

Light-Induced Switching between Structural Forms with Different Optical Properties in a Single Gallium Nanoparticulate

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ABSTRACT

In a single gallium nanoparticulate, self-assembled (from an atomic beam) in a nanoaperture at the tip of a tapered optical fiber, we have observed reversible light-induced reflectivity changes associated with a sequence of transformations between a number of structural forms with different optical properties, stimulated by optical excitation at nanowatt power levels. The ability to change the optical properties of a nanoparticulate using structural transformations provides a new mechanism for photonic functionality on the nanoscale.

In this letter we report experimental evidence indicating a sequence of transformations involving several different structural forms in a single gallium nanoparticulate. Our results are consistent with the fact that phase transitions in nanovolumes of material are achieved through *continuous* and *reversible* surface-driven coexistences of different forms^{1,2} and demonstrate that such transformations can be stimulated and controlled by extremely low power optical excitation. We have been able to induce and monitor transitions between phases that differ in free energy by only a fraction of a meV per atom and found that the nanoparticulate's response to optical excitation settles within a few tens of microseconds. We observed that a nanoparticulate probed with low intensity cw laser light can be overcooled by more than 90 K before it returns to the low-temperature phase. With such techniques as confocal microscopy, "optical tweezers", and scanning near-field imaging, it is now possible to detect photoluminescence and Raman spectra and perform sophisticated transient spectroscopic measurements on single nanoparticles^{3–6} – essentially removing the inhomogeneous broadening characteristic of nanoparticle film spectroscopy. In nanoparticles, phase transition temperatures and optical absorption cross-sections depend strongly on particle size, so inhomogeneous broadening in nanoparticle films masks the characteristic changes in optical properties that accompany a transition. Studying transitions in a single nanoparticulate, as opposed to a nanoparticle film,^{7,8} leads to advantages similar to the

resolution improvements achieved in the optical spectroscopy of single particles.

We studied a single nanoparticulate, grown from an atomic beam, at the tip of a tapered optical fiber with a nanoaperture at its end. This location allows for precise coupling of optical excitations to the nanoparticulate for the stimulation of phase transformations, and simultaneously for collection of a probe signal reflected by the nanoparticulate and used to monitor its state. We used a gold-coated silica single-mode fiber tapered to a 100 nm aperture (see inset to Figure 1a). It was attached to a liquid nitrogen cryostat coldfinger at 80 K inside a vacuum chamber evacuated to $\sim 10^{-6}$ mbar. To grow the nanoparticulate, a gallium atomic beam with a mass flux of $f \sim 0.3$ nm/min was directed at the end of the fiber for $t = 60$ min (Figure 1a).

The accumulation of gallium in the nanoaperture was indicated by a change in the reflectivity of the fiber tip during deposition. (The nanovolume of gallium deposited in the aperture may or may not form a single continuous body of material and its exact geometrical form may not be known, but in terms of its optical properties as compared to those of a film comprising some 10^4 particles,^{7,8} we believe that it may be considered as a "single" nanoparticulate). A cw diode laser operating at 1310 nm was used as a probe and another at 1550 nm, typically modulated at $\nu = 2.3$ kHz, was used as the pump. The reflected probe signal was monitored using an InGaAs photodetector. A wavelength-division multiplexer (WDM) and band-pass filter prevented reflected pump light from reaching the photodetector (see Figure 1b). Structural transformations were observed by monitoring pump-beam-

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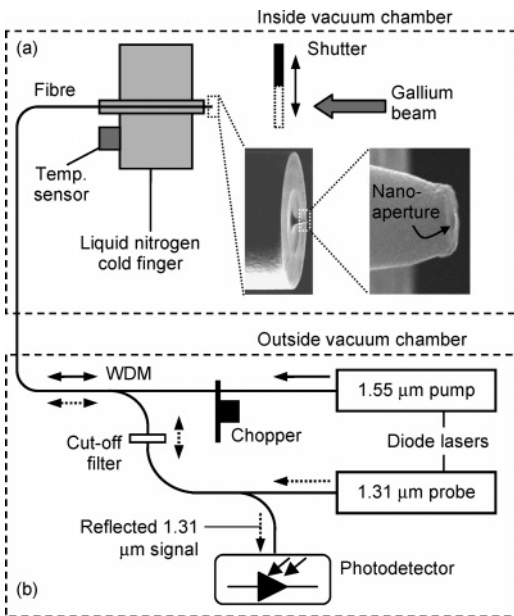


