Collective effects on semiconductor surfaces (GaAs)

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Collective effects were observed on semiconductor surfaces. These effects were investigated by measuring the low-temperature photoluminescence spectra of GaAs-insulator layer systems excited by laser radiation. A study was made of the profile, amplitude, and position of the photoluminescence line as a function of temperature, intensity, and polarization of the exciting radiation, electric voltage, mechanical stress, surface treatments, etc. The results indicated the appearance of an electron-hole condensate on the surface, whose properties differed considerably from the condensate in the bulk.

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1. INTRODUCTION

Much effort is being put currently into theoretical and experimental investigations of collective effects which are observed on excitation of some crystals by laser radiation. These effects include the formation of electron-hole drops predicted by Keldysh[1,2] and several other phenomena (formation of biexcitons, Bose condensation, etc.—see, for example, Ref. 3).

Bulk collective effects are now known to occur in several crystals. However, no systematic investigations have yet been made of surface effects. Nevertheless, there is experimental evidence that such effects can occur for certain special states of the surface and the surface layers.[4,5] A detailed investigation of surface collective effects is of fundamental importance for a number of reasons. First of all, the appearance of such effects may give rise to a surface superconductivity due to the influence of excitons.[1,6] Furthermore, the condition for the appearance of collective surface excitons is different from that in the bulk because some fundamental characteristics are different on the surface. For example, the effective mass of electrons on the surface m_c^* is usually greater than the effective mass in the bulk m_b; the permittivity ϵ_s on the surface may be, because of the presence of the ambient medium, lower or much higher than the corresponding bulk value ϵ_b, etc. In view of this, the criterion for collective effects on the surface is considerably different from that for the bulk effects.

It should be pointed out that, in spite of the self-evident importance of the surface problem, there are some basic difficulties which arise, in particular, because of strong nonradiative losses on the surface and the destructive influence of the surface field on excitons. It is not always possible to observe radiative recombination on the surface even in the impurity absorption region[7-9] and such recombination occurs only for certain very specific states of the surface. In the case of GaAs, some of these states are favorable also for the manifestation of collective effects in the edge surface photoluminescence.[4,5] The present paper reports a detailed investigation of collective effects on the surface of a semiconductor (GaAs).

2. EXPERIMENTAL METHOD

Bulk collective effects in GaAs are usually investigated in high-purity epitaxial films with a majority carrier density n_0 below 10^{15} cm^{-3}.[10,11] However, it follows from control experiments that, in this case, the bulk edge luminescence bands mask the surface bands. Therefore, we employed, as before,[4,7,9] a different method in which residual impurities were removed only from a very narrow ($d_0 \sim 3000$ Å) strip of the surface region and surface radiation recombination centers were generated. We deposited, by the gas-transport method at T = 550–600°C, Si_3N_4 (Ge_3N_4) insulator films, ~0.1 μ thick, on the surfaces of n-type GaAs single crystals ($n_0 = 10^{17}$ cm^{-3}).

The photoluminescence was excited primarily by a cw He–Ne laser, which ensured that only a shallow surface region was excited ($k^{-1} \leq 0.5$ μ) and that the maximum light intensity L in a focused beam was 10^{21} photons · cm^{-2} · sec^{-1}. In some cases, the photoluminescence was also excited with a DRSh-500 mercury lamp ($L \approx 10^{16}$ photons · cm^{-2} · sec^{-1}) and by ruby laser pulses of $L \approx 10^{24}$ photons · cm^{-2} · sec^{-1} intensity. The photoluminescence signal was measured on the illuminated side and analyzed with PGS-2, ISP-51, and IKS-12 spectrographs. In the case of the PGS-2 spectrograph, whose dispersion was 0.7 nm/mm, the luminescence was recorded photographically. In the case of the other two spectrographs, we employed the integrated luminescence characteristics. In this case, we used an FÉU-62 photomultiplier.

