Reflectivity and transmission of amorphous thin films at the melting temperature

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A method to evaluate the evolution of the optical properties (reflectivity and transmission) of thin solid films as a function of temperature has been developed. A pulsed Ar+ laser focused on the sample surface to a 1/e-beam radius of 4 μm is used as a local heat source while the optical properties of the irradiated surface are monitored in real time by means of another laser focused to 1.7 μm. The use of laser pulses combined with real time optical measurements provides a suitable means to determine accurately the optical properties of thin-film materials for temperatures up to the melting point. In addition, the irradiation pulse can be sufficiently shortened to avoid crystallization prior to melting in the case of amorphous films and therefore the optical properties of amorphous films up to the melting point can be also determined. The analysis of the optical transients with a simple thermal model allows either the determination of the thermal conductivity of a transparent substrate if the film melting temperature is known or the film melting temperature if the thermal properties of the substrate are well characterized. The results obtained in Ge and Si amorphous thin films prove the accuracy of the method and the melting temperature of amorphous Ge is determined to be 987 K.

I. INTRODUCTION

An accurate knowledge of the optical properties of both bulk- and thin-film semiconducting materials at high temperatures is important for many applications and especially for those related to laser annealing. In particular, the use of finite difference heat flow calculations of pulsed laser annealing of materials requires accurate values of the temperature evolution of the reflectivity and the absorption as input parameters. The determination of such evolution is usually difficult and involves the use of different techniques such as polarization modulated ellipsometry,\textsuperscript{4} time-resolved ellipsometry,\textsuperscript{5} or pseudo-Brewster angle-based methods.\textsuperscript{6} In the case of amorphous materials, the determination of the temperature dependence of the optical properties is especially complex because long-time high-temperature procedures will lead to structural transformations in the samples for temperatures well below the melting point. If thin-film materials are involved then additional difficulties arise from the presence of both optical and thermal coupling between the film and the substrate. This coupling strongly influences the surface damage thresholds\textsuperscript{7} and the cooling rates achieved upon pulsed laser irradiation.\textsuperscript{7}

In this work we present results of real-time optical measurements obtained during the irradiation of Si and Ge amorphous thin films with 50 μs Ar+ laser pulses. This pulse length is long enough to neglect the time required for heat transfer from the film to the substrate and therefore to neglect thermal gradients in the film thickness during the energy deposition process. At the same time, the selected pulse length is also short enough to avoid the crystallization of the films prior to melting. The results are analyzed with a simple thermal model that allows a very accurate determination of the evolution of both the reflectivity and the transmission of the film as a function of temperature up to the melting point, providing a method to determine straightforwardly either the thermal conductivity of the substrate or the film melting temperature. The result for the melting temperature of amorphous Ge is in excellent agreement with previous estimations based on thermodynamical analyses.

II. EXPERIMENT

The experimental setup used to perform the irradiations and real-time optical measurements has been extensively described elsewhere.\textsuperscript{8} The irradiations are performed by means of an Ar+ laser (all lines) pulsed to 50 μs and focused on the sample surface to a 1/e-beam radius of 4 μm. A HeNe laser pulsed to 300 μs, 0.1 mW, and focused on the center of the irradiated region to a 1/e-beam radius of 1.7 μm allows real-time monitoring of the reflectivity and the transmission changes induced by the irradiation pulse.

In this work we have used 64 ± 1-nm-thick Si films and 50 ± 1-nm-thick Ge films both grown on glass substrates. The films are grown in a dc magnetron sputtering system using Si and Ge targets (99.999%). The residual pressure of the system is 3 × 10\textsuperscript{-6} Torr and the operating Ar pressure is 4 × 10\textsuperscript{-3} Torr. The deposition rates are 0.19 and 0.27 nm s\textsuperscript{-1} for Si and Ge films, respectively. The as-deposited films were characterized by transmission electron microscopy, electron diffraction, and energy dispersive x-ray analysis in a Philips EM420 electron microscope. The Si\textsuperscript{7} and Ge\textsuperscript{8} films are amorphous with no appreciable traces of impurities. The substrates are commercial glass slides provided by Superior (Germany) with a refractive index at 632.8 nm of 1.5 and unknown thermal conductivity. Previous works both on laser-induced mixing of Ge-based multilayers\textsuperscript{8} and on laser treatment of amor-
phous Si films\textsuperscript{7} and using the same substrates allow one to discard any reaction between the films and the substrate.

