REVIEW ARTICLE

Single nanoparticle as photonic switch and optical memory element*

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Abstract

We review the concept of using nanoparticles undergoing light-induced transformations between structural phases with different optical properties as key components of optical gate and memory elements, with the potential to operate on picosecond timescales at femtojoule energy levels.

Keywords: nanophotonics, nanoparticle, nonlinear optics, optical memory, optical switching

1. Introduction: some 80 years ago

Nanoscale nonlinear optical devices will aim to meet the demand for controlling light with light and plasmonic signals in highly integrated circuits using very thin nanoscale-size quantities of material, or possibly just single nanoparticles. They will be used to switch and condition signals between elements of three-dimensional, highly integrated photonic-band-gap optical signal routers, two-dimensional plasmonic waveguides, or will perhaps be combined with two- or three-dimensional arrays of miniature semiconductor lasers in order to control their output. Controlling light by light in a nanoscale is a huge challenge. When we say the light signal is controlled, we mean that either its intensity or phase is changed substantially by the presence of a control signal. In an all-optical device this is achieved by using a control light-wave to change the optical characteristics of the medium as seen by a signal light-wave.

In 1926, Wawilow and Lewschin of Moscow State University in Russia set up the first experiment aiming to detect a light-induced change in a material's optical properties [1]. Using a spark light source they found that the transmission of a uranium-doped glass plate depended on the intensity of light (see figure 1). Saturation of the absorption of the doped glass was the reason for the effect. Wawilow and Lewschin clearly explained their results as a violation of the absorption law. They suggested that the absorption coefficient must
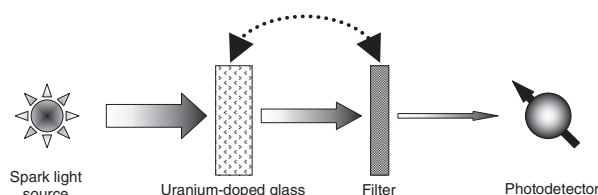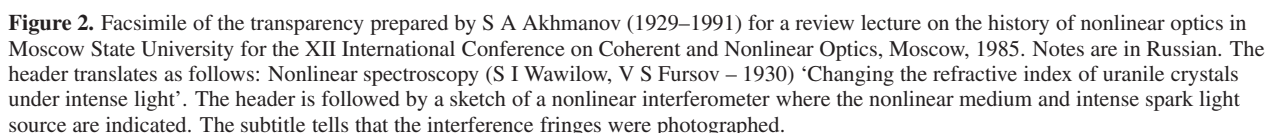

Figure 1. The first nonlinear optical experiment (Wawilow and Lewshin, 1926). The overall intensity of light which consecutively passes thorough the partially transparent filter and uranium-doped glass depends on their order. On interchanging the positions of the uranium glass and the filter, as indicated by the dotted double ended arrow, the light intensity received by the photodetector changes. This indicates that absorption in the glass is light-sensitive, i.e. is a function of the light's intensity.

be treated as intensity dependent. This was the first ever paper on nonlinear optics. With a reference to his successful experiment in 1926, Wawilow wrote in 1950: '*Nonlinearities in dissipative media should not only be observable with respect to absorption. This absorption is linked to dispersion, therefore, generally speaking, the speed of light in the medium will also depend on the light's power. For the same reason, generally, a dependence on the light's power, i.e. a violation of the superposition principle, should be seen in other properties of medium, such as birefringence, dichroism, polarization rotatory power, etc*' [2]. He thought, however, that the light intensities needed to see such violations of the superposition principle could only be found inside stars. In a story once told by Professor Sergei Akhmanov, a towering person in the

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Figure 2. Facsimile of the transparency prepared by S A Akhmanov (1929–1991) for a review lecture on the history of nonlinear optics in Moscow State University for the XII International Conference on Coherent and Nonlinear Optics, Moscow, 1985. Notes are in Russian. The header translates as follows: Nonlinear spectroscopy (S I Wawilow, V S Fursov – 1930) 'Changing the refractive index of uranile crystals under intense light'. The header is followed by a sketch of a nonlinear interferometer where the nonlinear medium and intense spark light source are indicated. The subtitle tells that the interference fringes were photographed.

history of nonlinear optics, Vasilii Fursov, once Wawilow's student at the Moscow State University and later its Head of Physics, was asked by Wawilow to set up an interferometric experiment to detect the light-intensity dependence of the refractive index with a spark source, but he failed (see figure 2). Wawilow passed away before the laser was invented and was not able to see the telecommunications revolution and the development of numerous photonic devices whose functionality is underpinned by the intensity dependence of the refractive index. However, 80 years ago, with the Wawilow–Lewschin experiment the Superposition Principle formulated by Christian Huygens in 1678 in 'Abhandlung über das Licht' as '*The most remarkable property of light is that light beams travelling in different and even opposite directions pass though one another without mutual disturbance*' was challenged and defeated forever. Remarkably, only a few years after the Wawilow–Lewschin pioneering work, Wood, an American physicist and Professor at Johns Hopkins University laid down the foundation of nonlinear spectroscopy, a fact which is often totally ignored in the canonical history of nonlinear optics.

