Formation of a metastable state of a liquid phase in the application of nanosecond laser pulses to GaSb

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The formation of metastable and stable states of liquid GaSb has been observed during the application of nanosecond laser pulses. The optical properties of the stable state correspond to those of the equilibrium GaSb melt.

This letter reports the formation, for times $\sim 10^{-8}$ s, of two states of liquid gallium antimonide (GaSb): a metastable state near the melting point of the semiconductor and a stable state at higher temperatures. The melting of the GaSb was studied by detecting the changes in the reflection coefficient for light which probed the surface of the semiconductor during the application of the laser pulses.

Group IV semiconductors and III–V compounds are known to be metals in the liquid state. The sharp increase in the reflection coefficient for probing light makes it possible to detect the time in which these substances melt in the course of the time evolution. When the applied pulse has an energy density sufficient to completely melt a surface layer of Si, Ge, or GaAs, the reflection coefficient reaches a steady-state value.[1,2] It has been established experimentally that for Si and Ge this value corresponds to the level of reflection from the melt which forms under equilibrium conditions.[1,3,4]

Crystalline GaAs(111) was illuminated with pulses from a Nd:YAG laser ($\tau = 25$ ns, $\lambda = 532$ nm) with a Gaussian intensity profile in the beam cross section. The surface of the semiconductor was probed with the beam from a cw He–Ne laser ($\lambda = 1.15$ μm and 0.63 μm). The ratio of the diameters of the probed region and the

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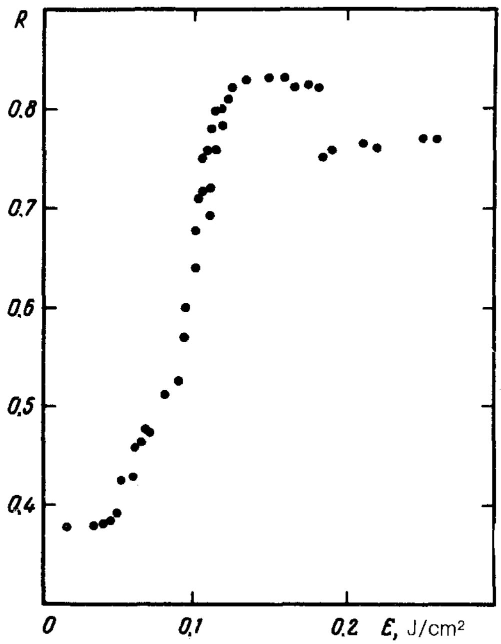

FIG. 1. Maximum reflection coefficient of gallium antimonide versus the energy density of the applied pulse. The probing wavelength is $\lambda = 1.15$ μm.

illuminated region was $\sim$1:20. The time resolution of the measurement apparatus was $\sim$1 ns.

In the experiments we detected the time evolution of the reflection coefficient for the probing light, $R(t)$, at various energy densities of the laser pulse. Figure 1 shows the maximum reflection coefficient as a function of the energy density E for $\lambda = 1.15$ μm. During probing with $\lambda = 0.63$ μm, the $R(E)$ dependence is similar. The increase in the reflection coefficient in the interval $E = 0.065$–0.15 J/cm^2 ($E = 0.065$ J/cm^2 is the threshold for the melting of GaSb) stems from an increase in the relative size of the liquid phase in the partially melted surface layer of the semiconductor with an increase in the applied energy density. At $E > 0.15$ J/cm^2, at which the surface layer melts completely, we detect two distinct levels of reflection from the GaSb melt. In the interval $E = 0.15$–0.19 J/cm^2, the reflection coefficient reaches a value of 0.83. A further increase in the energy density leads to an abrupt change in the reflection coefficient, to 0.76.

In the liquid state, GaSb thus behaves in a manner different from that of Si, Ge, or GaAs, for which only a single state of the liquid phase is detected over times $\sim 10^{-8}$ s. A behavior of the optical properties of the melt similar to that described above has been observed during the application of nanosecond laser pulses to InP (Ref. 5; more on this below).

To determine the reasons for the appearance of two levels of reflection for the liquid GaSb, let us compare the optical properties of a melt of this semiconductor under time-varying and equilibrium conditions. We have no direct data on the optical

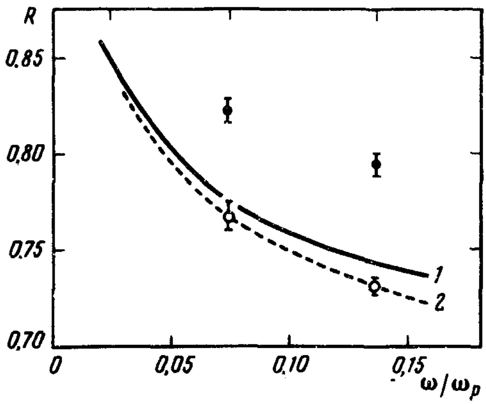

FIG. 2. Spectra of the reflection coefficient of liquid gallium antimonide at (line 1) a temperature T equal to the melting point T_m and (line 2) at $T = T_m + 200$ K. The points are experimental values of the reflection coefficient. ●—$E = 0.15$–0.19 J/cm^2; ○—$E = 0.19$ J/cm^2.

