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Melting kinetics of Sb under nanosecond UV laser irradiation

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Real time reflectivity measurements at the HeNe laser wavelength ($\lambda=632.8$ nm) have been performed in crystalline Sb under pulsed UV laser irradiation ($\lambda=193$ nm). For energy densities above 100 mJ cm^{-2} , a transient low-reflectivity phase is observed, which is related to surface melting. The change of reflectivity of the solid material upon heating is small, and a maximum variation of -0.02 relative to the room-temperature value ($R_{\text{Sb,rt}}$) is determined for the solid material at the melting point. The value of the reflectivity of the liquid material is determined to be $0.94R_{\text{Sb,rt}}(632.8 \text{ nm})=0.67$, which is lower than that of the solid and it is associated with a decrease of the absorption coefficient upon phase change. The analysis of reflectivity transients at energy densities just above the melting threshold suggests that melting nucleation proceeds inhomogeneously.

Antimony is a very interesting material for many thermoelectric and microelectronic devices. Lately, the interfaces of antimony/III-V semiconductors have attracted much attention because whereas most metals exhibit strong intermixing with these semiconductors, abrupt interfaces are formed with Sb overlayers.¹ UV laser pulse processing has been shown to be useful to planarize metal layers for multilevel interconnections.² As the absorption of the laser energy takes place at the surface,³ this technique has the advantage to drive the metal to the melting point while the semiconductor substrate remains virtually cold. Not only the lower melting point of Sb compared to GaAs, but also the high thermal gradient induced by the good thermal conductivity of both, the semimetal itself and the semiconductor, contribute to make possible this procedure.

Real time reflectivity (RTR) measurements have been proposed as a technique to determine the metal melt duration during the planarization process.² Such application requires an accurate knowledge of the properties of the material both in solid and liquid phase. Nevertheless, there are extremely few data about the properties of molten Sb. In particular, to the best of our knowledge, the reflectivity of this liquid semimetal has not been previously determined. Besides, real time optical measurements have been demonstrated to be a powerful tool to analyze the solid-liquid phase transformation in laser processing of semiconductors^{4,5} and oxidation processes.⁶ In this work we will analyze the solid-liquid transition induced in Sb by laser irradiation by means of RTR measurements.

In order to produce surface melting we have used ArF excimer laser pulses ($\lambda=193$ nm, $\tau=12$ ns FWHM), with energy densities at the sample site in the $90\text{--}450 \text{ mJ cm}^{-2}$ range. The laser beam is homogeneous within $\pm 5\%$ over the irradiated area. A HeNe ($\lambda=632.8$ nm) at near normal incidence is used to monitor in real time the induced reflectivity changes.⁵ The samples are cleaved Sb $\langle 111 \rangle$ high-purity single crystals. The surface of the crystals was polished with one micrometer alumina powder and rinsed in alcohol before processing.⁷ In order to determine the possible influence of any oxidation effects the samples were irradiated in air, and in a turbopumped system both

in an oxygen atmosphere and in vacuum ($\sim 10^{-4}$ mbar). For high oxygen pressures and in air processing a decrease in the reflectivity of the solid material was observed upon multipulse irradiation. This effect is related to the formation of an oxide overlayer at the surface. Formation of Sb oxides in air via solid-state processes has been reported at temperatures below the melting of Sb (903 K)⁸ and can be activated at temperatures close to room temperature via photonic effects by UV laser irradiation.⁹ At a pressure of 3×10^{-4} mbar no permanent changes in the sample reflectivity were observed. This pressure condition was selected for the present study.

