Abstract

The main objective of this project is to understand the mechanisms of the rapid phase transitions in metal nanoparticles driven up to their melting by femtosecond laser irradiation. Ultrafast electron diffraction (UED) is used to map the structural dynamics of the laser-irradiated nanoparticles. Molecular dynamics (MD) simulations with a realistic description of the laser energy coupling and partitioning in the nanoparticles complements the UED studies and provide atomic-level insights into the laser-induced phase transitions. Since melting and diffusionless solid-solid phase transitions can occur on a picosecond time scale, ultrafast measurements are needed to probe transient states along the transition pathways. Ultrafast laser melting of well-characterized, size-selected metal nanoparticles (In, Pb, and Bi) will be studied. The low vapor pressure of these nanoparticles enables structural studies near their melting point without affecting their size. The experiments are conducted on nanoparticles fabricated in an ultrahigh vacuum on substrates with weak surface van der Waals forces. The experiments are designed to study the structural pathways through which the phase transitions occur and their dependence on heating rate; electronic excitation effects; electron-phonon coupling; limits of superheating and supercooling; and interface and substrate effects on melting and solid-state transitions. MD simulations include the effect of the thermal pressure from the excited electrons, which is parameterized based on the predictions of ab initio calculations and the UED results.

Major outcomes of this grant are:

● The structural response and melting of indium NPs embedded in the ultrathin aluminum film were studied for slow thermal heating at ~1 K/min and for ultrafast laser heating at ~10^{15} K/s using electron diffraction. For slow heating, the indium NPs lost their structural order ~19 K below the bulk melting point (T_m) of indium. For ultrafast laser heating using a femtosecond laser pulse, a subset of the NPs was superheated in the range of 1.15−1.40 T_m. Superheating refers to the solid structure remaining intact above T_m, which is a transient phenomenon rarely observed.

● The melting of bismuth NPs was studied by electron diffraction for slow thermal heating and for ultrafast laser heating. For slow heating the onset of melting of the Bi NPs was detected ~44 K below T_m of Bi. For ultrafast laser heating the melting behavior was almost similar to that for slow heating showing no evidence of superheating. This is explained by the equilibrium rounded shape of the NPs, which are bounded by surfaces that melt below or at T_m. The results show the importance of the surface in initiating melting.

● The lattice dynamics of bismuth nanoislands induced by ultrafast laser excitation was studied by electron diffraction. For 5-nanometer thick flat islands, the decay time of some diffraction peaks is close to the decay of the laser induced high-energy phonons (lattice vibrations). When the nanoisland thickness was increased to ~16 nm, the excitation energy was dissipated into low energy phonons leading to a longer decay time. Size reduction is shown to result in a longer phonon decay time due to phonon bottleneck.

● The vibration of atoms in bismuth NPs after femtosecond laser excitation and the resulting hot electrons were studied. A fundamental parameter that denotes the change in the dimensions of solid bismuth due to the heating of its conduction electrons was measured.