Dynamics of light-induced reflectivity switching in gallium films deposited on silica by pulsed laser ablation

A. V. Rode, M. Samoc, B. Luther-Davies, and E. G. Gamaly

Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia

K. F. MacDonald and N. I. Zheludev

Department of Physics and Astronomy, University of Southampton, Southampton SO17 1BJ, UK

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We present what is to our knowledge the first experimental study of light-induced reflectivity changes at an α-Ga/Si interface irradiated by femtosecond and picosecond laser pulses. After exposure, the reflectivity can increase from $R \cong 0.55$, which is typical for α-Ga, to $R \cong 0.8$, which is close to that of liquid Ga. The initial step in the reflectivity change of 2–4 ps is resolved with 150-fs laser pulses. The light-induced reflectivity change relaxes during 100 ns–10 μs, depending strongly on the background temperature of the Ga mirror and the laser fluence. © 2001 Optical Society of America

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Elemental metallic Ga at a Si interface is an intriguing and potentially useful nonlinear optical system.[1] Changing the reflectivity of a Ga mirror manufactured on the tip of an optical fiber by more than 30% requires only a few milliwatts of continuous laser power.[1,2] This effect is very broadband: Ga–Si structures show reflectivity changes from at least 480 to 1800 nm.[3] Experiments with nanosecond pulsed laser excitation did not reveal the intrinsic speed of the reflectivity increase but demonstrated that the reflectivity recovers to its original level in a fraction of a microsecond.[4,5] An all-optical cross-wavelength gate function was demonstrated with a fiberized Ga mirror,[6] and a Ga-coated Si plate was used as a passive Q switch in Er^{3+}- and Yb^{3+}-fiber lasers operating at 1550 and 1030 nm, respectively,[7] and recently at 2.8 μm.[8] These findings have given an impetus to a detailed experimental investigation of the dynamics of the switching characteristics of Ga films. In this Letter we report what are believed to be the first time-resolved studies of the reflectivity behavior of α-Ga in confined geometry performed with femtosecond laser pulses.

We studied Ga films deposited on fused Si by use of ultrafast pulsed laser deposition. Films of 1–2-μm thickness were deposited from 6N-purity Ga targets onto Si substrates at $-100°$ C by use of a Q-switched mode-locked Nd:YAG laser ($\lambda = 1.064\ \mu$m; $\tau_{\mathrm{FWHM}} = 60$ ps; intensity at target, $\sim 10^{11}\ \mathrm{W\,cm^{-2}}$) in a chamber pumped to $\sim 2 \times 10^{-6}$ Torr.[9,10] This ultrafast process deposits Ga in a highly reflective form; Ga resolidifies in the α phase after melting. The samples have shown no degradation in optical properties over a period exceeding 1 year, despite repeated heating and cooling across the Ga melting point (29.8 °C). We attribute this structural stability to the presence of a transitional layer formed by the penetration of energetic Ga ions into the glass during deposition.

Transient pump–probe reflectivity measurements were performed with a Ti:sapphire laser composed of a regenerative amplifier and a Kerr-lens mode-locked oscillator at 800 nm and a repetition rate of 30 Hz. The pump and the probe beams, both 150 fs and s polarized, with a typical intensity ratio of 100:1, were incident upon the Ga–Si interface at ~10° to normal from the transparent Si side. The pump spot on the sample, which was 350 μm in diameter, overlapped the probe spot. We mounted the Ga mirrors on a Peltier cooler to allow the sample temperature to be varied. Our measurements have demonstrated that, following the excitation with a pump pulse, the reflectivity of the probe increases from $R \cong 0.55$ to $R \cong 0.8$ (Fig. 1).

The reflectivity change, measured 500 ps after pump excitation for a sample at room temperature (≈21 °C) has a clear threshold (Fig. 2): For pump-pulse energy-density levels below 0.5 mJ/cm^2, no reflectivity change in the probe pulse is seen. Above the threshold, the reflectivity increases rapidly with the pump energy density and then saturates at a level of ~20 mJ/cm^2. The largest relative change in reflectivity $(R_{t=500\mathrm{ps}} - R_{t=0\mathrm{ps}})/R_{t=0\mathrm{ps}} = 0.45$ was

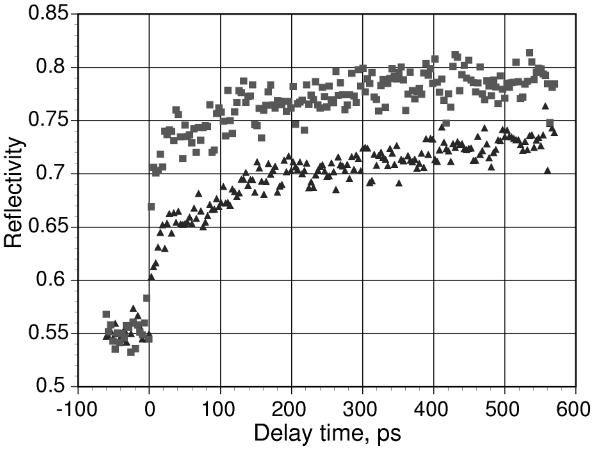

Fig. 1. Pump–probe measurements of light-induced reflectivity in Ga films induced by 150-fs 800-nm laser-pulse excitation at 21.5-mJ/cm^2 (squares) and 4.5-mJ/cm^2 (triangles) laser fluences. The zero point indicates the pump-laser excitation; the background mirror temperature was kept at 13 °C in both experiments.

