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Time resolved dynamics of rapid melting and resolidification of Sb thin films under ns and ps laser pulse irradiation

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Real time reflectivity measurements with ps time resolution at the wavelength $\lambda = 514.5$ nm have been used to analyze the rapid melting and solidification dynamics of Sb thin films on glass substrates irradiated with a visible laser pulse ($\lambda = 583$ nm) of duration either 30 ps or 2 ns. Significant differences in the solidification dynamics have been obtained for the three different film thickness investigated (25, 50, and 200 nm) as well as between ps and ns laser pulse excitation. Bulk solidification is the dominant mechanism observed at high laser fluence in the thinner films, no matter the pulse duration used, while interfacial solidification is the only mechanism observed in the thicker film for both pulse durations. These results have been interpreted in terms of the differences of the effective thermal conductivity of the films. The comparison of the behavior of these films with the case of Sb-rich GeSb ones makes it clear that relatively minor changes in the film composition can lead to big changes in the solidification dynamics under similar heat flow conditions that are beneficial for the application of such films in phase change optical recording with ultrashort pulses. The optical properties of molten phase of Sb and of the solid material at the melting temperature have been also been determined at 514.5 nm. © 2003 American Institute of Physics.
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I. INTRODUCTION

The semimetal antimony (Sb) has many interesting characteristics, such as a high thermoelectric capability¹ and behaving as an indirect narrow-gap semiconductor in ultrathin films.² It is also a surface active species (surfactant) and is widely used to form abrupt interfaces with III–V compounds.^{3,4} One of its many applications is as a component of rewritable phase change optical recording media such as the ternary system Ge–Sb–Te⁵ and quaternary system Te–Ge–Bi–Sb.⁶ The binary system Ge–Sb has also been shown to be a promising candidate for this application since the Sb-rich compositions (above the eutectics, ~ 85 at. % Sb) can be reversibly cycled between the amorphous (*a*) and crystalline (*c*) states under ultrashort laser pulses, showing high optical contrast.⁷ Also, Sb-rich GeSb films have been demonstrated to show sub-ns transformation times in both the *a*-to-*c* and *c*-to-*a* phase transformations under ps laser pulses.⁸ Since the fast solidification dynamics of these films is governed by antimony,^{9,10} it is essential to understand the effect of the heat flow conditions in the solidification dynamics of pure molten Sb. This can in principle be accomplished by the use of time-resolved reflectivity measurements with sufficient time resolution. However, while there have been several studies undertaken over the years to determine the optical properties of both solid crystalline¹¹ and polycrystalline^{12–14} Sb, there remains very little published data on its (highly unstable) liquid phase. One such study, performed by means of real time optical measurements with

ns resolution, determined the melting dynamics of bulk single crystals of Sb upon irradiation by ultraviolet excimer ns laser pulses.¹⁵

The aim of this work is to investigate the solidification dynamics of Sb films under different heat flow conditions which have been modified by varying the film thickness and the pulse duration and fluence. The difference of 1 order of magnitude between the thermal conductivities of the film and the substrate and the use of single-shot measurements with picosecond time resolution have allowed us to induce and observe in this material the occurrence of bulk solidification processes at extremely large nucleation rates. The use of a ps time resolution detection system based on the use of a streak camera^{16,17} has also allowed us to determine the optical constants of liquid Sb in the visible region as well as the reflectivity of the solid Sb films at the melting temperature.

II. EXPERIMENTAL METHODS

The samples used were 25, 50, and 200 nm thick polycrystalline Sb films grown on glass substrates at room temperature in a dc magnetron sputtering system from a pure (99.999%) Sb target. The optical constants of the films at 514.5 nm have been determined from spectroscopic ellipsometry data leading to a value for the complex refractive index ($n + ik$) of the as-deposited material of $(1.7 \pm 0.1) + i(4.2 \pm 0.1)$. This has yielded values for the reflectivity of $R = 0.73 \pm 0.02$ for the 50 and 200 nm films and $R = 0.66 \pm 0.02$ for the 25 nm film. These values are consistent with measurements of the reflectivity that have been carried out at nearly normal incidence at the same wavelength.