Describing his experiments on luminescence of atomic vapours he wrote explicitly: '... *the intensity of certain lines in the optically excited spectrum would increase with the square, and of others with the third power of the intensity of the exciting lamp... in the case of emission involving one absorption process... the intensity varies as the first power: where two absorptions are involved ... the intensity varies as the square of the intensity of the exciting light...*' [28].

Below we examine the most extreme departure from the superposition principle and analyse the situations when a very low level of optical excitation, perhaps absorption of only a singe photon, can radically change the properties of the nanoscale matter.

2. Back to Faraday, some 170 years ago

In this paper we are concerned with materials' nonlinearity that is needed for controlling light with light. This is sometimes referred to as *cubic nonlinearity* $\chi^{(3)}$ (generally a tensor). This notion comes from the nonlinear constitutive equation relating the electric field displacement $D = \varepsilon \cdot E + \chi^{(3)} \cdot$

E^3+ *higher field terms*, with electric field E of the light wave. More specifically, we are interested in '*cubic*' nonlinear media suitable for nanoscale photonic devices.

Let us assume that $N = n + i\kappa$ is the complex refractive coefficient of the medium for the signal wave, and that Δn and $\Delta\kappa$ denote the 'nonlinear' changes to its real and imaginary parts induced by the control wave. In nanoscale devices we will not have the opportunity to use optical resonators and interferometers to enhance manifestations of the nonlinear effects—a technique often exploited when the physical dimensions of a nonlinear device are several times larger than the wavelength. In nanophotonics we must rely on the nonlinearity of the medium itself. To achieve a strong induced retardation effect in a layer of nonlinear material with thickness L, $\Delta n L$ should be approximately $\lambda/2$, where λ is the signal wavelength. To have a strong effect in the intensity of the signal wave, one should fulfil the condition $\Delta\alpha L \sim 1$, where α is the absorption coefficient of the medium, or in terms of the complex refractive index $\Delta\kappa L \sim \lambda/4\pi$. For instance, in the case of the absorptive effect the required interaction length to see strong intensity modulation $L \sim \lambda/(4\pi\Delta\kappa) = (\lambda/4\pi)(1/\kappa)(\kappa/\Delta\kappa)$. So, to achieve a small value of L in the nanometre range, the second term in the right-hand side $(1/\kappa)$ must be as small as possible, i.e. κ must be as big as possible. Thus, to do nonlinear optics on the nanoscale, one must employ high-refractive-index materials that display extreme nonlinearities. The highest values of κ are found in metals. Taking a characteristic value for metals of $\kappa = 10$, we could achieve a substantial nonlinear interaction in a length of 10–100 nm only if $\kappa/\Delta\kappa \sim 1$–10. This is a very severe, nearly impossible, requirement on the light-induced change of a material's parameters.

Near-bandgap and excitonic transitions in semiconductors and the excitation of weakly bound electrons in organic polymers are probably the best sources of strong optical nonlinearities for controlling light with light that result from the anharmonicity of optical electrons [3–5]. However, whatever the system exhibiting electronic nonlinearity is, its maximum value is limited by the quantization of the light–matter interaction to

$$\chi_{max}^{(3)} = \tau \times \frac{a^3 (\mathrm{Im}\,\varepsilon)^2}{h}$$

where τ is the nonlinearity relaxation time, a is the characteristic distance between molecules in the medium of effective dielectric coefficient ε, and h is the Planck constant [6]. Even at this extreme level the electronic nonlinearity is not always sufficient to provide functionality of all-optical nanoscale switching devices.

A radically different approach to optical nonlinearities which only recently became a subject of intense investigation relies on the interaction between optical electrons and the crystalline lattice of a material. If light can somehow stimulate a structural phase transition, and the new structural phase has distinctly different optical properties from the ground state, this would constitute an optical nonlinearity. To be useful this process must be reversible—on withdrawal of the optical excitation the system must rapidly recover the initial structural phase and restore its optical properties. However, in bulk media transitions between different structural phases are often first-order transitions. When a critical condition is reached, there is a sudden change in the crystalline structure and optical properties. If the situation is restored, a hysteresis in recovery of the original state is seen. A typical example is bulk melting of ice: the melting temperature of 0 °C is sometimes noticeably higher than the water solidification temperature. If such a phase transition is stimulated by light in a bulk material, the original solid phase will not be recovered immediately after the excitation is withdrawn. Such a situation will not be suitable for controlling light with light for optical data processing.

