Nonlinear optics on the nanoscale

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We review the concept of achieving a large optical nonlinearity via a light-induced phase transformation in a confined solid. Nanoscale films and nanoparticles of gallium are examined as prime examples of materials displaying this type of optically broadband, fast and bright nonlinear response, which show promise for future all-optical switching applications.

It is not yet clear exactly where nanoscale nonlinear optical devices will be used. Will it be in all-optical switches, densely packaged on a chip? Or perhaps they will be used to condition optical signals between elements of a three-dimensional, highly integrated, photonic-band-gap optical signal router? Maybe they will be combined with two- or three-dimensional arrays of miniature semiconductor lasers in order to control their output? We simply do not know. What we do know is that the demand for devices capable of controlling light with light in a very thin, nanoscale layer, or possibly just a single nanoparticle of nonlinear material, will come in the near future.

But is it, at least in principle, possible to control light with light in a layer of nonlinear material only a few nanometres thick? When we say the light is controlled, we mean that either its intensity or phase is changed substantially by a control signal. In a nonlinear 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. 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 reality these two waves may be at the same wavelength but propagating in different directions or with different polarizations, and in the 'degenerate' case may simply involve the action of one wave on itself. For clarity of presentation, however, we will consider distinctly different control and signal waves (see figure 1).

In nanoscale devices we will not have the opportunity to use optical resonators to enhance the nonlinear effects—a trick often exploited when the physical dimensions of a nonlinear device are larger than the wavelength. Therefore, 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, ΔnL should be approximately $\lambda/2$, where λ is the signal wavelength. Similarly, to have a strong effect on 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 $\Delta \kappa L \sim \lambda/4\pi$. These are the requirements for strong transmission effects. The corresponding conditions for reflective effects are more complex, but in general, if a strong transmissive nonlinear effect is achieved in a nanoscale film, the reflective effect will also be strong.

Clearly, the stronger the nonlinear effect, the shorter the required interaction length L. But how short? Could it be in the nanometre range? Rearranging the above conditions for the observation of a strong effect helps to answer this question. For example, in the case of the absorptive nonlinearity, $L \sim \lambda/(4\pi\Delta\kappa) = (\lambda/4\pi)(1/\kappa)(\kappa/\Delta\kappa)$. So, to achieve a value of L in the nanometre range, i.e. much smaller than the wavelength, $(1/\kappa)$ must be as small as possible, i.e. κ must be as big as possible. The highest values of κ are found in metals. Taking a characteristic value for metals of $\kappa \sim 10$, we could achieve a substantial nonlinear interaction in a length of $10-100$ nm if $\Delta \kappa/\kappa \sim 0.1-1$. This is a huge nonlinear change. Thus, to do nonlinear optics on the nanoscale, one must work with high refractive-index materials that display extreme nonlinearities. But can we find such a nonlinear material?

In the classical Lorentz approach, molecular optical response is modelled by an ensemble of charged oscillators, each of which is an electron attached to a spring that

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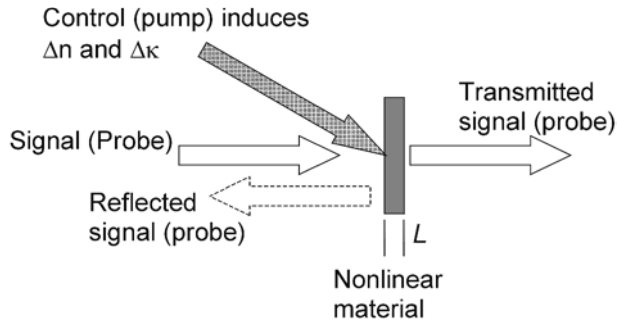
Figure 1. Controlling light with light in a sub-wavelength layer, L, requires a material with a huge optical nonlinearity.

restores the electron's position when it is displaced by the Lorentz force of a light-wave's electric field. An optical nonlinearity is then introduced as a departure of the restoring force from Hooke's elasticity law [1]. There is no apparent reason why the restoring force could not be extremely nonlinear and there is therefore no apparent limitation on the value of the optical nonlinearity in this classical model. So, might we then conclude that the search for optical media with fast and strong nonlinear optical responses has no end and, in principle, better materials may be found if we look hard enough for them?

Unfortunately not. The limit appears in the quantization of the light–matter interaction. Indeed, 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). The nonlinearity is maximized if such strongly excited molecules are packed as closely as possible. Ideally all of the molecules in the material structure will be involved and the quantum efficiency of the process will thus be 100%, giving the maximum possible nonlinear effect. Clearly, the change in the optical properties of the material will then be of the same order as its linear optical properties, which are described by the dielectric coefficient ε.

By following this argument we can easily arrive at a limit on the specific figure of merit for the optical nonlinearity. If the absorption length $L = \lambda/(4\pi\kappa)$ and all atoms within the absorption depth are to be excited once by quanta from the light wave, the energy density of the excitation requited would be $M L h\nu$, where M is the atomic density ($M \sim a^{-3}$, where a is the characteristic distance between molecules). Taking into account the excitation's relaxation time, τ, the corresponding light intensity required is $I = M L h\nu/\tau$. Now, by substituting $I = cnE^2/2\pi$, and introducing the specific figure of merit, $\chi^{(3)}$, for the cubic optical nonlinearity, via the nonlinear constitutive equation for the electric field displacement $D = \varepsilon E + \chi^{(3)} E^3 +$ higher field terms, we can

evaluate the ultimate cubic nonlinearity $\chi^{(3)}_{\max}$. As discussed above, $\chi^{(3)}_{\max} E^2 \sim \varepsilon$. Now recalling that $\mathrm{Im}\,\varepsilon = 2n\kappa$, we arrive at the following estimate:

$$\frac{\chi^{(3)}_{\max}}{\tau} = \frac{(\mathrm{Im}\,\varepsilon)^2 a^3}{h}.$$

For the sake of simplicity, we have assumed that only the imaginary part of the dielectric coefficient is affected by the excitation. For example for $\tau = 1$ ns, $a = 10^{-7}$ cm, $\mathrm{Im}\,\varepsilon = 10$ and $\chi^{(3)}_{\max}$ is about 0.1esu. A purist might argue that this nonlinearity concept may only be used for small light-induced changes and when changes in light intensity occur on time scales longer than the characteristic relaxation time of the system, τ. We are aware of these arguments [2] and accept them, however they do not really undermine the main findings of our analysis: first, that the limit on the nonlinearity contains the Planck constant, and there-fore — intriguingly enough — it is a quantum limitation. Secondly, the limit is higher in media with long relaxation times and, most importantly, in media with high dielectric coefficients.

