

Dynamics of Rapid Melting and Resolidification of Sb-based Phase Change Materials in Optical Disk

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ABSTRACT

Time-resolved static tester measurements and dynamical continuous write power measurements (DC-write) were performed to analyze the rapid melting and solidification dynamics of quaternary AgInSbTe phase change films with different Sb/Te ratios.

Significant differences in the crystallization kinetics have been observed for the different materials. As it is now well known, the Sb-rich compositions show a more pronounced crystallization ability. The related crystallization processes are investigated thanks to numerical simulations by considering a polymorphic crystalline growth process in which the temperature dependent atomic mobility via the viscosity plays a crucial role.

Surprising results have also been observed concerning the optical properties of the molten phase of the Sb-richest composition. The reflectivity values seem to indicate a drop of the imaginary part of the refractive index upon melting and we will see that this remarkable behavior of the optical properties versus (melting) temperature seems to act like a thermal regulator of the structure avoiding a drastic overheating during writing.

Keywords: Pure crystal growth process, Sb-rich phase change materials, solidification dynamics, real time reflectivity measurements, optical properties of the molten phase.

1. INTRODUCTION

AgInSbTe (AIST) films have attracted considerable interest as advanced materials for phase change recording. Despite the technological use of this material, little information has been reported on the solidification dynamics and crystallization process of this type of phase change materials. Moreover, while there have been several studies undertaken to determine the optical properties of both solid crystalline and amorphous AIST films, there remains very little published data on the liquid phase. In this paper, we propose to investigate the melting and solidification dynamics of these materials by the combination of the use of time-resolved reflectivity measurements and dynamical continuous write power measurements. The comparison of those experimental results with an optical, thermal, thermodynamics and kinetics numerical simulation allows to go towards a better understanding of the behavior (versus temperature) of these materials.

2. EXPERIMENTAL METHODS

The samples used were complete disc structures in which the Phase Change (PC) layer (17 nm) is sandwiched between two ZnS-SiO₂ layers and with an Al layer acting as a mirror and heat sink. Five compositions with a Sb/Te ratio comprised between 1.9 and 4.1 were investigated. Continuous write power measurements (DC-write) were performed on a dynamical tester with $\lambda=405$ nm and NA=0.85 and real time reflectivity measurements were performed at the wavelength $\lambda=650$ nm. Our microscope is equipped with two semiconductor laser diodes operating at 650 and 630 nm. The 650 nm laser operates in pulsed mode and allows the writing. The determination of the time evolution of the reflectivity of the films upon irradiation is conducted using the other laser working in the cw mode at a fairly low power. The two laser beams are focused (simultaneously and coincidentally) on the sample through the microscope objective (NA=0.85). The light reflected from the sample is collected by the objective lens and sent through a prism which separates the two laser beams and sends them to photodetectors. The reflected probe signal is measured using a fast photodetector coupled to a transient oscilloscope.

3. CRYSTALLIZATION BEHAVIOR ANALYSIS

3.1 REFLECTIVITY MEASUREMENTS UNDER CONTINUOUS-WRITE-POWER

Today, it is generally admitted that the crystallization mechanism of the AIST materials is not dominated by nucleation and is a pure crystal growth mechanism [1,2,3,4]. A means of considering this growth mechanism is to analyze the curves obtained in continuous write power at different linear speeds. In these experiments, the laser beam operates in cw mode and we measure for each linear speed the final reflectivity ratio ($=R_{\text{final}}/R_{\text{crystal}}$). In these writing conditions, the recrystallization proceeds via the growth of the crystalline grains surrounding the molten area. For a given composition, below a critical linear speed, it is impossible to achieve amorphization because recrystallization occurs in the tail of the spot (normalized reflection $R/R_c=1$). But above this critical speed, recrystallization is not complete because the crystal growth process is not sufficiently fast to keep up with the laser spot (the growth speed is too low to be able to follow the isotherms “favourable” to the growth) leading to a residual amorphous area ($R/R_c < 1$). Figure 1 shows the DC write power measurements realized on the samples with different Sb/Te ratios. From this figure, it is clear that the crystallization ability increases when the concentration of the metallic element (Sb) increases. With $\text{Sb/Te}=4.1$ (74 at% Sb), the crystalline growth process of the material is speed enough to work above 9 m/s.