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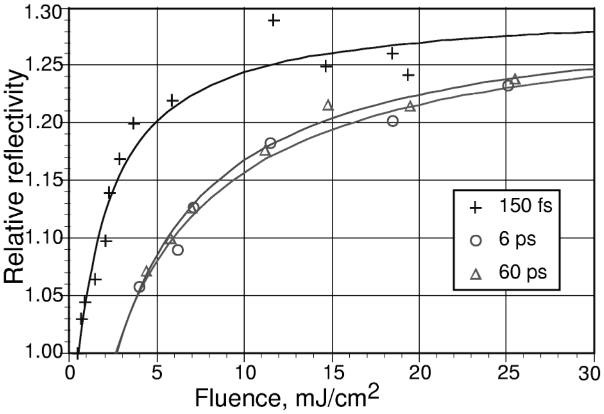

Fig. 2. Relative reflectivity ($R_{t=500\text{ps}}/R_{t=0\text{ps}}$) of Ga films on Si induced with 150–fs pulses at 800 nm (crosses) at 500-ps delay time at a sample temperature of 21 °C. For comparison the results are presented for 6-ps and 60-ps pulses at 1.053 μm.

observed at saturation for sample temperatures near 13°C. It decreased rapidly as the sample temperature approached the melting point of Ga. No damage to the film was detected after 10^5-10^6 laser pulses at energy density as great as ~40–50 mJ/cm^2. For comparison, we also present in Fig. 2 data obtained with 6- and 60-ps pump and probe pulses from a Nd:YLF laser at 1.053 μm. Comparison of the reflectivity changes obtained with picosecond (6–60-ps, 1053-nm) and femtosecond (150-fs, 800-nm) pulses shows that the phenomenon of reflectivity switching in Ga films is dependent primarily on the laser's energy-density (fluence): The maximum reflectivity change for femtosecond pulses only slightly exceeds that of picosecond pulses. This difference might also be attributed to the difference in photon energy at 1053 nm (1.18 eV) in comparison with that at 800 nm (1.55 eV), which is higher than the binding energy of 1.435 eV in covalent Ga$_2$. Photoexcitation of Ga$_2$ may affect the reflectivity change.

The increase of reflectivity is a two-stage process. Figure 3 shows the probe reflectivity measurements in the first 50 ps after excitation for pump-laser fluences of 3.3–8 mJ/cm^2, well above the threshold value of 0.5 mJ/cm^2. The initial fast rise in the reflectivity occurs in 2–4 ps and is shorter for higher fluences. Measurements at different temperatures from 6 to 25 °C show that the rate of increase in reflectivity during this initial fast stage does not depend on the background mirror temperature. In the second stage the reflectivity increases more slowly, reaching its maximum in 300–500 ps after the laser pulse. No reflectivity change was observed for sample temperatures exceeding 29.8 °C, the melting temperature of Ga.

The microscopic picture behind the observed light-induced reflectivity change is being investigated. At this stage it is clear that the reflectivity is related to light-induced conversion of Ga from the α phase to a phase with higher reflectivity. The relatively low semimetal reflectivity of α-Ga is explained by the coexistence of molecular and metallic properties,[11] whereas liquid[12,13] and amorphous[14] Ga are highly reflective and free-electron-like. Our observations, and previous studies with cw excitation, suggest that the optical properties of the skin layer change on illumination because a layer of a highly reflective metallic phase forms between the glass and the α-Ga.[1–5] The microscopic mechanisms of the melting process with ultrafast, femtosecond excitation should be radically different from those in the cw excitation regime, in which thermal conductivity rapidly removes heat from the skin layer.[15] Negligible heat diffusion during the femtosecond laser-pump pulse confines the pump energy to the optical skin depth of Ga. We expect that this will eventually lead to melting within, and possibly beyond, the skin layer and to a corresponding reflectivity increase. However, we do not exclude the possibility that in some regimes an intermediate metastable crystalline stage is formed after laser excitation, as α-Ga is known to melt through consecutive steps of intermediate metallic stages.[16]

Ga shows a remarkably low threshold (0.5 mJ/cm^2) for light-induced femtosecond melting, some 400 times lower than in semiconductors such as Si and GaAs.[17] This large difference can be readily explained. In crystalline Si, for instance, all the bonds are covalent, and so its specific enthalpy of melting is 8–10 times higher than that of semimetal α-Ga. Furthermore, the above-bandgap absorption depth in Si is 10 times greater than in Ga, leading to much higher laser fluence for melting of the skin layer. However, it is worth noting that similar changes in reflectivity (that do not require melting) can be obtained in semiconductor saturable Bragg reflectors.[18] In that case the switching generally saturates at fluences near 30 μJ/cm^2, more than 500 times lower than for gallium, although the spectral response of a saturable Bragg reflector is generally more limited.

