

Formation and Irradiation of Elemental Metallic Nanocrystals Characterized with EXAFS and SAXS

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Introduction

Elemental metallic nanocrystals formed in SiO₂ have applications including all-optical memory and switching devices. For this report, we have utilized a variety of analytical techniques to study the formation and irradiation of Cu, Pt and Au nanocrystals. In an as-formed state, we identify subtle structural perturbations relative to bulk material while following ion irradiation, we demonstrate the presence of a disordered and potentially amorphous phase not achievable in bulk material.

Methods and Materials

Elemental metallic nanocrystals were formed in a thin SiO₂ layer on a Si substrate by ion implantation and thermal annealing. Average nanocrystal diameters varied from 2-15 nm depending on the implantation and annealing conditions. Samples were characterized with cross-sectional transmission electron microscopy (XTEM), extended x-ray absorption fine-structure spectroscopy (EXAFS) and small-angle x-ray scattering (SAXS). XTEM analysis was performed at 300 keV, EXAFS spectra were measured at beamline 20-B of the Photon Factory in fluorescence mode at the Cu K, Pt L3 and Au L3 edges while SAXS exposures were recorded at beamline 15ID-D of the Advanced Photon Source with a Bruker 6000 CCD detector, a camera length of 1881 mm and x-rays of wavelength 1.09 Å. Our novel EXAFS and SAXS sample preparation methods involve the selective removal of the Si substrate as described elsewhere.

Results and Discussion

As formed, XTEM measurements demonstrated the Cu, Pt and Au nanocrystals were spherical in shape (Figure 1) and retained the face-centered-cubic structure characteristic of bulk material. EXAFS measurements however highlighted size-dependent differences in the structural parameters of Cu and Au nanocrystals relative to bulk material. For example, the bond-length decreased and Debye-Waller factor increased with a decrease in nanocrystal diameter as consistent with an increased surface-area-to-volume ratio. The bond-length contraction was readily fit using a simple liquid-drop model from which we calculated an increased surface tension relative to bulk material. Furthermore, the inter-atomic distance distribution was non-Gaussian, manifested as a negative third cumulant and skewed to shorter bond-lengths as consistent with a relaxed or reconstructed nanocrystal/matrix interface. The Cu, Pt and Au nanocrystal size distributions were determined from SAXS measurements using a maximum entropy method. Results were comparable with those extracted from XTEM analysis.

Heavy-ion irradiation (with MeV Sn ions) of Cu and Au nanocrystals yielded a disordered phase at intermediate ion doses followed by nanocrystal dissolution at higher ion doses.

For irradiated Cu and Au nanocrystals, we contend the disordered phase was amorphous as manifested by a decreased coordination number, increased bond-length and Debye-Waller factor and a positive third cumulant, all consistent with a dense random packing (DRP) of soft spheres model (Figure 2). Low temperature annealing returned the amorphised material to the nanocrystalline state. For irradiated Au nanocrystals, a distinct narrowing of the size distribution via inverse Ostwald ripening was observed. The eventual dissolution of the Cu and Au nanocrystals yielded either Cu monomers (bonded as Cu₂O) or Au monomers and small Au clusters within the SiO₂ matrix. No evidence of Au-O bonding was apparent.

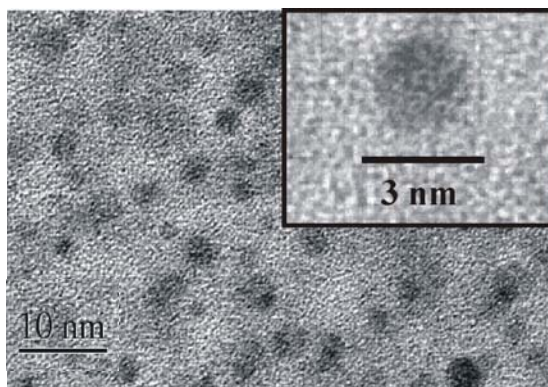


Figure 1: Electron micrograph of as-formed Cu nanocrystals in SiO₂.

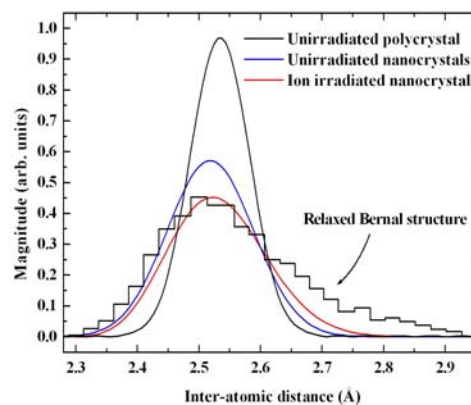


Figure 2: Inter-atomic distance distribution of Cu nanocrystals in SiO₂, before and after ion irradiation, compared with a bulk polycrystalline standard and a theoretical DRP distribution.