Investigation of excitons bound to phosphorus and arsenic impurity atoms in silicon

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We have investigated recombination radiation (RR) arising from the radiative decay of excitons bound to *P* and *As* impurity atoms in silicon within the temperature interval 2 K to 30 K. Particular attention is paid to excitons bound to pairs of impurity centers in samples subjected to uniaxial deformations along the [001] and [111] directions. We have determined conditions under which it is possible to observe these pair-bound excitons. It is shown that in the phonon-assisted region of the spectrum, pair-bound excitons radiate more effectively than excitons bound to individual centers. It is shown that more than one exciton can be bound at a donor pair. We have studied in detail the influence of uniaxially deforming the sample on the RR spectral distribution of excitons bound to impurity atoms of phosphorus and arsenic. It is established that deforming a sample in the [111] direction does not give rise to any significant change in the emission spectrum, while deformation in the [001] direction leads to a redistribution of intensities in the spectrum and the emergence of new emission bands. The change in the spectrum caused by deforming the sample is explained by a shift in the energy spectrum of the excitons bound to arsenic and phosphorous atoms, and the change in the energy distribution of excitons in an exciton-impurity band. We show that at low temperatures the energy distribution of excitons in this exciton-impurity band is determined by hopping of excitons from impurity atom to impurity atom, while at high temperatures it is also necessary to take into account the process of thermal emission of an exciton into the exciton band with its subsequent recapture by other impurities.

1. INTRODUCTION

At low temperatures ($kT < \varepsilon_0$, where ε_0 is the exciton binding energy at an impurity center) free excitons in silicon can be bound to impurity atoms belonging to the III and V groups of the periodic table. In crytals with low impurity concentrations, i.e., when the average distance between impurity atoms $r_{\text{av}} = (3/4\pi N_D)^{1/3}$ (N_D is the impurity concentration) is much larger than the exciton Bohr radius a_E, the excitons are bound to individual atoms, forming bound excitons $ED^{(1)}$ (Ref. 1) and multiexciton impurity complexes E_kD (Refs. 2,3). As the impurity concentration increases, the average spacing between impurity atoms decreases; as a consequence of this, the number of pairs, triads, etc., of impurity atoms in the crystal whose interatomic distances are comparable to a_E increases. Such groups of atoms are capable of trapping free excitons, creating the exciton-impurity complexes ED_2, ED_3, etc. We note that for $r_{\text{av}} \sim a_E$, excitons bound to impurity atoms (as we will show below) cannot be considered strictly localized; they may migrate through the crystal. Furthermore, at concentrations for which $r_{\text{av}} < a_E$ it would appear to be necessary to speak of an exciton-impurity band (EIB) in which propagating exciton states are present.[4]

An effective way to study these exciton systems is to investigate the recombination radiation (RR) arising from their decay, using magneto-piezospectroscopy methods. This is especially pertinent for E_kD, whose RR spectrum consists of extremely narrow lines whose spectral positions are directly related to their energy structure.[1,5,6] A host of difficulties attends the use of this method to study the exciton-impurity complexes ED_n. First of all, as opposed to E_kD, the emission spectra of ED_n complexes consist of broad bands which intersect each other, due to the random mutual separations of their constituent impurity atoms. Secondly, as we already have noted, for $r_{\text{av}} \sim a_E$ the excitons can migrate among the impurity atoms. This process leads to an exciton distribution in the EIB which depends on temperature and photoexcitation density, and which makes itself felt through the presence of deviations in the RR spectral density from the EIB density of states. In light of this statement, it is clear that the RR spectral distribution will be related to the energy spectrum of the ED_n complexes in a complicated fashion. It would appear that this is the reason why so little is known about the energy structure of ED_n and the EIB density of states. The situation is further complicated by the fact that theoretical analyses of ED_n are accompanied by considerable difficulties, and to date remain incomplete.

The low-temperature photoluminescence of silicon and germanium containing shallow donors (group V) in concentrations such that $r_{\text{av}} \sim a_E$ was investigated experimentally in Refs. 6–13. It was shown there that the exciton RR bands associated with phosphorous atoms in silicon, and phosphorus, arsenic and antimony atoms in germanium, are broadened nonuniformly and have long-wavelength "tails." The intensity and shape of the emission bands depend on the impurity concentration, temperature and photoexcitation density of the crystals (W). Based on comparisons of the RR spectra[10] with semi-quantitative calculations, the authors of Ref. 11 observe that it is necessary to include processes of energy transfer of the excitonic excitation in order to explain the experimental results. In Ref. 13, it was observed that for silicon at low temperatures, when a critical concentration ($N_D{}^{\rm cr} \approx 1.5 \times 10^{17}\,{\rm cm}^{-3}$) is reached, a sudden change in the RR spectra occurs—a shift in the maximum of the emission band to the long-wavelength side. The authors of Ref. 13 interpreted this phenomenon as an Anderson-type phase transition, i.e., the appearance of extended states in the EIB. We are constrained to point out that in many cases the results of papers devoted to the investigation of the questions alluded to above are contradictory and incomplete.

