Towards femto-Joule nanoparticle phase-change optical memory

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Phase-change functionality in gallium nanoparticles offers an innovative conceptual basis for the development of high density, low energy, non-volatile optical memories.

Phase-change materials, wherein structural forms with differing electronic and/or optical properties are used to encode digital information or control signal propagation, have recently attracted great interest due to their potential to address growing challenges of size and power consumption in data storage and memory applications, and to enable innovative photonic and plasmonic functionalities [1-4]. Their functionality may enable the shrinking of optical switching and memory devices all the way down to the nanoscale, thereby helping to achieve the ultimate goal of nanophotonics - that is, to create devices smaller than or comparable in size to the wavelength of the signals they handle (a relationship of proportions that is easily achieved in most electronic circuits).

Several problems hinder the nanoscale miniaturization of photonic circuits and data storage technologies: the need to guide optical signals in narrow and sharply bending waveguides; and the need to modulate these signals and encode information in very small active regions. The use of surface-plasmon-polariton waves as information carriers may address the guiding issue [5, 6] but the optical modulation and information storage problems seems to be much more difficult to tackle. In essence, both require very strong changes in the absorption or refraction of nanoscale volumes of material in response to external control excitations, be they temporary changes to effect signal modulation or more permanent bi- or multi-stable changes in the logic state of memory elements. Such large changes in absorption and refraction are only possible in media where there is something substantial to change, and in this respect metals fit the bill.

Large changes in the optical properties of metals can only be achieved through a phase change, and some metals, notably gallium, can exist in several phases with markedly different optical properties. Indeed, 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 [7, 8]. 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 [9]) are only separated by 3×10^{-4} eV/atom [10]. This is of considerable benefit for nanophotonics applications because it means that the energy requirements for switching are very low. Consider for example a 50 nm particle: to completely transform the particle from the δ to the β phase requires only ~20 fJ of energy – around three orders of magnitude less than the energy required to achieve a nonlinearity through the electronic excitation of every atom (assuming one 1 eV photon per atom).

Of crucial importance to the optical memory and switching functionality of metallic nanoparticles is the nature of the phase transition process itself (Fig. 1). Transitions in bulk materials are characterized by a discontinuous change in the state of the body, a sudden (irreversible) rearrangement of the crystalline lattice at a specific temperature. In nanoparticles

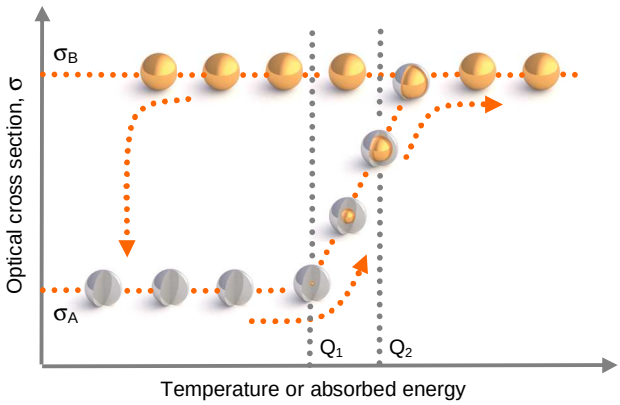

Fig. 1: Phase-change optical functionality in a nanoparticle. Dependence of optical cross-section on absorbed energy for a nanoparticle undergoing a phase transition. At low temperature particle is in phase A. Reversible changes in cross-section occur in the excitation range between Q_1 and Q_2 during the continuous transition to phase B (indicated by the mixed-phase shell structures). Excitation levels above Q_2 lead to a memory effect: once the transformation to phase B is complete, the particle remains in this phase even if the excitation is withdrawn. A transition back to phase A occurs abruptly only after overcooling. (After Ref. [3])

however, transitions from lower to higher energy phases proceed through a surface-driven dynamic coexistence of forms across a size-dependent range of temperatures [11-13]. Where, as in gallium, the two forms involved have different dielectric coefficients, this gives rise to a continuous change in optical properties. With decreasing temperature, the reverse phase transition occurs only after substantial overcooling. The resulting hysteresis in their optical properties forms the basis of gallium nanoparticles' memory functionality.