Each film has been irradiated at normal incidence by a single 30 ps or 2 ns laser pulse at 583 nm. The irradiation

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FIG. 1. Time evolution of the reflectivity at 514 nm of Sb films with thickness of (a) 25 nm, (b) 50 nm, and (c) 200 nm upon irradiation with a ps laser pulse as recorded with the streak camera in the 50 ns time window. The reflectivity values have been normalized to that of the film at room temperature.

pulses were delivered by a pulsed dye (Sulforhodamine B) amplifier seeded either by a synchronously pumped mode-locked dye (Rhodamine 6G) laser or by the same dye laser operated in cw mode and pumped by a frequency-doubled Nd-YAG laser. The diameter of the pump beam at the sample surface was $\sim 300 \mu\text{m}$ leading to fluence values typically in the $10\text{--}150 \text{ mJ/cm}^2$ range. The determination of the time evolution of the reflectivity of the films upon irradiation has been conducted using a single mode Ar^+ laser at 514.5 nm pulsed to a duration of $1 \mu\text{s}$ by means of an acousto-optic modulator. This probe laser beam, incident at 19° , is focused onto the center of the irradiated area to a diameter $\sim 50 \mu\text{m}$. The reflected probe signal has been simultaneously measured using a fast photo detector coupled to a transient digitizer giving a temporal resolution of $\sim 10 \text{ ns}$ and a streak camera with a single sweep unit providing ps time resolution. The time resolution of the streak camera depends on the amplitude of the time window used. For a time window of 5 ns, for example, it has a nominal temporal resolution of 35 ps. The actual time resolution achieved in a given time window is slightly slower than the nominal value due to post-acquisition Fourier transform filtering for improving the signal-to-noise ratio. Further details regarding the irradiation and reflectivity measurements setup have been presented elsewhere.^{16,17}

III. RESULTS AND DISCUSSION

A. Melting dynamics and optical properties of the molten phase

Typical real time reflectivity transients recorded by the streak camera for each film thickness under ps laser pulses are shown in Fig. 1. In this case, the time window used in the streak camera (50 ns) corresponds to a nominal time resolution of 350 ps. In each film, upon irradiation with a pump pulse of fluence above the melt threshold, the reflectivity is seen to abruptly decrease as anticipated for a solid-to-liquid transition in a semimetal thin film.¹⁵ The value of reflectivity at the initial minimum is a linear function of fluence until a saturation value is reached. This saturation value for the reflectivity decrease is independent of the duration of the pump pulse.

FIG. 2. Calculated dependence of the reflectivity of a 50 nm thick Sb thin film on the real part of the refractive index (n) calculated for several values of the imaginary part of the refractive index (k). The horizontal dotted lines, $R(\text{solid})$ and $R(\text{liquid})$, indicate the experimentally determined values of the reflectivity of the solid and molten phases of Sb. The vertical dotted line indicates the refractive index of the solid phase at 514 nm ($n=1.7$).

For the 50 and 200 nm films, the mean values obtained for the saturated reflectivity change upon melting are the same, a decrease of $12\% \pm 1.5\%$ with respect to the value of the solid at room temperature ($R_S = 0.73 \pm 0.02$). This indicates the formation of an optically thick molten layer with a reflectivity $R_L = 0.64 \pm 0.03$ at 514.5 nm. A slightly larger reflectivity drop of $14\% \pm 1.5\%$ was obtained for the 25 nm film, partly due to its lower initial reflectivity.

At this point, it is worth noting that the optical contrast observed between the solid and molten phase of Sb can be influenced by the time resolution of the measuring system used.¹⁷ In particular, we have seen that transients recorded with ns resolution using the digitizer showed a maximum optical contrast of only around $\sim 7\%$ between the solid and the liquid phase of the films. This would explain the difference between the value obtained in this work for the reflectivity of an optically thick liquid Sb layer ($R_L = 0.64 \pm 0.03$ at 514.5 nm) and the value reported by Serna *et al.*¹⁵ at 633 nm in bulk Sb samples ($R_L = 0.67$) which was obtained with ns resolution measurements.