In the present paper we present the results of an investigation of RR in silicon doped with phosphorus and arsenic at concentrations for which the samples contain a significant number of both "isolated" donors and donor pairs capable of capturing free excitons. Special attention is given to an investigation of the RR of the *ED* and ED_2 complexes in samples subjected to uniaxial deformations.

2. EXPERIMENTAL PROCEDURE

We investigated single crystals of silicon doped with phosphorous and arsenic, grown by either the Czochralsky method or by the crucible-less zone-refining technique. The samples used for investigating RR were cut out in the form of parallepipeds with dimensions $2 \times 2 \times 20$ mm^3 along the crystallographic [111], [001], and [112] directions. The procedure used to prepare the samples, and to create a homogeneous uniaxial compressive deformation, are described in Ref. 5. In order to investigate the RR spectra in the temperature interval 2 K to 4.2 K, the samples were immersed in liquid helium, and for the interval 6 K to 35 K in gaseous helium. The temperature was determined with the help of a calibrated resistor riveted to the lateral side of the sample. Samples were excited by radiation from a LG-106M-1 argon laser (0.5 W output power). The RR was analyzed with a CDL-1 transmission spectrometer. In cases where it was necessary to have higher resolution, we used an IT-28-30 transmission interferometer. The standard mirrors of the IT-28-30 were replaced by mirrors with multilayer dielectric coatings having a reflectivity maximum for $\lambda = 1.08\ \mu$m, which we used to obtain a finesse of ~ 50. In this case, the RR was recorded with a cooled FEU-62 photomultiplier, working in the photon-counting mode.

3. ANALYSIS OF THE RR SPECTRUM OF UNSTRESSED SILICON DOPED WITH PHOSPHORUS AND ARSENIC

We investigated samples of silicon doped with phosphorus and arsenic at concentrations $N_D = 10^{16}$ to 8×10^{17} cm^{-3}. For $N_D \leqslant 10^{17}$ cm^{-3} the mean distance between impurities $r_{\rm av} > 140$ Å, which is significantly larger than $a_E \approx 50$ Å.[14] This allows us to assume that for $N_D \approx 10^{17}$ cm^{-3} there will be a sizable concentration both of isolated impurities N_{ED} and of isolated atomic pairs N_{ED_2}. If we define an impurity atom as isolated if there are no other impurity atoms within a distance $r = 4a_E$, and a pair of impurity atoms as isolated if the two atoms are separated by a distance R from $1.5a_E$ to $3a_E$ from one another while out to a distance $r = 4a_E$ around the segment "connecting" these atoms there are no other impurity atoms, then it is not difficult to calculate the concentrations of such isolated atoms and atomic pairs. In Fig. 1 we show the dependences of N_{ED} and N_{ED_2} on N_D. From the figure it is clear that N_{ED} and N_{ED_2} increase up to a concentration $N_D \approx 10^{17}$cm^{-3}, and then decrease exponentially.

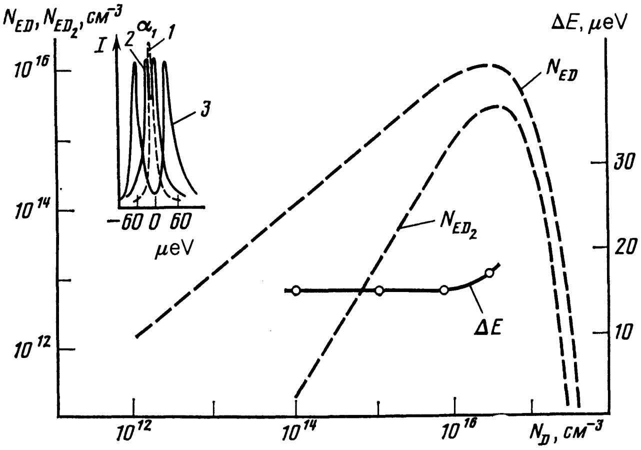

FIG. 1. The dependence of the half-width ΔE of the $\alpha_1 - NP$ emission band (experiment), the concentration of pairs N_{ED_2} and isolated centers N_{ED} (calculation), on the concentration N_D of phosphorous in silicon. The inset shows characteristic photoluminescence spectra of zone-refined silicon doped with phosphorous at $T = 4.2$ K (the spectral resolution is 8 μeV) for various values of N_D in cm^{-3}: 1—5×10^{15}, 2—1.1×10^{16}, 3—3×10^{16}.