The sharp phase transitions of bulk materials are characterized by the precise coexistence of different phases. However, this becomes a dynamic coexistence of structural forms if the material is placed in a restrictive geometry. Confinement erases the distinction between first- and second-order phase transitions in some systems. Moreover, the transition can become continuous and reversible. When a confined solid is brought to the verge of what would be a first-order structural phase transition in the bulk, it can become significantly more sensitive to external stimulation, offering an enhanced nonlinearity. The simplest forms of confinement are the formation of an interface with another material and forming material into nanoparticles. What is essentially happening with confinement is the creation of an interface with another medium.

To illustrate how an interface helps to achieve a reversible optical nonlinearity let us consider an ice cube at a temperature just below the melting point. It is covered by a very thin skin of water that develops, even below the bulk melting point, because the energy of the water–air interface is lower than that of the one between ice and air. This phenomenon is known as pre-melting and is a typical consequence of confinement. The thickness of the pre-melt layer increases with temperature, so the ice cube melts from the surface inwards. The delicate balance between water and ice may be shifted very easily, for example by heating the ice with light, if the ice cube is at a temperature close to the bulk melting point. The excitation will locally increase the surface temperature, leading to a *reversible* change in the water skin depth. Of course this change will be reversible only until the ice cube is not molten completely. Some overcooling of water below the melting point will then be needed to return it back to ice. Water and ice have similar optical properties, but if they were different, such an optical excitation would lead to a change in the material's reflectivity and transmission. Remarkably, the special properties of the ice surface were first mentioned by Michael Faraday in 1842: '*On a warm day, if two pieces of ice be laid one on the other and wrapped up in flannel, they will freeze into one piece. All this seems to indicate that water at 32.8 °F will not continue as water, if it be between two surfaces of ice touching or very near to each other...one surface of ice on water is not equal to the joint effect of two.*'

Thus, a combination of two ideas, confinement and bringing the material to the verge of a structural phase transition, can facilitate a strong reversible optical nonlinearity useful for controlling light with light in a reversible fashion (see figure 3). At the same time the irreversible response which we see when the ice has been molten completely could also be a useful property for designing optical memory elements.

Could we apply the ideas of exploiting a light-induced structural transformation as the source of a nonlinear optical
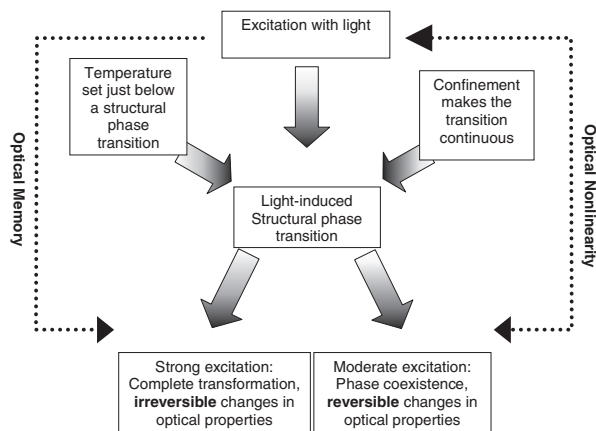
Figure 3. A general scheme for an optical nonlinearity and optical memory function achieved via a light-induced structural phase transition in a confined solid.
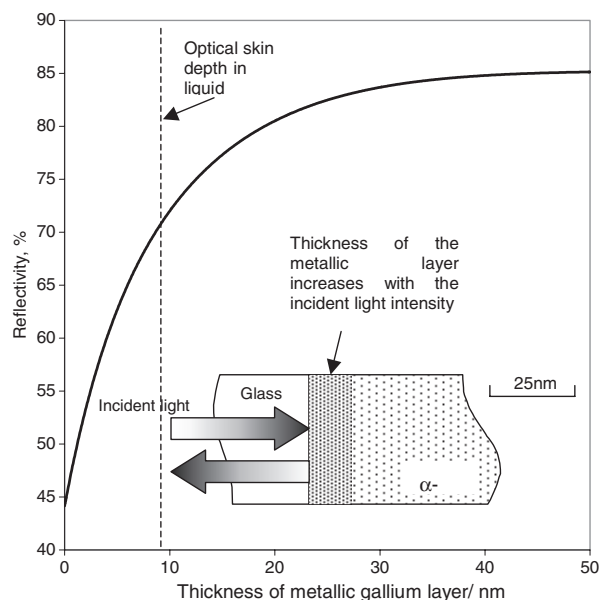

Figure 4. Surface light-induced metallization at a gallium/glass interface leads to a reflectivity increase. The graph shows the dependence of reflectivity on metallic layer thickness at a wavelength of 1.55 μm. The optical skin depth in liquid gallium is 9.7 nm.

response? Could this useful light-induced transition happen between solid phases of material? Could we achieve reversibility via confinement in metals, ultimately high-index materials? In spite of the common perception that all elemental metals have very similar optical characteristics, 'shiny as a metal mirror', elemental metallic gallium metal offers a high refractive index, the availability of several structural phases with widely different optical properties, easily accessible phase transition temperatures, and a susceptibility to light-assisted structural transformations.

