

All change, please

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Examples of structural phase changes abound in the natural world around us. But if we can exploit such changes on the nanoscale using light, new nanophotonics technology may be just around the corner.

Melting polar ice caps or the fantasy of freezing oceans in cataclysmic Hollywood films are graphic illustrations of often badly understood thermodynamic processes involving a structural phase change in water (Fig. 1). What is less widely known is that similar phase change events occurring on the nanoscale lie at the foundation of one of today's most important data-storage technologies, the re-writable digital versatile disk (DVD), and that they are lining up to underpin the next generation of super-reliable, high-capacity electronic memories. Ultrasmall devices exploiting structural phase changes could also form the basis for the design of future active nanoscale optical circuits.

A radical change in the arrangement of atoms is called a structural phase transition, or phase change. Liquid water, in which the molecules are randomly arranged, undergoes a phase change to the regular crystalline atomic construction of ice on freezing, and back on melting. This is a phase change between disordered and ordered states.

So what use are such transformations for photonics? It appears that phase-change functionality can provide a way of shrinking optical switching devices all the way down to the nanoscale. They can help achieve the ultimate goal of nanophotonics — that is, to create devices smaller than or comparable in size to the carrier wavelength of the signals they handle, a relationship of proportions that is easily achieved in most electronic circuits.

The concept of all-optical logical memory elements has been studied extensively since the 1980s. Optical nonlinearities can be used together with



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Figure 1 Processes similar to that of global climatic events involving melting icebergs also occur on the nanoscale, but quadrillions of times faster. By harnessing such phase changes, scientists could come up with fast and flexible nanophotonic circuit designs.

a feedback mechanism to enhance the switching response of a material and lock it into one of two or more possible stable states. However, the minimum spatial size of early bistable and multistable optical devices was limited to one wavelength — too large for nanophotonic technology — because they involved feedback from the interference of light¹.

Two main hurdles obstruct the nanoscale miniaturization of photonic circuits: the need to guide optical signals in the narrow and sharply bending waveguides of a highly integrated environment; and the need to modulate these signals in very

small active devices. It is now believed that the guiding problem can be successfully addressed using surface-plasmon-polariton waves as information carriers^{2,3}. However, the modulation challenge seems to be much more difficult to tackle.

In essence, the modulation of a signal in a waveguide requires that its amplitude or phase be changed substantially by a control signal either through a change in propagation losses or propagation delays. This is practically achieved by modulating the absorption coefficient and refractive index of a length of waveguide over which a change in amplitude or phase then