The assumptions described above are consistent with the experimental results presented in Figs. 1 and 2. In Fig. 1 we give the dependence of the width ΔE of the α_1 emission line (associated with the bound exciton) on phosphorous concentration.[2] As is clear from the inset of Fig. 1, for many of the samples we studied the α_1 line is split. This splitting we relate to the splitting of the valence band due to mechanical stresses which were present in our crystals. If this splitting is small (curve 2), then the separate components of the doublet are not broadened; we used their half-widths to construct the function ΔE shown. For larger splittings (curve 3) the components of the doublet are broadened due to stress inhomogeneities in the sample.

From the dependence of ΔE on N_D, it follows that up to a concentration of $\approx 2 \times 10^{16}$ cm^{-3} the *ED* complexes interact weakly with neighboring impurity atoms. In the concentration interval 3×10^{16}–10^{17} cm^{-3}, however, the α_1 line, although remaining well-defined as previously (this is clear from Figs. 1, 2), is significantly broadened; this is indicative of the strong interaction of the "bound" excitons with neighboring impurities. From this we can conclude that up to $N_D \sim 10^{17}$ cm^{-3} the impurity atoms and atomic pairs present in the crystal are "isolated", and are capable of trapping excitons. Their number decreases rapidly at higher concentrations.

Let us now investigate in more detail the evolution of the RR spectrum in phosphorous-doped silicon shown in Fig. 2(a) as a function of phosphorous concentration. In the

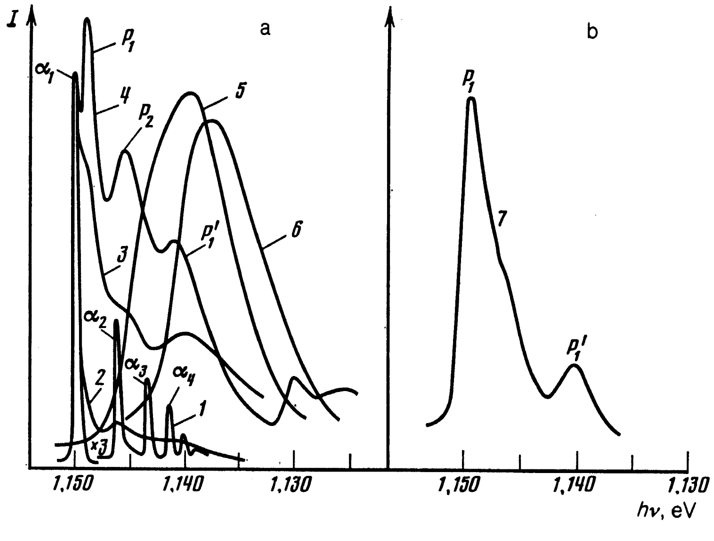

FIG. 2. Phononless emission bands of excitons bound to phosphorous atoms in silicon for $T = 2$ K and a photoexcitation density of (a) $W \sim 5$ W/cm^2 and (b) $W \approx 0.1$ W/cm^2, for various values of N_D in cm^{-3}: 1—10^{15}, 2—5×10^{16}, 3—7.5×10^{16}, 4—1.1×10^{17}, 5—4×10^{17}, 6—8×10^{17}, 7—1.1×10^{18}.

low- concentration region (curve 1) only the emission lines E_kD are present in the RR spectrum.[2,3] As N_D increases (curve 2) a long-wavelength shoulder appears on the α_1 line, while the α_2–α_5 lines are washed out into a long-wavelength "tail." At higher concentrations a structure begins to appear in the long-wavelength part of the spectrum, which for $N_D \sim 10^{17}$ cm^{-3} develops into sharply-defined bands P_1, P_2, and P_1', which disappear as the concentration is further increased. Radiation bands analogous to P_1 and P_2 appear also in the RR spectrum (see Fig. 3(a)) of arsenic-doped silicon (but at somewhat higher values of N_D).

We note that at low temperatures the emission bands P_1, P_2, and P_1' dominate the RR spectrum, as shown in Figs. 2 and 3. At high temperatures, the principal contribution to the spectrum (see curve 3 of Fig. 3(b), and Fig. 6(b) below) is emission arising from the decay of bound excitons (lines α_1, δ_1 and γ_1).[3)] The observed change in the RR spectral density is naturally explained by the temperature dependence of the population of the exciton levels in the EIB; we expect that at high temperatures the RR spectral distribution will correspond qualitatively to the density of states in the EIB. Actually, at high temperatures the lifetime of an exciton in the EIB is already determined not by the recombination time τ_r, but by the ejection time τ_T of an exciton from the exciton band, which is still present for the impurity concentrations under study (see Fig. 6 below, the *FE* line). The ejection time can be roughly estimated from the relation

$$\tau_T^{-1} = \alpha N_c \exp\left(-\varepsilon_0/kT\right),$$

where N_c is the exciton density of states in the exciton band and α is the capture coefficient for an exciton by an impurity atom. Substituting characteristic values for these parameters, we obtain $\tau_T \sim 1$ sec for $T = 2$ K, and $\tau_T = 10^{-11}$ sec for $T = 20$ K, i.e., for $T = 20$ K τ_T is significantly smaller than the time $\tau_r = 10^{-7}$ sec given in Ref. 17. An exciton can be ejected into the exciton band and subsequently retrapped by other impurity atoms; multiple repetitions of this process give rise to equilibration of the populations of the various levels in the EIB. This equilibration of populations can also be brought about by thermally-activated diffusion of excitons in the EIB. From this we can conclude that for $N_D \leqslant 10^{17}$ cm^{-3} the maximum density of states in the EIB occurs for excitons bound to "isolated" impurity atoms.

