

Light-induced metallization in laser-deposited gallium films

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Abstract: We have found that mirrors prepared on silica glass by ultrafast pulsed laser deposition of elemental gallium show a highly reproducible and fully reversible light-induced reflectivity increase. The effect is explained by non-thermal light-induced metallization of gallium at the interface.

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Gallium confined at a glass interface is one of the most intriguing and potentially useful nonlinear optical materials discovered recently^[1]. Just a few milliwatts of laser power are required to change an interface's reflectivity by more than 30%, and to induce an optical phase change of several degrees in reflected light^[2]. With pulsed laser excitation the change occurs very fast, in few picoseconds, and under the right conditions can recover to its original level in a fraction of a microsecond^[3]. This effect is very broadband - recent experiments^[4] show that the gallium/glass structure is sensitive to wavelengths from at least 480 to 1800 nm. Until recently gallium's nonlinearity had only been observed at interfaces formed either by squeezing molten gallium against a glass slide or by dipping a freshly cleaved optical fiber into a bead of the liquid metal^[1]. These are unreliable techniques and not suited to manufacturing interfaces for practical applications. Our attempts to deposit gallium on silica using electron-beam evaporation did not produce films of the common crystalline phase, called α -gallium, as required for the observation of the nonlinearity. We have now found that high-repetition-rate laser ablation with a picosecond-pulsed laser^[5] allows us to deposit high quality thin α -gallium films.

1-2 μm thick films were deposited from 6N purity gallium targets onto flat glass substrates at -100°C using a Q-switched mode-locked Nd:YAG laser ($\lambda = 1.064 \mu\text{m}$, $\tau_{\text{FWHM}} = 60$ ps, intensity at target $\sim 10^{11} \text{ Wcm}^{-2}$) in a chamber pumped to $\sim 2 \times 10^{-6}$ Torr. The emission spectrum of the laser plume, in the range from 220 to 400 nm, was found to be rich in lines of atomic and singly ionised gallium. This process deposits gallium in an amorphous form but after melting, it re-solidifies in the α phase. The samples have shown no degradation in optical and nonlinear optical properties over a period that now exceeds one year despite repeated heating and cooling across gallium's melting point (29.8°C). We attribute this structural stability, which is considerably better than that of the other interface types mentioned above, to the presence of a transitional layer formed by the penetration of energetic gallium ions into the glass during

deposition. Our optical measurements (see below) indicate that ions are implanted to a depth of ~ 3 nm, much deeper than would be expected for a thermal evaporation process. Using a Monte Carlo program^[6] we found that this required the ions to have rather high kinetic energies ~ 600 eV. However, an ion acceleration mechanism has been proposed recently that may give some ions energies of up to 1 keV during the laser ablation process^[7] and may thus explain the transitional layer's origins. The excellent stability and quality of the samples has helped us, for the first time, to obtain accurate, reproducible data on gallium/glass interface reflectivity at different excitation levels and temperatures, and subsequently to achieve a quantitative comparison with microscopic models for gallium's nonlinearity.

The properties of the gallium/glass interface were studied using a mode-locked Ti:sapphire laser ($\lambda = 810$ nm, pulse duration ~ 50 fs, repetition-rate ~ 87 MHz). We first performed pump-probe reflectivity measurements, directing both beams through the glass substrate onto the interface and detecting the reflected probe beam. They showed that when focused onto the sample, the energy density of the individual pulses (≤ 0.1 mJ/cm²) was not sufficient to noticeably change the interface's reflectivity. This is consistent with recent measurements^[3], performed with a high-power low-repetition-rate femtosecond laser, which have shown that the threshold energy density for the observation of such an effect is ~ 1 mJ/cm². Therefore, the output of the mode-locked Ti-sapphire laser used in the experiments reported here may be treated as "quasi-cw", although we retained the mode-locked regime for stability. We proceeded to investigate the dependence of the interface's near-normal-incidence reflectivity on temperature and time-averaged incident light intensity using the simple single-beam arrangement described below. As it will become clear below, such data are crucially important for testing different models of the mechanisms behind the observed effect.

