Gigantic optical nonlinearity in laser-deposited gallium films on the verge of a structural phase transition

K. F. MacDonald, N. I. Zheludev
Department of Physics and Astronomy, University of Southampton, Highfield, Southampton, Hampshire, SO17 1BJ, UK
kfm@phys.soton.ac.uk, n.i.zheludev@soton.ac.uk

K. Puech, L. Lefort, D. C. Hanna
Optoelectronics Research Centre, University of Southampton, Highfield, Southampton, Hampshire, SO17 1BJ, UK

A. Rode, B. Luther-Davies
Laser Physics Centre, Australian National University, ACT 0200, Canberra, Australia

V. I. Emelyanov
Department of Physics and International Laser Centre, Moscow State University, Vorobievy Gori, 119899 Moscow, Russia

Abstract: Gallium/silica interfaces prepared by ultrafast pulsed laser deposition have excellent optical qualities and structural stability. They show a gigantic optical nonlinearity in the visible and infrared, up to 1800 nm, which reaches $\chi^{(3)} \sim 1$ esu.

OCIS codes: (190.4350) Nonlinear optics at surfaces; (310.1860) Thin film deposition and fabrication

1. Introduction

We discuss a means of achieving a large optical nonlinearity in a material on the verge of a transition between structural phases with significantly different optical properties. We have found that films of gallium deposited on fused silica by ultrafast pulsed laser ablation show a fully reversible, surface-assisted metallization when approaching the transition from the α-phase (the normal crystalline form at room temperature and pressure) to the liquid. The nonlinearity has been probed in a quasi cw regime using a Ti:Sapphire laser and an Optical Parametric Oscillator (OPO) over a range of infrared wavelengths and is of the order of $\chi^{(3)} \sim 1$ esu (estimate for cw excitation).

2. Ultrafast pulsed laser deposition of gallium films

Until recently optical switching has been observed at gallium interfaces formed either by squeezing molten gallium against a glass slide or by dipping a freshly cleaved optical fibre into a bead of the liquid metal [1]. These are unreliable techniques but we have now found that high-repetition-rate laser ablation with a picosecond-pulsed laser [2] allows us to deposit high quality thin gallium films in the α-phase. 1-2 μm films were deposited from high purity gallium targets onto substrates at –100°C using a mode-locked Nd:YAG laser (λ = 1.064 μm, τ_{FWHM} = 60 ps, pulse energy ~60 μJ) in a vacuum chamber initially pumped to ~2×10^{-6} Torr.

3. Optical nonlinearity across the melting point

We have studied, in a quasi cw regime, the dependence of interface reflectivity on temperature and incident light intensity using a Ti:sapphire laser (λ = 810 nm). Also, by employing pump-probe techniques, we have measured the nonlinear response of the samples (again in a quasi-cw regime) in the 1500-1800 nm spectral range using a periodically poled $LiNbO_3$ optical parametric oscillator. At low incident light intensities (≤400 Wcm^{-2}) reflectivity varies with temperature across gallium's melting point as shown by curves i and i* in figure 1a. Curves ii-v show how the rising temperature part of this hysteresis curve changes with increasing light intensity. The temperature at which solidification occurs on cooling remains unchanged with increasing intensity. In figure 1b we present the magnitude of the light-induced change in the rising temperature parts of the hysteresis curves (the difference between curves ii-v and curve i from figure 1a as a fraction of the reflectivity level shown in curve i).

The pump-probe experiments with the OPO show that the nonlinear response is very broadband, and that a light-induced reflectivity change can be seen out to the OPO signal tuning limit at ~1800 nm (see e.g. fig. 2).

