Formation of metastable states of the liquid phase in the course of melting of III-V semiconductor compounds by nanosecond laser pulses

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(Submitted 17 May 1989)
Zh. Eksp. Teor. Fiz. **96**, 1459–1472 (October 1989)

Formation of two liquid phase states was observed when GaSb and InP were exposed to nanosecond laser pulses. In the case of GaSb one of these states was an equilibrium liquid phase and the other was metastable. In the case of GaAs the metastable state of the melt did not form even when picosecond pulses were used. The optical characteristics of liquid GaSb and InP were investigated in both states. In each of these states the GaSb and InP melts were metallic and their optical properties were described satisfactorily by a model of "almost-free" electrons. Possible structural differences between the metastable and stable liquid phases of binary compounds were analyzed. A study was made of the influence of the state of the melt on the properties of the material crystallizing from it.

1. INTRODUCTION

Interaction of semiconductors with nanosecond and picosecond laser pulses results in extremely fast (of order 10^9–10^{14} K/s) heating and cooling of the crystal lattice. The phase transitions (melting and crystallization) then occur under highly nonequilibrium conditions. For example, in the case of nanosecond pulses the velocity of the melting front can reach hundreds of meters per second, whereas the crystallization front can travel at tens of meters per second.[1,2] It is therefore not surprising that even in the case of elemental semiconductors such as silicon the experiments demonstrate that the kinetics of phase transitions considered over short time intervals differs from the traditional quasiequilibrium picture[2]; in particular, the kinetic melting and crystallization coefficients are asymmetric in the case of interaction with nanosecond laser pulses.

One of the most important distinguishing features of fast phase transitions is the possibility of forming intermediate metastable phases at some stage of the transition. A striking example of a metastable state is a crystal heated above its melting point. Significant overheating of crystalline semiconductors before melting, reaching 200–300 K above the melting point in the case of nanosecond pulses and 500–1500 K in the case of picosecond pulses, can be achieved only if short laser pulses are used (for a detailed discussion of this topic see Ref. 3). Another example is the formation of an amorphous phase during solidification of semiconductor materials from the melt created by picosecond laser pulses (see Ref. 4 and the literature cited there).

It should be pointed out that the amorphous phase is the most common example of a metastable state. The feasibility of formation of a crystal overheated above its melting point has been discussed frequently in the literature, but it has been observed experimentally as a result of interaction with laser pulses only quite recently. The possibility of formation of metastable states of the liquid phase when laser pulses interact with semiconductors is much less trivial. The latter possibility was pointed out in Ref. 5, where the postulated properties of one of such states were described: this state is a semiconductor liquid with a tetrahedral atomic environment typical of the crystalline and amorphous phases of group IV semiconductors and III-V compounds.

A recent investigation of the kinetics of melting of crystalline InP as a result of interaction with nanosecond laser pulses revealed[6] anomalous behavior of the optical characteristics of the melts of this semiconductor: two very different intensities of the reflected light used to probe the surface of the melt during irradiation were observed at different energy densities. This behavior was attributed tentatively to the formation, over intervals of $\sim 10^{-8}$ s, of a new metastable state of a liquid metallic phase of InP typical of binary semiconductors. Unfortunately, because of the lack of information on the properties of an equilibrium melt of InP, it was not possible to identify reliably the two states of the liquid phase observed experimentally. Therefore, a search was made for a material which would, on the one hand, manifest properties similar to those of InP and, on the other, would permit a comparison with the results obtained under equilibrium conditions. This model material was found to be GaSb, because—as in the case of InP—two different intensities of the reflected light used to probe the melt were recorded for gallium antimonide.[7]

Our aim was to carry out a comparative investigation of the conditions of the formation and the properties of two states of the liquid phase created by interaction of nanosecond laser pulses with crystalline samples of GaSb and InP. As a diagnostic we used the reflection coefficient of light to probe the surface of the semiconductor while the laser was acting. Full identification of the states created as a result of such phase transitions required probing of the surface at three wavelengths.

The paper is organized as follows. A brief description of the experimental methods is given in Sec. 2. The results of determining the reflection of a probe beam while the laser was acting are presented in Sec. 3. A comparative analysis is made of the experimental data demonstrating the existence of two different states of liquid GaSb and InP. These states are identified in Sec. 4; it is shown there that one of them is metastable. The main properties of metastable states are given. The influence of the state of the melt on the properties of the material crystallizing from it is demonstrated. Section 5 deals with the optical characteristics of metastable and stable states of liquid GaSb and InP, and it is shown that the optical properties of the melt in either state can be described

0038-5646/89/100827-09$04.00

by a model of almost-free electrons. An analysis of all the experimental results is used in Sec. 6 to discuss possible characteristics of the structure of the metastable states of liquid binary semiconductors.

2. EXPERIMENTAL METHOD

Our samples were chemically polished InP (100) and GaSb (111) plates cut from single crystals grown by the Czochralski method. These semiconductor crystals were irradiated with pulses of the second harmonic of a Q-switched YAG:Nd^3 laser ($\lambda_p = 532$ nm, TEM$_{00}$ mode, pulse duration $\tau_p = 20$ ns at half-height). A typical diameter of a region recrystallized after irradiation was 1.0–1.5 mm. The range of the energy densities E used in these experiments was 10–500 mJ/cm^2.