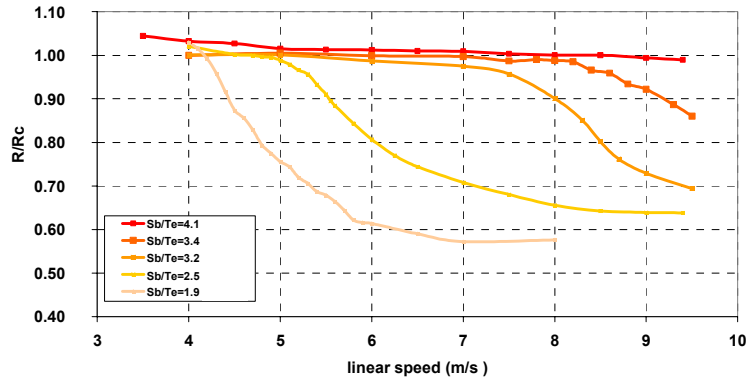


Figure 1 : DC-write curves showing the final reflectivity contrast ($R_{\text{after writing}}/R_{\text{crystal}}$) as a function of the linear speed for different AIST materials with a Sb/Te ratio comprised between 1.9 and 4.1.

3.2 CRYSTALLIZATION KINETICS

Given the very short involved crystallization times in the AIST materials [5,6], we consider only a crystalline growth mechanism without diffusion, it is the solid/liquid interface kinetics which governs the solidification process. The classical law for this behavior is given by eq.1 [7,8].

$$v = d \gamma \left(1 - \exp \left(- \frac{\Delta G_c}{kT} \right) \right) \quad \text{eq.1}$$

In this equation, the second term includes the thermodynamic component, with the driving force for crystallization (ΔG_c), and the preexponential factor which includes the kinetics of the reaction with the atomic jump frequency γ through the liquid/crystal interface. A means to have temperature dependent values of this parameter is to introduce a viscosity law in the Stokes-Einstein relation. We choose for the

viscosity law the Volger-Fulcher expression ($\eta = A \exp \left(a \frac{T_f}{T - T_0} \right)$) [9] which gives access to the atomic

mobility through an important temperature range, and especially in the highly supercooled liquid up to the glass transition temperature (T_g). Two elements allow us to think that the AIST materials may be considered in the supercooled range as “weak” liquids¹. First element, their viscosity at the melting point

¹ In a weak liquid, the viscosity of the material decreases rapidly above T_g and this labile state of the liquid is kept up to the melting temperature.

is low ($\sim 10^{-3}$ mPa.s). Second element, the very fast crystallization process implies probably that the viscosity reaches a low value above T_g with an important increase of the atomic mobility and a more efficient construction of the crystalline structure.

In order to analyze the crystallization process of the materials, we have tried to understand their behavior in the DC-amorphization conditions. For this, a complete simulation including optical, thermal² and PC models is a very efficient tool to guide the understanding.

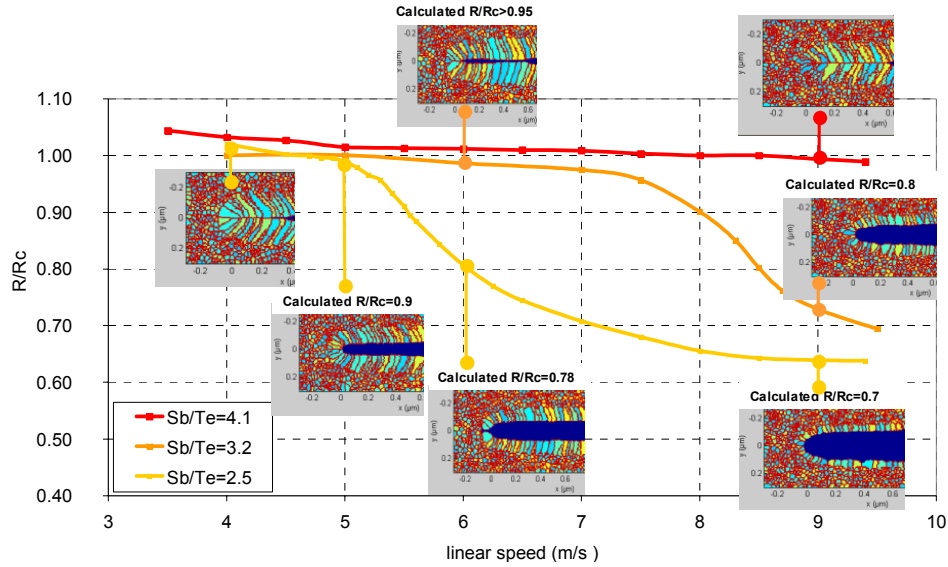


Figure 2 : Simulated amorphization results obtained for three different Sb/Te ratio.