The photoluminescence measurements were carried out in the temperature range 4.2-50°K. The nature of the observed bands was deduced from the temperature dependences of the photoluminescence intensity and from a series of other conventional experiments described in Sec. 3. In particular, measurements were made of the reflection and photoconductivity.

3. EXPERIMENTAL RESULTS

Before the deposition of the insulator films, we observed, at 4.2°K, two photoluminescence bands of bulk origin, shown in Fig. 1a (1.502 eV band, usually attributed to residual impurities such as Si, and 1.36 eV band, attributed to Cu atoms). Since these initial data were described in full earlier,[4,7] we shall not discuss in detail the spectral characteristics of these bands.

After the deposition of an Si_3N_4 (Ge_SN_4) insulator film, the 1.36 eV band did not change greatly but the 1.502 eV band disappeared completely. Moreover, several new bands were observed. They were the edge luminescence band and the 1.477, 1.444, and 1.411 eV bands. The reflection spectra of GaAs single crystals

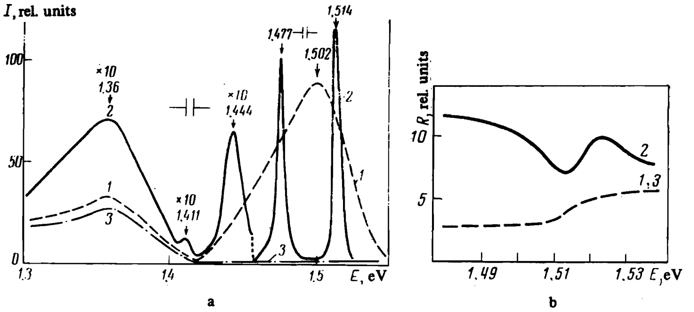

FIG. 1. Photoluminescence (a) and reflection (b) spectra of the original GaAs sample (curve 1), after deposition of an Si_3N_4 insulator film (curve 2), and after etching away of the Si_3N_4 film and a ~100 Å thick layer of GaAs (curve 3). Parallel vertical lines indicate the spectral slit width.

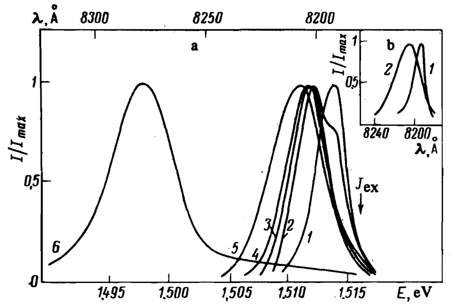

FIG. 2. a) Profile of the ESL band excited by a DRSL-500 mercury lamp (curve 1), a cw He-Ne laser beam (curves 2-5), and ruby laser pulses (curve 6). The excitation intensities L (photons$\cdot$cm$^{-2}\cdot$sec^{-1}) at T=4.2°K: 1) 10^{16}; 2) 10^{18}; 3) 7×10^{19}; 4) 3×10^{20}; 5) 10^{21}; 6) 10^{24}.
b) Comparison of the ESL band profile (L≈10^{21} photons$\cdot$cm$^{-2}\cdot$sec^{-1}, curve 2) with band J_{ex} (L≈5×10^{20} photons$\cdot$cm$^{-2}\cdot$sec^{-1}, curve 1), reported in [10].

coated with Si_3N_4 (Ge_3N_4) films exhibited a characteristic minimum (Fig. 1b), which was not observed before the deposition of the films. This minimum remained also after the insulator film was removed by etching and it disappeared only when a GaAs layer ≤100 Å thick was removed. A characteristic feature of this minimum was its considerable width and "nonclassical" profile.