The measured reflectivity change in the solid-to-liquid phase transition can be used to estimate the corresponding change in the complex refractive index ($n + ik$) upon the phase change. For that purpose, we have calculated the reflectivity of a 50 nm thick film as a function of the real part of the refractive index for different values of the imaginary part. The calculated values are shown in Fig. 2. For determining the complex refractive index of the molten phase, it is assumed that the melting process causes a negligible change in the real part n .^{15,18} Assuming a value of $n = 1.7 \pm 0.1$ (as measured in the as-deposited films by ellipsometry) and using the absolute reflectivity of the solid phase ($R_S = 0.73 \pm 0.02$) and the optical contrast upon melting ($\Delta R = 12\% \pm 1.5\%$, $R_L = 0.64 \pm 0.03$) observed in transients captured with the streak camera, the imaginary part of the refractive index of the liquid phase can be estimated from Fig. 2 to be $k_L = 3.4$. (The imaginary part of the refractive index corresponds to that curve which intersects the reflectivity line of the liquid at the n value of 1.7.) Upon melting, the change in the imaginary part of the refractive index is thus $\Delta k = -0.8$, which implies less absorption and a larger opti-

FIG. 3. Reflectivity transient acquired in the 50 ns time window of the streak camera corresponding to a 50 nm thick film irradiated with a ps laser pulse. Dotted lines *S*, *MT*, and *L* indicate the reflectivity levels at 514 nm corresponding to the solid at room temperature, the solid at the melting temperature, and an “optically thick” liquid layer, respectively.

cal skin penetration depth in the liquid phase as compared with the solid phase. This drop in k upon melting is very similar to the one measured ($\Delta k \sim -0.6$) by real time dielectric function measurements¹⁹ in polycrystalline GeSb films with a very large Sb content ($\text{Ge}_{0.06}\text{Sb}_{0.94}$).

The expected reflectivity evolution of the films upon melting has been simulated using the obtained complex refractive of the liquid phase of Sb ($1.7 + i3.4$). These simulations provide results which are consistent within experimental error with the reflectivity changes observed between the initial reflectivity of the films and the values observed when the maximum melt depth is achieved. It is indicated, for instance, that in the case of the 25 nm thick film, the reflectivity change expected upon melting the whole film should be slightly larger, (14% change), than the one obtained for the thicker films (12%), as experimentally observed. The reason for this difference is both the smaller initial reflectivity of the 25 nm thick film, as above indicated, and the fact that this thickness is only about twice the skin penetration depth d of molten Sb at 514 nm ($d = \lambda/4\pi k_L \sim 12$ nm). This causes the reflectivity of a fully molten 25 nm thick layer to be below that of an optically thick liquid film.

Figure 3 shows in more detail a transient corresponding to a 50 nm thick film irradiated with a ps laser pulse. It can be seen that upon melting, once the reflectivity “plateau” is reached, the reflectivity remains constant for several nanoseconds. Afterwards, the reflectivity increases again rapidly due to solidification when the molten layer thickness gets smaller than the skin penetration depth of the molten phase. After the fast initial recovery, the reflectivity increase shows an inflection which is followed by a recovery at a slower rate due to solid state cooling, finally reaching the value corresponding to the solid phase at room temperature. The reflectivity value where there is a distinct change in the rate of reflectivity recovery (i.e., a change in the slope of the curve), marks the time of complete resolidification and can be used to determine the reflectivity of the solid material at the melting temperature, $R_{S_{MT}}$.^{15,20,21} This gives a value of $R_{S_{MT}} = 0.71 \pm 0.02$ for the thicker films, which corresponds to “bulk” polycrystalline Sb. A somewhat smaller value ($R_{S_{MT}} = 0.64 \pm 0.02$) is observed in the 25 nm thick films.

FIG. 4. Reflectivity transient acquired in the 5 ns time window of the streak camera corresponding to a 25 nm thick film irradiated with a ps laser pulse. The time profile of the irradiation pulse, as determined in a shorter time window (~ 7 ps time resolution), has been included for comparison. The dotted lines *S* and *L* denote the reflectivity levels corresponding to the solid at room temperature and the liquid phases, respectively.

Obviously, in each case, the time that the film reflectivity remains below that of the solid film at the melting temperature corresponds to the duration of the melting process.