In recent years it was shown that when gallium is confined as a *film at an interface* with silica it exhibits light-assisted surface metallization (see figure 4) with switching times in the picosecond–microsecond range that lent themselves to applications in optical switching and laser modulation [6]. Below we will examine how *gallium nanoparticles* can lend themselves to the creation of ultra-low intensity optical gates and resonator-free optical bistable memory elements. We will demonstrate an extreme implementation of the water-on-ice situation explained above: the lump of material (elemental gallium in this case) undergoing structural transformation will be taken to be so small that its surface energy will be comparable with the cohesive energy of the atoms inside the lump. The thickness of the layer of the new phase will be comparable with the particle diameter and two structural phases will coexist in the particle. The optical properties of the nanoparticle will depend on the fragile and easy-to-control balance between two phases. Two regimes will be possible. Resulting from the low level of excitation the particle will transform into the new phase, solid or liquid, but only partially, through an increase in the skin layer thickness. This will be a reversible transformation, or more precisely, a controllable coexistence of phases. If the light excitation is withdrawn, the particle will recrystallize back into the initial phase. At a higher level of optical excitation, above a threshold, the particle will be transformed into the new phase completely and will change its optical properties irreversibly. In this case a memory function could be achieved: the particle will remain in the new phase even if the light is withdrawn. It will only convert back into the 'ground phase' if the temperature is reduced far below the phase transition point, analogous to the melting temperature of ice.

The phase transition mechanism of switching is extremely energy efficient. Indeed, in the case of electronic nonlinearity the maximum effect that a single quantum act of absorption can have on the optical properties of a medium occurs when it knocks the molecule out of the light–matter interaction process (for example, by saturating the absorption) or, in contrast, when it 'switches on' the optical response of the molecule (for instance, by forcing it into a resonance). Ideally all of the molecules in the material structure will be involved and the efficiency of the process will thus be 100%, giving the maximum possible nonlinear change of the material's properties. This requires a *photon* per atom to be expended. Clearly, the change in the optical properties of the material will then be of the same order as its linear optical properties. Using the phase transition mechanism of nonlinearity the same effect may be achieved by spending only the energy necessary for the phase change. This is given by the intra-phase enthalpy and is typically in the scale of characteristic *phonon* energy per atom. The difference between energies of *phonon* and optical *photon* makes the phase transition switching some 3–4 orders of magnitude more energy efficient than switching via electronic nonlinearity.

3. Nanoparticle to switch

Let us now examine in more detail the dynamic coexistence of structural forms in a nanoparticle [7, 8] in the presence of external stimulation. When a nanoparticle is brought to the verge of what would be a first-order structural phase transition in the bulk, its structural composition can become significantly more sensitive to external stimulation. If the structural phases involved have different dielectric properties, a continuous structural transformation will be accompanied by a continuous change in the optical properties of the nanoparticle [9], thus effectively providing an optical nonlinearity. This behaviour is
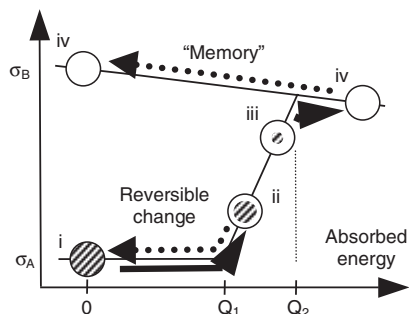
Figure 5. Dependence of optical cross-section on absorbed energy for a nanoparticle undergoing a phase transition. Reversible changes occur in the excitation range between Q_1 and Q_2; excitation levels above Q_2 lead to a memory effect.

illustrated in figure 5 for a nanoparticle undergoing a surface-driven phase transition from a low-temperature phase (grey shadow) to a higher-temperature phase (white). The transition may be activated by increasing the ambient temperature *or* by external optical or electron-beam excitation at a fixed ambient temperature. The later case the transformation is driven by laser-induced heating or excitation of the material's electronic structure [10, 11]. Increasing the level of excitation will sequentially convert the nanoparticle from stage I, through II and III, to stage IV. Reversible changes occur in the excitation range between Q_1 and Q_2. If the excitation is withdrawn before stage IV is achieved, the nanoparticle will return to its initial state, i.e. stage I. Excitation levels above Q_2 lead to a memory effect and the particle will remain in the fully converted phase IV. In all cases the point line indicates the route, which is followed when the nanoparticle excitation is withdrawn.

Stimulation of the particle with external excitation will change the phase composition of the particle and therefore its optical cross-section, thus modulating the transmission and reflection of the aperture. Let the optical cross-section of the nanoparticle in its low- and high-temperature phases be σ_A and σ_B respectively. We will consider a spherical nanoparticle of radius R and assume that the high-temperature phase develops as a skin layer around a core of radius r in the low-temperature phase. To a first-order approximation, the cross-section of the nanoparticle will be proportional to the volume occupied by each phase: $\sigma = \sigma_A (r/R)^3 + \sigma_B (R^3 - r^3)/R^3$.

