Optical nonlinearity and light-induced structural transformations in gallium nanoparticles

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Abstract: We report that gallium nanoparticles, prepared by light-assisted self-assembly, show a nonlinear response to low-power optical excitation. Reversible reflectivity changes of several percent are induced as the result of light-induced structural transformations in the metal.

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Gallium, confined at an interface with silica, has been found to respond dramatically to low power optical excitation when held at temperatures close to its melting point (29.8°C). Intensities of just a few kW/cm^2 can reversibly modulate the intensity (by up to 40%) and phase (by as much as several degrees) of reflected light as the result of a light-induced structural transition occurring in a layer of gallium ~30 nm thick [1].

Here, we report that this concept - of achieving a nonlinearity via a light-induced transformation in a confined solid at a temperature close to a phase transition temperature (see fig. 1) - can also be applied to gallium nanoparticles. We believe that inducing such a transition in gallium (an exceptionally polymorphic metal) in the nanoparticle geometry may be a means of enabling the development of nanoscale photonic devices [2].

We studied the optical properties of gallium nanoparticles prepared using the light-assisted self-assembly technique [3], wherein gallium is deposited on the cleaved end of a single-mode optical fibre, held at ~100K under high vacuum whilst pulses from an infrared diode laser are sent through the fibre from the other end. Nanoparticles, typically 80 nm in diameter, with a relatively narrow size distribution (± 22 nm) were thus formed on the fibre's core.

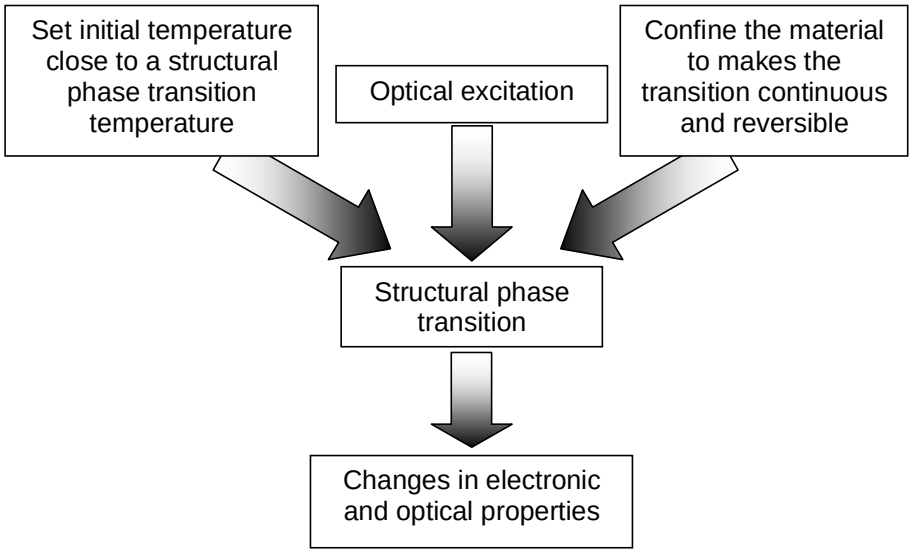

Fig. 1. Scheme for achieving a large optical nonlinearty via a light-induced structural phase transition in a confined solid at a temperature close to a phase transition temperature.

The nanoparticles' optical response was monitored using a reflective pump-probe technique, both during deposition, and afterwards at temperatures between 100 and 300K (fig. 2), without breaking the vacuum.