Figure 1. Experimental arrangement for studying light-induced phase transformations in a single gallium nanoparticle. (a) Components inside the UHV chamber, and SEM images of a tapered fiber tip. (b) Fiber-optic arrangement outside the chamber for reflective pump-probe measurements.

induced changes in the reflectivity of the nanoparticle as a function of temperature between 80 and 300 K (varied at a rate of ~ 2 K/min) using pump and probe powers of 30 and 20 nW respectively at the nanoaperture. Using an oscilloscope, we observed (in real time) that with each pump pulse the particulate's reflectivity changes (in response to the pulse) and recovers (after the pulse) in a reversible fashion, and that this continues for as long as pump pulses

are present. The magnitude of this modulation was recorded as a function of temperature using a lock-in detector referenced to the pump modulation frequency ν (thus, any reflectivity change induced by the cw probe beam is not recorded and may be ignored as the present study is concerned only with the existence of an effect rather than its absolute magnitude). With increasing temperature, we observe several narrow peaks in the induced-reflectivity-change signal at temperatures between 200 and 250 K, as shown in Figure 2a (no features are observed outside the range shown). The positive and negative peaks correspond to pump-induced increases and decreases in nanoparticle reflectivity, respectively. When the heating cycle is repeated, the peaks appear at the same positions, though their relative heights can vary.

Substantial changes in the optical properties of the nanoparticle may occur when it undergoes a transition between two phases or geometrical forms. Such changes are typically much more dramatic than temperature-dependent variations occurring within a single phase and the peaks observed in the pump-induced reflectivity change signal are characteristic of such transitions. Indeed, this type of asymmetric peaked optical response has been observed previously at gallium/dielectric interfaces⁹ and in gallium nanoparticle films,^{7,8} though these experiments did not resolve the fine detail of sequential transitions through several structural forms. The differences between the electronic density of states of gallium's various phases¹⁰ lead to pronounced differences between their optical dielectric coefficients. A phase change in a gallium nanoparticle thus affects its optical absorption cross-section,¹¹ and in the present case will change the reflectivity of the nanoaperture. One may thus detect phase transformations in a nanopar-

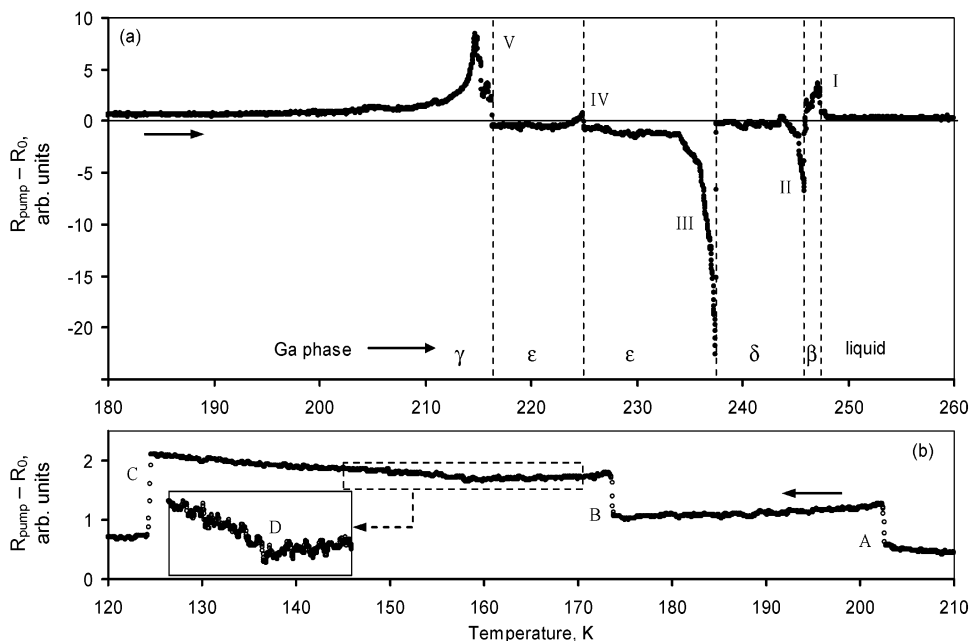


Figure 2. Magnitude ($R_{\text{pump}} - R_0$) of pump-induced reflectivity change for a single gallium nanoparticle as a function of (a) increasing and (b) decreasing temperature. (R_{pump} = reflectivity with pump illumination, R_0 = reflectivity with no pump present, cw probe power at aperture ~ 20 nW, pump peak power ~ 30 nW, plotted temp. = measured temp.) Note that the recorded temperature of the coldfinger is somewhat lower than the actual temperature of the gallium nanoparticle due to localized laser heating.