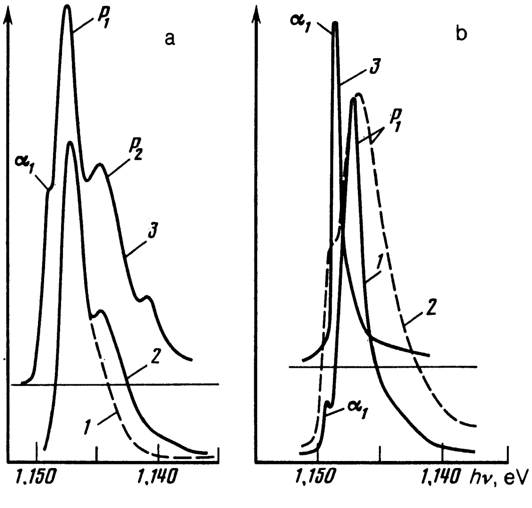

FIG. 3. Phononless emission bands of excitons bound to arsenic atoms ($N_D = 2.6\times10^{17}$ cm^{-3}) in zone-refined silicon (a) for various photoexcitation densities at $T = 1$ K: 1—$W \approx 0.05$ W/cm^2, 2—0.3 W/cm^2, 3—20 W/cm^2, and (b) at various temperatures for $W \approx 0.1$ W/cm^2: 1—$T = 2$ K, 2—4.2 K, 3—20 K.

We associate the emission bands P_1 and P_2, which dominate the RR spectra at low temperatures, with the decay of exciton-donor complexes corresponding to ED_2 and E_2D_2. These bands are observed within a narrow concentration interval which coincides closely with the function $N_{ED_2}(N_D)$ given in Fig. 1. The fact that the emission band P_1 corresponds to decay of the complex ED_2 is also suggested by its spectral position and form. The position of the maximum of the band P_1, which is shifted relative to the α_1 line into the low-energy region by 1.5 meV, corresponds to the binding energy of an exciton on an isolated pair with $R = 2a_E$.[11] The inhomogeneous broadening of the P_1 band into the low-energy region is explained by the fact that the binding energy of an exciton on D_2 increases as R decreases, while in this case

N_{ED_2} decreases. We note that the bands P_1 and P_1' are easy to observe at small photoexcitation densities, for which the intense α_1 and P_2 bands (see Fig. 2(b) and curves 1, 2 on Fig. 3(a)) disappear from the RR spectrum. In contrast to the bands P_1 and P_1' (the P_1' band will be considered below) the P_2 band is well-resolved in the RR spectrum at high levels of photoexcitation. The nonlinear growth in its intensity as the photoexcitation density increases allows us to assume that it originates from decay of the E_2D_2 complex, the formation of which requires direct capture of two excitons by an impurity pair.

We will now discuss two phenomena connected with the lack of thermal equilibrium in the EIB. The first of these is connected with the disappearance of the α_1 line from the $T = 2$ K RR spectrum as the photoexcitation density decreases. At $T = 2$ K an exciton cannot escape the EIB, because $\tau_T \gg \tau_r$. In addition, if we assume that in this case the time τ_H for an exciton to hop from D to D_2 ($ED + D_2 \rightarrow D + ED_2$) is smaller than τ_r, the most probable process is that of dissipative transfer of the exciton among the impurities. This assumption is a reasonable one because for $N_D \sim 5 \times 10^{16}$ cm^{-3} the time $\tau_H \sim 2\delta E/\hbar$ for the process $ED + D' \rightarrow D + ED'$ is 10^{-12} sec (δE is the interaction energy of ED with D) and we can be assured that τ_H is not too much larger for the process $ED + D_2 \rightarrow D + ED_2 + \hbar\omega_\varphi$ (where ω_φ is the frequency of phonon emission for this case). The process considered here is possible when nearest-neighbor centers are not occupied by excitons, i.e., in the case of low excitation density; as a result of this process free excitons, which are mostly captured by "isolated" impurity atoms (since N_{ED} is significantly larger than N_{ED_2}) will go off toward D_k groups of atoms, on which the exciton binding energies are larger ($ED \rightarrow ED_2 \rightarrow \ldots \rightarrow ED_k$). In this way, at low photoexcitation levels the "isolated" impurity atoms play the role of antennae, collecting the energy of exciton excitations and transferring it to isolated impurity pairs, similar to what takes place in photosynthesis. The second phenomenon is related to broadening of the P_1 band as the temperature increases from $T = 2$ K to $T = 4.2$ K (see curves 1,2 in Fig. 3(b)). This broadening is explained by the increase in exciton mobility in the EIB as the temperature increases, in view of the fact that within one lifetime an exciton succeeds in reaching deeper states in the EIB.