A single beam from the laser was circularly polarised and chopped at ~ 200 Hz. A pellicle beam-splitter directed part of the beam to a reference photodetector while the rest was focused through the glass substrate to a spot of ~ 20 μm diameter on the interface. A thermostat based on a Peltier heat pump allowed us to control the gallium/glass interface temperature to a nominal accuracy of 0.1K. At low intensities ($\leq 220 \text{ Wcm}^{-2}$) reflectivity varies with temperature across gallium's melting point as shown by curves *i* and *i** in Fig. 1a. To our knowledge, these measurements constitute the first observation of a continuous change in the reflectivity of a metal/solid interface just below the metal's melting point. This strongly suggests that a surface wetting layer of a different (more reflective) phase is formed, a phenomenon that has previously only been seen at liquid-crystal/glass and vacuum/metal (in particular gallium and lead) interfaces. From thermodynamical arguments we can immediately draw the conclusion that the surface energy of the wetting phase at a glass interface is lower than that of α -gallium^[8]. Overcooling of liquid gallium causes a reflectivity hysteresis with a width, of ~ 3 $^{\circ}\text{C}$, that is stable against repeated melting and solidification. This confirms the high purity of the gallium film.

Curves ii-v show how the rising temperature part of this hysteresis changes with increasing intensity. The reflectivity change becomes less abrupt with increasing intensity but the temperature at which bulk melting of the gallium film occurs (the bend point at ~ 30 $^{\circ}\text{C}$) remains constant at all excitation levels. In Fig. 1b we present the magnitude of the light-induced change in the rising temperature parts of the hysteresis curves, calculated as the difference between curves ii-iv and curve *i* as a fraction of the reflectivity level shown in curve *i*. This indicates that a considerable reflectivity change, $\sim 30\%$, can be achieved with modest excitation levels (~ 7 mW).

α -gallium has a relatively low reflectivity while several metastable phases of gallium are known to exist that have much more pronounced, approximately free-electron,

metallic properties^[9]. Liquid^[10] and amorphous^[11] gallium are also highly reflective and free-electron-like. Our observations suggest that the interface's optical properties change on illumination because a thin wetting layer of a highly reflective metallic phase forms between the glass and the α -gallium. The layer's thickness, and thus the sample's reflectivity, increases with applied light intensity. It was found recently that this model accurately predicts the intensity and phase of light reflected from a gallium/silica interface manufactured by dipping an optical fiber into molten gallium^[2]. Assuming that the optical properties of the metallic layer are the same as those of free-electron gallium and that there is a sharp boundary between the metallic and α phases, we have calculated the layer's thickness from our reflectivity data using standard thin-film formulae^[12]. Fig. 2 shows the results of this analysis. The plot indicates, as discussed above, that a high-reflectivity layer, of thickness $d_0 \sim 3$ nm, is always present at the interface and that a metallic layer ~ 25 nm thick is sufficient to achieve the full "liquid" reflectivity level (the inset to Fig. 2 shows this layered structure). From our calculations, the metallic layer's thickness d is very well represented by the formula $d = d_0 + \Delta \exp[-\mu(T_m - T)]$, where Δ and μ are fitting parameters and T_m is gallium's melting temperature. The exponential dependence on temperature of the metallic layer's thickness has been obtained previously for a gallium/vacuum interface from measurements of effective thermal capacity^[13]. As one can see from Fig. 2, this dependence is also valid for optically excited gallium at a glass interface if we assume that μ is a function of light intensity. So, the observed reflectivity increase may be interpreted as a light-induced "surface-metallization" effect. But what is the mechanism behind the metallization of α -gallium?

We have modelled the temperature distribution and heat-flow in the sample (Fig. 3) by numerically solving the 3D thermal conductivity equation for the sample structure and its immediate surroundings, taking into account the fact that the thermal conductivity of α -gallium

