



Optical switching at ZnSe–Ga interfaces via nanoscale light-induced metallisation

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Received 23 January 2005; received in revised form 2 May 2005; accepted 24 May 2005

Abstract

A structural transformation induced by optical impulse excitation of only a few mJ/cm^2 fluence affecting the nanoscale surface melt layer of gallium at a ZnSe–gallium interface leads to a fast, substantial and fully reversible change in reflectivity of up to 50%. Recovery occurs within a few μs after excitation is withdrawn and less than 1 μs at temperatures more than 4 K below gallium's melting point.

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PACS: 190.4350; 190.4720

Keywords: Nonlinear optics at surfaces; Optical nonlinearities of condensed matter

There is a growing demand for photonic materials that offer integration into current manufacturing technologies, and manifest strong nonlinearities suitable for all-optical switching, power limiting and laser control. Among traditional materials investigated for such applications are semiconductors with functionality underpinned by near bandgap and excitonic transitions, organic materials with weakly bound electrons,

and liquid crystals where performance relies on molecular re-orientation. Functionality underpinned by structural transformations is a new paradigm for meeting the demands of nanophotonic technologies. Here, research concentrates on highly correlated systems where structural changes may be effected by stimulating the electron and/or spin sub-systems [1], and polymorphic materials such as VO_2 [2] and metallic gallium. In polymorphic gallium [3], a light-induced metallisation transition at a gallium–glass interface affecting only a few atomic layers of the metal offers opportunities for broadband optical switches, photo-detectors and laser Q-switching.

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In this paper, we investigate a light-induced structural transformation in gallium interfaced with a semiconductor crystal of zinc selenide. Our research is motivated in part by the desire to ascertain whether the stimulated nanoscale structural transformation will readily occur on semiconductor interfaces, thus offering the potential of integration into semiconductor devices and structures such as lasers, detectors, waveguides and photonic crystals. It should be noted here that the interface assisted structural transformation is a dynamic manifestation of the surface melting effect [4] which has been studied at gallium–vacuum [5], gallium–diamond [6] and gallium–glass interfaces [7], but never at semiconductor interfaces. Moreover, a phase transition at a semiconductor–gallium interface could lead to a much stronger change in reflectivity than at the well-investigated silica interface due to a closer match between the dielectric properties of the semiconductor and that of the ground-state phase of gallium.

We investigated the light-induced structural transformation and associated transient reflectivity changes at gallium–ZnSe interfaces using a pump–probe technique. A Q-switched Nd:YAG-pumped optical parametric oscillator producing 8 ns pulses at a rate of 20 Hz was used as the pump source in the near infrared part of the spectrum. The probe beam was derived from a 0.5 mW, fibre-coupled, 1300 nm CW diode laser, and focused to a spot on the interface overlapped by the pump laser spot. The probe was circularly polarised to minimise the effect of gallium’s crystalline anisotropy at the interface. The probe beam reflected from the gallium–semiconductor interface was detected by a InGaAs photodiode and analysed with a digital storage oscilloscope. Gallium–semiconductor interfaces were prepared by squeezing molten gallium against optically polished wedges of ZnSe (angle = 0.5°, supplied by ISP Optics Corp.) then solidifying the gallium. In the experiment the sample temperature was controlled by a Peltier heat pump (see insert in Fig. 1(a)).

The linear reflectivity of the Ga–ZnSe interface (see Fig. 1(a)) manifests the characteristic features of the surface melting effect. As the temperature increases, the reflectivity stays approximately constant until about 27 °C, and then increases pro-