The surface of a semiconductor was probed during the interaction of a pulse; this was done using three wavelengths emitted by a cw He–Ne laser ($\lambda = 0.63$, 1.15, and 3.39 μm). The angle of incidence of the probe radiation (with the s polarization) on the sample was 20° relative to the normal. The diameter of the probe beam was $\approx 80\,\mu$m. The ratio of the diameters of the heating and probe beams ($\sim 15{:}1$) ensured that the relative error in the determination of the energy density at the point of interaction of the probe beam was less than 3%. The position of the point of incidence of the probe beam relative to the boundary of a recrystallized region was determined with the aid of a television camera. When the semiconductor was transparent to the probe radiation incident on its surface, the rear face of the plate was subjected to a roughening treatment to produce a matt surface so as to avoid interference effects. The reflected light was recorded with a fast-response photodiode; the time resolution of the recording system was ~ 2 ns.

The same optical system was used to determine the reflection coefficient of a crystalline semiconductor before studying the reflection of a probe beam. The values of the reflection coefficient R determined under kinetic conditions were then calibrated against the reflection coefficient of the crystalline material before irradiation. The error in a single measurement of R was less than 2%. When the maximum values of the reflection coefficient were determined, statistical analysis of the results reduced the error to 0.5%.

3. KINETICS OF MELTING OF SEMICONDUCTORS BY NANOSECOND LASER PULSES

The behavior of the reflection coefficient of a beam probing the surface of crystalline Si and Ge during interaction with nanosecond laser pulses has been investigated quite thoroughly.[8] At energy densities slightly above the melting threshold the time dependence of the reflection coefficient $R(t)$ is dome-shaped due to the formation of nuclei of the liquid metallic phase, their growth on arrival of further optical energy in the semiconductor, and disappearance after the end of a laser pulse. The rise of the reflection coefficient associated with the onset of melting coincides in time with the fall of the intensity of the heating pulse, which corresponds to the maximum increase in the temperature of the semiconductor. When the optical energy densities increase, the proportion of the molten material rises until the surface layer of the semiconductor melts completely. The amplitude of the reflection peak thus rises and then reaches a steady-state value governed by the reflection coefficient of the homogeneous molten material. When the energy density of the incident radiation is increased, the onset of melting is shifted toward earlier times, reaching the leading edge of the heating laser pulse.

Much less information is available on III-V semiconductor compounds, However, the data[9] available for GaAs demonstrate that its behavior is similar to that of Si and Ge. A direct comparison of these results with those obtained for GaSb and InP can be made by considering the maximum value of the reflection coefficient R_m reached in the course of a nanosecond interaction[9] as a function of the energy density E (curve 1 in Fig. 1). The rise of R_m in the range $E \lesssim 0.2$ J/cm^2 is, as already mentioned, due to an increase in the proportion of the molten material in the surface layer of the semiconductor. The steady value of R_m in the range $E \gtrsim 0.2$ J/cm^2 represents reflection from a homogeneous melt. It should be pointed out that this behavior of the dependence $R_m(E)$ is retained when laser pulses of picosecond duration are used,[10,11] as demonstrated by curve 2 in Fig. 1 (the shift of the melting threshold toward lower energy densities is due to both a reduction in the pulse duration and a transition to a shorter wavelength of the interacting light).

Our experiments on crystalline GaSb and InP revealed a completely different behavior of the reflection coefficient of the probe beam when nanosecond laser pulses interacted with the semiconductors. Figure 2 shows the time dependence of the reflection coefficient of the surface of GaSb at probe wavelengths $\lambda = 0.63$ and 1.15 μm, which were obtained at different energy densities. The curves labeled 1 ($E = 50$ mJ/cm^2) represent heating of the crystalline material without melting. Since the reduced density of states in GaSb for interband transitions at the wavelength $\lambda = 1.15$ μm increases with temperature, whereas at the wavelength $\lambda = 0.63\,\mu$m this density decreases with temperature, it follows that heating of a crystal at these wavelengths can result in an increase and a reduction in the reflection coefficient of the probe beam, respectively. At energy densities $E > E_0 = 55$ mJ/cm^2 (curves labeled 2) a dome-shaped peak, coinciding in time with the fall of the intensity of the heating pulse, appears superposed on the temperature-dependent reflection coefficient. This peak is manifested par-

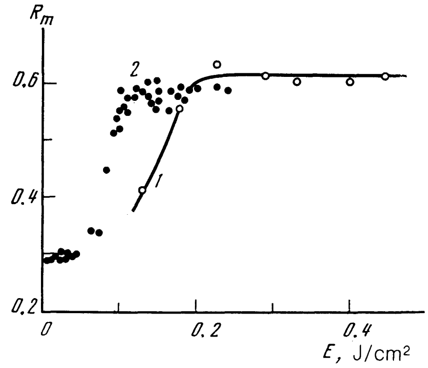

FIG. 1. Dependence of the maximum reflection coefficient of molten GaAs on the heating energy density: 1) $\tau_p = 12$ ns, $\lambda_p = 0.69$ μm, $\lambda = 0.63$ μm, angle of incidence of the probe beam $\theta = 45°$ (unpolarized radiation)[9]; 2) $\tau_p = 20$ ps, $\lambda_p = 0.53\,\mu$m, $\lambda = 1.06\,\mu$m, $\theta = 26°$ (p polarization); delay time $\tau = 3$ ns (Ref. 11).