Figure 2 shows the results of the simulation in which we have introduced the previously described crystalline growth law. We can see that for a given material the crystallization behavior (with the calculated optical contrast) versus the linear speed is rather well reproduced. The growth speeds (versus temperature) used for the different materials are represented Figure 3. Globally, we see that the shape of these curves is not classical. Contrary to the well-known shape which shows a maximum localized not far from the melting point, the growth speed presents an efficiency over an important temperature range. This shape illustrates in fact the hypothesis proposed above; namely a “weak” liquid behavior in the supercooled range. The labile state of the liquid appears to be extended over a more important temperature range when the Sb concentration increases (Figure 3). It should be noted that in this approach, we take care to keep the values of the viscosity above 10^{-3} mPa.s which is the lowest value (at the melting point) found in the published data on this type of materials [10].

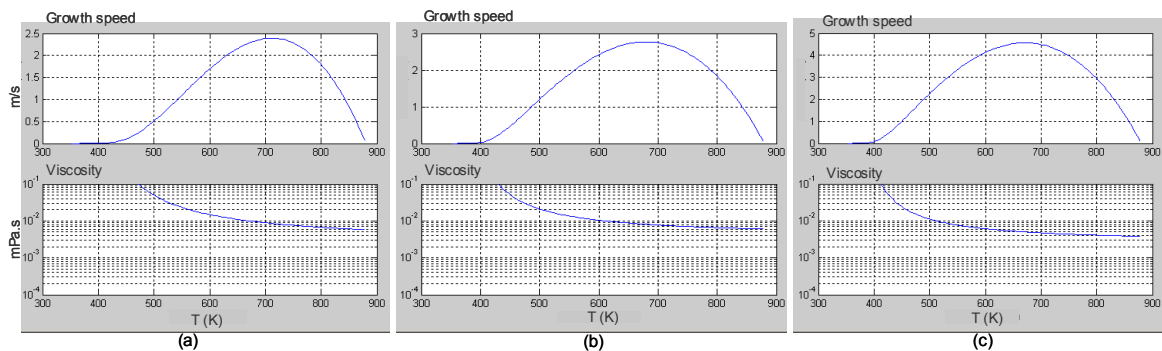


Figure 3 : Crystalline growth speeds used in the simulation for the three different material investigated Figure 2. (a), (b) and (c) are the growth velocities used for the materials with the Sb/Te ratio equal to respectively 2.5, 3.2 and 4.1. The lower figures show the related viscosity.

² The optical constants of the films introduced in the program are determined from ellipsometric measurements and the thermal parameters are from different sources.

Furthermore, static test measurements indicate a crystallization time (defined as the minimum duration of the erasure pulse for complete recrystallization of an amorphous mark written in the crystalline layer) of around 25-30 ns for the Sb/Te=4.1 material (Figure 13); the optimal erasing power (8 mW) being roughly half of the writing power (15 mW). If we use in the simulation the non-classical shape of the Figure 3.c for the growth speed, we can see on Figure 4 that the calculated crystallization time of the memory point is around 35 ns (by using an erasing power value half of the writing power) which illustrates rather well the observed experimental behavior.

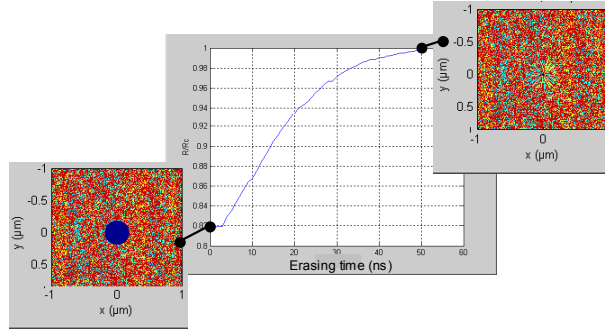


Figure 4 : Calculated time evolution of the reflectivity contrast (R/Rc) of a previously written mark (50 ns-15 mW) upon an erasing pulse (7 mW) and final resulting microstructure. The growth speed is the one described Figure 3.c.