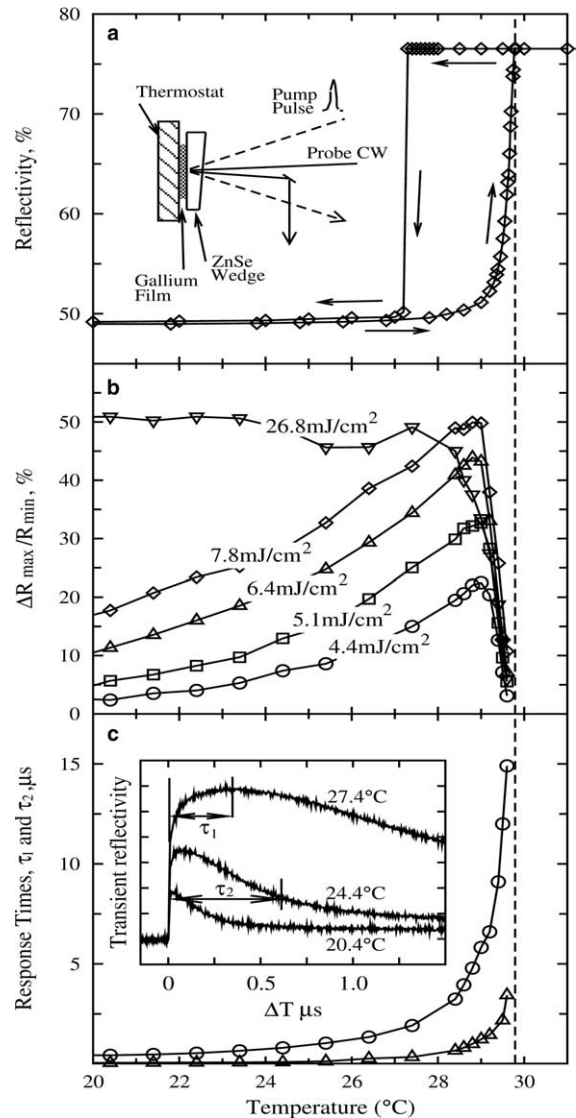


Fig. 1. Light-induced structural transformation at a gallium/zinc selenide interface. (a) Reflectivity of the interface as a function of temperature. (b) The peak pump-induced relative reflectivity increase ($\Delta R_{\max}/R_{\min}$) as a function of temperature for different pump fluences. (c) The relaxation time of the nonlinearity as a function of temperature (\circ) and the time from pump pulse excitation to peak response (Δ). The insert in graph (a) details the experimental set-up, and inset to (c) are typical real-time reflectivity traces with 6.4 mJ pump pulses.

gressively. As the gallium melting temperature of $T_0 = 29.8$ °C is approached, the reflectivity increases sharply to the level corresponding to liquid

gallium. Such behaviour is indicative of the gradual development of a layer of molten gallium at the interface with a thickness in the range of a few nanometres. Pronounced overcooling is evident in the 3 K wide reflectivity hysteresis seen on solidification of gallium in falling temperature. The reflectivity data may be used to derive the thickness of the intermediate liquid layer as a function of temperature, as presented in Fig. 2. Here, reflectivity was modelled for an α -gallium/liquid-gallium/ZnSe structure using standard thin film formulae [8] and dielectric properties of Ga from [9,10]. This analysis points to a similarity with what has already been seen at gallium–silica interfaces [7]: a 5.5-nm thick transitional layer with properties resembling those of liquid or amorphous gallium can explain the reflectivity levels intermediate between those of solid gallium interfacing with ZnSe and liquid gallium interfacing with ZnSe at temperatures far lower than the melting point.

Pump pulse excitation produces a rapid increase of reflectivity followed by a much slower relaxation to the initial reflectivity level (see inset in Fig. 1(c)). We have presented the peak relative reflectivity increase ($\Delta R_{\max}/R_{\min}$) as a function of

temperature for a range of pump fluences in Fig. 1(b). At lower fluences the pump-induced reflectivity increases monotonously with temperature, reaching a peak at about $T = 29^\circ\text{C}$, then decreases rapidly to zero at the melting temperature. At higher excitation levels the nonlinear signal becomes less dependent on temperature. The intrinsic transformation time from solid gallium into melt is expected to be of the order of a few picoseconds [11] and is not resolved in our experiments. In Fig. 1(c), we present the time lag (τ_1) between pump pulse excitation and the peak in reflectivity which occurs sometime later. We also plot the relaxation time measured at full width half maximum (τ_2). The relaxation time τ_2 increases from less than $1\ \mu\text{s}$ 10° below the melting temperature to about $15\ \mu\text{s}$ at a temperature 0.2° below the melting point. Although τ_2 always remains longer than τ_1 , the ratio between τ_2 and τ_1 slowly decreases from about 9 at 20°C , to about 4 at 29.6°C . The reflectivity change was experimentally observed to be repeatable over many thousands of optical pulses which leads us to believe that it would be repeatable ad infinitum.