It would not be a huge exaggeration to say that after the laser was invented the search for highly nonlinear materials was one of the main missions of optical physics. However, the search for optical nonlinearities began long before this time. In 1926 Wawilow and Lewschin published the first paper reporting a light-induced change in a material's optical properties [3]. Using a spark light source they found that the transmission of a uranium-doped glass plate depended on the intensity of light (see figure 2). Absorption of saturation in the doped glass was the reason for this observation. Wawilow and Lewschin clearly explained their results as a violation of the absorption law, $I = I_0 \exp(-\alpha L)$ and suggested that the absorption coefficient α must be treated as intensity dependent. This was the first ever paper on nonlinear optics. Wawilow's thinking was still ahead of its time when, in 1950, he wrote: '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.' [4]. He thought, however, that the light intensities needed to see such violations of the superposition principle could only be found inside stars. He passed away before the laser was invented.

The superposition principle is part of the foundation of linear optics and is a short way of saying that two beams travelling in a medium do not feel each other's presence. In this paper we examine the opposite situation.
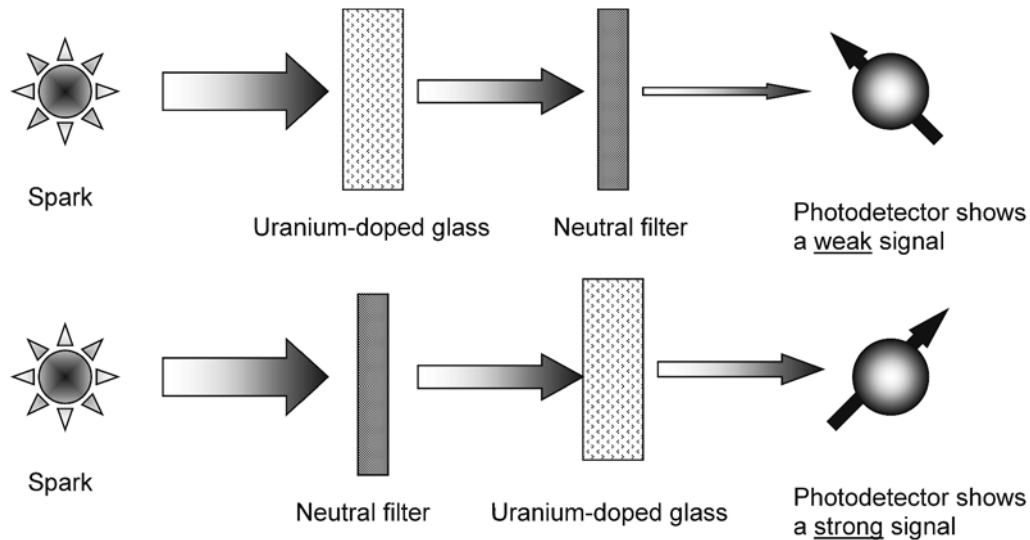
Figure 2. An illustration derived from the first nonlinear-optical experiment [3]. Nonlinear absorption in uranium-doped glass: transmission of intense light by the neutral filter and uranium-doped glass combination depends on their order, indicating that absorption in the glass is a function of light intensity following [4].

A systematic search for nonlinear materials unfolded after the invention of the laser. Remarkable successes were had in finding strong nonlinearities in condensed matter. 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 resulting from the anharmonicity of optical electrons [5–7].

A radically different approach to optical nonlinearities relies on the interaction between optical electrons and the crystalline lattice of a material. The idea of exploiting this interaction to achieve a large optical nonlinearity is very simple. 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 a true and useful optical nonlinearity this process must be reversible — on withdrawal of the optical excitation the system must recover the initial structural phase and optical properties. Herein lies the main problem.

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. If the situation is restored, a hysteresis is seen. A typical example is bulk melting: the melting temperature is sometimes noticeably higher than the 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. The non-linearity associated with the transition will not be reversible so would not be suitable for controlling light with light in applications such as 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 transition 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 form of confinement is the formation of an interface with another material.

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 a water–air interface is lower than that of 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. Water and ice have similar optical properties but if they were different, such an optical excitation would lead to a change in the cube'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°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 non-linearity (see figure 3).

Now we shall return to the arguments that higher limits on the magnitude of nonlinearities are to be found in solids with high refractive indices, and that only high-index materials, for instance metals, will be suitable for controlling light with light on the nanoscale. Could we apply the ideas of exploiting a light-induced structural transformation as the source of a nonlinearity, and of achieving reversibility via confinement, to metals? Do we have any metals whose phases have distinctively different optical properties? Can a transition between different phases be stimulated with light? Can this all happen at reasonable optical excitation levels and can it happen fast enough to be of any practical use?

In short, the answer is, surprisingly, 'yes'. We say 'surprisingly' it is fair to say that the dominant view for many years was that metals did not posses any sizable optical nonlinearity unless they were confined in nano-particles [8]. Indeed, there is no nonlinearity in the restoring force for free electrons in metals because the force itself is not present for ideally 'free' carriers. Other

sources of electronic nonlinearity, such as the multi-photon interactions, and the dependencies of free electron mass and relaxation time on the electron energy, are considered to be too small to be of any practical use for switching applications. Even the more pronounced spin-flipping nonlinearity [9] found in metals with significant spin–orbit coupling is still not particularly large.

The positive answer given above may also be surprising in light of the common perception that all elemental metals have very similar optical characteristics, 'shiny as a metal mirror'. So where are these phases with such different optical characteristics and can we induce a transition between them using light?

A material does exist which offers a unique combination of the required properties: a high refractive index, the availability of several structural phases with widely different optical properties, easily accessible phase transition temperatures, and most importantly, a susceptibility to light-assisted structural transformations. It is elementæ gallium. We will see below that when this metal is confined at an interface with silica, or prepared in the form of nanoparticles, it exhibits a huge optical nonlinearity via light-assisted surface metallization with switching times in the picosecond–microsecond range.

Let us first review the properties of gallium that make it a unique material for nanoscale nonlinear optics. It is a material known for its polymorphism [10]: forms called Ga(II) and Ga(III) are known, and others given the names β, γ, δ and ε-gallium have been seen in X-ray experiments.
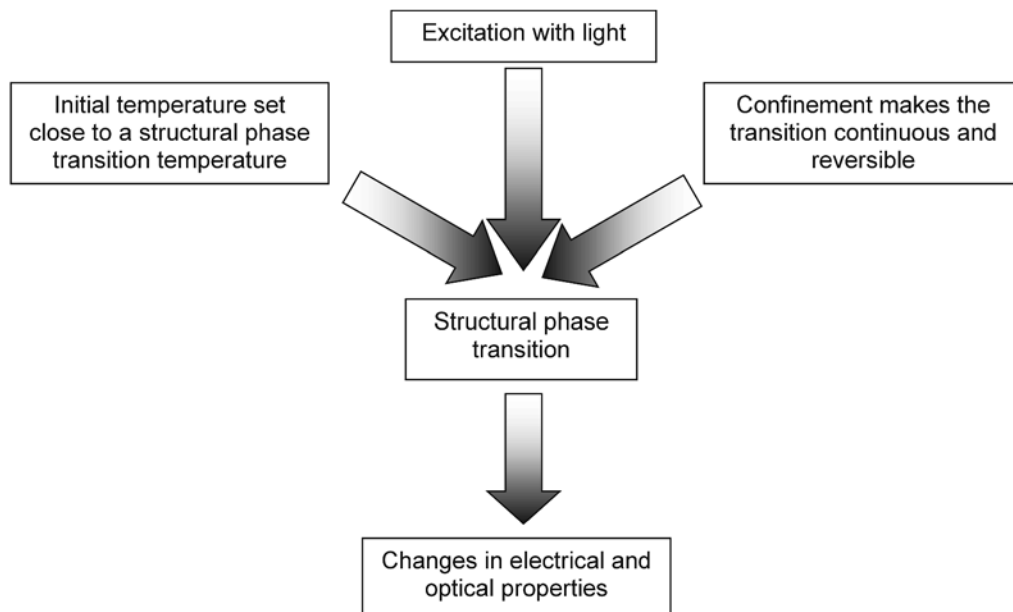
Figure 3. A general scheme for an optical nonlinearity achieved via a light-induced structural phase transition in a confined solid on the verge of a structural phase transition.