It was reported earlier[7,9] that etching away of the insulator film had practically no influence on the luminescence characteristics or the reflection spectrum. This observation and the identity of the characteristics obtained after the deposition of the Si_3N_4 and Ge_3N_4 films indicated that the optical, dielectric, and other properties of the insulator films had no significant influence on the characteristics of the observed peaks and that the photoluminescence was entirely due to the radiative recombination in the semiconductor. Moreover, removal of even a very thin layer (≤100 Å) destroyed the new photoluminescence bands. This indicated that the bands which appeared after the deposition of the nitride film were of surface origin. A complete recovery of the initial (curve 1) photoluminescence spectrum occurred when a layer of ~3000 Å thick was removed.

A detailed investigation of the 1.477, 1.444, and 1.411 eV series of bands, which were the surphon replicas of the zero-phonon band at 1.477 eV, was reported in[5,9,12] and several characteristics of surface phonons (surphons) were determined.

We shall now consider in detail the behavior of the edge surface luminescence (ESL) which has not yet been investigated. We shall use the results obtained for the 1.477 eV band solely for comparison with the ESL characteristics.

Figure 2a gives the ESL spectra obtained for different exciting radiation intensities L (control experiments indicated that the profile of the 1.477 eV band was independent of L). We can see that, at the lowest values of L, corresponding to the photoluminescence excitation by the mercury lamp, there is only one ESL band (1.5137 eV) shifted toward longer wavelengths, compared with the free-exciton line J_{ex} (1.5160 eV). An increase in L (by the use of the He—Ne laser) reveals two ESL bands (1.5137 and 1.5120 eV). Further increase in L (focusing of the He—Ne laser beam) reduces the number of ESL bands again to one: the half-width of this band increases and its position δE_m shifts toward longer wavelengths when the intensity L is increased. The maximum width H of the ESL band and its strong shift toward longer wavelengths are observed when the photoluminescence is excited by a ruby laser.

Figure 3a shows the dependences of the intensities I of the ESL and 1.477 eV bands on the excitation intensity. It is clear that the intensity of the 1.477 eV band depends almost linearly on L ($I \propto L^n$, where n = 1.2 ± 0.1), whereas the corresponding dependence of the ESL intensity is superlinear (n = 1.9 ± 0.1). Moreover, the spectral characteristics (δE_m, H) of the 1.477 eV band do not change with rising L. There are also other important differences between these two surface photoluminescence bands. In particular, the intensity of the 1.477 eV band is independent of the polarization of the exciting light, whereas the intensity of the ESL band excited by a focused He—Ne laser beam changes by a factor of about two when the polarization of light is altered by 90°.

We also studied the influence of low-temperature heating on the photoluminescence band intensities (Fig. 4b). Heating at 100°C in an inert atmosphere resulted in an identical increase in the intensities of all the bands observed in the Si_3N_4—GaAs or Ge_3N_4—GaAs systems. An increase in the heating temperature caused the ESL intensity to rise less than the intensities of the other photoluminescence bands.

Moreover, the intensity of the 1.477 eV band increased as a result of low-dose (≈10^7 rad) γ-irradiation, whereas the intensity of the ESL band fell (Fig. 4a). After such irradiation, scatter appeared in the energy position of the ESL band: it varied somewhat (within ~13 Å) when the laser beam scanned the surface (Fig. 5).

Figure 6a shows the temperature dependence of the intensities of the ESL and 1.477 eV bands, and of the first phonon replica of the latter (1.444 eV). We can see that strong quenching of the ESL band takes place in the range 4.2—20°K but the intensities of the other bands are not affected. It is particularly interesting that an inhomogeneous deformation has no effect whatever on the nature of the temperature dependence of the intensity of the 1.477 eV band. On the other hand, the intensity of the ESL band decreases as a result of such deformation by a factor of two even at 4.2°K and the temperature dependence of this band acquires a characteristics jump at T = 6.8°K.

Figure 6b illustrates the changes in the ESL band profile between 4.2 and 20°K. We can see that, when the temperature is increased, the ESL band broadens mainly in the direction of higher energies and the short-wavelength wing becomes less steep.