Si films are irradiated with powers ranging from 2 to 24 mW, whereas Ge films are irradiated with powers in the 3–14 mW interval. The sample is moved to a new position after each irradiation. The topography of the irradiated regions is analyzed by means of interference optical microscopy and scanning electron microscopy (SEM).

III. RESULTS

Figure 1 shows the evolution of the reflectivity ($R$) and the transmission ($Tr$) of Si films irradiated with low-power 50 ps pulses. It can be seen that for powers below a threshold ($P<14$ mW), the irradiation pulse induces a smooth and continuous reflectivity increase [Fig. 1(a)]. The reflectivity reaches a maximum at the end of the irradiation pulse and decreases afterwards, reaching an equilibrium value equal to the initial value. Within this power regime, the transmission changes behave symmetrically with respect to the reflectivity ones as evidenced in Fig. 1(b). The maximum (minimum) value of the reflectivity (transmission) transient increases (decreases) monotonically with the irradiation pulse power. If the same region is irradiated with more than one laser pulse, the optical changes are reproducible independently of the number of laser shots. The irradiated regions show no appreciable topography contrast when examined both by SEM and by interference optical microscopy.

Figure 2 shows a typical example of the reflectivity and transmission evolution of Si films for powers above 14 mW. Reflectivity [Fig. 2(a)] initially increases as in the low power regime. However, the transient reflectivity maximum is now reached while the irradiation pulse is still impinging on the sample and is followed by a sharp, almost vertical decrease (A). Subsequently, the reflectivity increases slightly and falls again (B) at the end of the irradiation pulse. The final reflectivity level is now lower than the initial one. The initial reflectivity increase is accompanied by a decrease in transmission [Fig. 2(b)]. However, the symmetric character in the behavior of $R$ and $Tr$ is broken when the reflectivity decreases abruptly (A) since the transmission shows also an abrupt descending step. Transmission continues to decrease until the end of the irradiation pulse (B) and increases then up to a final value lower than the initial one. The temporal position of the inflections (A) and (B) is the same in the $R$ and $Tr$ transients for a given power. When the irradiated regions are observed by SEM or interference optical microscopy, the irradiated regions exhibit a dome-like form.

The temporal position of the sharp step in $R$ and $Tr$ (A in Fig. 2) is a decreasing function of power while the reflectivity and the transmission values immediately before the step are constant. Let us define the normalized reflectivity and transmission changes as

\[ \Delta R = (R_{\text{max}} - R_{\text{in}})/R_{\text{in}}, \]
\[ \Delta Tr = (Tr_{\text{in}} - Tr_{\text{min}})/Tr_{\text{in}}, \]
\[ \Delta Tr(A) = [Tr_{\text{in}} - Tr(A)]/Tr_{\text{in}}, \]

where $R_{\text{in}}$ is the initial reflectivity level, $Tr_{\text{in}}$ is the initial transmission level, $R_{\text{max}}$ is the maximum transient reflectivity level, $Tr_{\text{min}}$ is the minimum transient transmission level, and $Tr(A)$ is the transmission level at time $A$. The normalized changes are plotted in Fig. 3 as functions of the irradiation pulse power.
FIG. 3. Normalized reflectivity (a) maximum values (○) and transmission (b) minimum values (△) as a function of the pulse power for amorphous Si films. The normalized transmission values immediately before the step [ΔΤr(A),●] are also included. The bars denote average values.

level, and Tr(A) is the transmission level immediately before the step A being R_{in}=0.32 and Tr_{in}=0.15 for our Si films.

Figure 3 shows the normalized transient reflectivity [Fig. 3(a)] and transmission [Fig. 3(b)] changes as a function of power. For powers below 14 mW, both ΔR and ΔTr are directly proportional to the irradiation power. Above this threshold ΔR reaches a saturation value while ΔTr suffers a clear discontinuity and ΔTr(A) remains constant within experimental error.

A systematic series of irradiations with 50 μs laser pulses on amorphous Ge films were also performed. The optical transients are qualitatively similar to those described above for Si films but the change of regime takes place at 9.3 mW. The results obtained are illustrated in Fig. 4 where the normalized transient transmission changes are plotted.