Some can be identified on a dc-resistivity versus temperature diagram [11]. A simplified sketch of gallium's phase diagram is shown in figure 4. The 'metallic' behaviour of Ga(II), Ga(III) 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 [12,13]. However, it is α-gallium, the stable 'ground-state' phase, which makes it a rather special metal [14–16]. It has a unique structure in which molecular and metallic properties coexist—some inter-atomic bonds are strong covalent bonds, forming well-defined Ga_2 dimers (molecules), and the rest are metallic bonds. This boron-like structure is what some authors call an inorganic polymer. The structure is highly anisotropic, with much better thermal and electrical conductivity in the 'metallic planes' than along the covalent bonds. Remarkably, α-gallium has a very low melting point, only 29.8°C. The covalent bonding leads to a dip in the density of states at the Fermi level, and gives rise to a strong optical absorption peak centred at 2.3 eV and spreading from approximately 0.68 eV (~1820 nm) to about 4 eV (~310 nm). The pronounced difference between the electronic structure of α-Ga and the more metallic phases manifests itself as a marked difference in the optical properties. The difference between the moduli of the dielectric coefficients of liquid gallium and α-gallium is huge, at a wavelength of 1.55 μm this difference, $|\varepsilon_{\text{liquid}}|-|\varepsilon_\alpha| \sim 180$. The reflectivity of α-gallium is more like that of semiconductor materials, in contrast with the high reflectivity of the metallic phases. β-gallium also displays some marked departures from true free-electron properties due to a zigzag arrangement of covalent bonds in its structure [17].

α-gallium near its melting point is an ideal material to illustrate the concept of using a high refractive-index medium, confinement and a light-induced structural transformation to achieve a substantial nonlinear response on the nanoscale. Let us first focus our attention on the phases of gallium between which a light-induced transition would produce a strong change in the optical characteristics. This must be the semiconductor-like α-phase and one of the highly metallic metastable phases or liquid gallium. How can one stimulate a transition from the α-phase to a metastable phase? The metastable states lie above the ground state, and energy must be expended to achieve such a transition. Remarkably, in gallium the specific energies of the transitions from the ground state to the metastable phases such as Ga(II) and Ga(III) are very similar to the energy needed to melt gallium. The energy required to achieve melting is relatively small, about 60 meV atom^{-1} [13]. This corresponds to a specific enthalpy for the phase
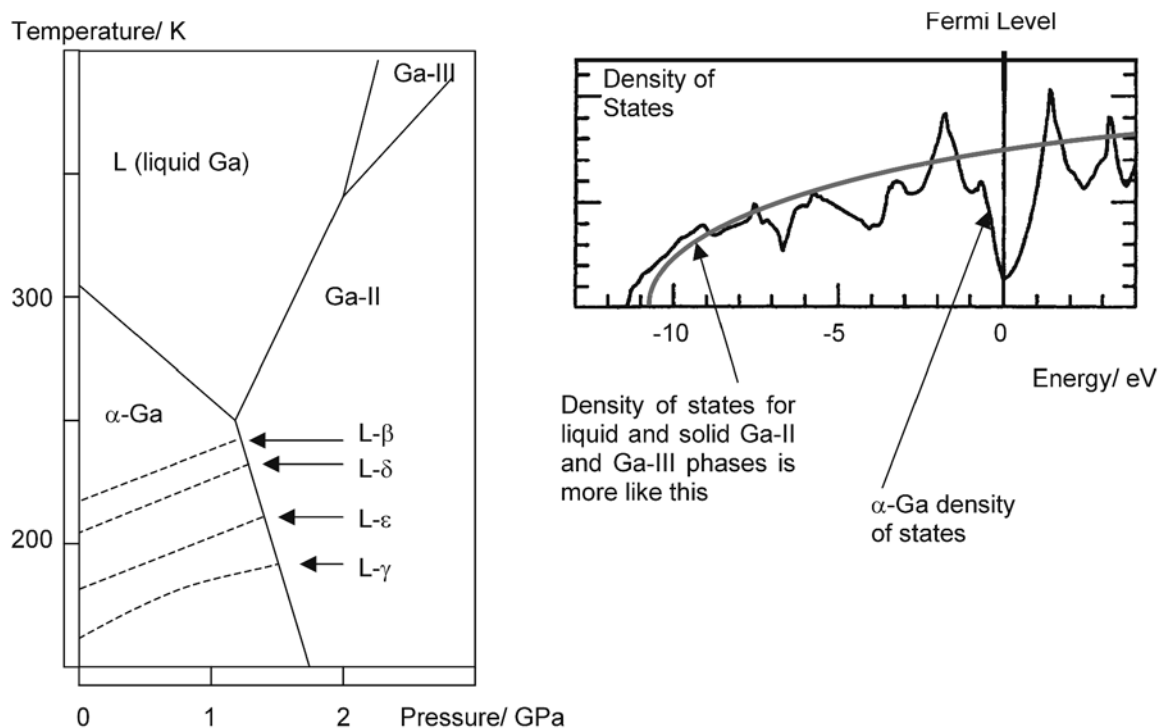

Figure 4. The phase diagram shows liquid gallium, L, Ga(III) and Ga(II), α-gallium (Ga(I)) and metastable phases β, δ, ε and γ. The electronic density of states of α-gallium shows a strong dip near the Fermi level as compared with the free-electron density of states (references in the text).

transition some 8–10 times lower than in silicon. The metallic metastable phases may be achieved by simple heating as a result of light absorption. Gallium, however, also presents another means of obtaining these phases, namely a non-thermal transition [18,19].