Further information on the nature of the ESL band was obtained by investigating the influence of a longitudinal electric field on the photoluminescence and photoconductivity (Figs. 7 and 8).

It follows from Fig. 7a that, in fields up to $E = E_{cr} = 0.87$ V/cm, the ESL band intensity is independent of the field but a sudden change in the intensity occurs at $E = E_{cr}$ (this change is less marked in the photoconductivity—Fig. 8). This is accompanied by a broadening of the photoluminescence spectrum with the short-wavelength wing becoming wider, after the application of E_{cr}, than the long-wavelength wing (Fig. 7b).

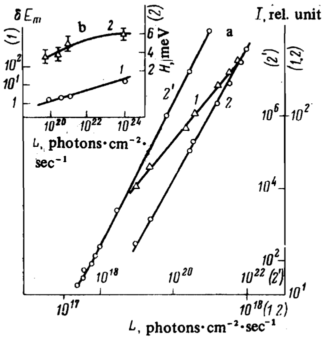

FIG. 3

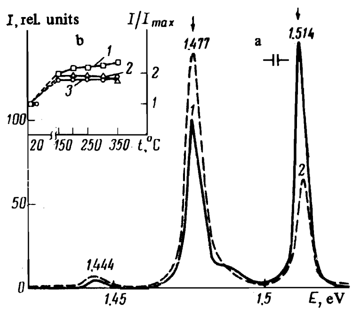

FIG. 4

FIG. 3. Dependences of the intensities (b) of the 1.477 eV (curve 1) and ESL (curves 2 and 2′) luminescence bands and of the spectral characteristics of the ESL band (b) on the exciting light intensity L.

FIG. 4. a) Influence of γ-irradiation (~10^7 rad) on the surface luminescence spectrum: 1) before irradiation; 2) after irradiation. b) Influence of low-temperature heating on the intensity of the impurity bulk (curve 1—1.36 eV band), impurity surface (curve 3—1.477 eV band), and edge surface luminescence (curve 2—1.514 eV band) excited by light of $L=10^{20}$ photons·cm^{-2}·sec^{-1} intensity.

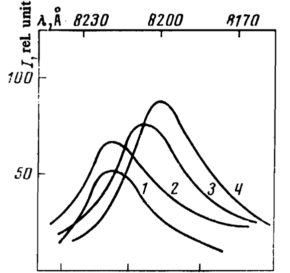

FIG. 5. Edge surface luminescence band recorded at different points on a sample of GaAs, covered with an Si_3N_4 film and irradiated with γ rays (~10^7 rad); curves recorded at T= 4.2°K for $L\approx10^{21}$ photons·cm^{-2}·sec^{-1}. Curves 1–4 were recorded at four arbitrarily selected points on a sample.

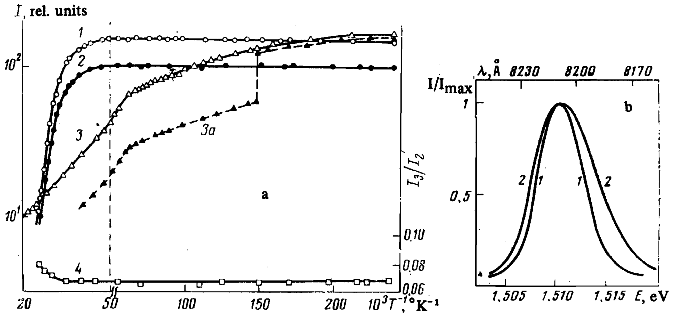

FIG. 6. a) Temperature dependences of the surface photoluminescence band intensities: 1) 1.477 eV band; 2) 1.444 eV band (1×10 scale); 3) ESL band; 3a) ESL band after inhomogeneous deformation; 4) ratio of the intensities of the 1.444 and 1.477 eV bands; $L=10^{20}$ photons·cm^{-2}·sec^{-1}. b) Edge surface luminescence band at 4.2°K (curve 1) and 20.4°K (curve 2).

