

Formation and thermodynamics of GeSi nanoparticles investigated with dispersive XAS

Gustavo M. Azevedo and Antonio A. M. Gasperini

Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), Zip Code 13083-970, Campinas, Sao Paulo, Brazil.

gustavo.azevedo@lnls.br

Nanoparticles have been attracting considerable attention since it has been realized that the reduction of dimensionality offers an alternative pathway to manipulate and control material properties, besides the more traditional control over chemical composition. The tailoring of nanoparticles properties requires excellent control over the formation and growth processes, which are, nevertheless, still incompletely understood in several systems. Due to their reduced dimensions, the early stages of formation and growth of nanoparticles are not amenable to conventional characterization methods, requiring the use of time-resolved and short-range-order sensitive techniques.

In this contribution, the formation of GeSi nanoparticles encapsulated in silica thin films has been followed in situ by time-resolved Dispersive X-ray Absorption Spectroscopy (DXAS). Our samples are thin films prepared by sputtering, consisting of a supersaturated mixture of silica doped with germanium and silicon atoms. The samples were annealed in situ, and time-resolved XAS measurements were performed in transmission mode at the LNLS DXAS beamline.

Our measurements enable identification of the thermal decomposition of the supersaturated mixture, the nucleation of small molten metallic GeSi clusters at the early initial stages of annealing and their subsequent growth during a two-hour annealing plateau at 1100°C. Upon cooling, the XANES spectra change continuously, presenting distinct spectral features that permit identification and quantification of the liquid-solid/metal-semiconductor transition. The linear combination fit analysis of XANES spectra yielded the molten and solid fractions as a function of temperature. Melting/solidification cycles of the nanoparticles were also investigated and are characterized by a significant temperature hysteresis of 300K around the bulk melting temperature.

We discuss our findings considering the influence of the nanoparticle size distribution, nanoscale phase diagram and possible kinetic pathways to melting and solidification of encapsulated nanoparticles.

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