IV. DISCUSSION

A. Optical transients and melting threshold

The results obtained in Si films show that for powers lower than 14 mW, the reflectivity and transmission levels before and after the irradiation are equal. This fact together with the reproducibility of the induced transient processes independently of the number of laser shots clearly show that the changes in R and Tr for powers below 14 mW are caused by a purely thermal process that involves no microstructural changes. For the Si film thickness used, crystallization should be accompanied by a non-reversible reflectivity increase. The lack of distinct features in the reflectivity transients further confirms this conclusion. Surfaces irradiated with powers above this threshold show an irreversible reflectivity change [Fig. 2(a)] together with a clear hemispherical topography. These features clearly evidence that surface melting has taken place and therefore we may conclude that 14 mW is the power required to bring the solid material to the melting temperature in the present experimental conditions. This threshold would be different if other beam diameter, pulse length, film thickness, or substrates were used.

The liquid phase of both Ge and Si presents a metallic character and therefore a dramatic change in the refractive index (n) and the absorption coefficient (k) at the solid-liquid transition is expected. Melting should be then evidenced in the optical transients by a strong reflectivity increase (transmission decrease). However the solid-liquid transition may be also accompanied by topography changes that cause the surface of the liquid phase to be no longer flat. The amount of light reflected towards the surface normal is then strongly reduced. In such case the melt onset is evidenced in the reflectivity transients by an abrupt decrease whereas the transmission transients behave normally, i.e., melting is evidenced by a transmission decrease since transmission is not surface sensitive and the molten phase is metallic. This behavior has been widely reported during the irradiation of semiconducting films with focused (Gaussian) laser beams and is the one that we observe in the transients for powers above the melting threshold [A in Fig. 2(a)]. Once the topography has changed, the reflectivity increases as the lateral extension of melted material increases due to metallic character of the liquid phase. Upon solidification, reflectivity decreases again since the metallic liquid phase disappears.

The discontinuity observed in ΔTr for $P \approx 14$ mW and the constant value of the transmission level immediately before the sharp descending step further support the previous reasoning. This constant value, which is 17% lower than the initial one, corresponds to the transmission level of the solid material at the melting temperature. The presence of a metallic liquid phase induces a strong decrease in
The solidified material is not completely amorphous and the melting material increases. Finally, after the energy deposition is over, the material cools down and solidifies. The solidified material is not completely amorphous and therefore the transmission level is lower than the initial one.

The transients obtained in the Ge films are in agreement with the previous discussion. Therefore, 9.3 mW is the melting threshold in the present experimental conditions and the transmission of the solid amorphous material at the melting temperature is 12% lower than its transmission at room temperature.

B. Thermal properties of the substrate and melting temperature of amorphous Ge

We will now focus the discussion on the reflectivity and the transmission transients induced in the low-power regime by reversible heating of the material. The results will be analyzed in the framework of a simple thermal model which will allow us to determine the temperature evolution during the transient process and the substrate thermal conductivity.

The temperature change $\Delta T$ at the center of a pulsed Gaussian heat source with $e^{-1}$ radius of $r_0$ on the surface of a half-infinite medium, switched on at time $t=0$ and with a pulse length $t_0$ is given by

$$\Delta T(r=0,z=0,t) = \frac{P}{k r_0^2 \pi^2} \arctan \left( \frac{4 D t}{r_0^2} \right) 0 < t < t_0 \tag{1}$$

and

$$\Delta T(r=0,z=0,t) = \frac{P}{k r_0^2 \pi^2} \arctan \left( \frac{4 D t - \sqrt{D(t-t_0)}}{2 D t \sqrt{D(t-t_0) + r_0^2/2}} \right)$$

where $z=0$ corresponds to the sample surface and $k$ and $D$ are the thermal conductivity and diffusivity of the substrate ($D=\kappa/\rho C_p$ where $\rho$ is the density and $C_p$ is the specific heat).