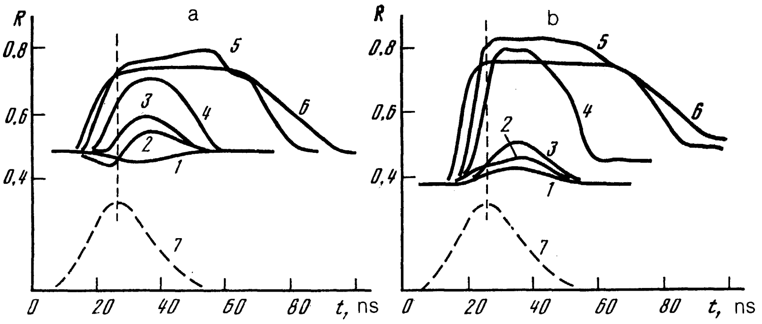

FIG. 2. Time dependence of the reflection coefficient ($\theta = 20°$, s polarization) of light probing the surface of GaSb: a) $\lambda = 0.63$ μm; b) $\lambda = 1.15$ μm. Heating energy density (mJ/cm^2): 1) 50; 2) 65; 3) 75; 4) 130; 5) 160; 6) 190; 7) profile of the heating pulse.

ticularly clearly at the probe wavelength $\lambda = 0.63$ μm, which is preceded by a reduction in the reflection coefficient associated with the heating of the crystal. The reason for the appearance of a reflection peak is partial melting of the surface layer of the semiconductor. A further increase in the energy density (curves 3 and 4) to $E \approx 150$ mJ/cm^2 increases the fraction of the molten material and, consequently, enhances the amplitude of the reflection peak. By analogy with GaAs we could expect that in the range $E > 150$ mJ/cm^2 the amplitude of the reflection peak would cease to rise and reach a level representing reflection by a homogeneous liquid phase. However, the experiments revealed a completely different picture, an increase in the energy density from $E = 160$ mJ/cm^2 (curves labeled 5) to $E = 190$ mJ/cm^2 (curves labeled 6) did not cause saturation of the amplitude of the reflection peak, but reduced it.

In order to show this effect more clearly, we used the $R(t)$ curves to plot the maximum reflection coefficient R_m vs the density E of the heating radiation energy. The dependences are plotted in Fig. 3 [which includes also the values of the reflection coefficient of the heated crystal recorded at the $\lambda = 0.63$ μm wavelength at the reflection minimum of the $R(t)$ curve]. It is clear from Fig. 3 that, in contrast to GaAs, Si, and Ge, in the case of GaSb there were two different levels or intensities of reflection from the molten semiconductor. In the range $150 < E \lesssim 180$ mJ/cm^2 the value of R_m reached 0.79 at $\lambda = 0.63$ μm and 0.82 at $\lambda = 1.15$ μm, whereas in the range $E \gtrsim 180$ mJ/cm^2, the coefficient R_m fell to 0.73 for 0.63 μm and 0.76 for 1.15 μm. The transition from one value of the reflection coefficient to the other was abrupt and it occurred when the energy density reached a critical value $E_c = 180$ mJ/cm^2.

Analogous behavior of the reflection coefficient of the probe beam was observed also in the case of nanosecond heating laser pulses interacting with crystalline InP. Figure 4 shows the dependence $R_m(E)$ obtained for InP at the probe wavelengths $\lambda = 1.15$ and 3.39 μm [as in the case of GaSb, $R_m(E)$ was plotted from the $R(T)$ curves]. Clearly, two different levels of reflection from the melt were observed also in the case of InP, but in contrast to GaSb the difference between these levels or intensities was considerably greater. In the energy density range $145 < E \lesssim 170$ mJ/cm^2 the reflection coefficient reached 0.77 at $\lambda = 1.15$ μm and 0.86 at $\lambda = 3.39$ μm. In the range $E \gtrsim 170$ mJ/cm^2 the value of R_m fell to 0.55–0.56 at $\lambda = 1.15$ μm and 0.67–0.73 at $\lambda = 3.39$ μm. As in the case of GaSb, the transition from one value of the reflection coefficient to the other was abrupt and occurred at a critical energy density $E_c = 170$ mJ/cm^2.

We thus found that, in contrast to GaAs, both GaSb and InP exhibited different levels of reflection of the probe beam by the liquid phase at different energy densities. The molten GaSb and InP exhibited metallic properties in each of the energy density intervals, but the reflection coefficient increased as a function of the probe wavelength.

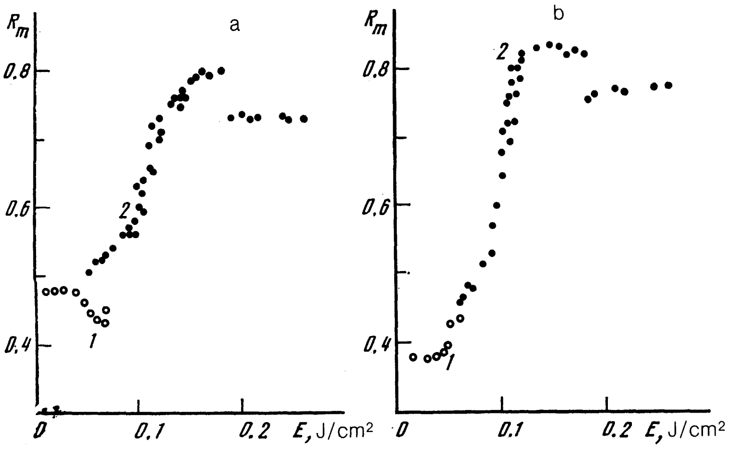

FIG. 3. Dependence of the maximum value of the reflection coefficient of light probing the surface of GaSb on the heating energy density ($\theta = 20°$, s polarization). Probe wavelength: a) 0.63 μm; b) 1.15 μm. 1) Reflection from the crystalline material; 2) reflection from the melt in the case of partial and complete melting of the surface layer.

