Gallium Nanoparticles Based Heterostructures for Full Color Thermally Stable Plasmonic and Photonic Platforms

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Gallium, Ga, a group-III metal, is of fundamental interest due to its polymorphism, unusual phase transition behaviors and optical properties. In recent years, substrate-supported Ga nanoparticle ensembles have been shown to be efficacious for plasmonics applications in the full NIR-VIS-UV spectral range [1]. Although bulk Ga is liquid under ambient conditions, new solid phases have been observed when Ga is confined at the nanoscale. Herein, we discuss structural, thermal and optical properties of Ga nanoparticles (Ga NPs) creating heterostructures with silicon, silicon carbide, graphene, and sapphire. We show that at the nanoscale the support plays a fundamental role in determining Ga nanoparticle phases. Specifically, we demonstrate the stable coexistence in sapphire/Ga NPs and SiC/Ga NPs of the Ga solid γ-phase core and a liquid shell. The driving forces for the nucleation of the γ- phase are a combination of surface energies, the Laplace pressure in the nanoparticles and its epitaxial relationship to the substrate. Amorphous, deformable substrates, like glass and graphene as well as chemically reactive substrates, such as Si, inhibit solid phase nucleation. Sapphire and SiC, which are rigid and non-reactive with Ga, creates a semi-coherent lattice nucleating a γ-phase solid core when the nanoparticles are above 50 nm. The solid-liquid phase coexistence is stable from 180K to 800K [2]. We present extensive correlations between structural, using HRTEM and TERS, and optical characterisations using ellipsometry and magneto-spectroscopy, from the infrared to visible and ultraviolet range, to describe phenomena arising from coupling wavelength-resolved light into the various heterostructures. Therefore, impacts of the stable solid-liquid phase coexistence and of superheating and supercooling in core-shell NPs on plasmonics are discussed.

The study is extended also to a variety of Ga-based bimetallic nanoparticles to provide a general framework for understanding how nanoscale confinement, metals interfacial and surface energies, and crystalline relationships to the support (graphene, semiconductor, or insulator) enable and stabilize the coexistence of unexpected phases providing criteria for choosing heterostructure type to control nanoparticle optical behavior and interfacial charge transfer.

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