Observation of surfons in surface photoluminescence spectra (GaAs)

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Two zero-phonon bands of low-temperature near-edge surface photoluminescence were observed in GaAs (1.515 and 1.477 eV), as well as two phonon replicas of the latter. The energy and average number of emitted surface phonons (surfons), the Franck–Condon shift, and other characteristics of the electron-phonon interaction on the surface were determined.

1. The study of surface phonons (surfons) of various types has been attracting great interest of late. In particular, surface polaritons were theoretically predicted for crystals with strong polar-bond fractions. [1-3] Owing to the presence of long-range Coulomb forces that alter the vibrational spectrum of the surface sections of the lattice, the contribution of the surface oscillators in these crystals turns out to be appreciable. To determine the surfon energy in an ordinary single crystal one uses either the method of total internal reflection[4] or the Raman scattering method. [5,6]

Observation of radiative recombination on the surfaces of superconductors[7] offers new possibilities of investigating surfons by a method that uses laser-induced photoluminescence (LPL). We report here the first data on the appearance of surfons in LPL spectra.

2. The phonon replica lines were best resolved in the impurity photoluminescence bands of n-GaAs samples doped with tellurium or silicon ($n_0 = 10^{18}$ cm^{-3}) and coated with a Si_3N_4 or Ge_3N_4 film (deposited by a gas-transport method at 550–600 °C), as well as in epitaxial films of high purity ($n_0 = 10^{14}$ cm^{-3}).

The samples were etched and exposed to a low dosage ($D = 10^7$ rad) of γ rays. The luminescence was excited with a stationary helium-neon laser ($\lambda = 0.6328$ μ) with a maximum intensity 10^{18} quanta/cm^2 sec. The use of such laser sources makes it possible (i) to excite a very thin ($\leqslant 0.05$ μ) layer of GaAs, making the contributions of the volume and surface luminescences to the LPL

commensurate, (ii) to detect the luminescence even at a low density of emitting centers, and (iii) to perform the measurements in the absence of band bending on the illuminated surface, i.e., when the conditions on the surface are highly homogenized.

The LPL signal was recorded from the side of the illuminated sample surface and was analyzed with IKS-12 and ISP-51 spectrometers and an FÉU-62 photomultiplier. The measurements were made in the range of T from 4.2 to 50 °K.

3. Figure 1 shows the LPL spectrum obtained for doped GaAs samples at 4.2 °K. Prior to the coating with the Si_3N_4 film, two broad emission bands are observed at 1.502 and 1.36 eV, and their spectral characteristics are independent of the surface treatment, thus indicating that these bands, which have been thoroughly studied in the literature, are of volume origin.

Coating with an Si_3N_4 film led to a small change in the intensity of the 1.36 eV band and to an extinction of the 1.502 eV band (a similar result was obtained for the SiO_2—GaAs system in[8]). New bands appeared simultaneously in the energy region 1.4—1.52 eV, namely $I_1(1.515$ eV), $I_2(1.477$ eV), $I_3(1.444$ eV), and $I_4(1.411$ eV). Etching off the Si_3N_4 film did not affect the form of the spectrum, but removal (by etching) of even a very thin (< 100 Å) layer of GaAs caused all four bands to be extinguished. This indicates that they are of surface origin. Band I_1, which we attribute to surface excitons, is discussed in a separate paper. We shall deal below with the behavior of bands I_2, I_3, and I_4. These bands are apparently due to radiative recombination via a shallow surface center of structure origin (of the "surface vacancy $+N$" complex type). This is indicated by the increase of these bands following low-dosage γ irradiation, that leads to the production of mainly surface defects.

Figure 2 shows the temperature dependence of the intensity of bands I_2 (curve 1), I_3 (curve 2), and I_1 (curve 3), and also of the ratio I_3/I_2 (curve 4). With increasing T, the attenuation of peaks I_2 and I_3 proceeded at almost the same rate, while the temperature dependence of peak I_1 differed appreciably from that of I_2 and I_3, a strong temperature extinction of peak I_1 taking place while peaks I_2 and I_3 remained unchanged.

For comparison, we measured the LPL spectrum of an epitaxial GaAs film. Two bands of volume origin were observed at 1.488 and 1.452 eV. The parameters of the bands (energy position and intensity) did not
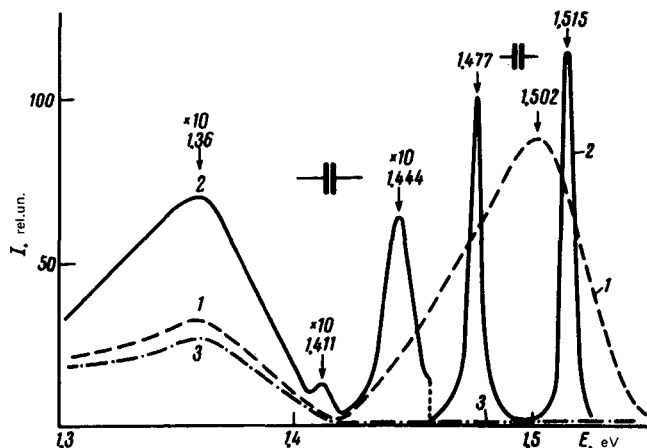

