Heterophase with inhomogeneous distribution of free carriers in GeTe

B. Yu. Vengalis and A. A. Kastal'skiĭ

A. F. Ioffe Physicotechnical Institute, USSR Academy of Sciences
(Submitted June 23, 1977)
Pis'ma Zh. Eksp. Teor. Fiz. **26**, No. 5, 355–358 (5 September 1977)

A fine structure has been observed in the spectra of the plasma reflection of light from single-crystal GeTe. It is attributed to the onset of a phase transition of the "gas-liquid" type in the free hole-acceptor subsystem, with formation of a spatial inhomogeneity in the distribution of the free carriers.

PACS numbers: 78.20.Dj, 81.40.Ef, 81.40.Tv

We report here the results of an investigation of the spectra of the plasma reflection $R(\lambda)$ in GeTe and their variation in the course of annealing of the samples at temperatures $T_0 = 200$—$460°C$. The observed singlarities, in our opinion, lead to the conclusion that spatial inhomogeneity appears in the distribution of free holes with fixed concentrations.

We used for the investigation single-crystal samples with Te percentage content within the region of homogeneity of the GeTe phase (50.1—52 at.%). The samples were obtained by the Bridgman method. For the homogenization we used annealing for 100 hr at $T = 550°C$. The free-hole concentration, determined from Hall measurements at liquid-nitrogen temperature, varied in the

 0021-3640/77/2605-0236$00.60

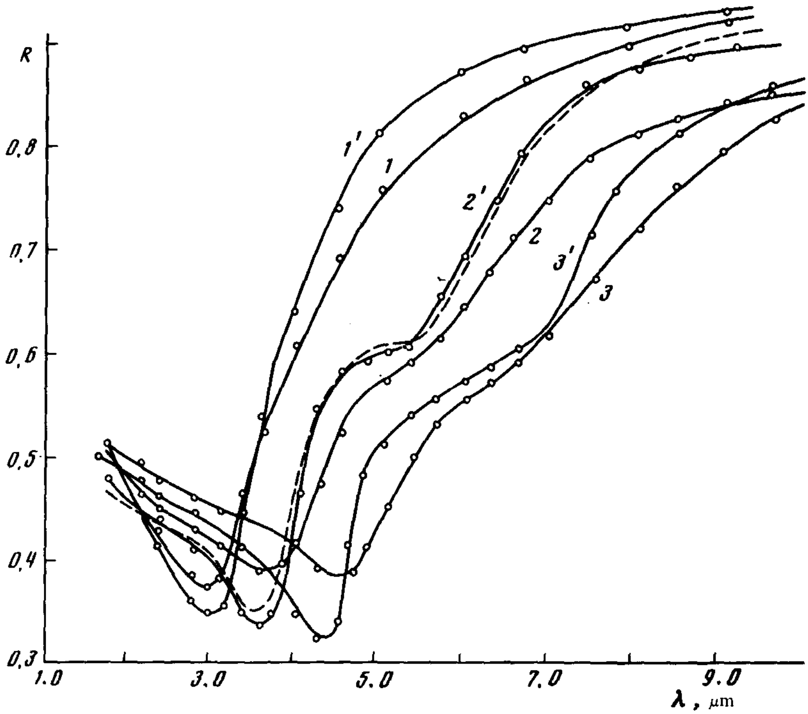

FIG. 1. Reflection spectra $R(\lambda)$ plotted after annealing for 100 hours at the following temperatures, °C : 1, 1'—550°; 2, 2'—300; 3, 3'—360. Measurement temperatures, K: 1, 2, 3—300°; 1', 2', 3'—80°. Dashed curves—theoretical $R(\lambda)$ obtained by summing three spectra with plasma minima 2.25, 3.5, and 5.5 μm and relative fractions 0.05, 0.55, and 0.4, respectively. $\omega_p\tau = 5.0\epsilon_{opt} = 37.5$ for all the spectra.

range P_{0H} (78 K) = (9.0—20) × 10^{20} cm^{-3}. The reflection spectra, obtained each time by using a freshly polished and etched surface, had the usual plasma minimum $\lambda_{min} = \lambda_0$, which shifted with increasing hole density from 3.7 to 2.3 μm respectively (Fig. 1, curve 1).

Subsequent annealing of the original samples at temperatures T_0 = 200—460°C, followed by quenching, led to substantial changes in the spectra. We note primarily the appearance of a fine structure (Fig. 1, curves 2 and 3) and a general tendency of λ_{min} to shift towards longer wavelengths. In the low-temperature measurements, the structure is more pronounced (curves 1'—3') and the minima shift towards shorter wavelengths.

Analysis has shown that the observed spectral dependence is the result of a superposition of two or three independent spectra with different plasma frequency ω_p and different relative fractions. The indicated spectral singularities were most pronounced in samples with smaller Te contents (50.1—50.8 at.%) and smaller concentration of free holes P_{0H}(78°K) = (9.0 to 12.0) × 10^{20} cm^{-3}. Three characteristic annealing-temperature regions can be discerned for these samples:

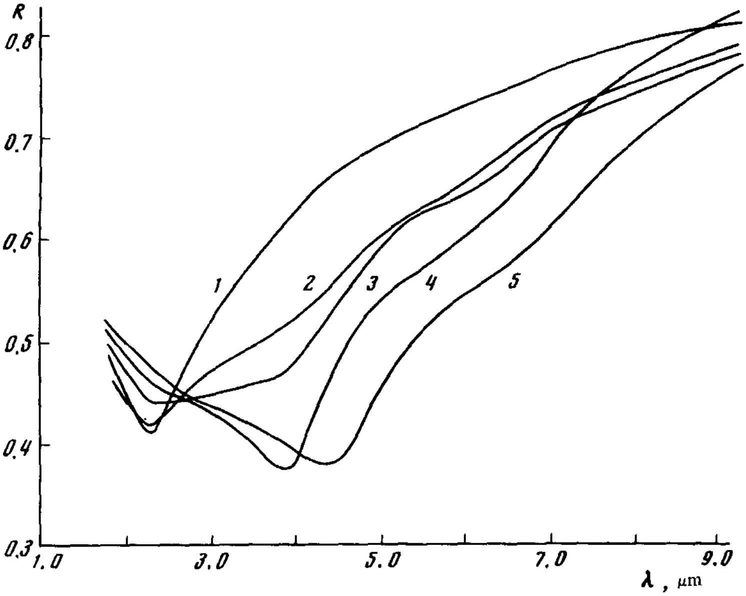

FIG. 2. Variation of reflection spectra with degree of etching of the sample. Depth of removed layer (μm): 1—0; 2—0.2; 3—0.5; 4—1; 5—100. The initial spectrum 1 was obtained by annealing the sample with $\lambda_{min}=4.5$ μm (Fig. 1, curve 3) for 1 hour at $T_0=270$ °C.

1) $T_0=200$—320°C. Annealing for ~100 hr at these temperatures produced in the spectra singularities with three fixed wavelengths: $\lambda_1-2.25$ μm, $\lambda_2=3.75$ μm, and $\lambda_3=5.5$ μm (Fig. 1, curve 2). The hole density p_H (78 K) obtained from Hall measurements was close to 8.5×10^{20} cm^{-3}.

2) $T_0=320$—400°C (near the temperature of the ferroelectric phase transition of GeTe). The spectra of samples annealed at these temperatures for ~100 hr had only two singularities, λ_2 and λ_3, shifted towards longer wavelengths, with maximum values $\lambda_2=4.5$ μm and $\lambda_3=7.0$ μm (Fig. 1, curve 3). In this case the Hall density P_H (78 K) was 5.0×10^{20} cm^{-3}.

3) $T_0=400$—460 °C. The spectra had minima with $\lambda_2=3.75$ μm and $\lambda_3=5.5$ μm, and were outwardly similar to curve 2 of Fig. 1.

Heating the samples above 480°C led to vanishing of the indicated structure, and the spectra resumed the initial form with a single plasma minimum.

In samples with high initial hole density P_{0H} (78 K) = (12—20) × 10^{20} cm^{-3} (as obtained by Hall measurements), only insignificant changes took place in the spectra, mainly as a result of the appearance of singularities at $\lambda_1=2.25$ μm ($T_0=200$—320°C).

It must be emphasized that, in all the considered temperature ranges, the spectral position of the indicated minima is independent of both the duration and temperature of the annealing within the selected range.

Somewhat different regularities are obtained in the surface layer of thickness 1 μm when the spectra of $R(\lambda)$ are obtained with a surface that is not finished prior to each measurement. The previously indicated singularities λ_1, λ_2, and λ_3 appeared in the course of annealing at $T_0 = 200-320°C$. The final spectrum had a clearly pronounced minimum at $\lambda_1 = 2.25$ μm (Fig. 2, curve 1). Gradual removing of layers by etching led to a reversed evolution of spectra (Fig. 2, curves 2, 3, and 4).

We thus arrive at the conclusion that annealing the sample leads to the appearance of an additional structure on the $R(\lambda)$ spectra. This is equivalent to the appearance of regions with different fixed hole densities. The appearance of the plasma minima $\lambda_2 = 3.75$ μm and $\lambda_3 = 5.5$ μm, corresponding to the concentrations $P_2 \approx 9.0 \times 10^{20}$ cm^{-3} and $P_3 \approx 1.0 \times 10^{20}$ cm^{-3}, can be attributed, in our opinion, to a phase transition of the gas—liquid type in the subsystem made up of the free holes and acceptors (doubly charged vacancies of Ge). Similar phenomena were observed earlier in Si(Li).[1] The state with uniform distribution of the acceptors and the associated free holes is unstable with respect to the formation of regions with increased ("liquid") and decreased ("gas") concentrations. The reason for such a phase transition lies in the existence, in the indicated subsystem, of an additional energy minimum corresponding to the "liquid" phase. It appears that the temperature at which spectra lose the structure in question (~480 °C) is in fact the critical temperature of this phase transition.

The shifts of λ_2 and λ_3 towards longer wavelengths when the samples are annealed near the ferroelectric phase-transition temperature can be due to a "softening" of the lattice and a decrease of the deformation contribution to the total energy balance.[1)]

As to the minimum at $\lambda_1 = 2.25$ μm, its cause is still unclear.

The strong temperature dependence of the time required to produce the observed singularities is connected with an activation mechanism of migration (or generation) of the Ge vacancies, which is needed for spatial inhomogeneity to set in.

[1)]In accordance with[2], the rhombohedral angle in the ferroelectric phase of GeTe depends on the hole density. Therefore the coexistence of regions with different densities will give rise to a spatially-inhomogeneous deformation.

[1]A. A. Kastalskiĭ and S. B. Maltsev, Solid State Commun. 17, 107 (1975).
[2]G. S. Bushmarina, T. B. Zhukova, E. Ya. Lev, and L. M. Sysoeva, Fiz. Tekh. Poluprovodn. 11, 467 (1977) [Sov. Phys. Semicond. 11, 270 (1977)].