The time interval from the maximum of the pump pulse to the time when the reflectivity reaches its minimum value provides an estimate of the solid-to-liquid phase transition time. This has been more accurately measured by capturing transients with the streak camera operating in a short acquisition time window (5 ns) where the nominal time resolution is ~ 35 ps. One such transient for the 25 nm thick film is presented in Fig. 4. The mean time taken to reach the minimum reflectivity level is ~ 60 ps, which is independent of the incident fluence and film thickness. Since this time corresponds to that required by the liquid–solid interface to travel a distance on the order of twice the optical skin penetration depth of the liquid phase ($2d \sim 24$ nm), we can estimate the corresponding melt-in speed to be ~ 400 m/s. An upper limit for the maximum liquid–solid interface velocity expected upon melting at high fluences is given by the speed of sound in Sb ($\sim 1.0 \times 10^3$ m/s).²² The lower value observed can thus be related either to the relatively low maximum fluences used in these experiments or to a possible underestimation of the transition time caused by the resolution of the streak camera (35 ps) in the time window used to record the transient plotted in Fig. 4.

The melting dynamics of the films under ns pulses show comparable features regarding the observed evolution of the reflectivity and its characteristic values. The transition time to the molten state is though nearly 2 orders of magnitude slower (typically 2–4 ns), which leads to a melt-in speed correspondingly smaller (~ 10 m/s) when compared to that induced upon ps laser pulse irradiation.

Presented in Table I are the estimated values for the melt and (for comparison where achieved) ablation thresholds for each pump pulse/film thickness combination. Each of the thresholds are lower for the shorter pump pulse. This is related to the higher intensity ps pulse depositing its energy in a much shorter time interval such that less energy is lost through conduction to the surrounding volume before a phase transition occurs. Also, each threshold increases with increasing film thickness due to the increased effective ther-

TABLE I. Threshold fluences for ns and ps laser pulse induced transitions in Sb thin films.

Process		Thickness (nm)		
		25	50	200
Process	Pulse duration	Threshold fluence (mJ/cm ²)		
Melting	ns	25 ± 5	45 ± 9	90 ± 20
Ablation	ns	90 ± 10	115 ± 12	~140
Melting	ps	16 ± 4	33 ± 7	50 ± 10
Ablation	ps	57 ± 9	...	...

mal conductivity of the film. It is important to bear in mind that the thermal conductivity of (bulk) Sb is around 24 W/m K, significantly larger than that of the glass substrate (~1 W/m K). For the 25 nm film, for example, the interaction volume and the heat affected zone comprise regions of both the film and the substrate, clearly giving rise to a lower average thermal conductivity than the one corresponding to thicker films. Similar trends have been obtained for ablation induced by the ns pump pulse. It was not possible to induce ablation in the 50 and 200 nm films using ps pulses with the maximum available laser fluence.

B. Solidification dynamics

Figure 5(a) shows the evolution of the melt duration induced upon irradiation with ps laser pulses in the different films as a function of the laser fluence. The melt duration has been determined as the time interval during which the reflectivity of the film remains below the value for the solid phase at the melting temperature ($R_{S_{MT}}$). As can be seen in the

FIG. 5. Dependence of the melt duration (t) on the laser pulse fluence (F) for: (a) ps laser pulse induced melting 25, 50, and 200 nm thick films and (b) ns laser induced melting of a 50 nm thick film. The solid lines correspond to the best linear fit at fluences below the appearance of visible recalescence effects. The dashed lines are a guide to the eye.

FIG. 6. Reflectivity transient acquired in the 50 ns time window of the streak camera corresponding to a 50 nm thick film irradiated with a ns laser pulse of fluence: (a) 89 and (b) 96 mJ/cm². The arrow denotes the minimum associated with the appearance of recalescence effects after bulk solidification at high fluence.

figure, in the studied interval, the melt duration shows an overall linear dependence with fluence with a clear exception in the case of the 50 nm thick films. In this film the dependence is linear until an additional laser fluence threshold of ~80 mJ/cm² is reached whereupon the melt duration increases abruptly from ~18 to ~25 ns. A globally similar behavior is found upon ns laser pulse irradiation although the discontinuity in the evolution of the melt duration in the 50 nm thick film is much clearer as shown in Fig. 5(b), where it can be seen that around 95 mJ/cm² the melt duration jumps from values about 25 ns to values above 40 ns.