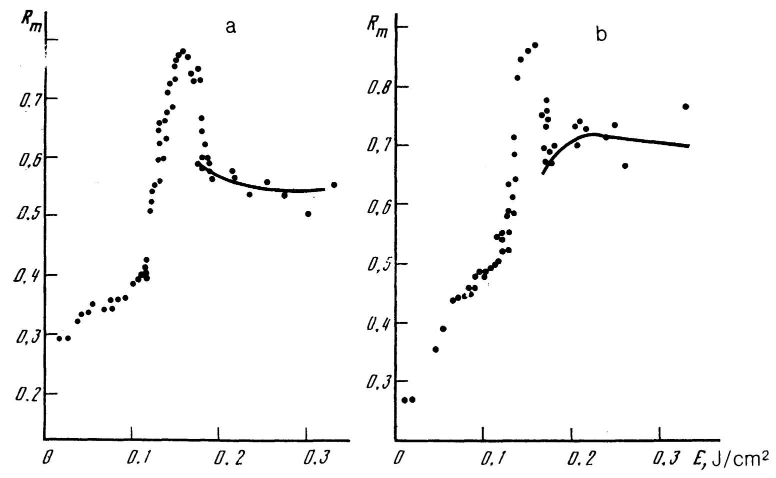

FIG. 4. Maximum value of the reflection coefficient of light probing the surface of InP as a function of the heating energy density ($\theta = 20°$, s polarization). Probing wavelength: a) 1.15 μm; b) 3.39 μm.

4. FAST FORMATION OF METASTABLE STATES OF THE LIQUID PHASE OF BINARY SEMICONDUCTORS

The behavior of the optical characteristics of molten GaSb and InP described in the preceding section shows that two different states of the liquid phase are formed in different energy density intervals. This effect had not been observed for GaAs (Fig. 1). Investigations of III-V semiconductors under steady state conditions (see Refs. 12 and 13 and the literature cited there), including studies of the phase diagrams of GaAs, GaSb, and InP (Ref. 14) show that the materials melted, forming a single equilibrium liquid phase. Therefore, the observation during the initial moments of two states of molten GaSb and InP was unexpected. Below we show that in the case of GaSb the available experimental data indicate directly that one of these states is metastable. In the case of InP the subsequent analysis of the experimental results is difficult because the information on the properties of its equilibrium liquid phase is incomplete. Therefore, in the present section we shall give additional information on the luminescence characteristics of InP crystallized from different states of the melt.

The liquid phase states can be identified by comparing the optical characteristics of the melt created by interaction with laser pulses and those obtained under steady-state conditions. In the case of GaSb the optical properties of the melt could be reconstructed from the data on the electrical conductivity of the liquid phase[12,13] (the reconstruction procedure is described in detail in Sec. 5).

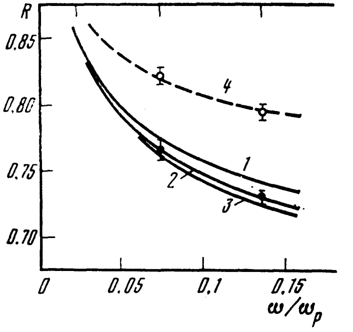

FIG. 5. Spectral dependence of the reflection coefficient of liquid GaSb ($\theta = 20°$, s polarization) calculated using the model of almost-free electrons at different temperatures of the melt: 1) $T_0 = 985$ K; 2) $T_0 + 200$ K; 3) $T_0 + 400$ K. Curve 4 is calculated assuming that $\omega_{pl} = 2.2 \times 10^{16}$ s^{-1} and $\tau = 3.5 \times 10^{-16}$ s. Experimental results: ●) stable liquid phase; ○) metastable liquid phase.

Figure 5 shows the spectral dependence of the reflection coefficient of liquid GaSb calculated using a model of almost-free electrons with parameters deduced on the basis of the data[12,13] on the electrical conductivity of the melt (the calculation method and the validity of the model are discussed in Sec. 5). Curve 1 represents liquid GaSb at its melting point $T_0 = 985$ K, whereas curves 2 and 3 represent the liquid phase overheated above T_0 by 200 and 400 K, respectively. This figure includes experimental results on the kinetics of the reflection coefficient of the melt recorded in the energy density ranges $150 < E \lesssim 180$ mJ/cm^2 and $E \gtrsim 180$ mJ/cm^2. The optical properties of molten GaSb formed in the range $E \gtrsim 180$ mJ/cm^2 are consistent with the properties of the liquid phase. On the other hand, the values of the reflection coefficient recorded in the range $150 < E \lesssim 180$ mJ/cm^2 were located well above the curves plotted for the equilibrium liquid phase. Therefore, the state of the melt created by laser pulses with energy densities $150 < E \lesssim 180$ mJ/cm^2 was unstable.

We now consider the main properties of the metastable state of molten GaSb. It is clear from Fig. 3 that this state is formed in a narrow energy density range lying directly above the melting threshold of the semiconductor. The transition to the stable state of the liquid phase, observed at the critical energy density $E_c = 180$ mJ/cm^2, is abrupt. It is possible that this may be due to an instability of the metastable phase at energy densities $E > E_c$. For $E \lesssim E_c$, decay of the metastable state with time and formation of a stable state of liquid GaSb are observed in some cases (curves labeled 5 in Fig. 2). However, it should be pointed out that directly after the decay of the metastable state the $R(t)$ curve exhibits a steep fall of the reflection coefficient due to arrival of the crystallization front on the semiconductor surface. The superposition of these two effects makes it difficult to interpret them reliably.