4. ANALYSIS OF THE RR SPECTRUM OF SILICON DOPED WITH PHOSPHOROUS AND ARSENIC AND SUBJECTED TO UNIAXIAL STRESS

Let us first note that compressing samples along the [111] crystallographic directions does not cause any qualitative change in the RR spectra if we ignore the fact that the recombination radiation is strongly polarized. For such deformations, which split only the valence band, the donor-bound exciton binding energy ε_0 is only slightly affected[3] (see below Fig. 5(b)). From this it follows that the characteristic size of an ED, and hence the quantities which characterize the interaction of ED with neighboring impurity atoms, are only slightly changed.

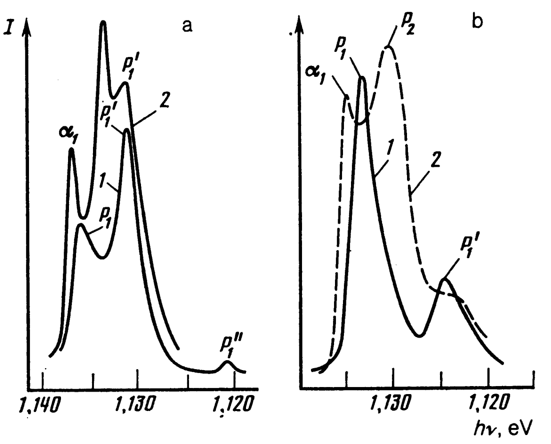

FIG. 4. Phononless emission bands of excitons bound to impurity atoms of phosphorous and arsenic in silicon stressed along the [001] axis at $T = 2$ K: (a) silicon doped with phosphorous, $N_D = 1.1 \times 10^{17}$ cm^{-3}, $P = 2280$ kg/cm^2; (b) silicon doped with arsenic, $N_D = 2.6 \times 10^{17}$ cm^{-3}, $P = 2250$ kg/cm^2, for various values of W; 1—$W \approx 0.2$ W/cm^2, 2—$W \approx 30$ W/cm^2.

A qualitatively different picture emerges when samples are compressed along the [001] and [112] directions. Deformation of silicon in these directions causes a splitting of the conduction band, and a variation in the wave function and binding energy ε_0 of the bound exciton related to it.[16] As a consequence of this the energy scale in the *EIB*, the matrix transfer and overlap integrals, etc., are all changed, which eventually changes the processes of energy transfer in the EIB and the RR spectral distribution.

In Figs. 4–6 we show typical RR spectra, along with the dependences of the spectral positions of selected emission bands on the applied pressure P; it is clear from these figures that the spectral positions and intensities of the emission bands $P_1, \alpha_1, P_2, P_1', P_1'', \delta_1, \gamma_1, FE$ present in the RR spectra depend strongly on pressure, photoexcitation density and temperature. Thus, the intensity of the P_2 band, which we associate with decay of E_2D_2 complexes, increases with increasing photoexcitation intensity, just as in the case of undeformed samples; its spectral position relative to α_1 remains unchanged.

Let us now discuss RR which originates from the decay of ED_2 complexes (the P_1 and P_1'' bands). The dependence of the spectral position of the P_1 band on pressure shown in Fig. 5(a) was obtained for low photoexcitation density, when the P_1 band is most clearly evident in the RR spectra (see curves 1 in Fig. 4). In the low-pressure region this dependence is practically identical to the dependence of the position of the α_1 band on pressure, as is clear from Fig. 5. Such a dependence of the α_1 band position on pressure, as was shown in Refs. 5 and 6, is related to the presence of excited states of the ED, and to the fact that the inner electron orbital of the ED is close to the orbital of an isolated donor. If we now take into account that for $R \sim 2a_E$ (for $R \sim 2a_E$ the basic contribution to the RR spectrum comes from ED_2) the inner electronic orbitals in ED_2 interact weakly among themselves, and are close to donor-like, then we can assume that the properties of ED_2 will be in most ways analogous to those of ED. Therefore it is natural to