Figure 6 shows two illustrative transients acquired with the streak camera at fluences below and above the nominal threshold of ~95 mJ/cm² for observation of this effect under ns pulses. For a fluence below the threshold, the reflectivity recovery to the solid phase value at the melting temperature occurs rapidly (see also Fig. 3). Above threshold, the initial recovery leads to a maximum in which the film reaches a value close to $R_{S_{MT}}$ (eventually above it) followed by a subsequent decrease and a final recovery at a slower speed. This behavior indicates that the material undergoes an initial solidification stage followed by remelting and finally solidifies, thus evidencing a recalescence mediated solidification process.

Recalescence is a phenomenon whereby the rapid and massive nucleation of the solid phase throughout the whole molten volume causes the release of sufficient solidification enthalpy to reduce effectively the supercooling of the liquid phase eventually leading to re-melting of the material.^{8,16,23} The fluence threshold for observing recalescence effects is given by two factors. On the one hand, it is required to induce a melt duration sufficiently long lasting to promote the homogenization of the liquid temperature and the bulk nucleation of the solid phase, something which is film thickness and substrate dependent. On the other hand, a minimum melt volume is required to provide the latent heat necessary to induce a substantial reduction of the liquid phase supercooling upon the initial nucleation of the solid phase. With these requirements, the amount of solidification enthalpy released in a film of a given thickness will thus depend both on the pulse duration and fluence. In the 50 nm thick film, at high fluences, when the solid-liquid interface gets close to the

substrate, the large difference between the thermal conductivity of *I*-Sb and glass enables a rapid homogenization of the molten layer temperature promoting the bulk nucleation of the solid phase throughout the whole molten volume.

The discontinuity in the evolution of the melt duration as a function of fluence in the 50 nm thick film (Fig. 5) is thus a clear indication of a change in the solidification scenario from a bulk process at high fluence to an interfacial one at low fluence. In the latter, after propagation of the melt front into the material, the melt front proceeds to return to the surface driven by conduction of heat from the liquid. In this case, the melt duration induced does not allow an homogeneous in-depth temperature profile to be established in the liquid and the typical interfacial solidification front speeds that can be estimated from the transients are, respectively, ~ 2 and ~ 5 m/s for ns and ps laser pulses.

In contrast to the case of the 50 nm thick film, the transients measured in 25 nm and 200 nm thick films under both ps [Fig. 5(a)] and ns (results not shown) laser pulses provide melt duration values which depend linearly on the laser fluence in the whole studied range. It would be expected at first glance however that at high fluences solidification should similarly occur via a bulk process followed by recalescence for these two film thicknesses. The reasons for no observation of recalescence effects are different in each case.

In the 200 nm film, the higher effective thermal conductivity of the film prevents the homogenization of the liquid layer temperature no matter the pulse duration used and thus solidification proceeds interfacially for any fluence above the melting threshold in the studied interval. The large initial thickness of the film makes it thus possible that a bulk-like Sb layer (with a thermal conductivity ~ 20 times larger than that of the glass substrate) remains solid underneath the molten layer even at the highest fluences used. This also explains the extremely short melt durations observed for this film [Fig. 5(a), about 10 ns under high fluence ps pulses] which show solidification front speeds similar to the ones estimated in the 50 nm thick film below the bulk solidification threshold.

With the above reasoning regarding the 200 nm thick film, it is clear that the fluence threshold for inducing bulk solidification decreases with decreasing film thickness. In particular, for the 25 nm thick film, the molten volume can extend to the substrate even for relatively small fluences above the melting threshold (the skin penetration depth of the solid phase at 514 nm is about 10 nm). However, the amount of latent heat released by this volume during the initial solid phase nucleation is not sufficient to manifest itself as a recalescence peak, i.e., to give rise to a sudden increase of the melt duration. A similar result has been observed in thin GeSb films under picosecond laser pulses in which recalescence effects in the solidification dynamics were minimized by decreasing the film thickness.⁸ In other words, the 25 nm film is simply too thin to support recalescence effects even if bulk solidification takes place at high fluence. To support this conclusion we have estimated the threshold for bulk solidification in the 25 nm thick film by comparing the melt durations induced in this film to those observed in the 50 nm thick one. We can assume that the

TABLE II. Dominant solidification scenarios at high and low fluence where (*I*) denotes interfacial solidification and (*B*) bulk, and thresholds for bulk solidification under ns and ps laser pulses in the different films studied.