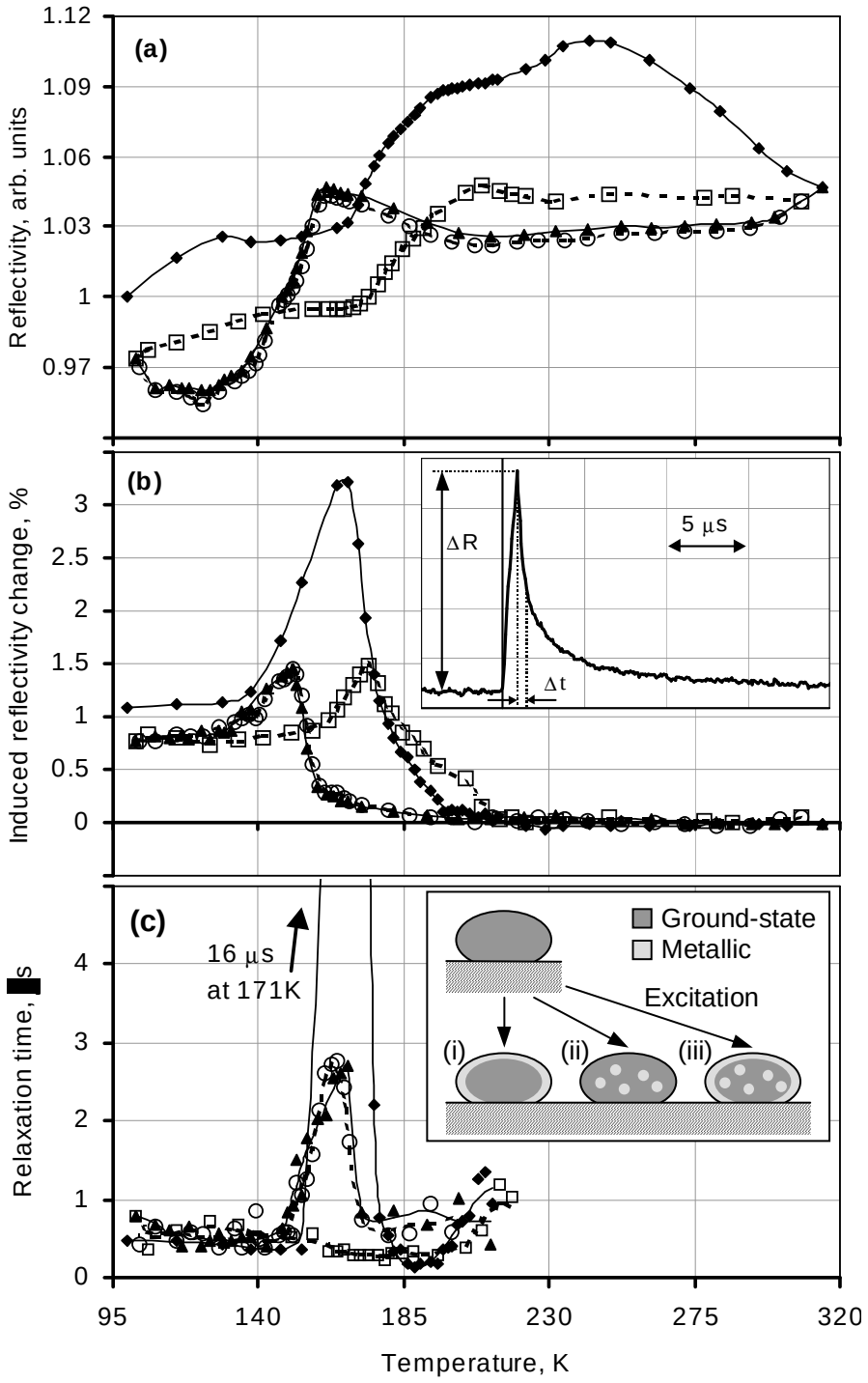

Fig. 2. Results of transient pump-probe experiments on the optical nonlinearity of gallium nanoparticles manufactured on the end of an optical fiber using the light-assisted self-assembly technique. Temperature dependencies of (a) reflectivity, (b) induced reflectivity change, (c) relaxation time. Four sets of experimental data are shown: —♦— increasing temperature for the first time after deposition; —▲— decreasing temperature; ---□--- increasing temperature again; ---○--- decreasing temperature again. The inset to (b) shows a typical reflectivity response curve from which the magnitude of the induced change (ΔR) and the relaxation time (Δt) are obtained. The inset to (c) illustrates how the metallization of a particle may occur by formation of: (i) a metallic shell; (ii) metallic inclusions; or (iii) both.

The nanoparticles' reflectivity, the light-induced reflectivity change and its relaxation time all show hysteretic behavior with temperature and in this respect their response is reminiscent of that of bulk α-gallium at an interface with silica [1]. However, there are significant differences between the nanoparticle and bulk behaviors. The phase transition temperatures and both the width and depth of the reflectivity hysteresis are different from those of planar films. Furthermore, nanoparticles show a strong response at temperatures far below the transition temperature whilst the nonlinearity of bulk films vanishes under similar circumstances. These observations indicate that the nanoparticles do not exist in the α phase at low temperatures, but in one (or a mixture) of gallium's various other solid phases.

The optical nonlinearity of bulk gallium/silica interfaces is the result of light-induced surface 'metallization' - a light-induced transition from the relatively non-metallic solid α phase to a more metallic phase, like the liquid [1]. The evidence suggests that a similar process occurs in nanoparticles where optical excitation initiates transitions between gallium's various solid phases and between these solid phases and the liquid phase. This metallization can take place either on the surface of the nanoparticles, leading to the formation of a metallic skin layer, in the body of the particle, creating metallic inclusions, or both (see inset to fig. 2c). Analysis of the induced reflectivity change and relaxation time data suggests that both thermal and non-thermal mechanisms contribute to the effect.

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