ticulate by monitoring its optical properties. A peculiarity of confined solids is that their phase transformations take the form of a dynamic phase coexistence extending across a certain temperature interval (as opposed to an abrupt transition at a specific temperature),^{1,2} with the surface of a nanostructure (where atoms have fewer nearest neighbors than internal atoms) acting as a boundary at which transformations start.^{12,13} At temperatures within or just below the transitional range, the phase equilibrium can be influenced by external excitations.¹⁴ In the current experiment, absorption of pump light leads to a periodic excitation of gallium's electronic structure and a periodic modulation of its temperature (both at the pump modulation frequency ν), which simultaneously affect the phase equilibrium in, and therefore the reflectivity of the particulate. To detail this process further, we may consider a nanoparticle (at a fixed temperature) consisting of a core in one phase covered by a thin shell of a different phase.² The thickness of the shell layer will increase with the level of external excitation and the optical properties of the particle will change continuously from those of the core phase to those of the surface phase. Depending on the level of excitation, this process may or may not be reversible: if the level is reduced *before* the transformation to the new phase is complete, i.e., while a nucleus of the core phase is still present, the transformation will be reversed, the skin layer will shrink to an appropriate equilibrium position and the reflectivity will return to its original level. However, when the core is fully consumed by the surface phase the particle becomes stable against a return to the core phase because this would require the creation of a nucleation center. At this point the applied excitation abruptly ceases to induce any significant change in the particle's optical properties, until the temperature approaches the next phase transition point.

The pump-induced reflectivity change signal observed during the cooling of the nanoparticulate (see Figure 2b) is very different from that observed during heating. It is somewhat smaller, always positive and shows abrupt step-changes (instead of sharp peaks) in the signal at temperatures different from those of any of the peaks. The peak/step temperature differences and the continuously low signal level are results of overcooling: with decreasing temperature the nanoparticulate remains in a given phase until its temperature is somewhat lower than the equilibrium transition temperature, and in these conditions pump excitation produces very little signal. When the overcooled particulate transforms abruptly into a lower energy form, the pump-induced probe modulation remains small because this change happens at a temperature far below the increasing-temperature signal peak for that phase. If the first/last peaks/steps (i.e., I and A, V and C) are associated with transitions into/out of the highest and lowest temperature phases, this implies overcooling of between ~ 45 and ~ 90 K. While five peaks are identified Figure 2a, there are only four features in the cooling part of the temperature cycle (Figure 2b): three distinct steps (A, B, and C) and a gradient change D (which is more clearly seen inset on an enlarged y-axis). This may be because features are harder to resolve at the reduced signal levels

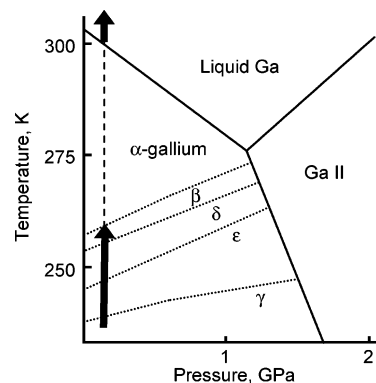


Figure 3. Phase diagram for (bulk) gallium after Bosio¹⁷ showing the sequence of phase transitions expected in a gallium nanoparticle undergoing adiabatic heating from 180 to 300 K. (The α phase is not found in nanostructures, so β transforms directly to liquid.)

recorded during cooling (e.g., with heating, peaks I and II are very closely spaced – their cooling counterparts may overlap), or perhaps because the sequence of transitions undertaken by the particulate with decreasing temperature is not simply the reverse of the increasing temperature sequence. Such “nonreciprocity” in the sequence may easily result from the fact that the transition mechanisms for heating and cooling are very different: with increasing temperature transitions are continuous and surface-driven, but with decreasing temperature they occur more abruptly following the formation of a nucleation center within the particle. The fact that the pump-induced reflectivity change is always positive with decreasing temperature (while switching between positive and negative with increasing temperature) may result from such nonreciprocity or may be an indication that there are two components to the excitation of the nanoparticulate: one that gives rise to a small positive “background” signal with a magnitude that depends on the phase of the metal but not on temperature, and another that produces a larger positive/negative component in the vicinity of the transition points.