Unfortunately, the properties of liquid InP have hardly been investigated under steady-state conditions. Therefore, in the case of this material we cannot compare directly the optical characteristics of the melt created by nanosecond pulses and those of the equilibrium liquid phase. However, a comparison of Figs. 3 and 4 demonstrates that the $R_m(E)$ curves of GaSb and InP behave identically. Using this analogy, we assume that in the energy density range $145 < E \lesssim 170$ mJ/cm^2 a metastable state forms in liquid InP and that this state has a higher reflection coefficient, whereas in the range $E \gtrsim 170$ mJ/cm^2 the liquid phase of this semiconductor is stable (a liquid formed in the range $E \gtrsim 170$ mJ/cm^2 exists in a wide range of energy densities right up to the damage threshold of the InP surface, demonstrating once again that this phase is stable).

The reflection coefficients of liquid GaSb and InP are very different in the metastable and stable states. This is particularly striking in the case of InP when the difference between the reflection coefficients of the stable and metastable phases ΔR_m reaches ~ 0.2 at the wavelength of $\lambda = 0.63$ μm. Since molten GaSb and InP are metallic in each of these states, such a large difference between the optical characteristics of the metastable and stable states could be due to a considerable structural modification of the liquid phase (discussed in greater detail in Sec. 6).

Although no data are available on the properties of the equilibrium melt of InP, additional information can be obtained by studying the properties of the material crystallized from the melt. Investigations of the photoluminescence of laser-recrystallized semiconductor lasers showed that the properties of the material formed from the metastable and stable liquid phases were quite different and the behavior of InP (Ref. 15) differed considerably from the behavior of GaAs (Ref. 16), which did not exhibit a metastable melt.

Figure 6 shows the intensity of the edge photoluminescence I_{pl} of recrystallized GaAs and InP as a function of the energy density of the heating radiation (in this case the luminescence signal was normalized to the value of the intensity of the luminescence emitted by the unirradiated material and the energy density of the heating radiation was measured in arbitrary units). In the case of GaAs immediately after the melting threshold E_0 was exceeded, the ability to emit photoluminescence was seen to fall abruptly, indicating the formation of a large number of point defects as a result of faster crystallization of the melt.[16] In the case of InP such degradation occurred only at high energy densities (region labeled 3 in Fig. 6b). There was also a narrow energy interval (region 2) where this degradation of the radiative properties was absent. It is clear from Fig. 6b that immediately after the melting threshold of InP there was a region 1 where the radiative characteristics of this material became degraded by recrystallization. An increase in the laser pulse lengths and the wavelength of the heating radiation destroyed this region. Degradation in region 1 was due to suppression of epitaxial crystallization during rapid cooling of the melt.

The trace plotted in Fig. 6b was obtained for InP irradiated with heating pulses characterized by $\lambda_p = 0.69$ μm and $\tau_p = 50$ ns. The difference in the behavior of the photoluminescence signal in regions 2 and 3 was observed also after the semiconductor was irradiated with pulses characterized by $\lambda_p = 0.53$ μm and $\tau_p = 20$ ns, but in the latter case this effect was less striking because of the considerable overlap of regions 1 and 2. A comparison of the results of these luminescence measurements and the results of an optical investigation of the kinetics of melting of InP demonstrated that crystallization from the stable melt created a material with a large number of defects, whereas crystallization from the metastable melt did not produce defects in a number sufficient to cause significant degradation of its radiative (photoluminescence) properties. In the case of crystalline GaAs the metastable state of the liquid phase did not form as a result of laser irradiation so that the degradation of the radiative properties of this compound occurred immediately after the melting threshold was reached.

5. OPTICAL PROPERTIES OF LIQUID SEMICONDUCTORS IN STABLE AND METASTABLE STATES

The experimentally observed behavior of the reflection coefficient of liquid GaAs and InP (Secs. 3 and 4) was fairly complex. Interpretation of the results obtained required comparison of the optical properties of the melt formed during the first few moments with the properties of the equilibrium liquid phase. However, published information on the properties during steady-state melting is available only for Ge (Ref. 17) and Si (Ref. 18). There is no information at all on the optical constants of liquid III-V semiconductors.

The optical characteristics of an equilibrium melt can however be deduced from the electrical conductivity of the liquid phase.[12,13] In fact, it is shown in Refs. 17 and 18 that the optical properties of Ge and Si melted under steady-state conditions can be described satisfactorily by the model of almost-free electrons.[19] According to this model the spectral dependence of the permittivity is given by the expression

$$\varepsilon(\omega) = 1 - \frac{\omega_{\mathrm{pl}}^2 \tau_p^2}{1+\omega^2\tau^2}\left(1 - \frac{i}{\omega\tau}\right), \tag{1}$$

where ω is the frequency of light; τ is the electron momen-

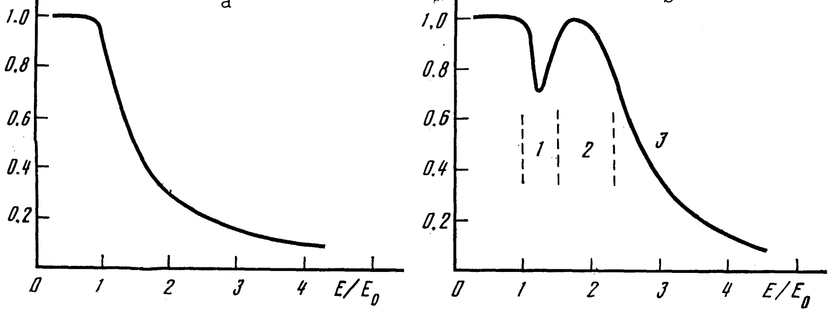

FIG. 6. Dependence of the intensity of the edge photoluminescence of GaAs (a) and InP (b), recrystallized by nanosecond pulses ($\tau_p = 0.69$ μm, $\tau_p = 50$ ns), on the heating energy density.