4. DISCUSSION OF RESULTS

1. Low-dose γ-irradiation (≤10^7 rad), used in our experiments, creates structure defects which accumulate mainly on the surface and in a thin surface layer[1)] of GaAs.[8] Therefore, the increase in the intensity of the 1.477 eV band which occurs after γ-irradiation (Fig. 4b) is direct evidence that this band is due to radiative recombination involving surface structure defects (such as vacancies or vacancy + N complexes). It has been shown[7,9] that it is this luminescence, corresponding to the impurity absorption region, which is characteristic of semiconductor surfaces.

2. We shall now consider the edge surface luminescence (ESL), which has been investigated less thoroughly. It follows from Fig. 2 that, at moderate excitation rates, the photoluminescence spectra include a band at 1.5137 eV. The reflection spectra have a minimum whose energy position is close to that of this ESL band.

The ESL band and the corresponding reflection minimum are due to noncollective surface excitons (J_S). These may be free excitons which experience the influence of the surface. Such an influence on excitons and on exciton-photon (polariton) modes was investigated, subject to spatial dispersion, both theoretically[13-16] and experimentally in the case of CdS[17] and GaAs.[18] Moreover, these may be excitons bound to surface centers.[9,12]

Since J_S is quenched by etching away a very thin surface layer, which destroys surface radiative recombination centers, it is more likely that J_S is due to bound surface excitons. The presence of bound excitons is favored by the giant oscillator strengths f of GaAs ($f^t_{ex}/f^0_{ex} \sim 5\times10^5$, where the indices t and 0 refer to the bound and free excitons, respectively) because the surface radiative recombination velocity is $S_r \propto f$.[19] The considerable half-width of the reflection spectrum, compared with—for example—the results reported in[18], is evidence of a very strong exciton—phonon interaction on the surface. The "nonclassical" form of

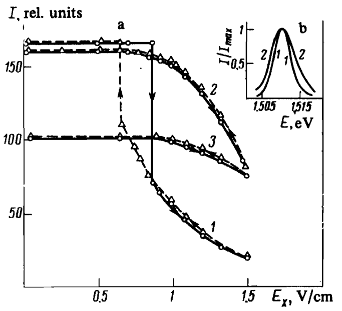

FIG. 7

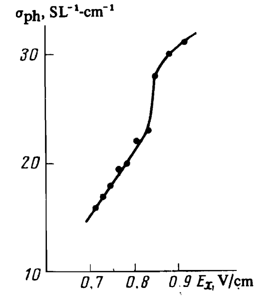

FIG. 8

FIG. 7. a) Influence of a longitudinal electric field on intensities of the ESL (curve 1), 1.477 eV (curve 2), and 1.36 eV (curve 3) bands; $L=10^{20}$ photons·cm^{-2}·sec^{-1}. b) Profile of the ESL band in the absence of an electric field (curve 1) and after application of this field E_x=1 V/cm (curve 2).

FIG. 8. Dependence of the photoconductivity of a sample of GaAs coated with an Si_3N_4 film on the electric field applied at T=4.2°K in the presence of excitation of $L\approx10^{18}$ photons·cm^{-2}·sec^{-1} intensity.

the reflection spectrum may be due to spatial dispersion in the presence of free or bound surface polaritons.[13-16] The appearance of noncollective excitons on the surface of GaAs will be discussed in greater detail in a separate paper.

It should be noted that the J_S band is observed only in a limited range of the exciting light intensities. This is due to the following circumstance. At low intensities L, the surface fields play a considerable role (these are accidental surface fields and the field in the space-charge region, which usually cause the dissociation of excitons).[2)]

At high values of L, the surface fields become much weaker but the photoluminescence spectra begin to be dominated by the band due to collective effects. Therefore, the probability of observing surface exciton bands is much less than the probability of observing the exciton effects.