The concept of non-thermal melting was originally suggested for covalently bound semiconductors [20,21]. With some adjustments it also works for gallium. To achieve a non-thermal effect in semiconductors, high-intensity femtosecond optical excitation is needed because the excitation de-localizes rapidly and the phase transition occurs through plasma-induced instability in the acoustic phonon mode. In contrast, the molecular character of the α-gallium structure results in highly localized excitation of the dimers. This is due to both very fast localization of the photo-generated electron–hole pairs on the dimers, and the local nature of the excitation itself. Consequently, light absorption can excite a dimer from the bonding to the antibonding state, reducing the stability of the surrounding crystalline cell (see figure 5). The α-gallium cell subsequently undergoes a transition to a new configuration (crystalline or disordered), creating a microscopic inclusion of the new phase without necessarily achieving the melting temperature. Since the inclusions of the new metastable phase are more 'metallic' than the α-gallium, the reflectivity of the interface increases. We call this process light-induced surface-assisted metallization (see figure 6).

Such a transition can be observed if the gallium interface is illuminated with light of a wavelength within the dimers' absorption line, which happens to be very broad. This non-thermal mechanism was found to be important for quasi-continuous wave excitation of gallium interfaces at intensities up to a few kW cm^{-2}. For example, in the experiments reported in [18] a laser beam at a wavelength of 810 nm was focused onto a gallium–silica interface and the reflected light was monitored. The heat was efficiently
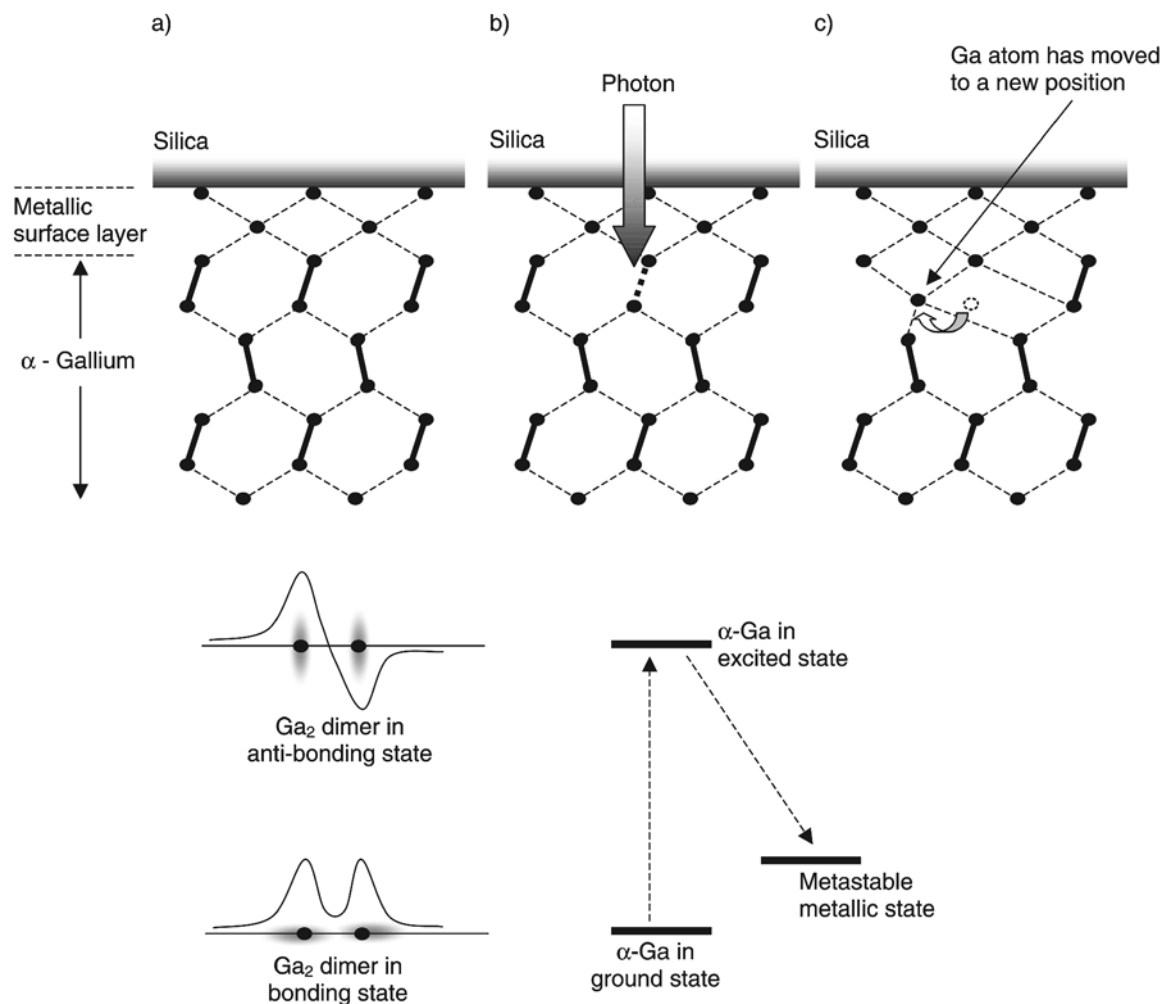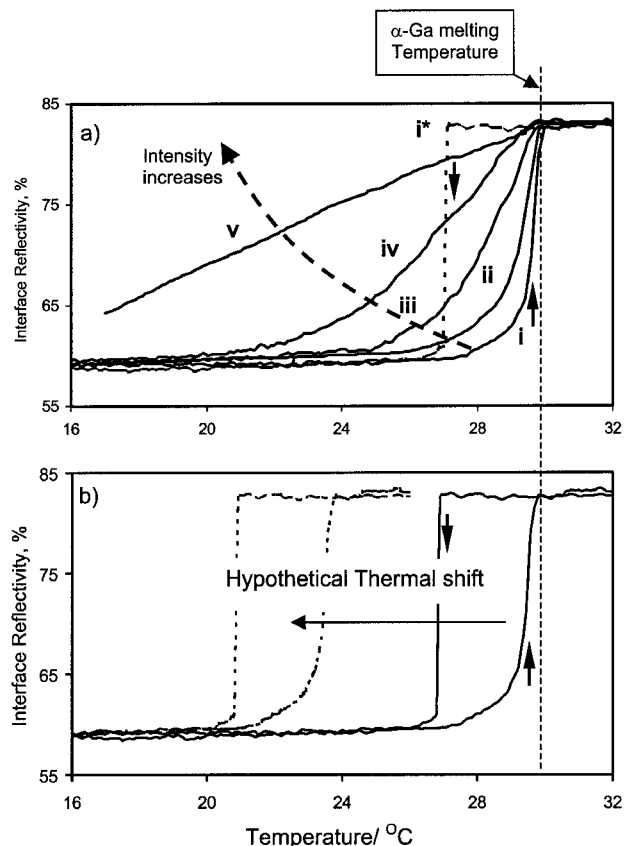