characteristics of an equilibrium melt of GaSb, but we can reconstruct them from results found in a study of the electrical conductivity of GaSb in the liquid state.[6]

The electrical and optical properties of molten Si and Ge can, as we know, be described well by the Drude model.[3,4] Regel' and Glazov[6] report that the density of electrons in liquid Si, Ge, and III–V compounds is approximately four per atom. Knowing the electrical conductivity and the density of the liquid semiconductor,[6] we can then determine the corresponding values of the plasma frequency ω_p and the momentum relaxation time τ. We can then calculate the dielectric constant and the reflection coefficient of the surface of the melt for the probing light. For liquid gallium arsenide, this procedure yields values for the reflection coefficient which agree within 2% with the value found experimentally by Lowndes and Wood.[2] In the case of gallium antimonide, the values found for ω_p and τ by this method are $\omega_p = 2.20 \times 10^{16}$ s^{-1} and $\tau = 2.48 \times 10^{-16}$ s at the melting point (T_m) and $\omega_p = 2.18 \times 10^{16}$ s^{-1} and $\tau = 2.39 \times 10^{-16}$ at a temperature 200 K above T_m.

Figure 2 shows the calculated spectra of the reflection coefficient of liquid GaSb at $T = T_m$ (line 1) and $T = T_m + 200$ K (line 2). Also shown here are experimental values of R found during the application of energy densities $E = 0.15$–0.19 J/cm^2 and $E > 0.19$ J/cm^2 to GaSb. We see that the values of R for $E > 0.19$ J/cm^2 lie close to lines 1 and 2. The values of the reflection coefficient for $E = 0.15$–0.19 J/cm^2, on the other hand, lie well above these curves.

The existence of two reflection levels is not a consequence of interference effects, and it cannot be explained in terms of a decrease in the reflection with increasing temperature of the liquid phase. In each of the energy intervals listed above, liquid GaSb exhibits metallic properties: The reflection increases with increasing wavelength of the probing light. It can be shown that the absorption length for the probing light in a GaSb melt which corresponds to the observed values of the reflection coefficient is substantially smaller than the wavelength. In this case the amplitudes of the interference peaks are negligible. With regard to the temperature dependence of the reflection coefficient, we note that R should fall off smoothly with increasing temperature. Experimentally, on the other hand, we see an abrupt decrease in R at an applied energy

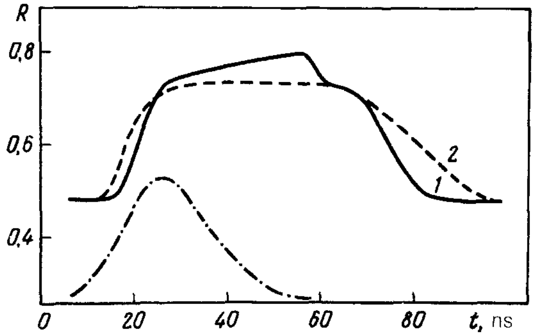

FIG. 3. Time evolution of the reflection coefficient during the application of nanosecond laser pulses. 1—the energy density of the pulse is 0.16 J/cm^2; 2—0.19 J/cm^2. The probing wavelength is $\lambda = 0.63$ μm.

density $E = 0.19$ J/cm^2. In each of the energy intervals $E = 0.15$–0.19 J/cm^2 and $E > 0.19$ J/cm^2 the reflection level remains constant.

We believe that the existence of two distinct reflection levels in different intervals of the energy density is a consequence of the existence of two states of liquid GaSb for times $\sim 10^{-8}$ s. The state observed at $E > 0.19$ J/cm^2 has optical properties which correspond to a GaSb melt produced under equilibrium conditions. The substantial difference between the optical properties of a GaSb melt at $E = 0.15$–0.19 J/cm^2 and the equilibrium optical properties suggests that the state of the liquid phase in this interval of energy densities is metastable. To test this suggestion, we carried out a further study of the time evolution of the reflection in the energy-density interval $E = 0.15$–0.19 J/cm^2. The experiments show that near $E \approx 0.16$ J/cm^2 the time evolution reveals, first, the formation of a molten state with an elevated reflection coefficient and then a transition to a state with a lower value of R (line 1 in Fig. 3). This $R(t)$ behavior is found at both probing wavelengths, $\lambda = 0.63$ and 1.15 μm. The observed time decay of the state of the liquid GaSb with the intensified reflection level is direct evidence that this state is metastable.

As we mentioned earlier, two states of a melt with different reflection levels have been detected[5] during the application of nanosecond pulses to InP. However, the absence of data on the properties of an equilibrium InP melt has made it impossible to compare the optical properties of liquid InP under equilibrium conditions and over times $\sim 10^{-8}$ s.

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