In this respect, we can draw an analogy with heavily doped Si crystals whose bulk free-exciton and biexciton bands are much more difficult to observe compared with the bulk band of electron-hole drops.[22]

3. When the excitation intensity is increased (by the use of unfocused and then focused He—Ne laser beams), the J_S band appears in the photoluminescence spectra first as an inflection (curve 2 in Fig. 2a) and then it disappears completely in the background of the superlinearly rising ESL band (curves 3—6). This type of dependence I(L) is typical of collective effects.[1-3]

It is also known that these effects appear in the corresponding spectral region. This is clear from Fig. 2b, which shows—for comparison—the ESL band and a band due to the appearance of an electron-hole condensate in the bulk of GaAs (this condensate is in the form of drops or a spread-out plasma).[10]

In addition to this condensate, we may observe several other collective effects (formation of biexcitons and of exciton-molecular complexes, exciton-electron interaction, etc.). Therefore, the effect observed can be identified only if all the experimental data are used comprehensively. In fact, the nature of the dependence of I(L) for the ESL band and the shift of its energy position toward longer wavelengths with rising L can be explained by assuming the formation of the condensate or by invoking the exciton-electron interaction (the formation of biexcitons can be rejected at once).

Further discrimination can be made on the basis of the temperature dependence of the ESL intensity (Fig. 6). Broadening of the ESL band with rising temperature because of the greater shift of the short-wavelength wing, in accordance with the calculations in[23], and the constancy of $E_{max}(T)$ are typical of the electron-hole condensate and do not agree with the exciton-electron interaction or with the formation of exciton-molecular complexes. Finally, the sudden change in the temperature dependence of the ESL intensity under inhomogeneous deformation conditions is also evidence of the appearance of the electron-hole condensate on the surface (critical conditions are established for the "gas-liquid" phase transition).[3)]

The profile of the luminescence band due to an electron-hole condensate in the bulk of pure Ge or Si crystals ($n_0 < 10^{14}$ cm^{-3}) and the energy position of this band are independent of the excitation intensity L. However, in the case of doped crystals, this band broadens with increasing L and shifts toward longer wavelengths.[22] A similar shift in the position of the band due to an electron-hole condensate in the bulk of Si is observed when the degree of doping of silicon with P and B atoms is increased.

In this respect, we can draw an analogy with our dependence of the ESL band profile on L in the case of unirradiated samples (Fig. 2a) and in the case of γ-irradiated samples when the surface is scanned by the laser beam (Fig. 5). In fact, the lower the intensity (after γ-irradiation) of the ESL band at a given point on the surface, the longer is the wavelength at which the maximum of this band is observed. A strong influence of the doping and excitation intensity on the profile of the electron-hole condensate band of Ge and Si is explained in[22] by the formation of small electron-hole drops in the bulk. Such small drops are the most stable and sensitive to the excitation intensity and to deformation and other agencies. Small drops are probably also formed on the surface of GaAs. This is favored by the short lifetimes of free excitons in GaAs ($\leq 10^{-9}$ sec) and relatively low exciton concentrations n_{ex} at which they condense. Therefore, the ESL band is extremely sensitive to γ-irradiation, application of longitudinal fields, inhomogeneous deformation, and polarization of the exciting light.

There is a correlation between a sudden reduction in the luminescence intensity I, observed in a critical field, and a sudden increase in the photoconductivity, which may be attributed to a reduction in the nonradiative losses as a result of dissociation of drops.

Low-temperature heating, known to alter the state of the surface, first increases equally the intensities of all the luminescence bands (Fig. 4b), which is direct evidence of a reduction in the nonradiative surface recombination velocity S. Further increase in heating temperature begins to weaken the ESL band (without affecting other bands) because this band is highly sensitive even to slight deformations.