Figure 5. Illustration of the non-thermal metallization in α-gallium: (*a*) gallium dimers in the bonding ground state of the α-gallium lattice; (*b*) excitation to the antibonding state by light absorption; (*c*) loose atom shifts to join the metallic layer at the interface. The corresponding 3-level system is also presented.
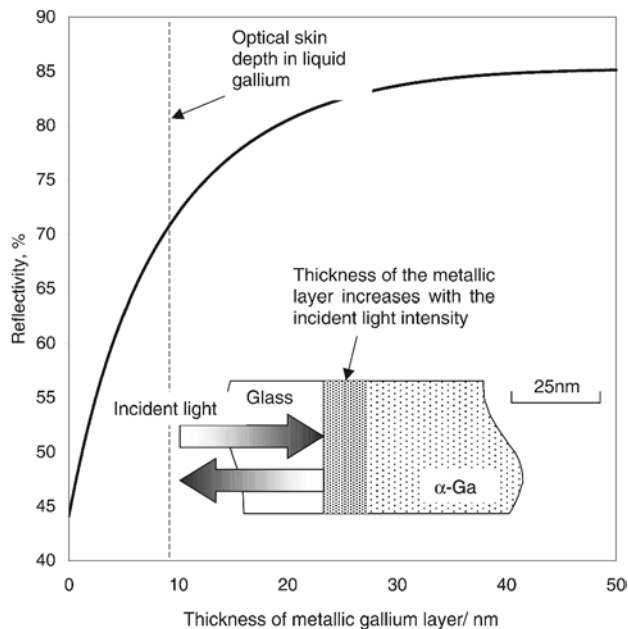
Figure 6. Surface light-induced metallization at a gallium–silica interface leads to a reflectivity increase. The graph shows the dependence of reflectivity on metallic layer thickness at a wavelength of 1.55 μm. Optical skin depth in liquid gallium is 9.7 nm and 38 Mm for α-gallium.

Figure 7. Nonlinear reflectivity at a gallium–silica interface prepared by ultrafast laser deposition. Graph (*a*) shows the reflectivity hysteresis of a gallium–silica interface as observed in the experiment for rising (i) and falling (i*) temperatures. It also shows the rising temperature curves for various laser intensities (curve (ii) to curve (v)). For comparison graph (*b*) again shows the reflectivity hysteresis measured at low intensity (curves (i) and (i*)) together with a hypothetical reflectivity hysteresis curve (dashed line) that would have been observed if laser heating was the main mechanism behind the effect (following [18], © Optical Society of America).

removed from the interface by thermal conduction, however a strong nonlinear response was seen at the interface. At low intensities ($\leq$220 W cm^{-2}) reflectivity varied with increasing temperature across gallium's melting point as shown by the solid experimental curve (i) in figure 7(*a*). Overcooling of liquid gallium caused a reflectivity hysteresis, with a width of $\sim$3°C, which was stable against repeated melting and solidification (curve (i*) shows the interface reflectivity for decreasing temperature). The rest of the curves (ii)–(v) show how the rising temperature part of the hysteresis changed with increasing light intensity, from 0.2 to 3.2 kW cm^{-2}. The reflectivity change became less abrupt but the temperature at which bulk melting of the gallium film occurs (the bend point at $\sim$30°C) remained constant at all excitation levels. A considerable reflectivity change, $\sim$30%, was achieved with quite modest intensities of just a few kW cm^{-2}.

The observed change in the reflectivity curves is somewhat different from that which might be expected from local heating effects (see figure 7(*b*)). Moreover, calculations of the temperature distribution created by laser heating in this experiment show only a small temperature increase. Altogether this firmly excludes thermal melting of gallium as the main mechanism responsible for the phase conversion. The dependencies of reflection on light intensity and temperature can, however, be modelled accurately by assuming that a thin wetting layer of a

highly reflective metallic phase forms between the glass and the α-gallium via the non-thermal metallization mechanism. The layer's thickness, and thus the sample's reflectivity, increase with applied light intensity as shown in figure 7(*a*). It should be noted that even without optical stimulation, gallium (like ice at a temperature just below its melting point) develops a thin ($\sim$ few nm) film of another phase at the interface [22]. This layer propagates into the α-gallium bulk with increasing light intensity. How does this happen? The working hypothesis is that when the interface is exposed to light and inclusions of the new phase are created, the presence of these nuclei of the new metallic phase in the α-gallium bulk shifts the delicate energy balance at the interface, leading to an increase in the thickness of the metastable layer [18,19,23].

The energy needed to switch gallium's reflectivity from the α-gallium level to the metallic level is about 10 mJ cm^{-2}. The non-thermal light-induced phase transformation in gallium dominates its response in the cw regime and for excitation with pulses longer than a few tens of nanoseconds. However, with shorter optical pulses, from a few nanoseconds down to femtoseconds, thermal diffusion does not have enough time to remove heat from the skin layer during the pulse, and the temperature at the excitation point increases, inevitably leading to thermal melting of the gallium film. This thermal melting process is highly reproducible from heating cycle to heating cycle as it only involves a few atomic layers of gallium at the interface. This mechanism of surface metallization was the dominant one for the conditions of the pump–probe experiment performed with 3 ns optical pulses in the visible part of the spectrum, reported in [24] (where a more detailed description of the transient melting process — outlined in figure 8 — may be found). Conversion of α-gallium into the metallic phase changes the reflectivity until the molten layer's thickness exceeds the optical skin depth.

So there are two main mechanisms of metallization, a thermal mechanism and a non-thermal mechanism. Whatever the mechanism of metallization is, when the excitation is terminated the molten layer rapidly recrystallizes. It returns to the structural configuration and crystalline orientation that it was in before the melting due to the presence of the crystalline gallium behind the metallized layer. Correspondingly, the reflectivity is restored to its initial value. The reflectivity relaxation time depends on the velocity, v_r, of the recrystallization front between the α-gallium phase and metastable phase. It also depends on the rate at which the interface cools and on the depth d of the metallized layer. Under the conditions used in the experiments described in [19] the characteristic thermal diffusion time is shorter than the recrystallization time and the reflectivity's recovery is controlled by the interface velocity. In gallium, the interface velocity is slower at temperatures closer to the phase transition temperature [25]: $v_r \sim (1 - T/T_0)$. This explains why the recovery time $\tau = d/v_r$ increases critically on approaching the melting temperature T_0, as shown in figure 9. This graph also illustrates that the relaxation time increases with pulse duration, because higher radiation doses create a deeper metallic layer, which then takes more time to recrystallize.

