Structural phase transition as the mechanism of an optical nonlinearity in a nanoparticle film

V A Fedotov, K F MacDonald and N I Zheludev

School of Physics and Astronomy, University of Southampton, Highfield, Southampton SO16 7DH, UK

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Abstract
Optical control of phase coexistence, previously used as a mechanism for achieving a nonlinearity at planar gallium/glass interfaces, can be exploited as a nonlinear response mechanism in a metallic nanoparticle film. Experimental measurements of the reflective and transmissive nonlinear response of a gallium nanoparticle film, manufactured on the tip of an optical fibre using the light-assisted self-assembly technique, are shown to be consistent with an effective medium theory for the optical properties of a layer of closely packed nanoshells comprising a core and surface layer in two different structural phases of the metal.

Keywords: aggregated thin films, nanoparticles, optical properties, structural transitions, phase coexistence

1. Introduction
Continuing advances in the fields of nanofabrication and nano-optics are making nanoscale photonic devices a realistic possibility, but the full realization of their potential will require ‘active’ components, in which one optical signal is controlled (i.e. has either its intensity or phase is changed substantially) by another in a very thin, nanoscale layer of nonlinear material at very low power levels. This type of control is achieved by using a control light wave to change the optical characteristics of a medium as seen by a signal light wave. In conventional nonlinear materials such a response is achieved by exciting their electronic substructure (for example, to saturate their absorption), and is ‘built up’ into a strong induced retardation or intensity change effect over a long interaction length or inside an optical resonator. However, a different approach is required to obtain a large nonlinear response on reflection from or transmission through a nanoscale layer of material [1].

It has previously been reported that optically induced phase transitions in nanoscale layers of gallium at an interface with glass can be used to achieve a large reflective nonlinearity [2, 3]. More recently, a similar response to both optical and electron beam excitation has been observed in monolayers of gallium nanoparticles [4, 5]. In this paper we report that the reflective and transmissive nonlinear responses of a gallium nanoparticle film are consistent with predictions based on an effective medium theory for the optical properties of a layer of closely packed nanoparticles [6].

The response mechanism relies on the fact that certain materials (such as gallium) can exist in two or more structural phases with very different optical properties. If light can be used to induce a reversible transformation between two of these phases, then that can constitute an optical nonlinearity. The particulate nature of the film is crucial to the reversibility of the process: in bulk materials phase transitions are usually first order and often hysteretic, so in the case of an induced transition, for example, an abrupt change in the crystalline structure may be achieved at a very specific level of optical excitation but the original phase will not be recovered immediately if the excitation is withdrawn. In nanoparticles however, phase transitions occur through a surface-driven dynamic coexistence of structural forms [7], i.e. the new phase appears first at the surface and grows inwards with increasing temperature. Once the core of the particle is completely converted to the new phase, the nanoparticle becomes stable against a return to the old phase because that would require the creation of a nucleation centre. However, in the range where both phases are present, the balance between them can be reversibly controlled by external optical, or indeed electron beam, excitation [4, 5].
The properties of gallium’s various phases range from those of the almost semiconductor-like, partially covalent solid α phase to those of the almost ideally metallic liquid [8, 9]. While electronically very different, many of gallium’s phases are energetically very close to each other; for example the δ and β crystalline phases (normally metastable, but preferred to the α phase in the confined geometry of a nanoparticle [10]) are only separated by $3 \times 10^{-4}$ eV/atom [11]. This means that the energy requirements for switching are very low. Consider, for example, a 50 nm particle: the maximum nonlinearity achievable by electronic excitation will be obtained if every atom is excited, and using 1 eV photons this would require a total energy of around 60 pJ. To completely transform the particle from the δ to the β phase on the other hand only requires about 20 fJ—three orders of magnitude less.

Gallium’s unique morphology also provides the added advantage that optical excitation can induce structural transformations both thermally (i.e. via a laser-induced temperature increase) and non-thermally (by direct excitation and rupture of the covalent bonds found in some of its crystalline structures) [2].

In the following we summarize a theoretical model recently developed to describe the optical properties of a closely packed film of non-spherical, two-phase nanoparticles [6], and compare the predictions of this theory (which will be referred to as the ‘closely packed nanoparticle film’ or CPNF model) with experimental measurements of the reflective and transmissive nonlinear response of a gallium nanoparticle film.