On the other hand, if we introduce in the simulation a more classical shape for the crystalline growth speed with a marked maximum at temperatures relatively close to the melting point (Figure 5), it appears difficult to achieve a complete crystallization of the mark whatever the erasing power. We can see on Figure 6 that with a too low power (7 mW), the “incubation” time to efficiently heat the amorphous/crystalline boundaries and start the crystalline growth is too long, more than 40 ns, and with a too high power (9 mW) the center of the mark is molten and amorphized again.

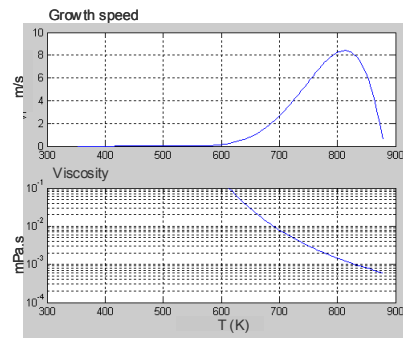


Figure 5 : Crystalline growth speed with a marked maximum not far from the melting point and related viscosity.

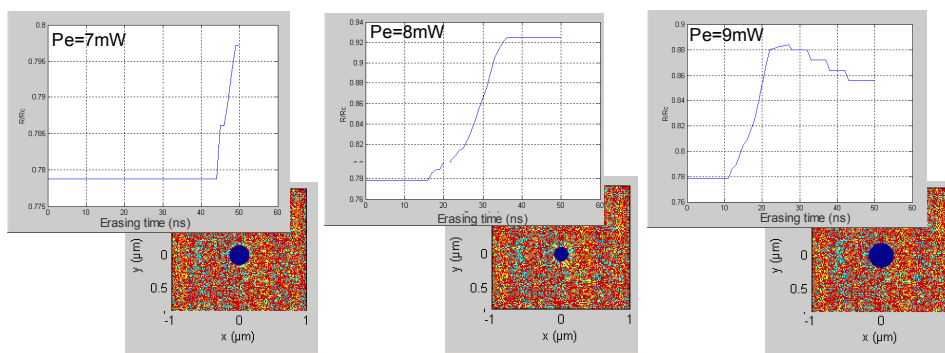


Figure 6 : Calculated time evolution of the reflectivity contrast (R/Rc) of a previously written mark (50 ns-15 mW) upon an erasing pulse with three different erasing powers (7-8-9 mW) and final resulting microstructure. The growth speed is the one described Figure 5.

It should be pointed out that such a growth speed (8 m/s) at its maximum requires the use of very low values for the viscosity near the melting point, less than the water viscosity, which seems to be ‘a priori’ unlikely.

4. OPTICAL PROPERTIES OF THE MOLTEN PHASE AND WRITING PROCESS ANALYSIS

In the following we study mainly the Sb/Te=4.1 material thanks to real time static measurements. We have observed on a quadrilayer stack³ an increase of the optical contrast upon melting ($R_{\text{melting}}/R_{\text{crystal}} > 1$). We can see on Figure 7 that this behavior appears whatever the pulse duration (50 ns to 200 ns).

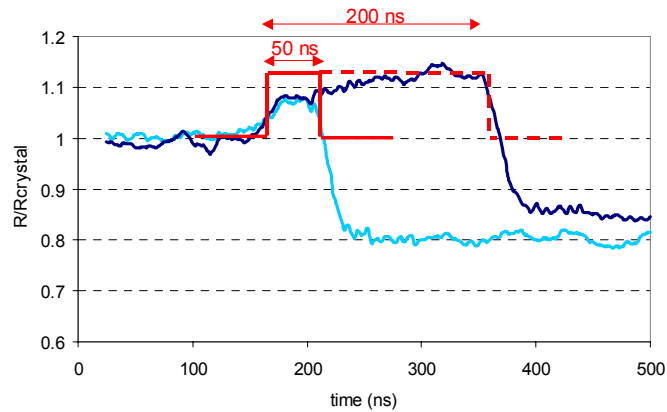


Figure 7 : Reflectivity contrasts (R/R_c) measured upon a 50 ns and a 200 ns pulse at 15 mW and 650 nm. The red curves correspond to the pulses temporal profiles.

This 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.