TABLE I. Plasma frequencies ω_{pl} and the momentum relaxation times τ of electrons in molten group IV semiconductors and III-V compounds (calculated using the model of almost-free electrons).

Semiconductor	From measured electrical conductivity				From optical measurements				Source
	T_0		T_0+200 K		stable state		metastable state		
	$\omega_{pl}\cdot10^{+16}$, s^{-1}	$\tau\cdot10^{-16}$, s	$\omega_{pl}\cdot10^{+16}$, s^{-1}	$\tau\cdot10^{-16}$, s	$\omega_{pl}\cdot10^{+16}$, s^{-1}	$\tau\cdot10^{-16}$, s	$\omega_{pl}\cdot10^{+16}$, s^{-1}	$\tau\cdot10^{-16}$, s	
Ge	2.41	2.72	2.39	2.45	2.50 2.66	2.47 2.16	–	–	[17] [20]
Si	2.63	1.97	2.59	1.95	2.56 3.22 2.39 2.50	2.17 1.61 2.43 2.12	–	–	[18] [20] [21] [22]
GaAs	2.46	1.50	2.42	1.54	...	...	–	–	–
InAs	2.18	1.62	2.14	1.48	...	...	...	...	–
AlSb	2.20	2.23	2.13	2.70	...	...	...	...	–
GaSb	2.20	2.48	2.18	2.36	2.18	2.37	2.20	3.50	our results**
InSb	2.05	2.56	2.03	2.43	...	...	...	...	–
InP	...	...	...	...	2.30	0.60	2.30	2.20	our results**

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*Comparison of the data deduced from the electrical conductivity and optical measurements is difficult because in the first series of experiments the temperature of the liquid phase was not normally determined. In the second series of experiments we quote the values at two temperatures showing how ω_{pl} and τ vary as T increases.

**These results were obtained from dynamic experiments; the error in the determination of the maximum value of the reflection coefficient in this case was 0.5%.

tum relaxation time; $\omega_{pl} = (4\pi n q^2/m)^{1/2}$ is the plasma frequency of the electron gas; q is the electron charge; m is the effective mass of an electron in the melt usually assumed to be equal to the mass of a free electron. The electron density n in liquid Ge and Si is close to four electrons per atom.[17,18]

In the case of irradiation with laser pulses the optical characteristics of liquid Ge are practically the same as those obtained under equilibrium conditions.[20] However, in the case of Si there is a discrepancy between the conclusions reached by different authors[20–22] about the relationship between the optical properties of the melts melted in a very short time and under steady-state conditions. A comparison of the analysis of these papers shows, however, that the optical properties of liquid Si are most probably the same under equilibrium and strongly nonequilibrium conditions.

According to the results of the Hall-effect measurements,[23,24] the electron density in molten InAs, GaAs, InSb, GaSb, and AlSb is close to four per atom. Knowing the density of these semiconductors in the liquid phase,[12,13] we can find the electron bulk density n and use it to calculate ω_p. The electron momentum relaxation time can be deduced[12,13] from the electrical conductivity of the liquid phase ($\tau = 4\pi\sigma/\omega_p^2$). Using the values of ω_p and τ found in this way, we can then apply Eq. (1) to calculate the permittivity of the melt corresponding to the light frequency ω.

This procedure for the determination of the optical constants was checked against a calculated reflection coefficient of unpolarized light of the $\lambda = 0.63\ \mu$m wavelength incident at an angle of $\theta = 45°$ to the surface of molten GaAs. The value $R = 0.64$ obtained in this way was in good agreement with the reflection coefficient $R_m = 0.61$ found experimentally in Ref. 9. Therefore, using the results of Refs. 17 and 18, we concluded that the above procedure for reconstructing the optical constants of liquid semiconductors of group IV elements and of III-V compounds from their electrical conductivity gives values in reasonable agreement with the experimental data. Parameters ω_p and τ found in this way for some III-V semiconductor compounds are presented in Table I.

We now return to the experimental data obtained for GaSb (Fig. 5) and discuss them in greater detail. A calculation of the spectral dependence of the reflection coefficient was made at the melting point T_0 and at temperatures exceeding T_0 by 200 and 400 K. Allowance was made for the influence of temperature on the density and electrical conductivity of molten GaSb (Refs. 12 and 13). It is clear from Fig. 5 that a study of the kinetics of the reflection coefficient of a stable melt yielded a curve[1)] similar to that corresponding to $T_0 + 200$ K. This was not surprising in view of the fact that a stable state of liquid GaSb did not form immediately at the melting threshold, but at a higher energy density $E_c = 180$ mJ/cm^2. The results obtained for a metastable state of the melt did not fit the curves calculated for the equilibrium liquid phase. However, they agreed well with the spectral dependence deduced from Eq. (1) by substituting the parameters $\omega_p = 2.20\times10^{16}$ s^{-1} (representing the value of ω_p for the equilibrium liquid phase) and $\tau = 3.50\times10^{-16}$ s.