2. Overview of the CPNF model

The CPNF model is a development of Yamaguchi, Yoshida and Kinbara’s effective medium theory (which we will call the YYK model) for calculating the dielectric constants of a discontinuous metal film on a transparent substrate [12]. The YYK model assumes the film to be a monolayer of small particles distributed on the points of a square lattice and seeks to determine the local electric field at a particle by considering electrostatic dipole interactions between the particle and its mirror image in the substrate, the surrounding particles and the images of the surrounding particles. However, its use of a point dipole approximation to describe the interaction between particles and their mirror images limits the applicability of the YYK model to spherical (or nearly spherical) particles: when a sphere is replaced with a spheroid the point dipole approximation only works at distances that are large compared to the size of the spheroid. As a spheroidal particle is flattened (increasing the diameter:height ratio) the distance $h$ between the centre of the particle and that of its mirror image decreases. In the YYK model this implies a rapid increase in the additional field produced by the image ($\propto h^{-3}$), leading to a discontinuity for discus-like particles. The model is also limited to low surface density films by the assumption (made to simplify the consideration of field contributions from surrounding particles and their images) that particle separation is much larger than particle size.

The CPNF model [6] overcomes these problems by using the exact expression for the electric field of an oblate spheroid to account for the interaction between a given particle and its

Figure 1. The calculated change in the reflectivity ($R$) and transmission ($T$) of a solid-core, liquid-shell gallium nanoparticle film on a silica substrate as a function of shell thickness. The inset is a plot of normalized shell thickness ($t$) against normalized shell volume ($\alpha$). A 25 nm shell thickness corresponds to full conversion of the particle to the liquid phase ($t = \text{particle radius}$) and therefore to the limit of reversibility.

24 nearest neighbours, their mirror images in the substrate and its own image. The effect due to the rest of the monolayer/substrate system is calculated using the dipole field approximation as in the YYK model.

To make it applicable to optically excited gallium nanoparticle films, the CPNF model was designed to cover the case of binary nanoshells consisting of a core and a single shell layer with different dielectric properties (the YYK model considers only homogeneous particles). This was achieved by introducing an effective dielectric constant for a homogeneous particle with the same polarizability as the binary nanoshell.

3. Reflectivity and transmission of a closely packed gallium nanoparticle film

Reference [6] reported on the use of the CPNF model to calculate the optical properties of a gallium binary nanoshell film at 1310 nm: the particles were considered to be spheres with a radius of 25 nm distributed on the surface of a silica substrate with a mean separation of 100 nm (an approximation to the sort of film typically produced by light-assisted self-assembly of gallium nanoparticles [13]). The solid core of the particles was assumed to have optical properties intermediate between those of the liquid and α phases, and the shell was taken to be in the liquid state. Figure 1 shows, for the same kind of film but at a wavelength of 1550 nm, the calculated change in the reflectivity and transmission of the film caused by the presence of the liquid surface layer on the particles (relative to the properties of a film of completely solid particles).

4. Experimental measurements

The results of an experimental study of gallium nanoparticles have subsequently been found to compare very well with the curves shown in figure 1: a film of ~50 nm nanoparticles was prepared on the cleaved end of a single-mode optical fibre using the light-assisted self-assembly technique [13]. The reflectivity and transmission of this layer were probed using a
and pump power, by using digital lock-in amplifiers to detect
pump power (see the inset to figure 1).

induced surface layer will be almost directly proportional to
pump power. The similarity between these data and the
reflective and transmissive nonlinear response as functions of
phase. The signal falls as more and more particles complete
formation of an increasingly thick surface layer of the new
phase. The signals rise to a peak as the transition temperature is
approached because the pump excitation is able to induce the
optical properties of a closely packed, two-phase, core–shell
nanoparticle film. The observed response is the result of a
reversible, light-induced, surface-driven structural transition
in the nanoparticles.

References

Figure 2. Temperature dependences of the pump-induced changes in reflection and transmission (normalized against the peak signal) in the vicinity of a phase transition for a gallium nanoparticle film on the tip of an optical fibre. cw probe power = 0.48 mW, peak pump power = 2.8 mW.

5. Conclusions

Experimental measurements of the reflective and transmissive nonlinear response of a gallium nanoparticle film on the tip of an optical fibre are found to be consistent with calculations based on effective medium theory developed to describe the optical properties of a closely packed, two-phase, core–shell nanoparticle film. The observed response is the result of a reversible, light-induced, surface-driven structural transition in the nanoparticles.

Figure 3. The peak pump-induced change in (a) reflection and (b) transmission of a gallium nanoparticle film as a function of the pump power.