The evolution of the reflectivity as a function of time for several irradiation energy densities, is plotted in Fig. 1. Before the laser pulse reaches the surface, the reflectivity has a constant value corresponding to the reflectivity of the solid material at room temperature ($R_{\text{Sb,rt}}=0.71$). For energy densities higher than 100 mJ cm^{-2} significant reflectivity changes are observed. Above this threshold, when the irradiation pulse reaches its maximum intensity, the reflectivity decreases to a minimum. Two different behaviors can then be distinguished. For the lowest energy densities ($100\text{--}150 \text{ mJ cm}^{-2}$), the reflectivity recovers once the minimum is reached and this minimum value increases as the energy density increases. Above 150 mJ cm^{-2} and once the reflectivity reaches its minimum, it remains constant during several tenths of nanoseconds. An increase of irradiation energy density yields to an increase in the duration of this plateau, whereas the minimum reflectivity value does not change. The transients end by recovering the initial reflectivity value. This indicates that no permanent optical changes have been induced in the material.

The observed behavior is consistent with the development at the surface of a high-temperature transient phase with well defined optical properties. This phase is most probably liquid Sb, and the plateau lasting corresponds therefore to the movement forwards and backwards of the melt front. An approximate calculation of the energy density required to bring the solid material to the melting temperature using the expression provided in Ref. 10 gives a value of 80 mJ cm^{-2} , which is in very good agreement

FIG. 1. Reflectivity transients obtained upon irradiation with ArF excimer laser pulses with (A) 119, (B) 144, (C) 218, and (D) 291 mJ cm^{-2} . The dashed line corresponds to the irradiation pulse temporal profile. The melt duration (t_m) for transient D is included, as an example of the criteria employed, and to show the change of slope observed during the cooling process.

with the threshold experimentally observed. This result together with the fact that the reflectivity behavior reported for metals upon melting is similar to the one shown by Sb supports our interpretation.^{2,11,12} The observed reflectivity change is opposite to that reported for semiconductors upon melting, which show a strong reflectivity increase related to the melting process, and originated by the metallic nature of the molten phase.^{4,5}

A more detailed observation of the transients for energy densities above 150 mJ cm^{-2} shows that the reflectivity recovery, related to the cooling process, is slower than the initial decrease, related to the heating and melting process. Before reaching the reflectivity value corresponding to the solid material at room temperature, the transients show two different slopes (see D in Fig. 1). This slope change in the case of semiconductors has been attributed to the end of the solidification process followed by solid phase cooling.^{5,13} A similar interpretation in our case allows us to determine the reflectivity value of the solid material at the melting temperature ($R_{\text{Sb,mt}}$). In Fig. 2(a), the reflectivity value at the change of slope during cooling has been included as a function of the energy density. It has a constant value, $0.99\text{--}0.98R_{\text{Sb,rt}}$, which clearly sustains the previous interpretation and provides a value for $R_{\text{Sb,mt}} \sim 0.70$. The small difference of this value with respect $R_{\text{Sb,rt}}$ shows that there is not a strong dependence of the optical properties of the solid material as a function of the temperature.

In Fig. 2(a), the minimum reflectivity value reached in each transient has been also plotted as a function of the irradiation energy density. Above the energy density threshold for observable reflectivity changes ($\sim 100 \text{ mJ cm}^{-2}$), the reflectivity minimum sharply decreases to reach a near constant value for energies higher than 150 mJ cm^{-2} . This value ($0.94R_{\text{Sb,rt}} \sim 0.67$), which corresponds to the already discussed plateau observed in the reflectivity transients (Fig. 1), provides the reflectivity of a homogeneous Sb liquid layer at the surface. When compar-

FIG. 2. Reflectivity (a) at the change of slope during cooling ($\square$) and at the minimum ($\blacksquare$); and surface melt duration (b, $\blacksquare$) both as a function of the energy density.

ing the relative reflectivity change of Sb upon melting (-6%) with that reported for semiconductors at the same wavelength (100% for Si,^{4,5} 50% for Ge,⁴ 44% for GaAs¹³) this change in Sb seems quite low. The result is not surprising since in semiconductors, melting is accompanied by a change from semiconductor to metallic state, whereas in the case of semimetals (Sb) melting is not expected to involve a change in the bonding nature.