If basically we use, for the liquid PC material, the optical values of the as-deposited amorphous material, the calculated temperature reached in the layer at the end of the 200 ns pulse (15 mW) is more than 1400°C, such “unlikely” temperature which should undoubtedly cause permanent damages of the device. Moreover, in this case the simulated reflectivity change upon melting is opposite to that experimentally observed (Figure 8). This means that contrary to a basic way of thinking, the optical properties of the molten material appears to be very different from the amorphous ones, especially for AIST.

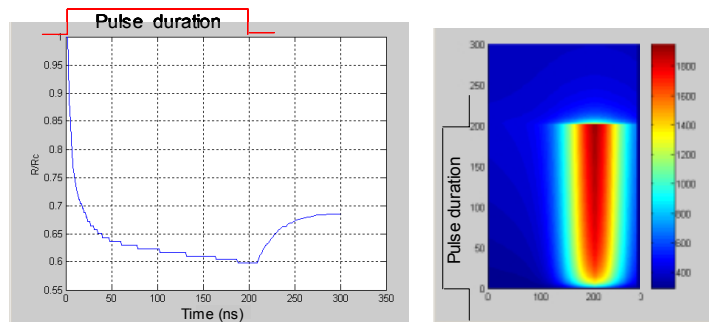


Figure 8 : Calculated reflectivity contrast (R/R_c) obtained upon a 200 ns pulse (15mW) by using for the molten PC material, the optical values of the as-deposited amorphous material (left figure), and time dependent temperature evolution in the PC layer during the pulse (right figure).

³ The PC material is sandwiched between two ZnS-SiO₂ layers and a AlTi film ends the stack.

In order to find what are the optical properties of the molten material, we have calculated the reflectivity ratio ($R_{\text{calculated}}/R_{\text{crystal}}$) of our multilayer stack as a function of the imaginary part of the refractive index (k). It is assumed, in a first approach that the melting process causes a negligible change in the real part [11,12]. The calculated values are shown in Figure 9. We can see that two cases may lead to the measured molten contrast ($R_{\text{molten}}/R_{\text{crystal}} > 1$): the first one is an increase of k of around 0.5 above the crystalline value ($k_{\text{crystal}} = 4.3$) and the second one is an important decrease of k up to the order of 0.5 (cf. green crosses on Figure 9).

In this paper, we will not consider in details the first case; in fact a mismatch between the experimental and the calculated (with $k_{\text{molten}} = 5$) threshold power for melting the PC material seems to indicate that this optical solution does not illustrate the real behavior of the material. In the following, we will focus on the second behavior; the data from literature supporting this interpretation, that is to say a decrease of the imaginary part of the refractive index for a solid-to-liquid transition in a metal or semi-metal material, like pure Sb [11,12].

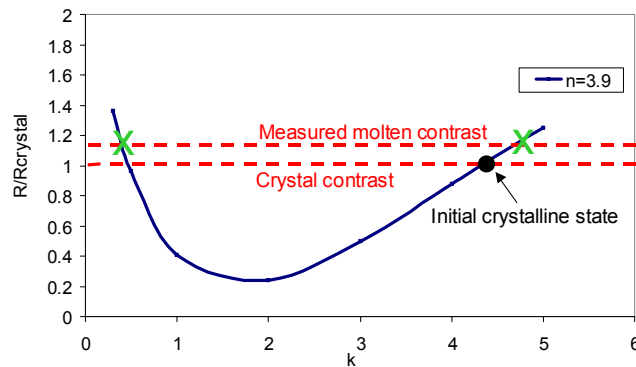


Figure 9 : Calculated dependence of the reflectivity contrast (R/R_c) of a 17 nm thick AIST material sandwiched in a quadrilayer structure on the imaginary part of the refractive index (k) calculated for $n = n_{\text{crystal}} = 3.9$. The horizontal dotted lines indicate the experimentally determined values of the reflectivity contrast of the crystalline and molten phases of the material.

We have then made simulations considering a quasi non absorbing molten PC material to know its effect on the thermal behaviors and consequently on the writing processes. Figure 10 shows the calculated evolution of the reflectivity contrast (R/R_c) versus time during the 50 ns writing pulse and the subsequent cooling (Figure 10.a), the evolution of the temperature in the middle of the phase change layer during and after the pulse (Figure 10.c) and the simulated final microstructure (Figure 10.b).