Let us now examine the case of a structural transformation induced by optical heating. We assume that the nanoparticle absorbs an optical pulse of energy Q with duration $\tau_p \ll \tau_{therm}$, where τ_{therm} is the characteristic thermal diffusion time from the particle into the substrate. The excess excitation energy above Q_1 will provide the latent heat of conversion and lead to the growth of a skin layer of the high-temperature phase on a core of decreasing radius in the low-temperature phase: $Q - Q_1 = 4\pi (R^3 - r^3)\xi/3$, where ξ is the specific latent heat of the phase transition. This conversion will lead to a change in the optical characteristics (e.g. the optical cross-section) of the nanoparticle. By combining the equations mentioned above we arrive at a figure of merit for the sensitivity of the nanoparticle's optical properties to optical excitation $M\sigma/MQ = (\sigma_B - \sigma_A)/4\pi R^3 \xi$. This mechanism for controlling the optical properties of a nanoparticle is deeply rooted in the nanoscale

nature of the effect and its efficiency increases in inverse proportion to the cube of the particle radius. Finally, for $Q > Q_2$, where $Q_2 = Q_1 + 4\pi R^3 \xi$, the particle is fully converted into the high-temperature phase and any further increase in the excitation level will increase its temperature but not change its phase composition. The gradient $M\sigma/MQ$ is inversely proportional to the specific latent heat of the phase transition and differs from one transition to another. For example, the lowest value of ξ in gallium is observed between the δ and β solid phases, $\xi_{\delta\beta} = 0.48 \times 10^{-22}$ J/atom, or 2.54×10^7 J m^{-3} [11]. Thus, in a nanoparticle with a radius $R = 15$ nm, $M\sigma \approx \sigma_B - \sigma_A$ at $MQ = 0.4$ fJ. So, the absorption of about 2000 photons at a wavelength of 1 μm would be sufficient to alter the phase equilibrium and achieve a substantial change in the nanoparticle's optical properties. From here it immediately follows that the energy obtained by absorbing just a *single photon* could be sufficient to completely convert a nanoparticle with diameter of a few nanometres into a new phase, this making a single-photon all-optical switch a reasonable possibility. Transitions between other structural phase in gallium are characterized by higher latent heats, between 2.79×10^{-22} and 3.27×10^{-22} J/atom, and would therefore require excitation levels of the order of a few femtojoules.

As long as the level of external excitation does not exceed Q_2, i.e. as long as a complete transformation into the high-temperature phase does not take place (stage IV in figure 5), any light-induced change in optical properties will be reversible. Thus, a nanoparticle located in a nano-aperture can act as an optical gate. The switch-on time of such a gate, i.e. the intrinsic time needed for conversion from the low-temperature phase to the high-temperature phase, may be very short. For instance, the initial response time for a thin α-gallium film undergoing a light-induced transition to the melt is only about 2–4 ps [12]. The relaxation time of the optical properties (and therefore the bandwidth of the gate) is determined by the time taken for the metastable high-temperature phase to be converted back into the low-temperature phase. This is determined by the longer of two characteristic times, τ_{therm} (which determines the time for the particle to return to its initial, pre-excitation temperature) and τ_{rec} (the recrystallization time). A rough estimate of τ_{therm} for a nanoparticle in good contact with a substrate acting as a thermostat can be obtained using the equation $\tau_{therm} \sim R^2/\chi$, where χ is the thermal diffusivity of the material that the nanoparticle is made from. Thus, for a liquid gallium nanoparticle ($\chi = 1.2 \times 10^{-5}$ J m^{-3} K^{-1}) [13] with a radius $R = 15$ nm, $\tau_{therm} \sim 20$ ps. τ_{rec} depends on overcooling because the velocity v with which the boundary between two phases moves towards the surface of the nanoparticle ($\tau_{rec} \sim d/v$, where d is the distance moved by the phase boundary) is a strong function of overcooling: $v \propto \mu\Delta T$ [14, 15]. Given that $\mu \sim 5$ mm s^{-1} K^{-1} for the liquid-to-α-gallium transition, we can estimate that the recrystallization time in a particle of radius $R = 15$ nm subject to overcooling $\Delta T = 3$ K would be ~ 1 μs. This is much longer than τ_{therm} and is therefore the controlling factor. Sub-nanosecond relaxation times may nevertheless be possible if the 'explosive crystallization' regime, which has been observed in thin gallium films [16] and where crystallization velocities reach tens of metres per second, can be achieved in nanoparticles.
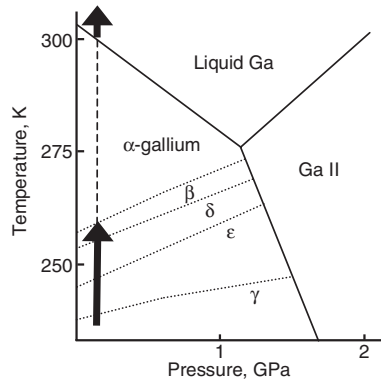
Figure 6. Phase diagram for gallium showing the sequence of phase transitions expected in a gallium nanoparticle undergoing adiabatic heating from 180 to 300 K. These transitions can also be induced optically. The α phase is not found in nanostructures so the β phase transforms directly to liquid.