The model is valid if we assume that the absorptance and the thermal conductivity are independent of temperature. The equation accounts for radial heat diffusion effects. In our case, the power absorbed by the medium is $P=P_A$, where $P_A$ is the incident pulse power and $A$ is the film absorptance since the absorption in the transparent substrate is negligible. Deviations caused by the finite film thickness are negligible for times $t > t_1 = h^2/D_1$, where $D_1$ is the film thermal diffusivity and $h$ is the film thickness. In our case, with a thermal diffusivity of $\approx 0.2$ cm$^2$/s for amorphous Si, $t_1 \approx 2$ ns, which is much smaller than the pulse length (50 µs). Since $r_0$ (4 µm) $> h$ (50-60 nm), the radial diffusion effects in the film are also negligible.

If $t, \Delta T, A, P_A, r_0, C_p$ and $\rho$ are known, Eq. (1) yields to implicit transcendental equation for the thermal conductivity of the substrate, $k$:

$$C_1 k = \tan^2(C_2 k), \tag{2}$$

where

$$C_1 = 4t/(\rho C_p r_0^2) \quad \text{and} \quad C_2 = \Delta T \pi^2 r_0/(P_A A).$$

From the results in the previous section it is known that the power required to bring the surface of an amorphous Si film to the melting temperature at the end of the irradiation pulse is $P_\text{p} = 14$ mW. The temperature increase at that time ($t=50$ µs) is therefore $\Delta T = T_m - T_a$ ($T_m = 1420$ K, melting temperature of amorphous Si) and $T_a = 291$ K, room temperature, 18° C). These values together with the ones shown in Table I as the input parameters in Eq. (2) lead to a value for the thermal conductivity of the substrate of $k=0.00281$ W cm$^{-1}$ K$^{-1}$.

Since both the Si and the Ge films were grown on the same substrates we can combine the power melting threshold obtained from the optical transients in Ge with the obtained value of $k$ to calculate the temperature increase at the end of a 9.3 mW, 50 µs laser pulse and therefore calculate the temperature increase needed to induce melting in an amorphous Ge film. The value obtained is $\Delta T = 696$ K, that is equivalent to a melting temperature for amorphous Ge of $T_m = 987$ K. This value is in excellent agreement with the commonly accepted value obtained from estimations on thermodynamic basis, $T_m = 965$ K, and shows both that the initial hypothesis (constant thermal conductivity and absorptance) are correct in a very good approximation and that the calculated value of the thermal conductivity of the substrate is very accurate.

**TABLE I.** Optical and thermal parameters used to calculate the surface temperature evolution of the substrate, the melting temperature of amorphous Ge, and the temperature dependence of the reflectivity and the transmission of Ge and Si films. The absorbance of the films was determined by a numerical simulation using the optical constants and thicknesses of the films shown also in the table.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$a$-Si</th>
<th>$a$-Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time, $t$ (µs)</td>
<td>50.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Substrate density, $\rho$ (g/cm$^3$)</td>
<td>2.32</td>
<td>2.32</td>
</tr>
<tr>
<td>Substrate specific heat, $C_p$ (J/g K)</td>
<td>0.737</td>
<td>0.737</td>
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<tr>
<td>Film thickness, $h$ (nm)</td>
<td>64.0</td>
<td>50.0</td>
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<tr>
<td>$e^{-1}$ beam radius, $r_0$ (µm)</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Refraction index at 488 nm, $n$</td>
<td>4.47</td>
<td>4.193</td>
</tr>
<tr>
<td>Extinction coefficient at 488 nm, $K$</td>
<td>0.969</td>
<td>2.502</td>
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<tr>
<td>Refraction index at 514 nm, $n$</td>
<td>4.46</td>
<td>4.24</td>
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<tr>
<td>Extinction coefficient at 514 nm, $K$</td>
<td>1.22</td>
<td>2.42</td>
</tr>
<tr>
<td>Film absorptance at 488 and 514 nm, $A$</td>
<td>0.53</td>
<td>0.487</td>
</tr>
<tr>
<td>Melting temperature, $T_m$ (K)</td>
<td>1420</td>
<td>965</td>
</tr>
</tbody>
</table>

*CRC Handbook of Materials Science, edited by Ch. T. Lynch (CRC, Boca Raton, FL, 1980).*

**Handbook of Optical Constants of Solids, edited by E. D. Palik (Academic, Orlando, FL, 1985).**


C. Temperature dependence of $R$ and $T_r$

In the previous section we have established the validity of the thermal model employed. The combination of the experimental optical transients with the temperature evolution calculated with the model allows a numerical determination of the evolution of both the reflectivity and the transmission of the films as a function of temperature in a general case.