is anisotropic. It was established recently that gallium dimers in the liquid phase tend to be oriented perpendicular to an interface^[14]. Therefore we expect that after solidification this orientation would prevail near the interface. Our measurements of the intensity and phase of light reflected from α -gallium/glass interfaces support this expectation^[2]. In the direction perpendicular to the interface the thermal conductivity is $\lambda_c = 15.9 \text{ Wm}^{-1}\text{K}^{-1}$ and in the plane of the interface it is anisotropic with principal coefficients $\lambda_a = 41 \text{ Wm}^{-1}\text{K}^{-1}$ and $\lambda_b = 88 \text{ Wm}^{-1}\text{K}^{-1}$ (ref. 15). As fig. 3 shows, in a steady-state regime laser heating could account for a temperature increase of $\sim 4.8 \text{ }^\circ\text{C}$ over the thermostat level. In practice this increase would be smaller because our calculations use a relatively low value, $0.8 \text{ Wm}^{-1}\text{K}^{-1}$, for the thermal conductivity of glass and they ignore radiative heat losses and losses from the sides of the sample. Nevertheless, this analysis does not provide a clear argument that laser-induced thermal melting of bulk gallium can be ruled out completely as a possible explanation for our observations. However, an explanation based on thermal melting has some serious difficulties: The same calculations show that the temperature difference across the whole gallium film is only $\sim 0.5 \text{ }^\circ\text{C}$. Therefore, if the laser were simply heating the gallium it would melt the whole film, and we would expect to see the low-intensity reflectivity curve just shifted down the temperature axis by an amount equal to the laser-induced temperature increase. Instead, we see that the melting temperature remains constant at any level of excitation, while the reflectivity's dependence on temperature becomes less steep with increasing intensity.

We thus propose that there is another, non-thermal mechanism contributing to the metallization of α -gallium and we have developed a non-thermal model that satisfactorily describes the reflectivity's dependence on temperature and light intensity. This model relies on the unique structure of α -gallium in which molecular and metallic properties coexist - some bonds are covalent, forming Ga_2 dimers and leading to an optical absorption band spreading

from ~ 0.68 eV (1820 nm) to ~ 4 eV (310 nm)^[16], the remaining bonds are metallic. The model assumes that light absorption at 810 nm results in highly localised excitation of gallium dimers from the bonding (*b*) to the antibonding (*a*) state, reducing the stability of the surrounding crystalline cell. The cell subsequently undergoes a transition to a new metastable configuration (crystalline or disordered), creating a microscopic inclusion of the new phase (*m*-state of the cell). From the standard equations for populations in a multi-level system one can now calculate the relative number density of crystal cells in the *m*-state, sustained by the presence of light: $n_m/n = (\gamma_m/\gamma_b) \Gamma/[2\Gamma + \tau^{-1} + \gamma_m(1 + \Gamma/\gamma_b)]$, where n is the number density of cells, γ_m and γ_b are, correspondingly, transition rates from the excited (*a*) to the metastable (*m*) state, and from the metastable to the ground (*b*) state, and τ is the lifetime of the excited state. $\Gamma = (1 - R) I \alpha / h \nu n$, where R and α are, respectively, the optical reflection and absorption coefficients of α -gallium and I and ν are the intensity and the frequency of the laser light. Since the metallic state is metastable when $T < T_m$, the equilibrium number density of “metallized” cells can achieve a high value at relatively low optical excitation levels. The presence of nuclei of the new metallic phase in α -gallium shifts the delicate energy balance at the interface, leading to an increase in metastable layer thickness. By minimising the free energy of the surface layer, an equation for its equilibrium thickness can be obtained: $d = d_0 + \Delta \exp[-\mu_0(1 - n_m/n)(T_m - T)]$. Comparing this to the earlier formula, it can be seen that the factor μ is replaced with the intensity dependent $\mu_0(1 - n_m/n)$. From here the interface’s reflectivity can be calculated using standard thin film formulae^[12]. For the purpose of these calculations we used a number density of α -gallium crystal cells $n = 6.5 \times 10^{21} \text{ cm}^{-3}$, a value $R = 0.6$ for the reflectivity of an α -gallium/glass interface and an absorption coefficient $\alpha = 4 \times 10^5 \text{ cm}^{-1}$. We also used typical values for the lifetime of the excited state in direct-gap semiconductors, $\tau = 10^{-8} \text{ s}$, and the transition rate from an excited to a metastable state in metals, $\gamma_m = 3.3 \times 10^{10} \text{ s}^{-1}$, and took

values of $\Delta = 18.4$ nm and $\mu_0 = 16.5$ (consistent with the results of the thermal capacitance measurements^[13]). The only free parameter in these calculations is the lifetime of the metastable state, γ_b^{-1} . By taking a value ($\gamma_b = 5 \times 10^3$ s⁻¹) that fits a curve of the correct form to a plot of μ against incident intensity (inset to Fig. 1b), a good fit to the experimental reflectivity data can be obtained for a wide range of temperatures and light intensities (see Fig. 1b). The model could be improved, in particular by taking more accurate account of changes in the sample's reflectivity with intensity, which should give a better fit at higher intensities, by considering multiphoton absorption, and by allowing for the fact that all of the various transition rates may depend on temperature, and that the relaxation rates γ_m and γ_b , for a given atom, may depend on the state of neighbouring atoms^[17]. However, the question remains as to whether the hypothesis of excitation localisation at the gallium dimers, which is crucial to the non-thermal model, is correct. An accurate study of the effect's spectral dependence, currently in progress, and independent measurements of γ_m may provide tests of the model's validity.