We find that the relaxation of the reflectivity change of the Ga–Si interface occurs on a much

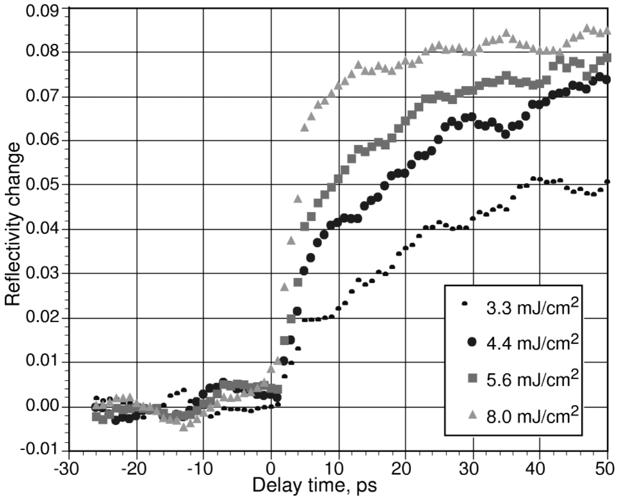

Fig. 3. Transient light-induced reflectivity increase in Ga films on Si measured with 150-fs 800-nm pump and probe pulses at various pump energy densities. The intrinsic response of 2–4 ps of the Ga films was clearly resolved. The sample temperature was kept at 21 °C in all experiments.

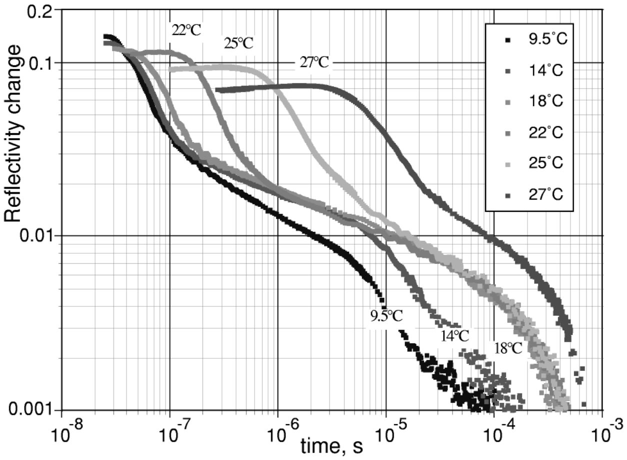

Fig. 4. Reflectivity recovery dynamics measured at various sample temperatures with a cw 632.8-nm probe beam at the pump-beam fluence 15 mJ/cm^2 of 1.053-μm 60-ps pulses.

longer, nanosecond-to-microsecond time scale. Measurements of the decay time after 60-ps Nd:YAG laser excitation at 15 mJ/cm^2 were performed with a cw 632.8-nm He–Ne laser as a probe. The relaxation dynamics of the reflectivity were determined at various sample temperatures by use of a photodetector with ~10-ns resolution. The reflectivity behavior depended strongly on the temperature of the sample and could be approximated by a double exponential (Fig. 4). For example, at a sample temperature of 9.5 °C the first stage of the decay process took 60 ns, followed by a much slower relaxation with a 16-μs decay time. The transient reflectivity at higher temperature [and (or) saturating fluences] remained constant for a relatively long time after excitation (it has a plateau). The length of the plateau depended on the excitation conditions and on the background temperature: The higher the absorbed laser energy and the closer to the melting point, the longer the plateau. In our opinion the relaxation of the reflectivity level is related to recrystallization of the quasi-melt back to the α-Ga phase. The speed of the recrystallization is controlled by the nonlinear heat flow from the excited spot, making the reflectivity relaxation a rather complex process. We are performing numerical simulations of the heat-flow dynamics and the reflectivity relaxation.

In conclusion, the experimental results described above underline the possibilities for using Ga mirrors prepared by ultrafast pulsed laser deposition for practical devices. A large, low-threshold reflectivity increase can be obtained within only a few picoseconds, whereas the fastest reflectivity cycle seen in our experiments takes a few microseconds. Therefore a Ga mirror can be used as a passive broadband fluence-dependent nonlinear switch and is particularly well suited for Q switching and possibly mode locking of a wide range of lasers.

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