How fast can the light-assisted metallization and reflectivity switching be achieved? At low light intensities, approximately a few kW cm^{-2}, the effect of the structural transformation has a cumulative nature. After the optical excitation commences, more and more crystalline cells are converted into the metallic phase. The thickness of the metallic layer, and thus the reflectivity, increase with time during the laser pulse (see figure 10). In a cumulative regime
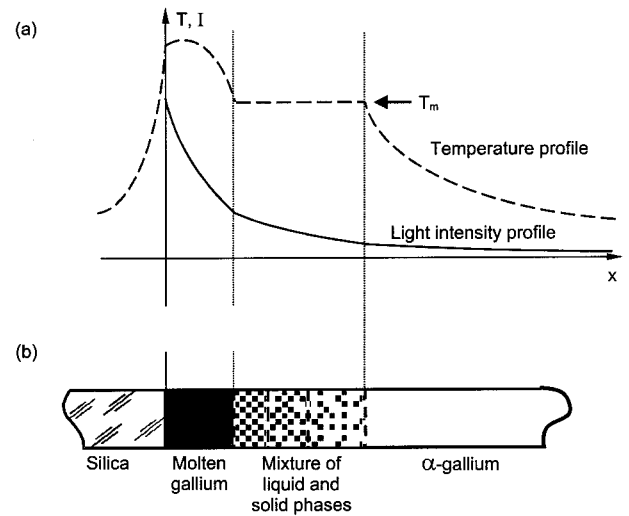

Figure 8. The thermal melting concept of light-assisted metallization at a gallium–silica interface in the pulsed excitation regime: (*a*) light intensity profile, and resultant temperature profile in gallium near to the interface with glass. (*b*) The absorbed laser energy is sufficient to completely melt the gallium immediately at the interface and to partially melt gallium further from the interface. The area affected by laser-induced meeting is only several tens of nanometres (following [21], © American Institute of Physics).
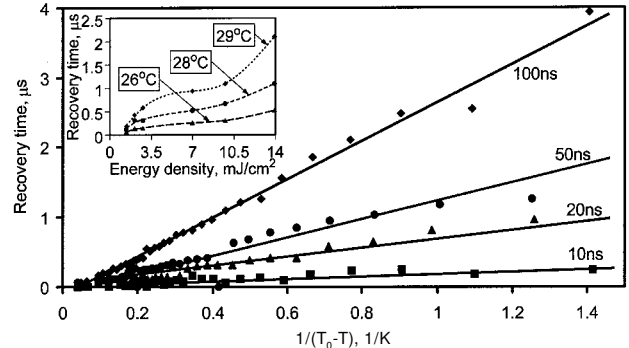
Figure 9. Light-induced reflectivity change recovery time, τ, in confined gallium, plotted as a function of $1/(T_0 - T)$, where T is the sample temperature and T_0 is gallium's melting temperature. Different lines correspond to different pump pulse durations at a peak pump power of 70 mW, $\lambda = 1.55$ μm. The inset shows the recovery time as a function of pulse energy density for three different temperatures (following [19], © American Physical Society).

such as this there is no point speaking about a characteristic, 'intrinsic' switching time. The higher the light intensity, the faster the switching occurs. Importantly, the reflectivity starts to increase immediately after commencement of the pump pulse — a signature of the non-thermal melting mechanism (in the early stages of the excitation, the temperature increase is very small and thermal melting is

a)
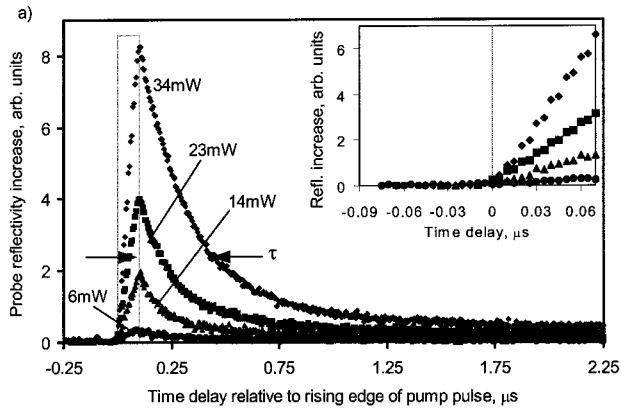
Figure 10. Dynamics of the reflectivity change in a gallium – silica interface after excitation with 100 ns pump pulses (dashed line) of varying peak power, at a temperature $T = 24°C$. The inset shows dynamics near the rising edge of the pump pulse with an enlarged time scale (following [19], © American Physical Society).

Figure 11. Measurement of the 'intrinsic' reflectivity increase time for a gallium – silica interface at $T = 21°C$, induced by a femtosecond light pulse at $\lambda = 810$ nm. The reflectivity change is in arbitrary units (following [26], © Optical Society of America).

impossible). However, with very short laser pulses, in the femtosecond time domain, the medium's reaction time is long in comparison with the duration of the light pulse and the concept of an intrinsic switching time can be introduced. It has been measured for a gallium – silica interface, using mutually delayed 150 fs pump and probe pulses at a wavelength of 810 nm [26], and was found to be 2 – 4 ps (see figure 11). The particular phase of gallium achieved in the femtosecond experiments is not yet clear. We only can guess as to whether this intrinsic switching time is the time needed for the α-gallium lattice to melt, or to convert it into another metastable crystalline phase. Interestingly enough, a recent femtosecond X-ray study of a light-induced phase transformation in VO_2 indicated that a transition to a new crystalline phase, but not into the melt [27].

This excellent reproducibility of the metallization – recrystallization process, which only involves few atomic layers of material, allows for such applications as all-optical switching and laser Q-switching. The moderate dependence of the nonlinear mirror's efficiency on wavelength in the visible to near-infrared spectral range makes them useful at any wavelength from 400 to 2000 nm and beyond (see figure 12). The uniquely broadband character of gallium's nonlinearity is explainable on the one hand, by the very broad nature of the gallium dimers' absorption line (~ 0.4 to ~ 1.8 μm)—the basis of the non-thermal metallization mechanism. On the other hand, α-gallium's total absorption (interband and free-electron), as for many metals, is strong in the infrared, thus providing for the thermal mechanism of the nonlinearity at wavelengths from the visible out to 2.7 μm in the mid-infrared [28].
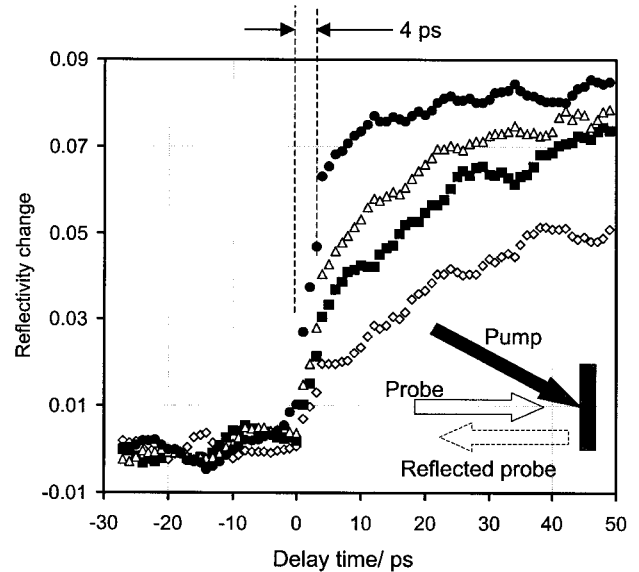
We will now consider a practical example of how gallium's nonlinearity may be used in all-optical switching applications. The simplest implementation of an AND-type switch may be achieved using the nonlinearity and two diode lasers operating at different wavelengths, as shown in figure 13. The radiation from laser B is assumed to carry information in the modulation of its intensity that needs to be cross-coded into the intensity modulation of laser A, at a different wavelength. This is achieved by mixing radiation from the two lasers on a nonlinear gallium mirror [29]. Stimulation of the mirror by the modulated radiation from laser B changes its reflectivity and therefore the intensity of reflected light from laser A. At C, the output of the gate, the now modulated radiation from laser A is spectrally filtered. Such a gate requires only a few milliWatts of laser power to operate and has a frequency bandwidth of several hundred kiloHertz. Using a similar arrangement, cross-wavelength all-optical switching was demonstrated between two telecom spectral bands at 1.55 and 1.31 μm [30].