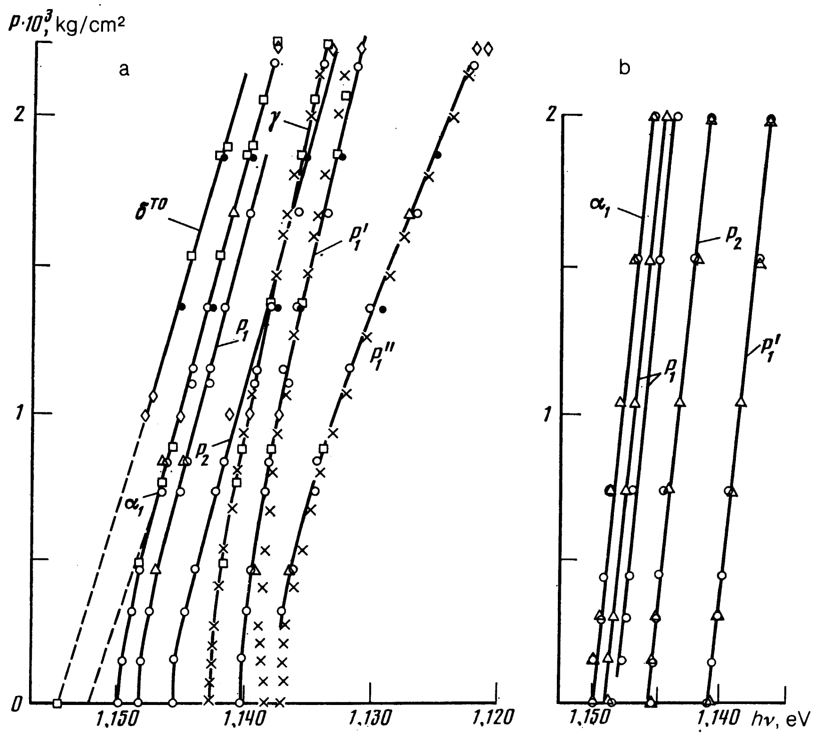

FIG. 5. Dependence of the spectral position of the *NP* emission band for silicon doped with phosphorous on applied pressure. To construct the dependences presented here, we used spectra obtained at various temperatures, impurity concentrations and photoexcitation densities. For convenience, the dependence of the position of the δ-line on stress is shifted from the *TO* to the *NP* region of the spectrum. (a) Stress applied along the [001] direction: □—$N_D = 1.1\times10^{17}$ cm^{-3}, $T = 20$ K; ◇—5×10^{16} cm^{-3}, 20 K; △—1.1×10^{17} cm^{-3}, 2 K; ○—1.1×10^{17} cm^{-3}, 4.2 K; ●—7.5×10^{16} cm^{-3}, 4.2 K; ×—calculation carried out using formulae from Ref. 16. (b) Stress applied along the [111] direction, N_D—1.1×10^{17} cm^{-3}; ○—$T = 4.2$ K; △—$T = 2$ K, $W = 0.2$ W/cm^2.

suppose that ED_2 has an excited state whose interaction with the ground state also gives rise to the observed nonlinear dependence of the spectral position of the P_1 band on pressure. The dependence of the spectral position of the P_1'' band on pressure also indicates that for $R \sim 2a_E$ the electronic states of D_2, and consequently the inner electronic orbitals of ED_2, interact weakly among themselves (see Fig. 5(a)). This emission band appears in the RR spectra of deformed crystals (see curve 1 in Fig. 4(a)) and is related to the decay of ED_2, as a result of which two donors are formed, one of which is in an excited state.

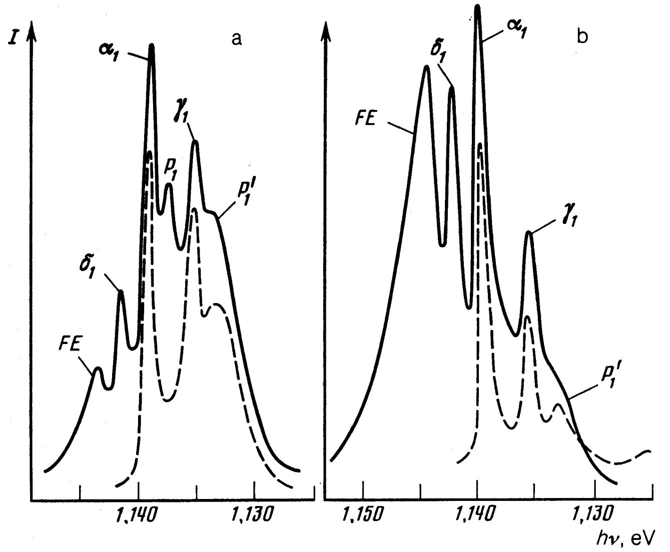

FIG. 6. *NP* (dashed curves) and *TO* (continuous) emission bands for excitons bound to phosphorous impurity atoms (N_D—7.5×10^{16} cm^{-3}) in silicon stressed along the [001] direction; $P = 1850$ kg/cm^2. *FE* is the free-exciton emission band. For convenience in comparison, the maxima of the α_1—*NP* and α_1—*TO* lines are superimposed; $W \approx 20$ W/cm^2, a—$T = 11$ K, b—$T = 20$ K.