It is also interesting to note a considerable shift in the energy position of the ESL band ($\Delta E \sim 18$ meV) when the He—Ne laser radiation is replaced with the ruby laser radiation (Fig. 2a). This shift should be mainly due to a reduction in the forbidden band width of the condensate. Theoretical predictions[24,25] give $\Delta E_g \sim 4.3 \times 10^{-5} n^{1/3}$ meV and a shift of E_g (for light intensity variations in the investigated range) of the order of 10—20 meV, which is in qualitative agreement with the experimental results (Fig. 3b).

4. We shall conclude by comparing the band which we attribute to the surface electron-hole condensate with the bulk band due to a similar condensate observed earlier in GaAs.[10,11] The spectra of such a condensate are plotted in Fig. 2b for similar experimental conditions.

First of all, we can see that the curve associated with the surface electron-hole condensate is shifted by 2.7 meV toward longer wavelengths compared with the bulk condensate band. This shift may be attributed to a change in the binding energy of the surface electron-hole condensate (E_{cs}) compared with the corresponding bulk value (E_{cb}). It should be pointed out that there is as yet no sufficiently rigorous theory for the calculation of even E_{cb} of GaAs. Only approximate values are available and these are strongly underestimated[26] possibly because the electron-hole correlation is not allowed for or slightly overestimated[27] compared with the experimental values of E_{cb}. The results given in[27] are closer to the experimental values and they are obtained on the basis of ideas developed in[1,2,28,29]. In estimating the reduction in the energy E_c of electrons (holes) due to their interaction in the process of condensation, one has to sum the kinetic energy (E_{kin}) with the exchange (E_{exch}) and correlation (E_{corr}) corrections

$$E_c = \frac{2.21}{(r_s/a_0)^2}\frac{m}{m^*_{e,h}}R - \frac{0.916}{r_s/a_0}\frac{R}{\chi} - \frac{0.88}{r_s/a_{c,h}+7.8}, \tag{1}$$

where R is the Rydberg constant, a_0 is the Bohr radius of the charge carriers, $m^*_{e,h}$ are the density-of-states effective masses of electrons and holes, and r_s is the distance between neighboring particles in the condensate.

The energy minimum of the Fermi gas of electrons and holes corresponding to the binding energy of the bulk condensate E_{cb} occurs at a nonequilibrium carrier density of 3×10^{16} cm^{-3}.[26,27] The value of E_{cb} calculated in[27] on the basis of Eq. (1) is 4.4 meV, which is close to the experimental value of 3.3 meV.

In the case of the surface electron-hole condensate, the value of E_{cs} should be calculated using the effective mass on the surface m^*_s, surface permittivity ϵ_s, surface exciton radius a_{exs} and the energy of formation of free excitons in the surface E_{exs}:

$$a_{exs} = \frac{\hbar^2\varepsilon_s}{m_s{}^*e^2}, \quad E_{exs} = \frac{1}{2}\frac{e^4 m_s{}^*}{\varepsilon_s{}^2\hbar^2}. \tag{2}$$

Weakening of chemical bonds may increase the effective mass on an unmodified surface by a factor of 1.5–2 compared with the mass in the bulk,[30-32] whereas ϵ_s is usually less than ϵ_b.[33] According to Eq. (10), this should reduce somewhat a_{exs} and increase considerably E_{cs}, which is indeed observed experimentally.[4]

The band due to the surface electron-hole condensate had a profile different from that of the bulk condensate band (mainly because of the greater half-width of the surface band). It is shown in[10] that the profile of the band due to the bulk electron-hole condensate (particularly its short-wavelength wing) can be described qualitatively by a theoretical formula for a degenerate electron-hole plasma in direct gap semiconductors subject to the selection rule governing the wave vector k. On the other hand, a similar line is described satisfactorily in[34] by a relationship for an electron-hole plasma when the selection rule applying to k is violated in the course of radiative transitions (Fig. 9). The quasi-Fermi levels and the degree of unipolarity ($n/p \sim 10^4$), typical of our samples, give theoretical curves[11,34,35] which are not in agreement with the experimental data discussed in the present paper (this applies particularly to the short-wavelength wing). Hence, we may conclude that the theory developed for bulk plasma condensates cannot be applied directly to surface condensates. In particular, one must allow for a stronger exciton-phonon interaction on the surface.[12]