Figure 2(b) shows the melt duration as a function of the energy density evaluated from the transients, considering that the surface material is liquid whenever the reflectivity remains lower than $R_{\text{Sb,mt}}$. The melt duration increases monotonously as the energy density is increased, being 20 ns the minimum value observed experimentally. For low-energy densities ($< 300 \text{ mJ cm}^{-2}$), the melt duration shows an approximately linear dependence. For higher energy densities, a higher order of dependence is observed, related to the limited nature of the heat diffusion rate in the material while the energy deposition is continuously increasing. Heat-flow calculations of the melt duration curve both in metals¹⁴ and semiconductors^{15,16} below the evaporation threshold predict a behavior similar to this experimental curve.

The change of reflectivity measured in the liquid phase implies a change in the complex index of refraction ($n + ik$). Figure 3 shows the behavior of the reflectivity (R)

FIG. 3. Reflectivity curves as a function of the real part of the refractive index (n) calculated for several values of the imaginary part of the refractive index (k) at normal incidence.

at normal incidence as a function of the real part (n) of the refractive index, calculated for several values of the absorption coefficient (k).¹⁷ The optical constants of the Sb solid phase are $n_s=2.87$ and $k_s=5.03$.¹⁸ As R is a multivaluated function of n and k , both optical constants of the liquid phase cannot be determined straightforwardly from the measured reflectivity. However, since in our case the constant k_s curve does not intersect the reflectivity value determined for the liquid phase, it is clearly seen that this phase has necessarily a lower k value. It means that the molten material has a lower absorption and therefore the penetration depth of the probe beam is larger in the liquid than in the solid phase. Simulations of the reflectivity of a liquid layer growing on solid Sb were made taking into account n values different than that of the solid (and the corresponding k value from Fig. 3) and they always showed interference effects, which were not observed in the transients within the experimental resolution. Besides, the large change in reflectivity observed upon melting in the case of semiconductors is mainly associated to a change in the k value and a small change in n .¹⁹ Thus, we can assume a negligible change in n ($n_l=n_s$) which leads to $k_l \sim 4.5$.

The kinetics of the early stages of melting can be analyzed through the reflectivity transients obtained in the 100–150 mJ cm⁻² range. For this energy density range, reflectivity values between those corresponding to the solid material and the liquid material at the melting point are found [Fig. 2(a)]. The same effect has been widely discussed in the case of semiconductors, because of its implications in the nucleation of the liquid phase.^{4,5,13} It has been shown that melting is not induced homogeneously at the surface, and that there is a stage in which the solid and liquid phases coexist without a well defined (planar) interface. The relative amount of these phases induces the existence of reflectivity values intermediate between those of the solid and the liquid. Once the energy is high enough, an homogeneous liquid layer is formed. An alternative explanation for these intermediate values is based in the evolu-

tion of the reflectivity of the liquid/solid bilayer as a function of the increasing liquid layer thickness.²⁰ In the case of Sb, it is difficult to elucidate between these two effects, due to the narrow energy density range in which the transition takes place (50 mJ cm⁻²) and the small probe penetration depth both in the solid and the liquid. Nevertheless, experimental melting times lower than ~ 20 ns [Fig. 2(b)] have never been found, which clearly supports the inhomogeneous melting model.^{4,5}

In summary, we have determined the energy density melting threshold of Sb at 193 nm (~ 100 mJ cm⁻²). The results suggest that melting for energy densities below 150 mJ cm⁻² proceeds inhomogeneously. The reflectivity of the liquid phase at 632.8 nm ($R_{Sb,l}=0.67$) is lower than that corresponding to the solid material at room temperature due to a decrease in the absorption coefficient. The reflectivity of the solid material at the melting point is $0.98\text{--}0.99 \times R_{Sb,r}$, which shows that there is no significant dependence of the optical properties of the solid phase with temperature at this wavelength.

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