FIG. 1. LPL spectra of doped GaAs samples at 4.2 °K: 1 – prior to depositing the Si_3N_4 film, 2 – after the coating, 3 – after etching off the Si_3N_4 film and a layer of GaAs ($\leqslant 100$ Å).
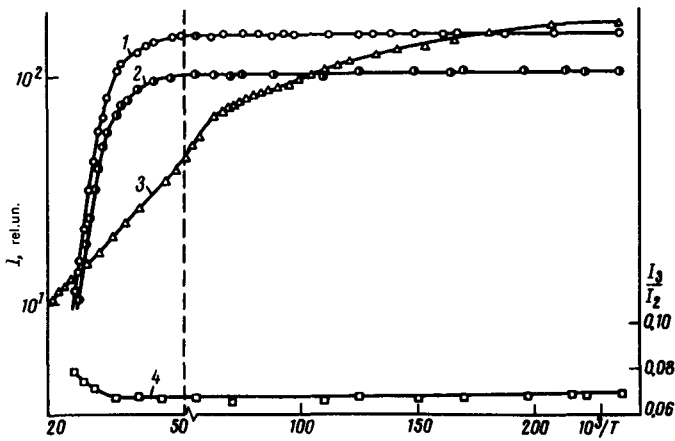
FIG. 2. Temperature dependence of the surface-luminescence band intensity: 1) I_2 (1.477 eV), 2) $I_3 \cdot 10$ (1.444 eV); 3) I_1 (1.515 eV), 4) I_3/I_2.

change when different surface treatments were used. The obtained intensity ratios of these bands ($\overline{N}_v = 0.044$) and the distances between them (36 ± 0.5 meV), corresponding to the energy of a volume LO phonon, coincide with the published data.

4. The waveform of the surface band I_2 turns out to be close to a Lorentzian with a half-width 6 meV. In this case the electron-phonon interaction is usually manifest in the form of a phonon replica of the zero-phonon band.[9,10] Actually, the peaks I_2, I_3, and I_4 are equidistant in energy, the ratio I_3/I_2 is independent of T at $T \leqslant 20\,^\circ$K and depends weakly on T at $20^\circ < T \leqslant 40\,^\circ$K, and the peak amplitudes decrease approximately according to the Poisson law[9,10]:

$$W_n = W_0 (\overline{N}^n / n!). \qquad (1)$$

Here W_0 is the photon emission probability for the zero-phonon band, W_n is the probability of emission of one photon and n phonons, and $\overline{N}$ is the average number of emitted phonons and determines the strength of the electron-phonon interaction[10]:

$$\overline{N} = \frac{e^2}{a} \; \frac{1}{\sqrt{2\pi}} \; \frac{1}{\hbar\omega_0} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right), \qquad (2)$$

where ϵ_∞ and ϵ_0 are the high- and low-frequency dielec-

tric constants of the material, a is a Bohr orbital radius, and $\hbar\omega_0$ is the phonon energy.

If account is taken of the change in the parameters of formula (2) on the surface in comparison with the volume, then the value $\overline{N}_s \sim 0.05-0.06$ estimated from the last formula is close to the experimentally determined value (0.063) of the ratio I_3/I_2. The aggregate of the indicated data proves the existence of a phonon replica of the 1.477-eV surface-emission band and allows us to determine from the distance between the bands I_2, I_3, and I_4 the surface-phonon energy, which equals 33 ± 0.5 meV. This value agrees qualitatively with the predictions of the theory,[1-3] according to which the energy of the surface polaritons should exceed the energy of the exchange TO phonon (32 meV) and be less than the energy of the LO phonon (36 meV). It is also typical that $\overline{N}_s$ is 50% larger than the exchange value of $\overline{N}_v$ for an equal-energy center, while the Franck-Condon shift, determined from the data of Figs. 1 and 2 ($\delta E_{FC}^s = 13$ meV), is 20% larger on the surface. These data, together with the broadening of the surface exciton band, point to an appreciable increase of the electron-phonon interaction on the surface.

Thus, an investigation of the radiative surface recombination has made it possible to observe a manifestation of surface phonon in LPL spectra and to determine a number of important characteristics of the electron-phonon interaction on the surface.

[1]R. Fuchs and K. L. Kliewer, Phys. Rev. 140, A2076 (1965).

[2]R. Englman and R. Ruppin, J. Phys. Chem. Sol. 1, 630 (1968).

[3]V. V. Bryksin and Yu. A. Firsov, Fiz. Tverd. Tela 11, 2167 (1969); 14, 1148 (1972) [Sov. Phys.-Solid State 11, 1751 (1970)]; [14, 98 (1972)].

[4]V. V. Bryksin, Yu. M. Gerbshtein, and D. N. Mirlin, ibid. 13, 1603 (1971) [Sov. Phys.-Solid State 13, 1342 (1971)].

[5]D. L. Molls and A. A. Maradudin, Phys. Rev. Lett. 31, 372 (1973).

[6]V. M. Agranovich, ZhETF Pis. Red. 19, 28 (1974) [JETP Lett. 19, 16 (1974)].

[7]V. A. Zuev, V. G. Litovchenko, G. A. Sukach, D. V. Korbutyak, ibid. 16, 126 (1972) [16, 87 (1972)]; Phys. Stat. Sol. (a) 17, 353 (1973).

[8]V. V. Diyakov et al., Phys. Stat. Sol. (a) 1, K45 (1970).

[9]M. A. Krivoglaz and S. I. Pekar, Trudy Inst. Fiz. AN Ukr. SSR 4, 73 (1953).

[10]J. J. Hopfield, J. Phys. Chem. Sol. 10, 110 (1959).