We report here on phase-change memory functionality in films of gallium nanoparticles and in single particles, demonstrating that data can be written to bi- and multi-stable memory elements both optically and via electron-beam excitation, and that logic states can be identified through measurements of the particles' reflectivity and cathodoluminescent (CL) emission. Together these results offer an innovative conceptual basis for the development of high density phase-change memories.

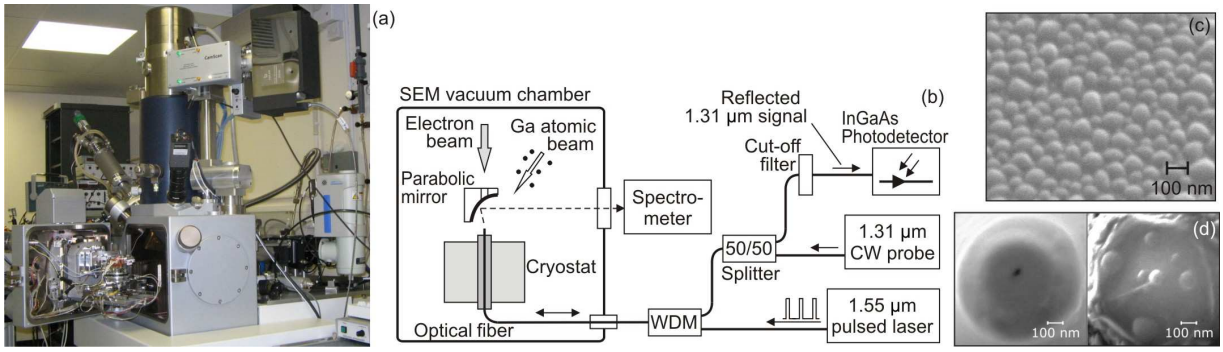

Fig. 2: (a and b) Integrated system, based on a modified scanning electron microscope, for growth, imaging, cathodoluminescence study, and optical interrogation of gallium nanoparticle films; (c) Secondary electron image of part of a gallium nanoparticle film grown on the core area of a single-mode fibre end face; (d) Scanning electron microscope images of the nano-aperture at the tip of a near-field microscopy probe before (left) and after (right) gallium deposition. A single nanoparticle is formed in the aperture.

In the experiments reported here, nanoparticle growth, imaging, optical measurements, and CL studies were all performed under high vacuum inside a scanning electron microscope (SEM) equipped with an effusion cell for gallium deposition and a nitrogen-cooled cryostat to control sample temperature in the 100–305 K range (Fig.'s 2a and b).

Monolayer films of gallium nanoparticles were grown on the end faces of cleaved single-mode fibres using the light-assisted self-assembly technique [14]. With the fibre tip held at a temperature of 100 K, gallium was deposited at 0.3 nm/min for 50 min (giving a mass thickness of 15 nm) while 1 μs pulses from a 1550 nm diode laser (19 mW, 1 kHz repetition rate) were launched into the fibre from outside the SEM chamber. This process produces a monolayer of particles with a mean diameter of 60 nm on the optical core area of the fibre end face (Fig. 2c).

Single, isolated nanoparticles were formed by depositing gallium, typically for 30 min. at a rate of 0.3 nm/min., onto near-field optical microscopy probes - tapered, gold-coated fibres with nano-apertures at their tips. Here, they are ideally located for optical interrogation and excitation via the fibre (Fig. 2d).

The integrated experimental system allows for particles to be imaged in situ by the SEM and for their cathodoluminescence to be probed, with the emitted light being directed out of the chamber by a bespoke parabolic mirror to a spectrum analyzer comprising a Horiba Jobin–Yvon CP140 spectrograph and a liquid nitrogen-cooled CCD array for wavelength-sensitive detection in the 400-1000 nm range. Samples' reflective optical properties can also be studied via the fibre, and phase transitions can be stimulated in the particles by both optical and electron beam excitations.