As is clear from Fig. 5(a), the experimental dependence of the position of the P_1'' band on pressure agrees well with the calculated dependence (the crosses in Fig. 5(a)) of the spectral position of the emission line which arises from decay of *ED*, as a result of which a donor in a 1*s*-like state is created (the calculations were performed based on the formulae of Ref. 16). From the fact that these dependences are analogous, it follows that the donors in a D_2 are only slightly less separated than the isolated donors. The significant spatial extent of the ED_2 apparently is suggested also by the fact that the relative intensity of the ED_2 emission (see Fig. 6(a)) in the *TO* component of the RR spectrum is noticeably larger than in the *NP* component. Thus, in the intervals of concentration and temperature investigated by us, the main contribution to the RR is from ED_2, whose internal electron orbitals are close to donor-like.

We should note that we were unable to observe those *ED* and ED_2 decays which result in conversion of a donor to a 2*s*-like state; apparently, this is because these states interact strongly with the impurity atoms, since the size of a 2*s*-like state is approximately four times that of the 1*s*-like state.

The most difficult task is to explain the origin of the emission band P_1', which is present for even the weakest photoexcitation densities (curves 1,2 of Fig. 4) and whose relative intensity increases sharply both with an increase in impurity concentration and with an increase in pressure for samples compressed along the [001] and [112] directions. This band is observed in the RR spectra of silicon doped both with phosphorous and arsenic. As the temperature rises from 10 K to 20 K its intensity decreases linearly.

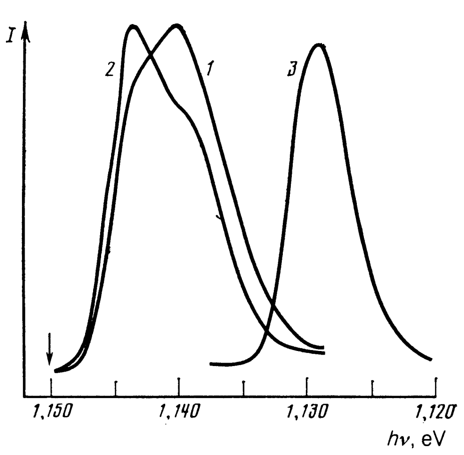

FIG. 7. Phononless emission bands of excitons bound to phosphorous atoms ($N_D = 4\times10^{17}$ cm^{-3}) in silicon subjected to uniaxial strain in the [001] direction at $T = 2$ K; 1—$W\approx15$ W/cm^2, $P = 0$ kg/cm^2; 2—$W\approx0.2$ W/cm^2, $P = 0$ kg/cm^2; 3—$W\approx15$ W/cm^2, $P = 2180$ kg/cm^2. The arrows indicate the position of the bound exciton at low phosphorous concentrations.

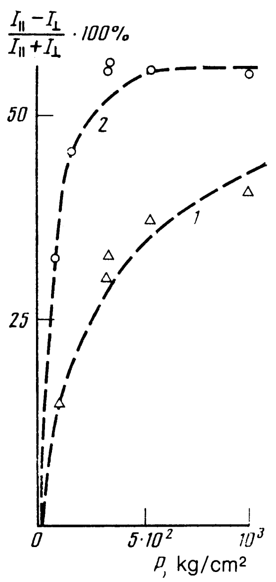

FIG. 8. Dependence of the degree of polarization of the *NP* emission band for excitons bound to phosphorous atoms ($N_D = 4\times10^{17}$ cm^{-3}) in silicon under stress applied along the [111] axis at $T = 2$ K; 1—$W\approx20$ W/cm^2, 2—$W\approx0.15$ W/cm^2.

The P_1' band can be explained by relating it to the decay of long-lived excited states of the ED_2 complexes, as a result of which a D_2 complex is created one of whose donors is in an excited state. In particular, this is suggested by the agreement of the experimental dependence of the spectral position of this band on pressure given in Fig. 5(a) with the analogous dependence (the γ-transition in *ED*) calculated by using the formulae given in Ref. 16. However, in order to understand why, e.g., the relative intensity of the P_1' band grows with increasing stress, it is necessary also to assume that the excited states of ED_2 are populated due to excitons hopping from the ground state of *ED* complexes. Such an assumption allows us to explain qualitatively the results we have obtained in our experiments.