The light-induced increase in reflectivity results from a dynamic laser-induced increase in the thickness of the more reflective layer between the solid gallium and semiconductor through a light-induced structural transformation. The normal ground phase, α -Ga, contains covalent dimers leading to a broad absorption peak centred at 2.3 eV [12] and significantly lower reflectivity in the visible and NIR spectrum than the more metallic phases. The transitional layer of surface melt and the crystalline bulk exist in a delicate equilibrium which may easily be altered by the addition of energy to the interface. The energy supplied from a pump pulse changes this balance, pushing the solid–liquid phase boundary further in to the crystal bulk [7]. This brings about a large and fully reversible change in reflectivity: the reflectivity recrystallisation recovers through of the transitional layer into the bulk α phase. The relaxation time τ_2 is controlled by the velocity of recrystallisation. We found that τ_2 is proportional to ΔT^{-1} where $\Delta T = T_0 - T$ is the temperature difference from the phase transition temperature T_0 . A study of the growth kinetics of the solid–liquid phase

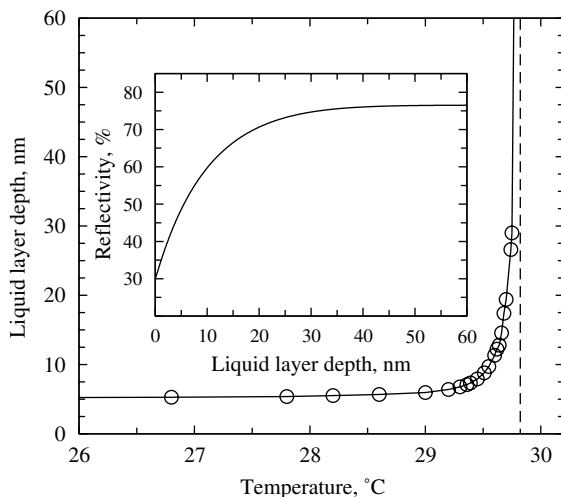


Fig. 2. Modelling surface melting of gallium at the ZnSe interface. An estimate of the melt thickness at the interface is achieved by comparing the observed reflectivity with that modelled for an α -gallium/liquid-gallium/ZnSe structure (inset). Circles represent experimental points.

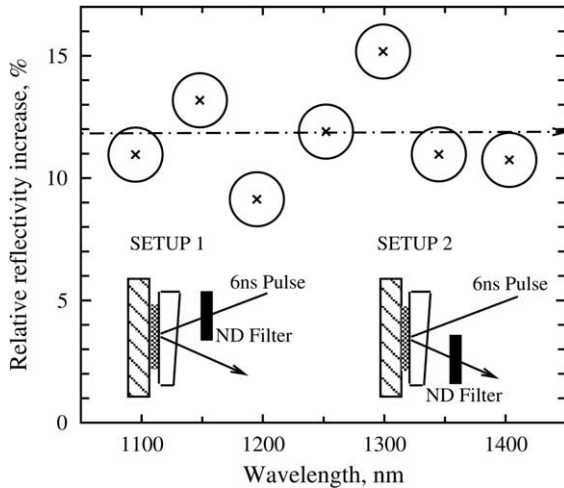


Fig. 3. Spectral dependence of the reflectivity nonlinearity of ZnSe–gallium interface at $T = 27.4^\circ\text{C}$ and excitation level of 10 mJ/cm^2 . The circles are the experimental measurements of relative reflectivity increase at 4 ns after the onset of excitation. Measurements were made by recording the difference in the intensity of the reflected pulse between set-up 1 and set-up 2.

boundary using the Seebeck effect [13] found that the growth *velocity* for dislocation assisted growth was proportional to ΔT for low supercooling, in good agreement with our observations. When a pump pulse arrives at the interface the energy that is absorbed is deposited within approximately the first 15 nm. Redistribution of the heat within the sample may explain the delayed peaking (τ_1) of the reflectivity change that continues to increase after cessation of the pump pulse.

We also measured the spectral dependence of the nonlinear response at the gallium–ZnSe interface in the range from 1.1 to $1.4\ \mu\text{m}$ (Fig. 3) in a single beam “self-action” experiment. This experiment shows a optically broadband nonlinear response, with an essentially flat wavelength dependence in keeping with expectations based

on gallium and ZnSe dielectric constants in this wavelength range.

In summary, we report the observation of a fully reversible broadband optical nonlinearity at an interface of gallium and zinc selenide, that is initiated by a nanoscale light-induced structural phase transformation of gallium at the interface.

Acknowledgements

The authors acknowledge V.A. Fedotov’s contribution to discussions on this work and the support of the Engineering and Physical Sciences Research Council, UK.

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