Gallium mirrors are also suitable for controlling the dynamic characteristics of lasers. So-called passive Q-switching, i.e. forcing the laser to generate short pulses instead of continuous radiation, was achieved using a gallium mirror in low power erbium and ytterbium lasers operating at wavelengths of 1550 and 1030 nm respectively [31]. The mirror replaced a dielectric mirror in a Fabry – Pérot laser resonator. In this situation, the gallium mirror acts as a nonlinear dumping element
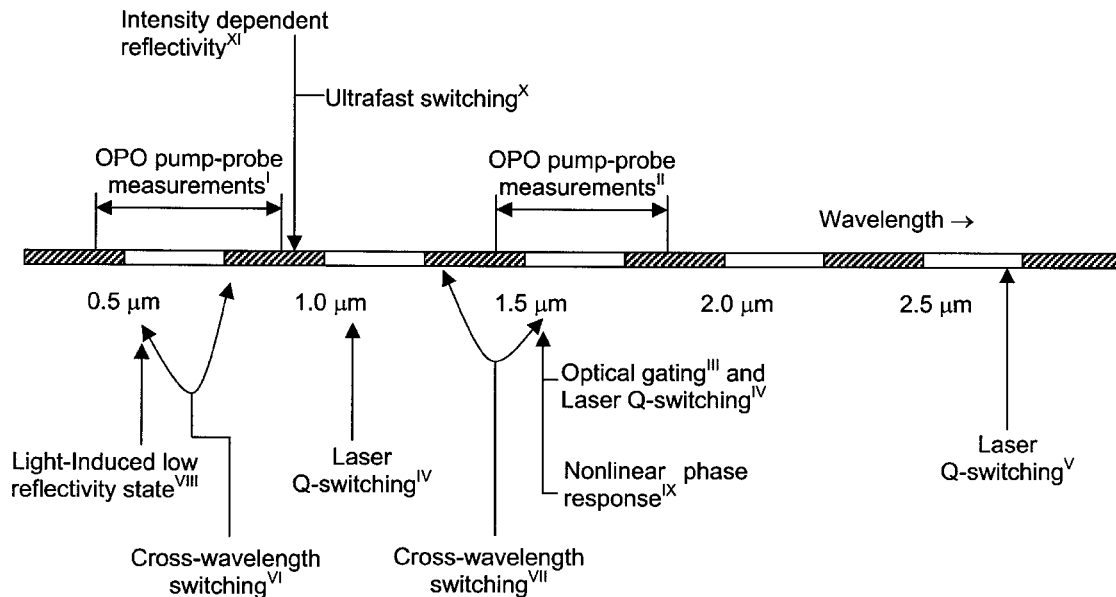
Figure 12. Confined gallium as an extremely broadband nonlinear material. Arrows show wavelengths at which various experiments involving confined gallium's nonlinearity were performed. References are as follows: I, [24]; II, [28]; III, [19,32]; IV, [34]; V, [31]; VI, [29]; VII, [33]; VIII, [30]; IX, [23]; X, [26]; XI, [18].
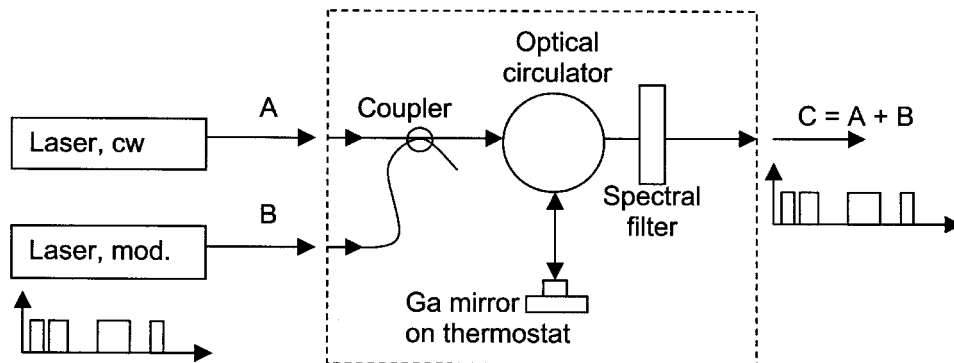
Figure 13. Schematic of an AND gate exploiting the nonlinearity of a gallium mirror and operating with standard telecom diode lasers. Here an unidirectional optical circulator is used to couple light at inputs A and B into the gallium mirror, and to route the light reflected from the mirror to the gate output C (following [32], © American Institute of Physics).

and controls the losses in the cavity: the higher the intensity in the cavity, the higher the mirror's reflectivity and the lower the losses. With such a mirror, the laser rapidly attains the pulsed mode of operation after being switched on, generating optical pulses several tens of nanoseconds long with repetition rates from tens to hundreds of kiloHertz, depending on the conditions. A similar regime was also achieved in a ZBLAN fibre-laser operating at 2.7 μm [27].

In order to be incorporated into highly integrated waveguide structures, the future all-optical switch will have to be small in all dimensions. This brings us to our current study of gallium nanoparticles. Nanoparticles are the ultimate confined geometry: leading to dramatic modifica-

tions of gallium's properties and phase diagram, facilitating the reversibility of the phase transformation underpinning its optical nonlinearity and offering local field-enhancement effects which could improve the characteristics of gallium-based all-optical devices. This means that gallium nanoparticles may be one of just a few ways to realize nanoscale all-optical switching devices. We have developed a technique for depositing gallium nanoparticles directly onto the end of optical fibres, from an atomic beam source [32] — a technique that ensures very convenient compatibility with optical signal carriers.