The estimates given above have recently been largely confirmed in a series of experiments with nanoparticle films and single gallium nanoparticles. Gallium is known for its polymorphism [12]. A simplified sketch of gallium's phase diagram is shown in figure 6. α-gallium is the stable 'ground-state' phase in the bulk [13–15]; it has a very low melting point, only 29.8 °C. Here some interatomic bonds are strong covalent bonds, forming well-defined Ga_2 dimers (molecules), and the rest are metallic bonds. This so-called boron-like structure is what some authors call an inorganic polymer. The transition between the α-gallium and molten phases underpins the optical nonlinearity in gallium confined at the interface with silica and some semiconductor materials [16]. This phase, however, is not normally observed in nanoparticles. A high-pressure form called Ga(II) and low-pressure forms β-, γ-, δ- and ε-gallium have been seen in x-ray diffraction experiments. Some phases can be identified on a DC-resistivity versus temperature diagram [17]. The 'metallic' behaviour of Ga(II) and amorphous gallium may be expected since their densities of states deviate little from the free-electron model and are similar to those of liquid gallium, which in terms of its optical and electronic properties is very close to an ideal free-electron metal [18, 19]. However, β-, γ-, δ- and ε-gallium are expected to display some marked departures from true free-electron properties and therefore should have optical properties different from liquid gallium. For instance the β phase has a zigzag arrangement of covalent bonds in its structure [20].

To illustrate how the optical cross-section of the nanoparticle depends on its structural phase let us consider an oblate spheroidal shaped gallium nanoparticle with a radius of 20 nm and an aspect ratio 2. For the purposes of illustration, we take α- and liquid gallium, the only phases of the metal for which dielectric constants are known with certainty ($\varepsilon_A = -3.5 + i1.6$, $\varepsilon_B = -26.6 + i7.3$). These dielectric constants give vastly different absorption cross-sections (per unit area at wavelength of 400 nm) in the two phases: $\sigma_A/\pi r^2 = 2.6$ and $\sigma_B/\pi r^2 = 0.07$, respectively. Such a nanoparticle, when positioned in a nano-aperture matching its largest absorption cross-section, will show a high switching contrast for transmitted light.

Light- and electron beam-induced structural transformations and the associated change in optical properties
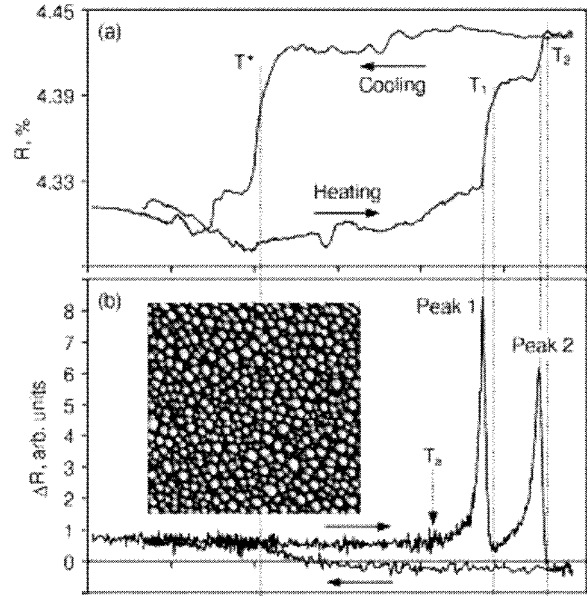

Figure 7. Temperature dependences of (a) reflectivity R and (b) pump-induced reflectivity change ΔR, for gallium nanoparticles on the core of a single-mode optical fibre. The inset to (b) shows an atomic force microscope image of a 2×2 μm area of the fibre core.

have recently been demonstrated in gallium nanoparticle films [21, 22]. In the all-optical experiments [21] the structural transformations were monitored by recording the optical reflectivity of the films. The particles, typically 50 nm in diameter with a relatively narrow size distribution, were prepared on the tips of silica optical fibre, using the light-assisted self-assembly technique. This process produced a nanoparticle film on the fibre's core comprising about 10^4 nanoparticles. Phase transitions in the nanoparticles were stimulated by a mW power range modulated 'pump' laser, a 1.55 μm fibre-coupled diode laser providing a 'peak' excitation power of approximately 40 nW per nanoparticle. Another low-power cw diode laser operating at 1.31 μm was used to probe the reflectivity of the film (see figure 7). In essence these experiments confirm that reversible structural transformations, induced by optical excitation, may be stimulated in nanoparticles between the β, γ and liquid phases of gallium. Only a few tens of nanowatts of optical excitation per particle were required to control the transformations that took the form of dynamic phase coexistence and were accompanied by substantial changes in the optical properties of the nanoparticle film. It was found that the time needed to achieve phase equilibrium is in the microsecond range, and increased sharply near the transition temperatures.