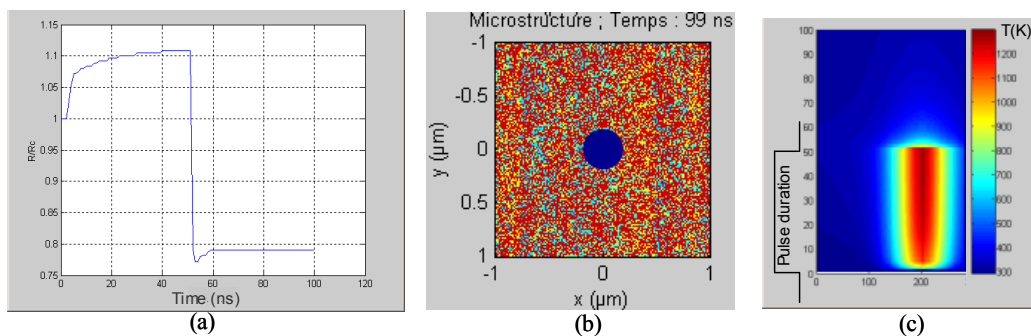


Figure 10 : Calculated reflectivity contrast (R/R_c) obtained upon a 50 ns pulse (15 mW) by considering a quasi non absorbing molten PC material (a), simulated final microstructure of the amorphous mark (b) and time dependent temperature evolution in the PC layer during the pulse (c).

The three graphs of the Figure 11 show the same simulated characteristics but with a writing pulse of 200 ns.

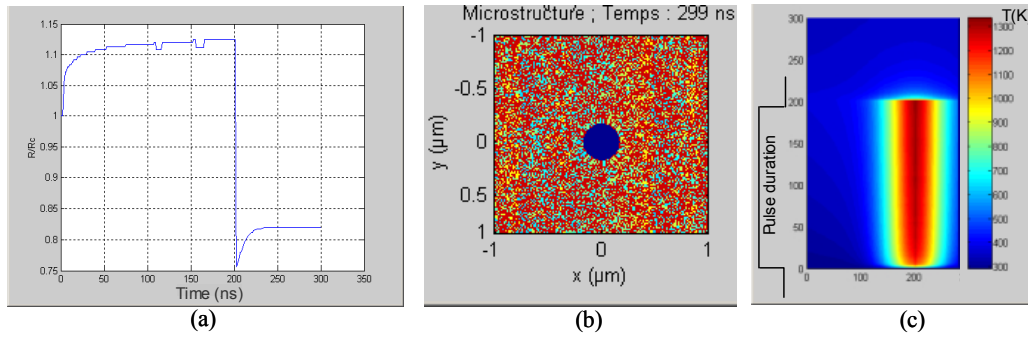


Figure 11 : Calculated reflectivity contrast (R/Rc) obtained upon a 200 ns (15mW) pulse by considering a quasi non absorbing molten PC material (a), simulated final microstructure of the amorphous mark (b) and time dependent temperature evolution in the PC layer during the pulse (c).

As expected, we observe an increase of the R/Rc contrasts during writing for the two pulse durations. We can see on the microstructure that the final size of the marks is very close in the two writing conditions but we can observe a small quantity of recrystallization from the crystalline edge during the cooling in the case of the long pulse. This recrystallization phenomenon causes a small increase of the contrast at the end of the cooling. The final ratio R/Rc in this case is comprised between 0.8 and 0.85 whereas the final contrast at the end of the short pulse is a little bit better, around 0.8, due to a more efficient quenching which prevents recrystallization. These results are consistent with the experimental curves of the Figure 7 and with the diffraction limited optical microscope ($\lambda=514$ nm and NA=0.85) image (Figure 12). If we consider now the temperature profiles, we can see that with a short pulse the temperature of the liquid material is around 900°C which is reasonable compared to the melting point of this material family. For the long pulse, we see that the temperature in the PC material doesn't increase with time and is maintained at around 900°C. The liquid material seems to be not significantly overheated which should prevent irreversible damages and troubles in the eventual subsequent erasing process.

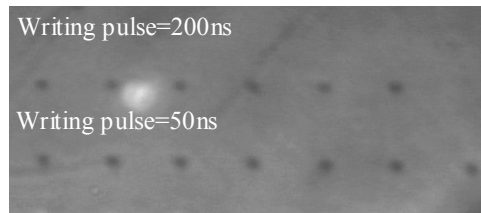


Figure 12 : Diffraction limited optical microscope ($\lambda=514$ nm and NA=0.85) image of the memory points written with two different pulses durations (50 and 200 ns)

The experimental subsequent recrystallization process of the amorphous marks written in 50 and 200 ns seems to support the latter discussion because, as we can see on Figure 13, the recrystallization time of the amorphous marks is the same for the two writing conditions. This means that the long writing pulse did not perturb the subsequent erasing process.