The work on the nonlinearity of gallium nanoparticles is at an early stage [33], however it is already clear that the mechanisms underlying the nonlinearity in nanopar-

ticles are similar to, but certainly not the same as those responsible for the response of gallium films. Figure 14 shows the results of an experiment in which a gallium nanoparticle mirror, consisting of thousands of particles approximately 80 nm in diameter, was grown on the fibre's tip. The mirror's nonlinearity was then measured in a reflective pump–probe experiment. A 400 μW probe beam at a wavelength of 1.31 μm and a 800 μW pump
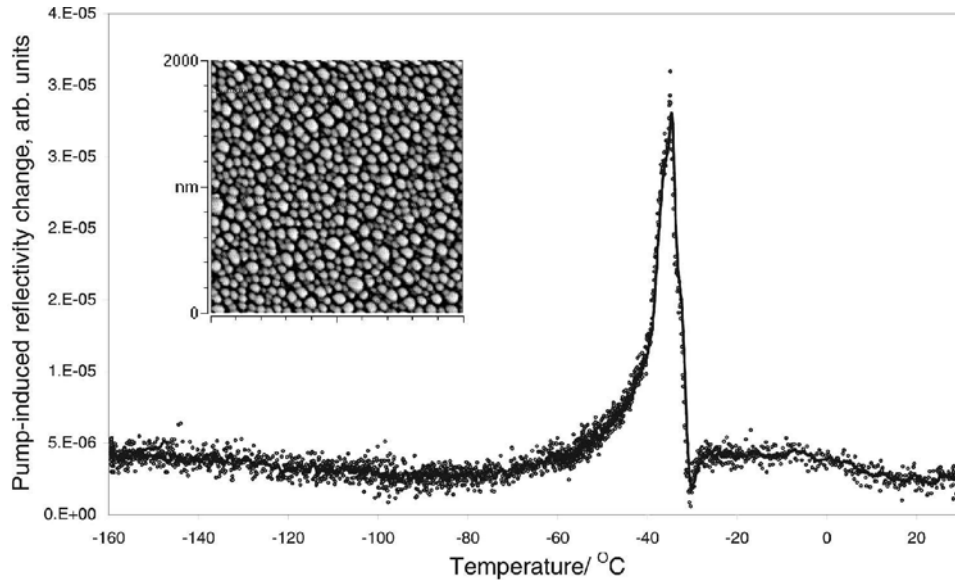
Figure 14. Temperature dependence of the nonlinear response of a gallium nanoparticle mirror. Note the strong peak at a temperature of about −35°C, close to the melting temperature of β-Ga. The inset shows an atomic force microscope scan of a typical gallium nanoparticle mirror as used in the experiment.
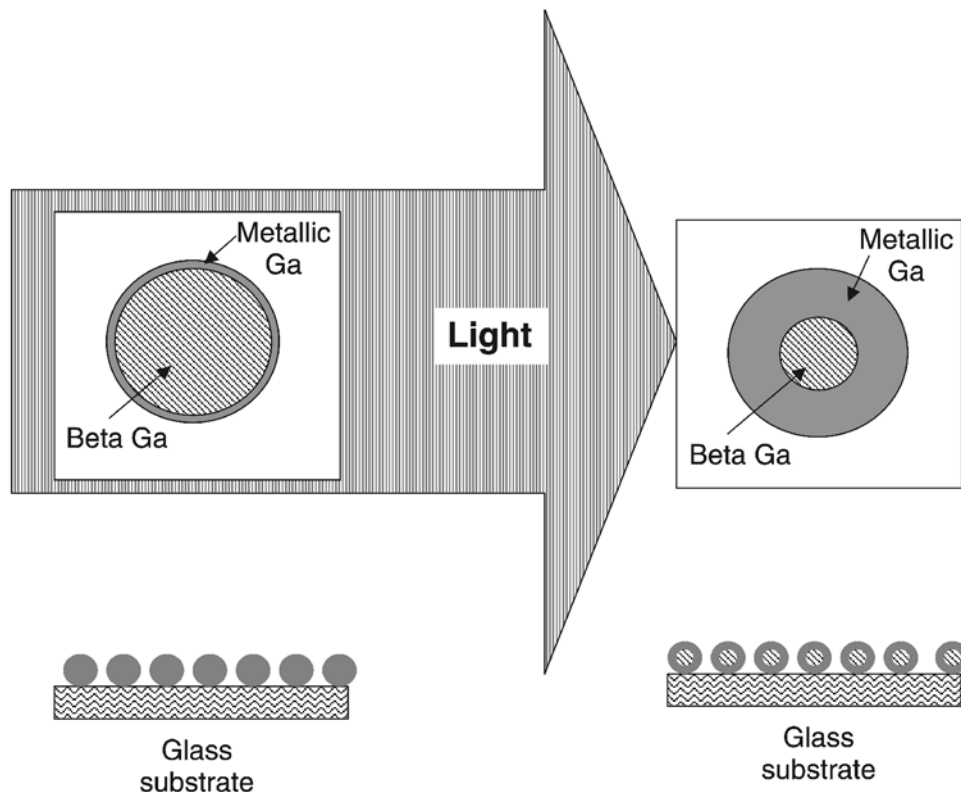
Figure 15. Light assisted metallization of gallium nanoparticles leads to an increase in the film's reflectivity.

beam at 1.55 μW, modulated at different frequencies in the kHz range, were generated by diode lasers. The reflected probe intensity-modulation induced by the pump (the figure of merit for the nanoparticle mirror's nonlinear response) was measured using the lock-in detection technique. Notice the sharp increase in the nanoparticles' response at a temperature of about $-35°C$, similar to the peak at $+30°C$ in the temperature dependence of the response of α-gallium films. In nanoparticles, β-gallium, a phase with a lower melting temperature than α-gallium, is probably the main ground state phase (see figure 4). Our working hypothesis is that as a result of optical excitation, a thin surface layer of a new, highly metallic phase, a 'shell', is created on the core of the β-phase nanoparticle. The shell's thickness increases with the intensity of excitation, and the particle's reflectivity grows accordingly, providing for a substantial change in the reflectivity of the nanoparticle film (see figure 15). Again, the light-induced structural phase transition in a confined geometry is achieved more easily by bringing the material near to a phase-transition temperature, thus increasing the magnitude of the optical nonlinearity.

Finally, some 17 years ago, Gibbs, in his famous book *Optical Bistability: Controlling Light with Light* [5], outlined the ideal characteristics for an all-optical data-processing device. He wrote that 'the device should be small, i.e. of characteristic dimension of a micrometer ... the holding power should be less than 1 mW and the switching energy should be less than 1 fJ'. Gibbs said that the device '... should be fast (< 1 ps), so that high-speed operations can be accomplished', but admitted that 'response times as slow as 1 ms are acceptable for some parallel-processing applications'. Gibbs required that the device 'should be operable at room temperature' and 'it should be integrable to permit a large number of interconnections'. Summarizing this set of requirements, Gibbs concluded that 'clearly, none of the demonstrated devices is a good approximation to the ideal device'. Seventeen years later we are still in the same position and widespread all-optical data processing remains a dream. However, it is intriguing to see how close the nonlinearities of confined systems on the verge of a structural phase transition, with that of gallium – silica interfaces the prime example, have brought us to Gibbs' ideal device. Here we have a switching device on the tip of an optical fibre, which may in the future be based on just a single nanoparticle. Its switch-on time is just a few picoseconds and it has a recovery time in the nanosecond range, it works at room temperature and allows for a very high level of integration. It operates at only a few milliWatts of laser power. It requires more energy to switch than Gibbs' ideal switch, about 10 nJ, but a single nanoparticle device would only require about 10 pJ to switch — much closer to the 'ideal' energy.

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