Using gallium's phase diagram (Figure 3) and the available information on the relative stability of its crystalline forms, we can attempt to ascribe transitions to the peaks in Figure 2a. We may reasonably assume that peak I is associated with a transition from a solid state to the liquid. An X-ray diffraction study of gallium nanoparticles found that α -gallium, the stable solid state of bulk gallium, is completely absent in small particles¹⁵ so it then follows from Defrain's analysis of the free energies of gallium's metastable phases¹⁶ that the only possible sequence of phase transformations in gallium nanostructures is $\gamma \rightarrow \epsilon \rightarrow \delta \rightarrow \beta \rightarrow$ liquid ($\gamma, \epsilon, \delta, \beta$, all crystalline) – a progression that is in agreement with the established phase diagram for gallium shown in Figure 3. (The pressure inside a particle may be estimated using the Laplace–Young equation $P = (4\sigma/3)(2/d + 1/h)$, where σ is the surface tension ($\sim 0.7 \text{ J}\cdot\text{m}^{-2}$ for liquid gallium), $d = 100 \text{ nm}$ is the particle diameter, and $h \sim ft = 18 \text{ nm}$ is its height, giving $P \sim 0.1 \text{ GPa}$.)

Thus, according to this sequence, peak I in Figure 2a (at $T_1 = 248 \text{ K}$) would correspond to a transition from monoclinic β -gallium to the melt. (The bulk melting point of

β -gallium is 257 K (ref 16), but transition temperatures are suppressed in nanoparticles.¹⁸ If we assume, in accordance with the above sequence and with its strong presence in gallium nanoparticle X-ray spectra,¹⁵ that the γ phase is the “ground state” (lowest temperature) phase, then we are left with three phase transitions ($\gamma \rightarrow \epsilon \rightarrow \delta \rightarrow \beta$) and four peaks (II, III, IV, and V), suggesting that one of the peaks is associated with something other than a phase change – a shape change for example. Peak IV differs from the others in a number of ways and is therefore perhaps the most likely candidate: aside from being the smallest peak and the only one that crosses the zero level, there is a change in the retardation between pump and probe modulations associated with it that is at least an order of magnitude larger than for any other peak. So, if peak IV relates to a shape change, that leaves peak V as the γ - to ϵ -gallium transition, peak III as ϵ -to- δ , and peak II as δ -to- β . In the absence of any data on the dielectric constants of gallium’s metastable crystalline phases, no information on the phase transition sequence can be derived from the signs or relative magnitudes of the peaks in Figure 2a.

The light-induced reflectivity changes are observed at very low levels of optical excitation. Such levels can be used because the differences ΔG between the free energies of some of the metastable phases involved are very small: for example, $\Delta G_{\delta-\beta} = 0.3$ meV/atom, $\Delta G_{\gamma-\delta} = 1.7$ meV/atom.¹⁶ Thus, the absorption of a “pump” quantum with an energy of 0.8 eV should be sufficient to convert about 2700 atoms from the δ phase to the β phase, and about 500 atoms from the γ phase to the δ phase. The light-induced transitions are likely to be driven primarily by thermal excitation (i.e., laser-induced heating) but there may also be a contribution from a temperature-independent, nonthermal mechanism where the phase change is caused by band-structure collapse and lattice instability resulting from electronic excitation.¹⁴

To summarize, we have for the first time investigated reversible light-induced transformations in a single gallium nanoparticulate and observed a sequence of reversible transitions between different structural forms. The low energy requirements for such optically induced phase transitions, and the phase stability on overcooling suggest that such

single nanoparticles could provide a means of creating key logical and bistable memory elements for nanophotonic devices operating at extremely low power levels, in which for example, they may be placed in optical nanoapertures, incorporated into a chain waveguides,¹⁹ or used as scattering centers in photonic-band gap or plasmon-polariton waveguides.²⁰

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