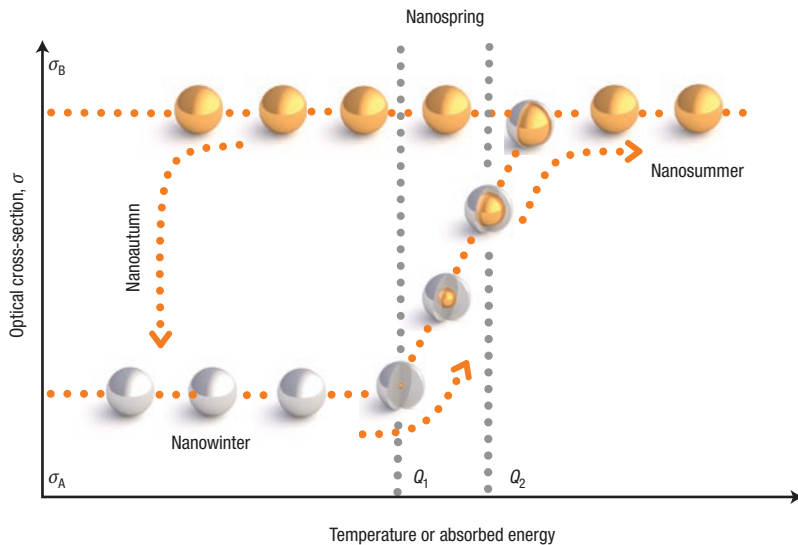


Figure 2 Phase change optical functionality in a nanoparticle: the dependence of optical cross-section σ on absorbed light energy Q for a nanoparticle undergoing a phase transition. At low temperature, the particle exists in phase A (nanowinter). Reversible changes occur when a light pulse of energy between Q_1 and Q_2 is used to excite the system (nanospring). Excitation energy levels above Q_2 herald in nanosummer and a memory effect: phase A fully transforms into phase B, and the particle remains in this metastable phase even as the excitation is withdrawn. A transition to the low-temperature phase takes place abruptly and only after overcooling (nanoautumn). The spherical structures indicate nanoparticles in phase A (silver), phase B (gold) and transitional mixed-phase states (silver and gold) occurring in the energy range between Q_1 and Q_2 .

accumulates. But in optical nanocircuits, individual components are spaced on the nanoscale and there is not enough propagation distance to obtain effective modulation.

The only way to overcome the lack of propagation distance is to use nanometre-scale materials that can undergo a very strong change in absorption or refraction in response to an external control wave; for example, for a refractive index the real and imaginary parts would need to change on the order of unity. Traditional approaches such as the use of optical resonators to enhance modulation do not help here; any resonator must be at least one wavelength long (longer if possible, as resonator performance improves with length), and it will therefore simply not fit into nanoscale circuits. The required large changes in absorption and refraction are only possible in media where there is something substantial to change. And on this score, metals, which refract and absorb light strongly, fit the bill.

PHASE-DEPENDENT OPTICAL PROPERTIES

Large changes in the optical properties of metals can only be achieved through a phase change, and some metals — gallium, for example — can exist in phases with vastly different optical properties.

This is the first piece of good news for nanophotonics. The stable ground-state phase in bulk is α -gallium, which has a very low melting point of only 29.8 °C and is likened to an inorganic polymer. When α -gallium melts at about room temperature, the modulus of its dielectric coefficient changes by more than a hundred. The α -phase is not normally observed in nanoparticulate form, but gallium nanoparticles can exist in a variety of other phases: from the highly metallic liquid phase to forms known as β -, γ -, δ - and ϵ -gallium, which display some marked departures from metallic behaviour. When gallium melts, the absorption and scattering cross-sections at the plasmonic resonance frequency change by an order of magnitude.

ENERGY EFFICIENT

The second piece of good news is that the energy difference between phases is often small, making phase-change-based devices extremely energy efficient. For instance in the case of optical nonlinearity associated with the bound electrons of a material, the maximum effect that the absorption of a single photon can have on the 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). This requires one photon per atom. A similarly strong effect on the optical properties of a material may be achieved by providing the energy needed to move it from one phase to another. This energy ‘price’ is typically of the order of the characteristic phonon energy per atom. As phonon energy is three to four orders of magnitude lower than photon energy, changing the optical properties through a phase transition is much more energy efficient than relying on electronic nonlinearity. So the energy of only a handful of photons should be enough to convert an entire nanoparticle from one phase to another, say from a weakly absorbing ‘semiconductor’ phase to a strongly optically absorbing ‘metallic’ phase.

NANOSEASONS

The third piece of good news for nanophotonics is that structural phase transitions in nanoscale objects are different from those in bulk media. Depending on the regime of excitation, one can obtain either reversible or irreversible phase changes. Continuous and reversible changes occur through the intermediate coexistence of phases, and are suitable for controlling light with light. Irreversible changes are better suited to nanoscale optical memory elements.

Consider, for example, a nanoparticle that can exist in two different phases depending on temperature (Fig. 2). Continuing with the climatic analogy, the low-temperature phase represents winter when water is frozen into ice, whereas the high-temperature phase is that of summer, when ice melts into water. The seasons of spring and autumn in the nanoworld are interesting for photonics. Just as sunlight melts some of the ice on a spring day, a nanoparticle still in its low-temperature phase but with a rising ambient temperature, can be converted to the high-temperature phase by only a small amount of extra heat provided by a control light beam. If this phase change is only partial, then on removing the control light beam the particle will return to the low-temperature phase, like ice re-forming overnight in spring. These ‘nanospring’ processes can be reversible.