In conclusion, the light-induced transition is of considerable interest for low power light-by-light control applications, and particularly for photonic switching devices, laser Q-switching^[18] and possibly mode-locking. The phenomenon we observe cannot be quantified in terms of the cubic optical susceptibility, $\chi^{(3)}$, but it is interesting to estimate what value of $\chi^{(3)}$ a hypothetical homogeneous medium would have to have in order to show an effect of the same magnitude: $\chi^{(3)} \sim |\epsilon_\alpha - \epsilon_m| / (4 \pi E^2)$ where ϵ_α and ϵ_m are the complex dielectric coefficients of α -gallium and metastable gallium respectively and E is the electric field in gallium (calculated in esu). Assuming that ϵ_m is close to the dielectric coefficient of liquid gallium, $|\epsilon_\alpha - \epsilon_m| \sim 67$, so taking a value of E consistent with our experiments gives an effective value of $\chi^{(3)} \sim 1$ esu (1×10^{-8} m³V⁻²).

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Figure Captions

Fig. 1: (a) Gallium/glass interface reflectivity against increasing temperature for incident intensities of i: 220, ii: 320, iii: 950, iv: 2230, v: 3180 Wcm^{-2} and i*: against *decreasing* temperature at 220 Wcm^{-2} . (b) Magnitude of light-induced reflectivity change for intensities of v: 320, vi: 950, vii: 2230 Wcm^{-2} with fittings (dashed) derived from the light-induced metallization model. Inset is the intensity dependence of the fitting parameter μ .

Fig. 2: Thickness of the metallic layer present at the gallium/glass interface that would explain the observed dependence of reflectivity on temperature. Curves were calculated from the data presented in Fig. 1a using complex refractive indices for α ^[19] and free-electron^[20] gallium of $2.11 + 3.38i$ and $2.22 + 8.64i$ respectively. Fittings (dashed) are of the form $d = d_0 + \Delta \exp(-\mu(T_m - T))$. Inset is a diagram of the interface structure.

Fig. 3: Sample cross-sections showing, on the left, structure and on the right; (a) lines of constant laser-induced temperature increase (in thousandths of $^{\circ}\text{C}$); (b) direction of heat flow. Temperature distributions were calculated for an average intensity $I = 1115 \text{ Wcm}^{-2}$ (2230 Wcm^{-2} chopped with 50% duty cycle) using the following parameters: $\lambda = 810 \text{ nm}$, laser spot radius at Ga layer = $10 \mu\text{m}$, thermostat temperature $T_0 = 26^{\circ}\text{C}$, steady state interface reflectivity under these conditions = 0.7. Radiative losses and losses from the sides of the sample are neglected.