As pointed out already, there is no information at all on the carrier density and electrical conductivity of the equilibrium liquid phase of InP. Therefore, we determined the optical constants of molten InP in the stable and metastable states using the experimental values of the reflection coefficient obtained at different wavelengths. The results obtained at the probe wavelengths of $\lambda = 0.63$, 1.15, and 3.39 μm are plotted in Fig. 7. The following procedure was adopted to test whether these results were in agreement with the almost-free-electron model. The electron density in the melt was assumed to be four electrons per atom. Using the crystal density $\rho = 5.05$ g/cm^3 (Ref. 25), we found that in the case

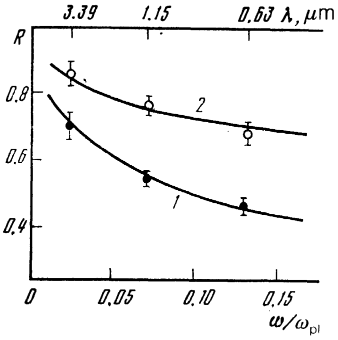

FIG. 7. Spectral dependence of the reflection coefficient of liquid InP ($\theta = 20°$, s polarization) calculated using the model of almost-free electrons with the following parameters: 1) $\omega_{\rm pl} = 2.3\times10^{16}$ s^{-1}, $\tau = 0.6\times10^{-16}$ s; 2) $\omega_{\rm pl} = 2.3\times10^{16}$ s^{-1}, $\tau = 2.2\times10^{-16}$ s. Experimental data: ●) stable liquid phase; ○) metastable liquid phase.

of liquid InP the density was $n \approx 1.67\times10^{23}$ cm^{-3} ($\omega_p = 2.3\times10^{16}$ s^{-1}). The relaxation time τ was found by ensuring the best agreement between the values of the reflection coefficient calculated with the aid of Eq. (1) and the experimental data (the values of τ obtained in this way are listed in Table I). The results of calculations of the spectral dependence of the reflection coefficient of liquid InP were plotted in Fig. 7. The optical properties of liquid InP were thus found to be described reasonably well by the model of almost-free electrons. Therefore, in spite of the extreme simplicity of the model, it could be used to describe the properties of liquid Ge, Si, and GaAs and also of the two liquid phases of GaSb and InP. In the case of InP, for which information on the electrical conductivity of the equilibrium liquid phase was missing, we were able to compare the experimental data with the one-parameter spectral dependence of the permittivity (this one free parameter was the relaxation time τ, the value of ω_p was determined independently). It was found that the values of τ for the stable and metastable states of molten InP differed approximately by a factor of 4.

It should be pointed out that among all the III-V semiconductors the compound InP is distinguished by an anomalously short electron momentum relaxation time in the stable liquid state (Table I). For this reason the absorption length for the $\lambda = 1.15$ and 3.39 μm probe beams is fairly large and comparable with the depth of the layer melted by laser pulses. We could therefore expect that the dependence $R_m(E)$ could be influenced by interference effects in the region of appearance of the stable state of the liquid phase.

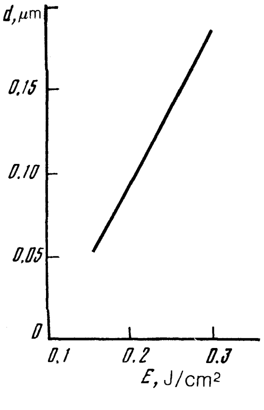

FIG. 8. Dependence of the thickness of the molten InP layer on the heating energy density, reconstructed from the results of measurements of the reflection of a probe beam during irradiation.

In fact, at the wavelength $\lambda = 1.15$ μm the function $R_m(E)$ obtained for $E \gtrsim E_c$ was of the smoothly falling type, whereas at the wavelength $\lambda = 3.39$ μm the value of R_m first increased with increasing energy density, then fell, and reached saturation (Fig. 4). This effect could be described using the values of ω_p and τ found above and calculating the dependence of the reflection coefficient of the probe beam ($\lambda = 1.15$ and 3.39 μm) on the thickness of the molten layer d. A comparison of the calculations with the experimental results (Fig. 4) made it possible to reconstruct the dependence $d(E)$; the results of this procedure are plotted in Fig. 8. The values of the reflection coefficient corresponding to this dependence are represented by continuous curves in Fig. 4.

In the case of the metastable state of molten InP the absorption length of the probe beam was considerably less than the depth of the molten layer at all the wavelengths used in our investigation. Therefore, the interference effects were not observed.

6. POSSIBLE STRUCTURE OF STABLE AND METASTABLE STATES OF LIQUID III-V SEMICONDUCTORS

The considerable difference between the optical characteristics of the two states of liquid InP and GaSb formed as a result of interaction with nanosecond laser pulses and the influence of the state of the melt on the properties of the material crystallized in the case of InP demonstrated that the metastable and stable liquid phases were structurally different.

In the case of binary compounds the structure of the liquid phase can be described by the coordination number (representing the number of the nearest neighbors of a given ion[2)]) and by the degree of correlation in the relative positions of ions of different kinds. A quantitative measure of the correlation is the difference between the partial structure factors of the liquid for identical ions and for ions of different kinds.[26] We shall consider the likely influence of each of these factors on the optical properties of the liquid phase and on the properties of the material which crystallizes from it.