However, as the temperature increases further, there comes a point when the particle is converted completely into the high-temperature phase and it remains locked in ‘nanosummer’. Full conversion to the high-temperature phase may also be achieved by providing sufficient energy in the form of a control light pulse hitting the nanoparticle, rather than by

changing the ambient temperature. Under these conditions the fully converted particle remains in the high-temperature phase even after the optical excitation is withdrawn. It could be said that the particle has a memory of past events written into its phase: reducing the temperature to the lowest nanospring level will not revert the particle back to its low-temperature phase. Much stronger cooling to a few tens of degrees below the lowest nanospring temperature (known as overcooling) is needed to trigger 'nanoautumn'. In fact, in some cases the nanoautumn transition may be stimulated by a short optical pulse.

Under the right conditions, therefore, a polymorphic nanoparticle can be locked into a metastable state, in which it remains regardless of changes in temperature. As the different crystalline phases of a single nanoparticle possess different optical absorption and scattering cross-sections, one can build a logical memory element by coding each distinct optical characteristic with a unique label. The transitions between the different phases, or equivalent logical states, may be activated by increasing or decreasing the temperature of the medium. In the case of optical data storage, this could be done by external excitation using optical pulses.

The phase-change approach to controlling the optical properties of a nanoparticle is deeply rooted in the nanoscale nature of the effect. The smaller the particle gets, the more rapidly and easily its optical properties (absorption, in this case) can be modulated by energy from an external light beam. Nanoparticles are particularly promising for all-optical data-storage applications because they provide intrinsic

mechanisms of phase metastability, offer outstanding information-storage density in the terabits-per-square-inch territory and require a very small amount of energy per logical state to write. For example, in gallium an energy of just 0.4 fJ, which is equivalent to the energy of about 2,000 photons at a wavelength of 1 μm , is in principle enough to convert the state of a nanoparticle with a radius of 15 nm from the δ - to the β -solid phase. And absorbing the energy of just one photon could be sufficient to completely convert a particle with a diameter of a few nanometres into a different phase, thus making a single-photon all-optical switch a feasible proposition.

The ten orders of magnitude size difference between a melting iceberg and a nanoparticle changing its phase has welcome implications for nanophotonics: in the nanoworld spring and autumn may take only a few billionths of a second. Because the phase change proceeds through the coexistence of two phases, it involves the propagation of a boundary between the phases. Although this phase front does not travel particularly fast, and is normally much slower than the speed of sound, in nanoparticles it does not have far to travel, so switching times in the nanosecond range are possible. Subnanosecond switching times may even be possible if the 'explosive crystallization' regime — observed in thin metal films when crystallization velocities reach tens of metres per second — can be achieved in nanoparticles. A transition from a low-temperature to a high-temperature phase induced by an optical pulse may be even faster if the high-temperature phase is a disordered state of matter and the

low-temperature phase is highly ordered. It only takes a few angstroms of atomic movement in a random direction to achieve such a transition. These processes occur on the picosecond timescale or even faster.

Nanophotonic switching and memory functionality underpinned by phase change has already been demonstrated using gallium nanoparticles. Solid-to-solid and solid-to-liquid light-induced phase transitions have been observed in various crystalline and amorphous phases of gallium⁴. Similarly, resonator-free all-optical memory has been achieved in this system^{5,6}. The size of the memory element, which is equal to the size of the nanoparticle itself, is comparable to that of magnetic domains in state-of-the-art hard disks. Moreover, the energy needed to switch the nanoparticle (that is, to store one 'bit') is an order of magnitude smaller than that needed in DVD/DVR technology. These findings suggest that in the future photons driving structural phase changes could offer a practical way of controlling signals in plasmonic⁷ and nanophotonic circuits⁸.

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