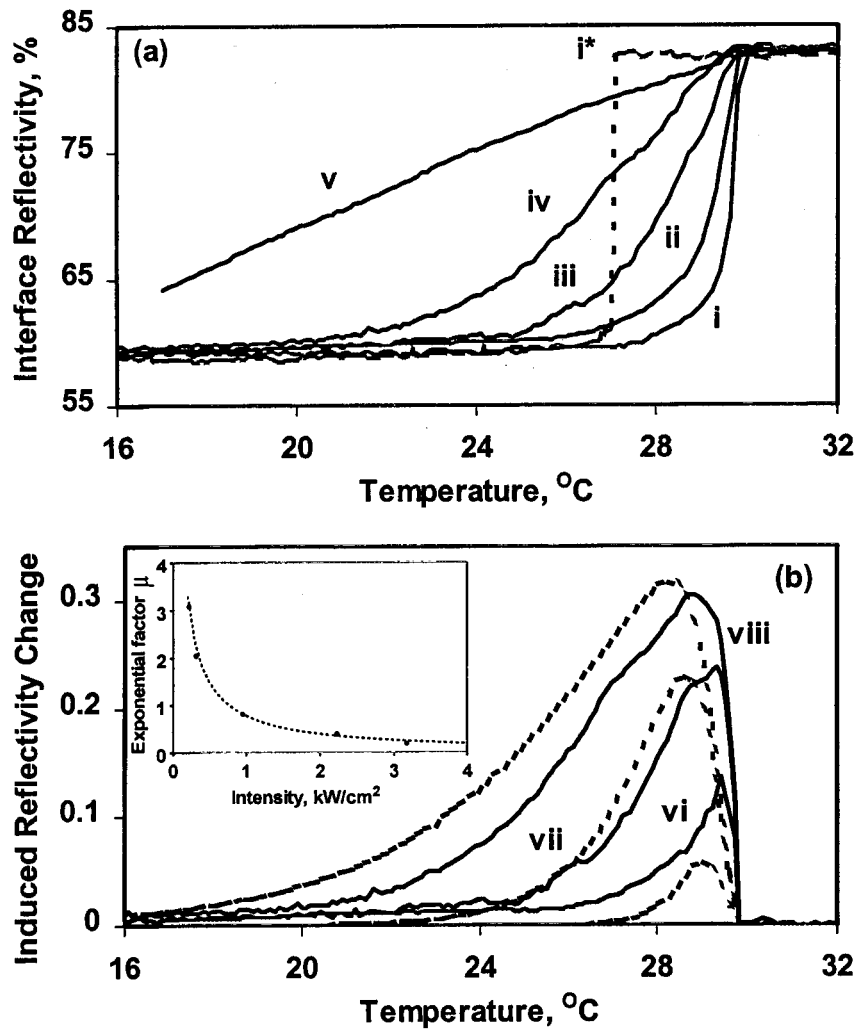


Figure 1

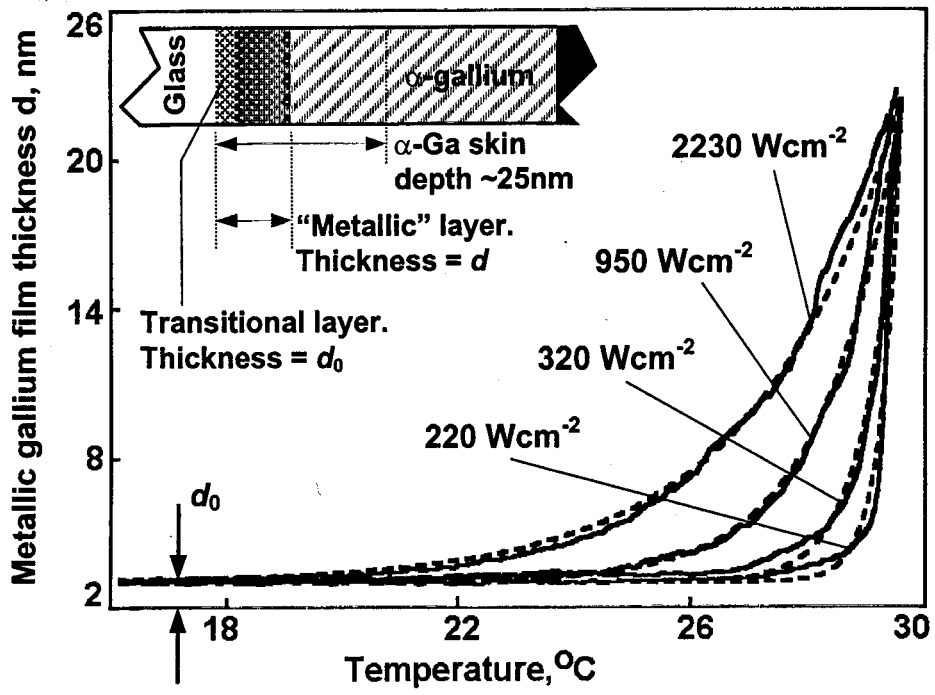


Figure 2

(a)