For the Si and Ge samples used, the maximum transient reflectivity and the minimum transient transmission are linear functions of the incident pulse power, for powers below the melting threshold (see Figs. 3 and 4). In addition, this maximum (minimum) occurs at the end of the irradiation pulse which is the time at which the temperature reaches also its maximum value for a given power according to Eq. (1). Since the maximum temperature is also a linear function of power [see Eq. (1)], it is obvious to conclude that the reflectivity and the transmission of the Si and Ge samples used are linear functions of temperature, for temperatures below the melting point. Therefore, an analytical expression for the temperature dependence of the reflectivity and the transmission can be given in this case. For each power up to the melting threshold in Figs. 3 and 4, the temperature can be easily calculated using Eq. (1) and making $t$ equal to the pulselength ($t_0=50 \mu s$). The obtained temperature dependence of the reflectivity and the transmission of amorphous 64-nm-thick Si and 50-nm-thick Ge films at 632.8 nm is

$$R(Si, T) = R(Si, T_a) \left[1 + 1.40 \times 10^{-4}(T - T_a)\right], \quad (3)$$

$$T_r(Si, T) = T_r(Si, T_a) \left[1 - 1.44 \times 10^{-4}(T - T_a)\right], \quad (4)$$

$$T_r(Ge, T) = T_r(Ge, T_a) \left[1 - 1.72 \times 10^{-4}(T - T_a)\right], \quad (5)$$

where $T_a = 291$ K (room temperature), $R(Si, T_a) = 0.32$, $T_r(Si, T_a) = 0.15$, and $T_r(Ge, T_a) = 0.1$.

The linear behavior is not surprising. It has been reported for both amorphous Ge$^3$ and crystalline Si$^3$ a temperature dependence of $n(\lambda)$ and $k(\lambda)$ in the form $S_0(\lambda) \exp(T/T_0)$, [$S_0(\lambda)$ and $T_0$ constant values]. It is relatively easy to show$^3$ that such behavior of $n$ and $k$ results, to a good approximation, in a linear dependence of the reflectivity and the transmission on the temperature$^{35}$.

In Fig. 5 we have plotted the experimental evolution of the reflectivity of a Si film irradiated with a 12-mW, 50-µs laser pulse together with the theoretical evolution calculated from Eqs. (1) and (3). The theoretical fit is in excellent agreement with the experimental results. The small deviation observed after the end of the irradiation pulse is probably related to a heating effect caused by the probe beam. Using the same thermal model employed in the discussion, it can be shown that maximum temperature increase included in the sample surface at the end of the probe pulse is lower than 20 K. This temperature increase becomes important only when the irradiation pulse effect has finished and the material approaches room temperature.

It is worth noting that assuming that $R + T_r + A = 1$, we may obtain from Eqs. (3) and (4) the temperature dependence of the absorptance of the amorphous 64-nm-thick Si films at 632.8 nm:

$$A(Si, T) = 0.537 - 2.32 \times 10^{-5}(T - T_a), \quad (6)$$

which shows a variation from room temperature to the melting point lower than 5% and confirms again that the approximation of constant absorptance for the calculations is quite correct. The simple thermal model used can be combined with real time optical transients to obtain also the evolution with temperature of the optical properties of thin-film materials even when they exhibit a nonconstant absorptance. The absorptance change as a function of time can be calculated from the reflectivity and transmission transients as $A(t) = 1 - R(t) - T_r(t)$. Equation (1) can be then used to calculate the temperature increase in those time intervals in which the absorptance changes are lower than a fixed value (5%, for instance). The final result leads again to an accurate determination of the evolution of the reflectivity, the transmission, and the absorptance as a function of temperature.

V. CONCLUSIONS

A simple method to evaluate the evolution of the optical properties of amorphous thin films as a function of temperature has been developed. The reflectivity and transmission of amorphous Si and Ge films for temperatures up to the melting point have been determined. In addition, this method allows one to evaluate straightforwardly the thermal conductivity of a transparent substrate if the thin-film material at the substrate is well characterized. The melting temperature of amorphous Ge has been determined to be 987 K.

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