Recently a much more detailed sequence of *solid-to-solid* light-induced phase transitions followed by a light transition to melt was seen in a single gallium nanoparticle [23]. The particle was grown (from an atomic beam) in a 100 nm nano-aperture at the tip of a gold-coated tapered optical fibre (figure 8). A series of structural transformations between γ, ε, δ, β and liquid phases of gallium were observed in the temperature range from 80 to 300 K. The phase coexistence could be controlled by only a few nanowatts of pump light power changing reflectivity of the fibre tip for the probe beam a different wavelength, propagating in the same fibre. It was also found that a particle probed with low-intensity cw laser
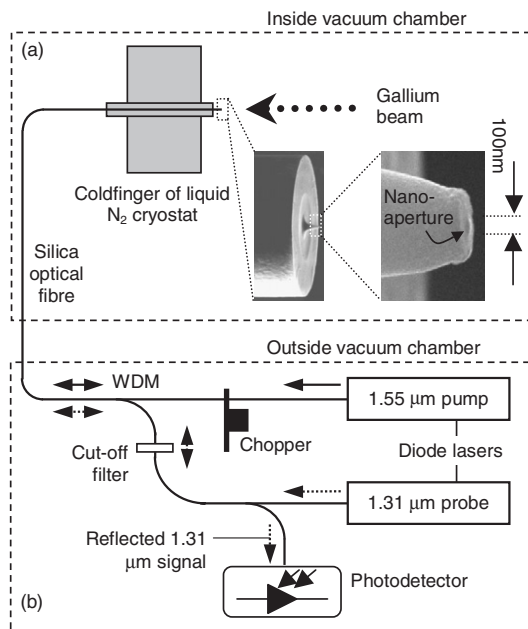
Figure 8. Experimental arrangement for observing light-induced phase transformations in a *single* gallium nanoparticle at the tip of optical fibre. (a) Inside the UHV chamber a tapered fibre tip is exposed to a beam of gallium atoms. A gallium nanoparticle grows on the tip. (b) After the particle is grown, a pump–probe arrangement is used for detecting light-induced structural transformations in the particle. The pump laser at $\lambda = 1.5$ μm induces the phase transition in the nanoparticle leading to a change of reflectivity in the fibre aperture. This change is then detected thorough monitoring the reflected light of the probe laser at $\lambda = 1.31$ μm.

light could be overcooled by more than 90 K before it returned to the low-temperature phase. Studying transitions in a single nanoparticulate, as opposed to a nanoparticle film, has led to

advantages similar to the resolution improvements achieved in the optical spectroscopy of single particles. Without the masking effect of inhomogeneous broadening characteristic in nanoparticle films it has been possible to detect a much more detailed series of phase transitions and identify them against the phase diagram of gallium (see figure 9).

4. Nanoparticle to remember

A remarkable characteristic of a nanoparticle undergoing a structural transition is the memory effect: when the excitation has exceeded the level Q_2 needed for complete transformation of the particle into the high-temperature phase (or the ambient temperature has increased beyond the point at which the phase transition is complete), the particle will not return to the low-temperature phase without substantial overcooling (see figure 5). For example, a gallium nanoparticle probed using low-intensity cw laser light needs to be overcooled by more than 90 K before it returns to the low-temperature phase. Such a nanoparticle is therefore an inherently bistable object, and this presents an opportunity for creating an optical memory element.

Resonator-free optical bistability has recently been demonstrated in gallium nanoparticle films [24] (see figure 10). In this experiment an impulse semiconductor laser generating 1 μs *control* pulses at a wavelength of 1.5 μm was used to write information by switching gallium nanoparticles from the low reflectivity phase '0' into the high reflectivity phase '1'. The state of the bistable nanoparticle film was monitored by a second low-intensity *reading* laser through measuring the reflectivity R of the film. In the absence of the *control* pulse the reflectivity shows a well-pronounced hysteresis on cycling the temperature. If the temperature of the nanoparticle film was set low (at T_{0*}) the *control* pulse produced only a reversible change in the state of the film (figure 10(a)). Here particles