Let us now discuss what from our point of view is the most natural explanation for the appearance of the P_1' band. To do so, let us once more turn to Fig. 2. From a comparison of curves 5 and 4 of Fig. 2 it is clear that as the phosphorous concentration increases up to $N_D \approx 2\times10^{17}$ cm^{-3}, the RR spectrum is restructured: the bands α_1, P_1 and P_2 disappear, and in place of the P_1' band a broad emission band appears, the position of whose maximum corresponds approximately to the position of the maximum for emission from electron-hole droplets (EHD) in silicon.[18] From Fig. 7 it is clear that the form of this band depends weakly on the photoexcitation density. However, the degree of polarization depends in a significant way on the density of exciting radiation (see Fig. 8). For low levels of photoexcitation the degree of polarization is saturated even in the low-pressure region, i.e., it behaves like the polarization of bound excitons.[19] For larger photoexcitation densities the dependence of the degree of polarization on pressure is analogous to that of EHD emission,[20] which suggests an insulator-to-metal transition of the excitons in the EIB. We thus conclude that at least for low photoexcitation densities the band we have investigated arises from recombination of excitons in the EIB.

The restructuring of the spectrum as N_D increases described above is explained in Ref. 13 as an Anderson transition in the bound-exciton system, which is characterized by the appearance of extended states along with weakly localized states in the EIB when $N_D > N_D^{\rm cr}$. According to Refs. 21, 12, the extended states appear when the magnitude of the fluctuations of the potential V of the impurity atoms become smaller than the width B of the exciton-impurity band, i.e., for $V/B\sim1$ where $B = 2zI$, $z = 2$, $I = 2\varepsilon_0\exp(-r_{\rm cr}/a_E)$. As a consequence of the appearance of extended states, the mobility of excitons in the EIB increases, leading to a decrease in their energy and thus to a shift in the emission maximum.

In an analogous way we can explain the changes in the RR spectrum we observed which occur when samples are uniaxially stressed along the [001] and [112] axes. When the stress applied to the crystals exceeds 10^3 kg(force)/cm^2, it causes a decrease in ε_0 by roughly a factor of three, and thus a significant decrease in ΔE and in the spacing between levels in the EIB. For a given temperature this will lead to a noticeable increase in the exciton mobility in the EIB. The motion of excitons among the impurity atoms at low temperatures, accompanied by relaxation of their energy, gives rise to a change in their energy distribution within the EIB: the number of excitons with high energy decreases while the number with low energy increases. This change in the exciton distribution within the EIB explains the rise in intensity of the P_1' band that we observed along with the simultaneous decrease in intensity of the P_1 band in the RR spectrum of silicon doped with phosphorous or arsenic, which are shown respectively in Figs. 4(a) and 4(b). It is obvious that this process is most clearly marked at concentrations such that $r_{\rm av}\sim a_E$. The change in the spectral position of the P_1' band observed as the pressure increases, which is evident from its proximity to the α_1 line, is explained by the decrease in the width of the EIB. The drop in intensity of the P_1' band as the temperature rises is explained by the fact that at high temperatures, as we showed above, the contribution of the various D_n atomic groups to the RR is approximately proportional to the corresponding density of states in the EIB, which for groups of atoms corresponding to the P_1' band is small. We note that the appearance of the P_1' band in the case of silicon samples doped with arsenic occurs for N_D larger than in the case of phosphorous-doped samples. From these considerations we can explain the constriction of the emission bands of phosphorous-doped silicon for $N_D > N_D^{\rm cr}$ which is shown in Fig. 7, which is observed when samples are stressed in the [001] direction.

5. CONCLUSION

A characteristic feature of a system of the sort under discussion, i.e., a system of excitons bound to impurity atoms, is the absence of a well-defined relation between the EIB density of states and the RR spectral distribution, which is caused by the absence (in the usual sense) of exciton localization in the EIB; it is this feature which makes its investigation difficult. We also note that a further source of complexity in the investigation of EIB is the absence of even a semiquantitative theory which can describe the excitonic energy transfer and distribution of the density of states in the EIB. For this reason, some of the conclusions reached in this paper are ambiguous and lacking in precision. In addition, concepts such as "isolated impurity atoms" and "isolated pair of impurity atoms", which are widely used to explain the experimental results, partially lose their meaning for concentrations where $r_{\rm av} \sim e_E$. One of the basic results of this paper is the suggestion that the energy of excitonic excitations can be transferred from one group of atoms to another; the use of uniaxial strain allows us to make this process controllable. In this paper we have investigated the EIB which appears in crystals of phosphorous-and-arsenic-doped silicon. It would be of undoubted interest, in our view, to study the EIB in silicon crystals doped simultaneously with two kinds of impurities, e.g., phosphorous and arsenic or phosphorous and boron. In such an EIB it might be possible to bring about energy transfer from impurity atoms of one type to impurity atoms of the other type.

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[1)] In this article we denote by $E_k D_n$ a system consisting of n neutral donors and k excitons bound to them; a system consisting of neutral donors alone we refer to as D_n.

[2)] Crystals of silicon obtained by the Czochralski method cannot be used to determine the functions shown in Fig. 1, because they have large amounts of oxygen in them, which according to Ref. 15 causes strong broadening of the α_1-line.

[3)] We have adopted the terminology we used in Ref. 16.

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