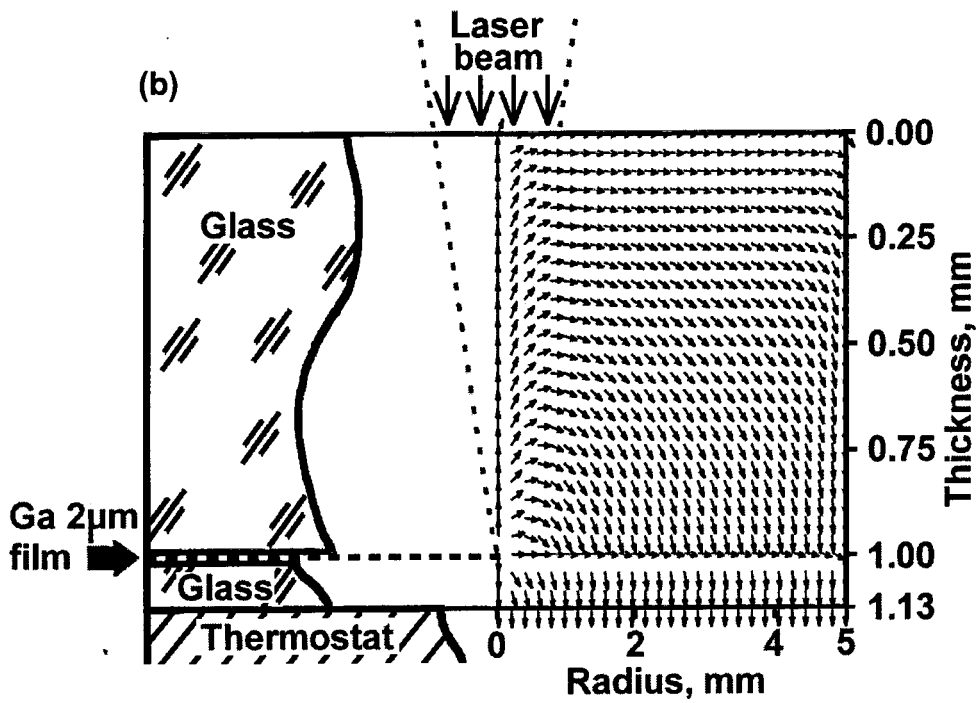
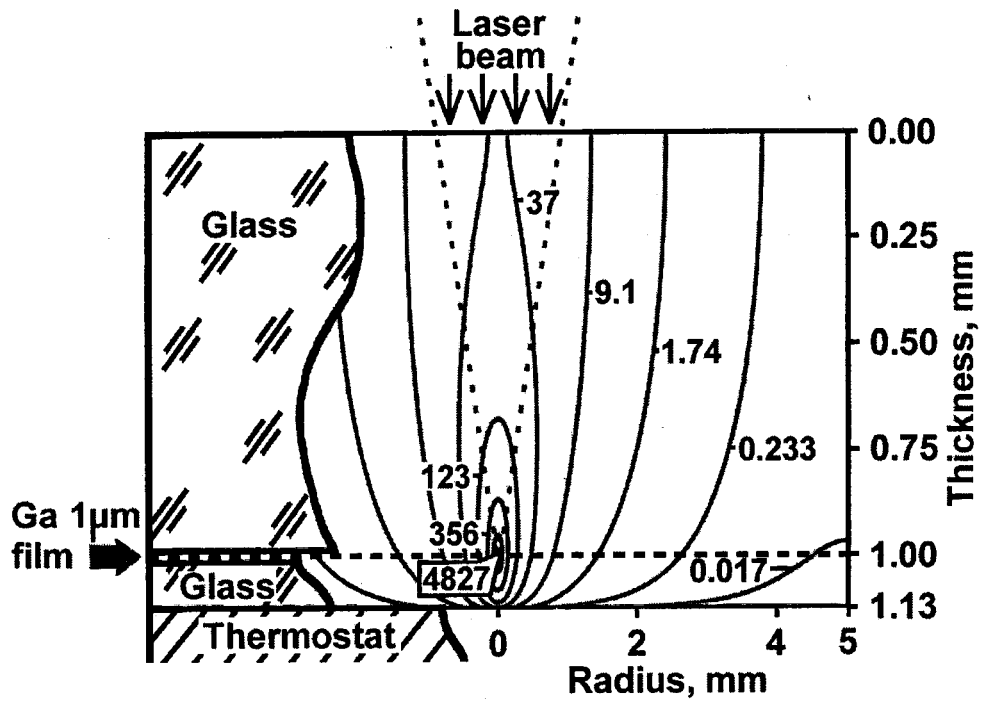


Figure 3