

The Crystal Structure and Sintering of Coalescing Gold Nanoparticles and its Alloys

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Gold nanoparticles are used in a range of applications including electronics, catalysis, sensors, plasmonic biosensing and target-specific drug delivery as therapeutic agents. On the other hand, bimetallic nanoparticles exhibit superior or even novel properties than their parent materials. Physical properties (e.g. reactivity and ligand adsorption of gold nanorods) of such nanostructures depend on the particles crystal structure and surface facet orientation. Even though particle characteristics such as size distribution, primary particle and agglomerate size and morphology have been investigated extensively (Goudeli et al., 2015) little is known about particle crystallinity in atomistic scale. Experimental investigation of particles' nanocrystallinity with electron microscopy leads to incomplete characterization as it is based on the analysis of 2D projections of nanoparticles. However, Molecular Dynamics (MD) simulations can be used to provide physical insight in crystal structure changes and dynamics with atomistic detail (e.g.g Ag by Buesser and Pratsinis, 2015) and can complement the above experiments, especially for very small nanoparticles.

Here, MD simulations are used to systematically investigate the sintering mechanism and crystallinity dynamics of gold (Goudeli and Pratsinis, 2016) and its alloy nanoparticles with silver of various size and temperatures. The stage of crystallinity is theoretically investigated by the deviation of each gold atom from a perfect face cubic centered crystal. This deviation is quantified by the so-called bond order parameters (Steinhardt et al, 1983) which are measures of the local and extended orientational symmetries of the particle. The local degree of distortion of coalescing Au particles is described by the disorder variable (Kawasaki and Onuki, 2011). During adhesion, particles reveal increased degree of distortion compared to later stages of sintering, regardless of particle size and sintering temperature, while they form grains of different size and orientation. Large particles (e.g. 4 nm in diameter) form twin boundaries, consistent with experiments of Au nanoparticles coalescing by electron beam irradiation (Yuk et al., 2013).

Figure 1 shows snapshots of cross-sections of two unequally-sized coalescing Au nanoparticles at 800 K with diameter 3 and 4 nm at $t = 0, 0.01$ and 0.1 ns. To eliminate the effect of initial crystal structure on the orientation of the formed grain the bigger particle has amorphous structure (no "blue" atoms exist at this temperature), while the smaller one is crystalline. After adhesion, a spherical amorphous particle is formed rapidly ($t = 0.1$ ns), but at sufficiently long times it recrystallizes forming polycrystalline particle.

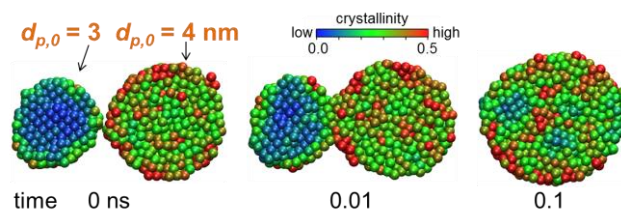


Figure 1: Cross-sections of Au nanoparticles of 3 and 4 nm in diameter coalescing at 800 K for $t = 0, 0.01$ and 0.1 ns.

Figure 2 shows the evolution of normalized surface area of two Au nanoparticles of equal (3-3 or 4-4 nm) and different diameters (3-4 nm) undergoing sintering or coalescence at 800 K. Initially ($t = 0$ ns), the particles have different crystallinity state (such as in Fig. 1) that affects the evolution of surface area reduction and therefore the sintering rate, especially for large particle sizes. So amorphous nanoparticles sinter faster compared to crystalline ones of the same size.

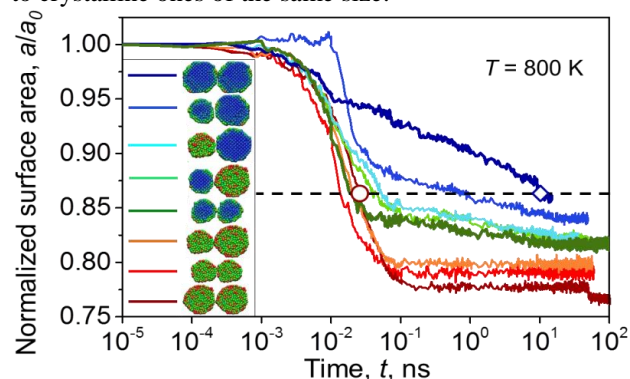


Figure 2: Evolution of the surface area fraction of Ag-Au nano-alloys with $d_{p,0} = 3$ nm during sintering at 600 (red line), 700 (green line) and 800 K (blue line).

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