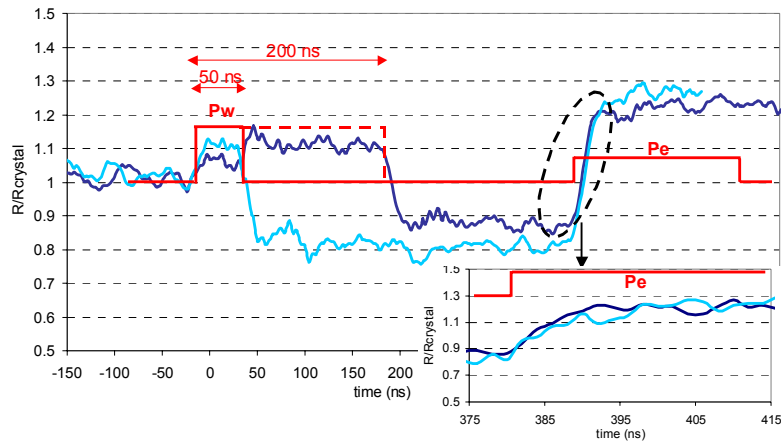


Figure 13 : Reflectivity contrast (R/R_c) measured upon a writing pulse and a subsequent erasing pulse. The bright blue curve corresponds to the 50 ns writing pulse and the dark blue curve corresponds to the 200 ns writing pulse. The red curves correspond to the pulses temporal profiles.

5. CONCLUSION

We have investigated the rapid melting and solidification dynamics of the AIST phase change materials. We have seen that in order to make physically realistic simulations, it is necessary to consider the behavior of a weak liquid in the supercooled range leading to a non classical shape for the temperature dependent growth speed. Moreover, the reflectivity change observed during the writing pulse when the Sb/Te=4.1 material is molten may be explained by considering a drop of the complex refractive index of the liquid phase. These remarkable optical properties of the liquid material seem to regulate the thermal behavior during writing avoiding an overheating of the liquid material and allowing a trouble-free subsequent erasing process. However, we are conscious that this interpretation requires further investigations and especially the measurements of the optical properties of this Sb-rich phase change material both in crystal phase and in molten phase. The corresponding measurements will have to take into account the possible formation of a perturbing layer resulting from the chemical reactivity with environment of the Sb-rich layer when the liquid state is reached.

REFERENCES

1. G. F. Zhou, H. J. Borg, J. C. N. Rijper, M. H. R. Lankhorst and J. J. L. Horikx: Proc. SPIE, Vol. 4090, p.108 (2000)
2. L. van Pieteron, M. van Schijndel, J. C. N. Rijpers and M. Kaiser: Appl. Phys. Lett., Vol. 85 (7), p.1373 (2003)
3. P. K. Khulbe, T. Hurst, M. Horie and M. Mansuripur: Applied Optics, Vol. 41 (29), p.6220 (2002)
4. S. J. Price, A. L. Greer and C. E. Davies: Proc. SPIE, Vol. 4090, p.122 (2000)
5. H. J. Borg, P. W. M. Blom, B.A. J. Jacobs, B. Tieke, A. E. Wilson, I. P. D. Ubbens and G. F. Zhou: Proc. SPIE, Vol. 3864, p.191 (1999)
6. G. F. Zhou: Mater. Sci. Eng. A, Vol. 304-306, p.73 (2001)
7. F. Spaepen and D. Turnbull: Am. Inst. Phys. Conf. Proc. 50, p.73-83 (AIP, New York 1979)
8. M. Von Allmen, *Laser Beam Interactions with Materials* (Springer, Berlin, 1987)
9. G. S. Fulcher: J. Am. Ceram. Soc, Vol.8, p. 339 (1925)
10. F. Herwig and M. Wobst: Z. Metallkd, Vol. 83, p.35 (1992)
11. S. M. Wiggins, W. M. Gawelda, J. Solis, R. Serna and C. N. Afonso: J. Appl. Phys., Vol. 94 (8), p. 4961 (2003)
12. R. Serna, J. Solis and C. N. Afonso : J. Appl. Phys., Vol. 73, p.3099 (1993)

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