It is also interesting to note that, in the case of the bulk electron-hole condensate, the luminescence band intensity should be a cubic function of L (for moderate values of L): $I \propto L^n$, where n = 3. In our case, the exponent is $n \sim 1.8$–2. This can be explained qualitatively by the transition from spherical drops in the bulk to flattened drops on the surface; a calculation similar to that in[1,23] gives $n < 3$.

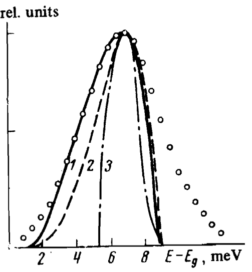

FIG. 9. Comparison of the experimentally determined ESL band profile (points) with theoretical calculations (curves): 1) k selection rule not satisfied and parameters typical of our samples ($n/p \sim 10^4$, $F'_p = 6$ meV, and $F'_n = 1$ meV, where n, p, F'_n, and F'_p are the densities of electrons and holes and the corresponding quasi-Fermi levels); 2) similar profile of a luminescence line of an electron–hole plasma ($n \sim 5\times10^{16}$ cm^{-3}, T=2°K); [34] 3) profile of a luminescence line of an electron-hole plasma in the case when k selection rules are satisfied ($n_0 = p_0 = 1.1\times10^{16}$ cm^{-3}, T=3.8°K) [10].

There are also several other characteristics which distinguish the surface electron-hole condensates: the condensate can form at lower carrier densities than in the bulk, it is more sensitive to external agencies, it is affected more strongly by an increase in the injection level, etc.

In fact, the value of n_{ex} can be found from the condition of formation of a surface condensate:

$$n_{ex} l_{ex} a_{exs}{}^2 \sim 10^{-1} - 10^{-2}, \tag{3}$$

where l_{ex} is the depth of extraction of excitons to the surface, which is governed by the smallest of the following quantities: depth of exciton generation k^{-1}, diffusion length of excitons l_{Dex}, or thickness of the purified surface layer d_0. If the condition $l_{ex} \gg a_{exs}$ is satisfied, the collective state is established near the surface at exciton concentrations much lower than in the bulk. This condition may be satisfied by purifying a sufficiently deep surface layer (in our experiments, $d_0 \sim 3\times10^3$ Å) or by increasing l_{ex} at higher excitation rates by free-carrier screening of the surface fields and of the fields of the impurity atoms. In the case of very small values of l_{ex}, a condensate fills completely the whole "active" surface region.

It is also interesting to note that the formation of a surface electron-hole condensate is facilitated by the appearance of condensation centers of the surface. Such centers may be surface structure defects responsible for the 1.477 eV band and surface centers at which excitons are bound. In fact, quenching of the ESL band in our experiments on etching away a thin layer of GaAs occurs simultaneously with the quenching of other surface bands.

Thus, the results obtained indicate that, in principle, it is possible to observe collective effects on the surface of a semiconductor and that the principal characteristics of the luminescence bands associated with these effects are different from the characteristics of the bands associated with the bulk effects.

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[1] Further increase in the radiation dose causes intensive generation of bulk structure defects.

[2] The formation of a "dead"—for excitons—surface zone is also possible for other reasons which are discussed in theoretical [16, 20] and experimental [21] papers.

[3] The position of the observed ESL line does not agree with the exciton-exciton (Auger) interaction mechanism.

[4] It should also be noted that purification of the surface region used in our experiments was different from that employed in [10] and corresponded to a higher dopant density. According to [22], this could also shift the position of the electron-hole condensate bands in the direction of longer wavelengths.

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