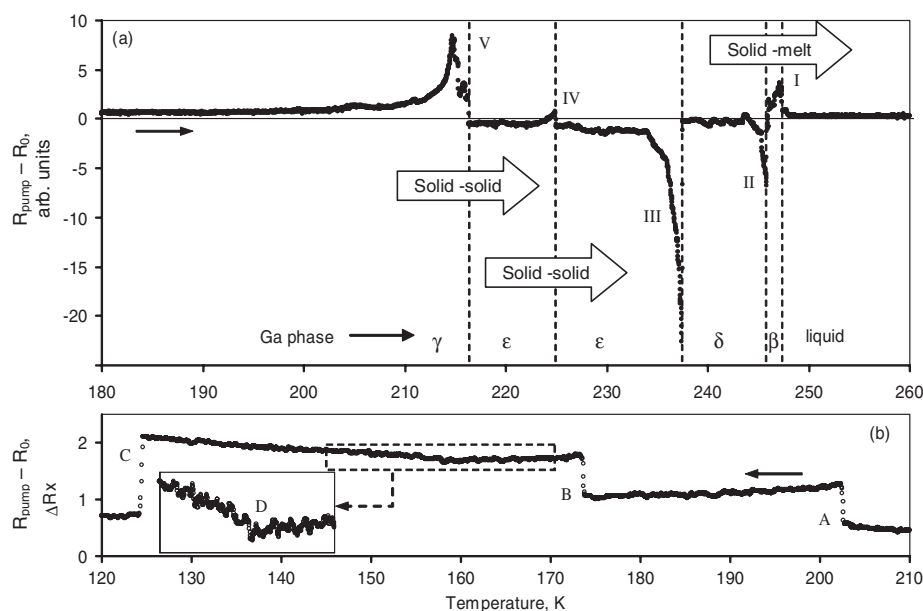**Figure 9.** Detecting light-induced structural phase transition in a *single* gallium nanoparticle. The graphs show magnitude ($R_{pump} - R_0$) of pump-induced reflectivity change of the fibre occupied by gallium nanoparticulate as a function of (a) increasing and (b) decreasing temperature. (R_{pump} = reflectivity with pump illumination, R_0 = reflectivity with no pump present; cw probe power at aperture ∼20 nW, pump peak power ∼30 nW.) Note that the recorded temperature of the cryostat cold finger is somewhat lower than the actual temperature of the gallium nanoparticulate due to localized laser heating.
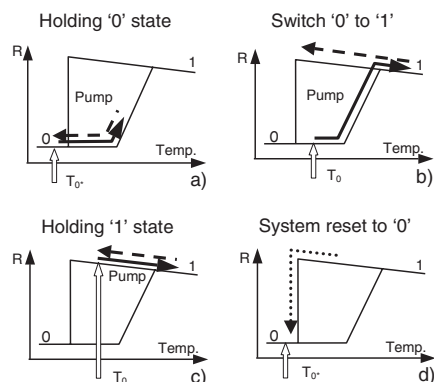
Figure 10. Nanoparticles undergoing light-induced structural transformation as an inherently bistable element. Vertical arrows indicate temperature set points. Solid lines show the action of the *control* optical pulse. Dashed lines show the evolution of the system on termination of the *control* pulse. The dotted line shows system reset (d).

are only partially converted into the high reflectivity phase and on withdrawal of the control pulse the system recovers state '0'. At a higher set temperature T_0 the *control* pulse energy is sufficient to convert the nanoparticles completely into the high reflectivity phase (figure 10(b)). On withdrawal of the pulse the particles remain in the high reflectivity state. The system remains in the high reflectivity state '1' regardless of the presence of the *control* pulse (figure 10(c)). In order to restore state '0' the nanoparticles need to be cooled down to a temperature T_{0^*}, below the hysteresis boundary (figure 10(d)). This completes the cycle of writing and erasing information in the optical memory element. In fact the temperature set point need not necessarily be controlled only by the cryostat. The initial set point also depends on the power of the continuous *reading* signal due to laser heating of the nanoparticle film. Thus, if the initial nanoparticle temperature is set at T_0^*, the film may be brought to and from the operational temperature T_0 simply by adjusting the *reading* signal power, as was seen in the experiment. Thus, a nanoparticle may constitute an optical memory bit, which can be read by a weak probe beam and erased by substantial cooling or switching off the read beam.

5. Conclusions

Recent experimental results outlined above have clearly demonstrated that a nanoparticle undergoing a structural transformation may offer a variety of applications as an active optical gate and memory elements operating at extremely low power levels in future nanophotonic devices. These are still only proof-of-principle demonstrations and much more work is needed on finding suitable polymorphic materials operating in a convenient temperature range, such as perhaps selenium. For various device solutions the nanoparticle could be placed in an optical nano-aperture, incorporated into a chain waveguide [25], or used as a scattering centre in a photonic-bandgap or plasmon-polariton waveguide [26].

Among the very recent developments in the field of nanoparticle optics we shall mention the finding that the power-flow lines of light interacting with a metallic nanoparticle, in the proximity of its plasmon resonance, form whirlpool-like nanoscale optical vortices [27]. The vortex structure, with

light passing through a nanoparticle several times backwards and forwards, resembles a standing wave in a dissipative Fabry–Perot resonator. One may therefore ask the intriguing question of whether such a 'nano-resonator' could provide conditions for a hysteresis and bistability in the nanoparticle's optical response, if its dielectric properties depend on the intensity of light, even if the structural phase of the particle does not change, or changes without an irreversible structural transformation.

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