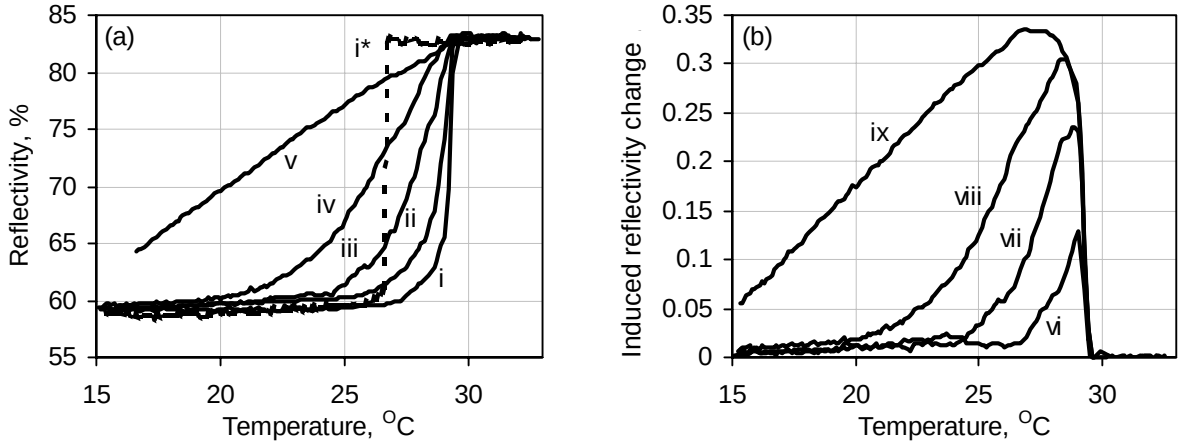

Fig. 1. (a) Variation of PLD gallium/glass interface reflectivity with increasing temperature for incident intensities of i: 400, ii: 570, iii: 1700, iv: 3960 and v: 5660 Wcm^{-2} and i*: with *decreasing* temperature for an intensity of 400 Wcm^{-2}. (b) Magnitude of light-induced reflectivity change for incident intensities of vi: 570, vii: 1700, viii: 3960 and ix: 5660 Wcm^{-2}.

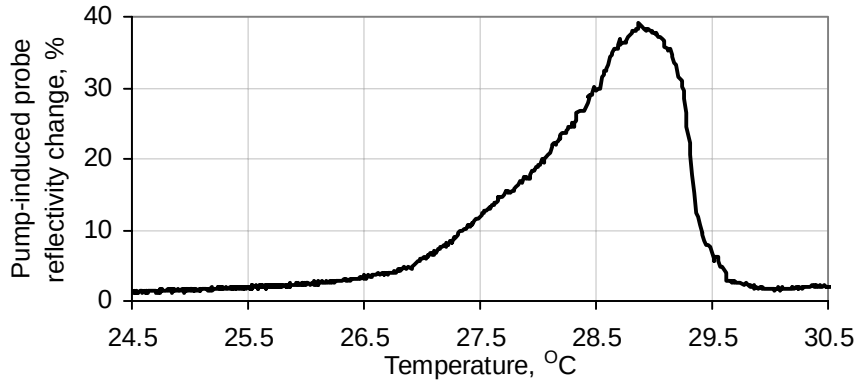

Fig. 2. Magnitude of pump-induced probe reflectivity increase. λ = 1630 nm, Mean pump intensity = 7500 Wcm^{-2}.

4. Light-induced, surface-assisted metallization model

The high sensitivity of the interface's reflectivity to optical stimulation can be accurately explained by light-induced conversion of α-gallium to a new, more metallic, more reflective phase. This metallization is made possible by the unique structure of α-gallium in which molecular and metallic properties coexist - some inter-atomic bonds are strong covalent bonds, forming Ga_2 dimers, and the rest are metallic bonds. The covalent bonding leads to a strong optical absorption peak spreading from ~0.68 eV (~1820 nm) to ~4 eV (~310 nm). Light absorption excites a dimer from the bonding to the antibonding state, reducing the stability of the surrounding crystalline cell. α-gallium subsequently undergoes a transition to a new metastable configuration (crystalline or disordered), creating a microscopic inclusion of the new phase. The presence of these inclusions changes the delicate energy balance at the interface and the thickness of the metallic layer increases, changing the reflectivity accordingly. A light-induced layer 25 nm thick is sufficient to achieve full 'metallic' reflectivity. We believe that excellent optical quality and high stability of the structure against repeated temperature cycling is explained by a transitional interface layer formed by Ga-atoms implanted into the substrate at high energies during the PLD process.

5. References

[1] P. J. Bennett, S. Dhanjal, P. Petropoulos, D. J. Richardson, N. I. Zheludev, and V. I. Emelyanov, *"A photonic switch based on a gigantic, reversible optical nonlinearity of liquefying gallium"* Appl. Phys. Lett. **73**, 1787 (1998).

[2] E. G. Gamaly, A. V. Rode and B. Luther-Davies, *"Ultrafast ablation with high-pulse-rate lasers. Part I: Theoretical considerations"* J. Appl. Phys. **85** (8), 4213 (1999); A. V. Rode, B. Luther-Davies and E. G. Gamaly, *"Ultrafast ablation with high-pulse-rate lasers. Part II: Experiments on laser deposition of amorphous carbon films"* J. Appl. Phys. **85** (8), 4222 (1999).