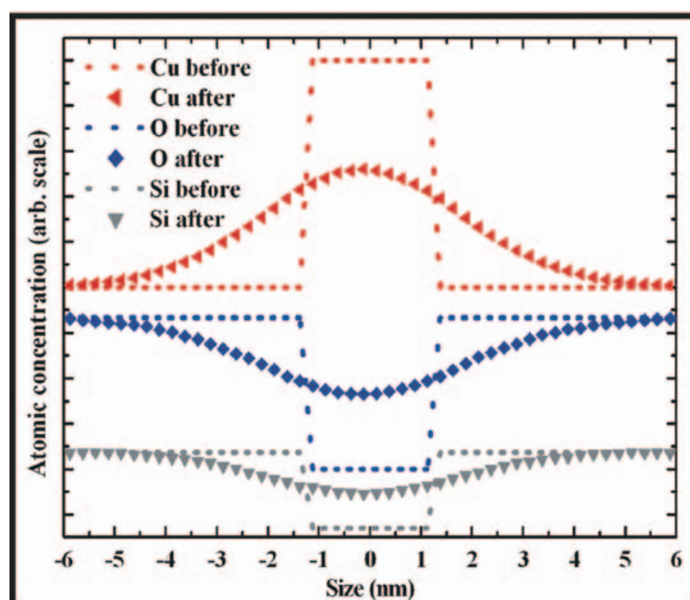

FIG. 4: *Simulation showing the extent of intermixing (Cu, O, Si) upon ion irradiation. Prior to irradiation there is only Cu within the central 2.5nm film.*

magnification including the O-ring.

Samples were analysed using a Philips CM300 microscope operating at 300 kV with a LaB_6 emitter. Fig. 3a shows a digital micrograph of the unirradiated sample displaying close-to-spherical nanoparticles of 2 – 3 nm diameter. The inset shows lattice fringes corresponding to the (111) lattice planes of Cu. Electron diffraction confirmed the nanoparticles to consist of Cu with the face-centered cubic (f.c.c.) structure. Figure 3b shows a micrograph of the irradiated sample taken under similar conditions to that of the unirradiated sample. The presence of Cu, albeit not in nanoparticle form, was confirmed by an energy-dispersive x-ray probe. Fig. 4 shows the extent of intermixing [3] of Cu, O and Si before and after ion irradiation. (The simulation is that for a 2.5 nm thick Cu layer centered around the origin for simplicity.) Clearly, intermixing caused by the ion irradiation resulted in the nanoparticles dissolving as indicated by the TEM micrograph and the smearing of the nanoparticle/matrix interfaces after ion irradiation as seen in the simulation. (The authors note that the simulation is that for a 2-dimensional film, which by nature is underestimating the amount of intermixing present for the 3-dimensional particles).

We conclude that the Cu nanoparticles are dissolved into the SiO_2 matrix under the irradiation conditions presented here, while suggesting that for an intermediate ion irradiation dose Cu nanoparticles are still present, however in an amorphous phase [4]. ■

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