Thickness (nm)	Dominant solidification mechanism					
	ps pump			ns pump		
	Low	High	Threshold (mJ/cm ²)	Low	High	Threshold (mJ/cm ²)
25	<i>I</i>	<i>B</i>	~ 40	<i>I</i>	<i>B</i>	~ 40
50	<i>I</i>	<i>B</i>	80	<i>I</i>	<i>B</i>	95
200	<i>I</i>	<i>I</i>	...	<i>I</i>	<i>I</i>	...

minimum melt duration required for achieving a molten layer at homogeneous temperature is obviously not longer than the corresponding value in the 50 nm thick film (i.e., ~ 15 and ~ 20 ns melt duration for fluences just below the bulk solidification threshold for ps [Fig. 5(a)] and for ns [Fig. 5(b)] pulses, respectively). We can thus infer that bulk solidification should clearly take place in the 25 nm thick films for fluences inducing melt durations above ~ 20 ns. This would lead to an estimation of ~ 40 mJ/cm² for the bulk solidification threshold under ps pulses [Fig. 5(a)] and an approximately similar value for ns laser pulses (results not shown).

A global picture of the different solidification scenarios expected upon ns and ps laser irradiation at high and low fluence in the different films is given in Table II where it can be seen that the dominant mechanism at high fluence in the thinner films is always bulk solidification while interfacial is the dominant mechanism in the thickest film no matter the fluence or the pulse duration used.

The comparison of the present results with those previously reported in Sb-rich GeSb films⁸ shows a strong difference in the solidification speeds under the same experimental conditions. In that work it was shown that 25 nm thick crystalline Ge_{0.07}Sb_{0.93} films on glass, irradiated in the same experimental setup used here with 30 ps pulses at 583 nm and fluences in the 30–45 mJ/cm² range, could be fully reamorphized via bulk solidification with a solidification time of just ~ 400 ps, i.e., 1–2 orders of magnitude smaller than the ones observed in this work for pure Sb films. The amorphous to crystalline phase transition could be also induced via melting upon irradiation at lower fluences (~ 15 mJ/cm²) with a similar solidification time.

Given the complex refractive index of the crystalline phase¹⁹ the reamorphization fluences used in Ref. 8 correspond to *absorbed* fluences of ~ 11 – 17 mJ/cm² and are those required to completely melt the film in depth. Comparing with the equivalent film thickness in the present work (25 nm), we can see in Fig. 5(a) that the larger fluences used here are similar (~ 50 mJ/cm² corresponding to an absorbed fluence ~ 13 mJ/cm²), which indicates that the pure Sb film must similarly melt in depth completely. This is also in agreement with the above estimated threshold for bulk solidification in the 25 nm thick film under ps pulses (~ 40 mJ/cm²). Hence the solidification mechanism at high fluence (bulk process) must be the same for both types of films (Ge_{0.07}Sb_{0.93} and Sb) but the transformation time is greatly increased in the pure Sb ones. It can therefore be concluded

that the ultrafast (sub-ns) transformation time of the Sb-rich GeSb is in fact related to the relatively small amount of germanium present. A plausible explanation for this could be that the Ge modifies the solid phase nucleation process via heterogeneous nucleation, increasing strongly the solidification speed. However, other important thermo-physical parameters of the film that can strongly affect the solidification speed, such as the latent heat, could also be affected by the incorporation of Ge. Whatever the origin of this behavior, whereas it has been previously believed that the essential role played by germanium in the Sb-rich GeSb films was to provide stability for the amorphous phase,¹⁰ it is now clear that the addition of Ge is also essential in greatly improving the solidification speed.

IV. CONCLUSIONS

The rapid melting and solidification dynamics of Sb thin films upon ps and ns pulse irradiation have been studied with picosecond time resolution. The dynamics show significant variations for the three film thicknesses that have been investigated (25, 50, and 200 nm) which originate from the large difference in thermal conductivity between Sb and the substrate material (glass). Most notably, for the 50 nm film, bulk solidification and recalescence effects have been observed in this material at laser fluences just over two times the melt fluence threshold. The use of ps resolution measurements has also allowed the optical constants of the liquid phase of Sb in the visible region to be accurately determined. A comparison of the behavior of these films with the case of Sb-rich GeSb ones makes it clear that relatively minor changes in the film composition can lead to changes in the solidification dynamics under similar heat flow conditions that are beneficial for the application of such films in phase change optical recording.

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