We start with the optical characteristics of molten semiconductors. Under equilibrium conditions the coordination number of liquid Si, Ge, and III-V compounds is 6–8 near the melting point and increases to 8–10 when the liquid phase is heated by several hundred kelvin.[13,27] However, the associated change in the optical properties of the melt (estimated, for example, from the electrical conductivity data such as those given in Refs. 12 and 13) is small compared with the change observed in our case in the transition from the metastable to the stable state. It should be noted that the reduction in the electron density in molten GaSb and InP cannot account either for the experimentally observed reduction in the reflection coefficient. In fact, estimates obtained using the model of almost-free electrons indicate that the carrier density has to be reduced by at least two orders of magnitude in order to alter the reflection coefficient by 10–15%. Such a change in the carrier density is possible only if the nature of the chemical binding in the liquid phase is modified. The experimental data are in conflict with this hypothesis: they demonstrate that strong metallic properties are exhibited by each of the liquid states of GaSb and InP.

On the other hand, it is known[19] that the scattering of electrons by the ionic potential in liquid metallic alloys is very sensitive to a change in the microscopic structure of the liquid in the first coordination sphere. The reason for this is the strong effect of the interference between electron waves scattered by the nearest neighbors on the total scattering probability. Therefore, the appearance of a correlation in the relative positions of ions of different kinds can significantly alter the conditions for the scattering of electrons in the melt, which in the final analysis is manifested by a major change in the relaxation time τ.

Therefore, if we assume that the metastable state of liquid GaSb and InP is characterized by a correlated distribution of ions of different kinds, whereas the stable state is characterized by a random distribution, we find we can explain the change in the reflection coefficient in the transition from one state to the other.

The nature of the possible correlation is undoubtedly important. In the case of binary semiconductors we can distinguish two cases: in one case the ions of the element A are surrounded mainly by the ions of the element B, whereas in the other case we have the converse when around the ion A (or B) there are mainly identical ions A (or B). The latter case is typical of eutectic alloys in which the interaction of ions in the liquid phase is repulsive. It is also known that the components of $A^{III}B^{V}$ compounds tend to form associates of the AB type in the liquid phase.[13] This means that molten GaSb and InP may exhibit correlations of the first type.

We shall now turn to the problem of the influence of the structure of the liquid phase on the properties of the material crystallizing from it. We shall begin by noting that a change in the coordination number in the liquid should not significantly affect the number of defects in the crystal, because the changes occurring in the semiconductor during crystallization (such as the formation of the tetrahedral environment and a change in the type of binding from metallic to covalent) are much stronger than the changes in the liquid phase itself, associated with a reduction on increase in the coordination number. On the other hand, the results of the luminescence measurements obtained for InP and GaAs (see Sec. 4) can easily be explained by the above hypothesis on the structure of the two states of the liquid phase of binary semiconductors.

The important point is that crystallization of a semiconductor which is melted in $\sim 10^{-8}$ s can be characterized by an additional defect-formation channel. In fact, in the case of nanosecond laser pulses the motion of the crystallization front occurs at velocities of the order of several meters per second. Under these conditions an additional defect-formation channel appears in the crystal, due to the possibility of capturing local fluctuations of the composition of the molten semiconductor by the phase boundary. We now take a brief detour from our topic.

When ions of different kinds are distributed at random in a melt, fluctuations should give rise to regions with a modified (nonstoichiometric) composition. If we assume that fluctuations are thermodynamic, we can estimate the mean-square deviation n in a certain selected volume V: $\xi^2 \propto n/V$. Fluctuations of the composition in the melt are dispersed by diffusion in a time $\tau_D \propto R^2/D$, where $R = V^{1/3}$ is the characteristic size of a fluctuation and D is the self-diffusion coefficient of a given component in the liquid phase. The crystallization front moving at a velocity v crosses the selected volume in a time $\tau_v R/v$. If $\tau_v < \tau_D$, then fluctuations of the composition are not dispersed in the available time and are "frozen in" in the solid phase. This requires velocities $v > D(\xi^2/n)^{1/3}$. Substituting typical values $D \sim 10^{-4}$ cm^2/s and $n \approx 5\times 10^{22}$ cm^{-3}, we find that at crystallization front velocities in excess of 0.2–1 m/s the solid phase contains trapped microinclusions with deviations from stoichiometry amounting to $\xi \sim 10^{19}$–10^{20} cm^{-3}. Characteristic sizes of the microinclusions are on the order of $(n/\xi^2)^{1/3}$, i.e., 100–500 Å. This level of deviation from stoichiometry in III-V semiconductors must be manifested in the experimentally observed state of the defect structure of the crystallized material and, in particular, it may be responsible for degradation of the radiative properties (photoluminescence).

Going back now to our case we note that the above mechanism can be effective in the case of a random distribution of ions of different type in the liquid phase and can be suppressed by the presence of correlations of the above type in the melt. Therefore, a semiconductor crystallizing from the melt with a random distribution of ions of a different type (stable liquid phase) should contain more defects. On the other hand, crystallization from the metastable liquid phase does not increase significantly the concentration of defects in the irradiated material.

It follows that the above hypothesis about the structure of the metastable and stable states of liquid GaSb and InP is in agreement with the results of the optical investigations of the kinetics of melting and with the results of measurements of the luminescence emitted by recrystallized InP and GaAs.

[1)] It is necessary to point out that these data cannot be used to determine reliably the temperature of the melt at which a stable state is formed, especially as at temperatures $T > T_0 + 200$ K the temperature dependence of the reflection coefficient becomes weaker (Fig. 5).

[2)] Melting of group IV semiconductors and III-V compounds ionizes practically completely the valence electrons.[12,13]

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Translated by A. Tybulewicz