Bistable memory functionality, engaging transformations between the solid (logic '0') and liquid (logic '1') states, has been demonstrated in films of nanoparticles on cleaved fibre tips (Fig. 3). In this case, the state of the nanoparticles can be read via measurements of film reflectivity using a low power optical probe beam, measurements of nonlinear reflective response to pulsed optical excitation (this technique discriminates strongly between the phases because their responses have opposite signs), or measurements of cathodoluminescent emission in response to low energy electron beam excitation (Fig. 3b, the advantage here being that an electron beam can probe small regions within the particle film).

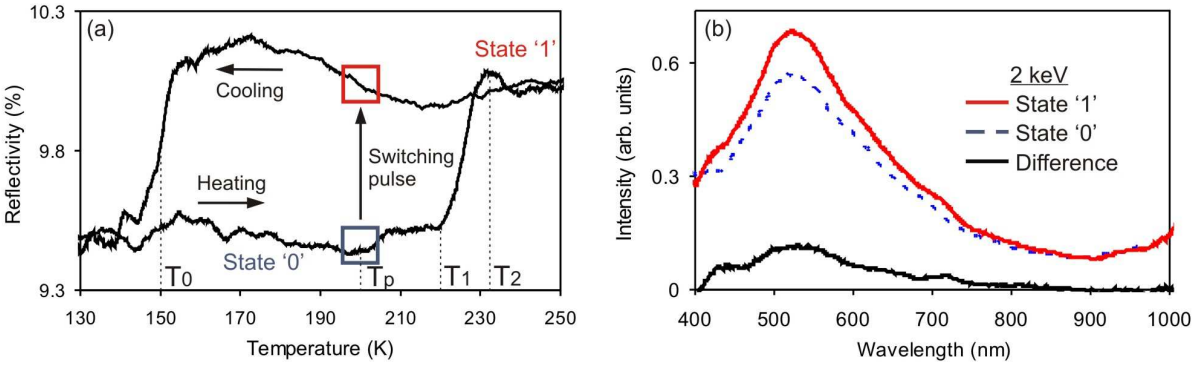

Fig. 3: (a) Reflectivity hysteresis of a gallium nanoparticle film on a fibre end face (measured via the fiber) as function of cryostat temperature. Single optical or electron beam pulses can be used to induce abrupt phase (memory state) switching at T_p = 200 K ($T_0 < T_p < T_1$); (b) Cthodoluminescence spectra obtained at T_p before and after excitation-induced switching between the two phase states, together with the difference spectrum.

At a fixed temperature (T_p in Fig. 3a) within the hysteresis loop, single 1 μs, 1550 nm optical pulses with a fluence of >0.3 fJ/nm^2 can irreversibly switch the nanoparticles from the low reflectivity solid phase ('0') into the high reflectivity liquid phase ('1'), thus providing memory 'write' functionality. Single electron beam pulses with a fluence of >35 fJ/nm^2 can also be used to perform the write function, with the advantage that they can selectively address small areas within a large film of particles. The 'erase' function is achieved by cooling the particles down to below their solidification point (T_0 in Fig. 3a), either by cooling the sample as a whole (non-volatile mode) or, in the case where the bistable operating temperature is maintained by the local heating effect of continuous probe laser illumination, simply by switching the laser off (volatile mode).

Single, isolated nanoparticles, free from the inhomogeneous broadening effects of the size distribution found in a particle film, show more complex phase change behaviour. Here, transitions between different crystalline solid states, and ultimately between solid and liquid, are observed. This multi-stable system has facilitated the first demonstration of a quaternary logic resonatorless optical memory element. Single pulse energies of just a few pJ are required to encode information in the phase state of the particle, and read-out is achieved through reflective optical pump-probe measurements.

To summarize, particulate phase-change memory elements offer the possibility of very high data storage densities. For example, if individual binary (two-phase) elements within a close-packed array of 60 nm particles could be addressed, as they might with a steerable tightly focused electron beam, a storage density of ~0.2 Tbit/ in.^{2} could be achieved. Smaller particles and higher-base logical elements would obviously further increase this value (for comparison, today's 'BluRay' disks offer an optical storage density of ~ 0.015 Tbit/ in.^{2}).

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