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Multiparticle impurity complexes in uniaxially deformed silicon doped with phosphorus

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The luminescence spectra of multiparticle impurity complexes were investigated at low temperatures in silicon doped with phosphorus and compressed along the [100] direction. It is shown that all the main features of the spectra—the character of line splitting, the line shifts, and the appearance of new lines upon deformation—can be explained on the basis of the shell model of multiparticle complexes.

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Many recent papers are devoted to the physical nature of the series of narrow luminescence lines[1] produced at low temperatures in silicon doped with elements of groups III and V and located in the energy region directly behind the emission line of the bound exciton. According to the interpretation proposed by us earlier[1] these lines are produced when electrons and holes recombine in the multiparticle complexes B_m that are produced as a result of successive binding of m excitons with the impurity atoms. Investigations of the kinetics of the formation and decay of the complexes[2-4] have confirmed this interpretation. However, in subsequent studies[5-7] of the splitting of these lines in magnetic fields and under uniaxial deformation, doubts were cast on the existence of multiparticle complexes. In the present paper, using as an example silicon doped with phosphorus, we show that the complex emission spectrum observed under uniaxial deformation agrees well with the shell model of multiparticle impurity complexes, which was proposed by Kirczenow.[8]

It should be noted that the investigation of the influence of uniaxial compression on the emission spectra of the complexes encounters at least two difficulties. The first is connected with the need for producing a uniform strain that does not cause additional splitting or broadening of the emission lines. In the present study, uniformity of the strain was attained by using long silicon samples measuring ~20×2×2 mm and having hemispherical ends. The pressure P on these ends were applied through lines of a 50% Pb+50% Sn alloy that solidifies at low temperatures.[9] The uniformity of the strain in our was attested by the absence of substantial broadening of the lines up to $P \approx 2000$ kgf/cm² when a large area of the crystal with dimension 0.2×7 mm was excited with an argon laser.

The second difficulty arises in the line identification. For reliable identification we used the method of constant additional illumination.[10] To this end we focused on the sample surface, besides the modulated exciting radiation, the beam of a second argon laser. This unmodulated radiation produced a certain stationary concentration of the B_m complexes. As shown in Refs. 1–4, the concentration of complexes with different m depends in nonlinear fashion and in various ways on the excitation levels. Therefore application of constant additional illumination altered the ratio of the amplitudes of the lines of the modulated part of the radiation registered by our apparatus.[10] The fact that the amplitudes of the groups of lines changed in identical fashion was evidence that these lines are connected with one and the same complex B_m.

Figure 1 shows the no-phonon (*NP*) component and the *TA* component of the emission of silicon doped with phosphorus and different pressures in the [100] direction. The emission spectra of the *TA* and *TO* components are similar, and the *TO* spectrum is therefore not shown in Fig. 1. The line designations correspond to the type of radiative transitions assumed in the shell model (Ref. 8). [1)] A number of lines were identified by using constant additional illumination. Thus the onset of the β_2'' line in the decay of the complex B_2 is indicated by the increase of the intensity of this line when the additional illumination is turned on; this increase is identical with that of the α'' line (Fig. 2). The intensity of the line $\alpha_1^{\Gamma_3}$ decreases following the additional illumination in the same way as the intensity of the α_1'' line (Fig. 3), thus indicating that it is produced in the decay of the bound exciton B_1. The spectral positions of the different emission lines of the complexes as functions of the applied pressure P are shown in Fig. 4.

We examine now in greater detail the change of the energy spectrum of multiparticle complexes bound to

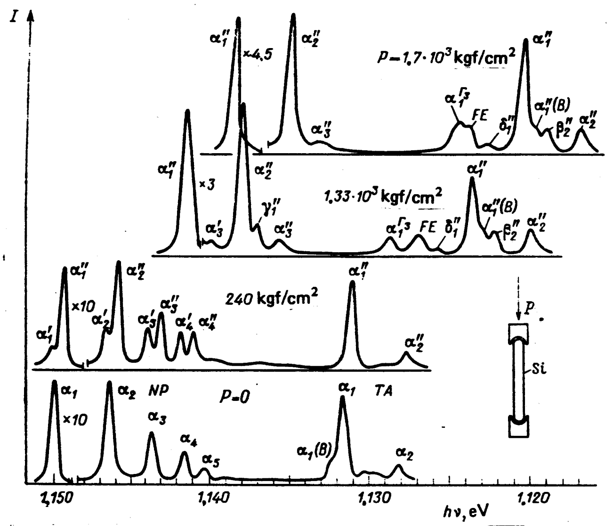

FIG. 1. *NP* and *TA* component of emission spectrum of multiparticle impurity complexes of silicon doped with phosphorous at a concentration 7×10^{14} cm^{-3}, at 4.2 K and at various pressures *P* in the [100] direction. The line $\alpha_1(B)$ is due to a residue of boron impurity.

phosphorus atoms, under uniaxial compression. The final state in the decay of the bound exciton B_1 are a neutral donor in the ground or excited states. In the absence of deformation, the ground state of the phosphorus atom is split into three states: Γ_1 (singlet), Γ_5 (triplet), and Γ_3 (doublet). The energy spacing between the levels Γ_1 and Γ_5 is $\Delta_1^0=11.6$ meV, and between Γ_1 and Γ_3 we have $\Delta_2^0=13.0$ meV (see e.g., Ref. 11). When silicon is compressed in the [100] direction[12] the state Γ_5 is split into a doublet $\Gamma_5(2)$ that shifts like $\Delta_1^0-\frac{1}{3}\Delta_c$, and a singlet $\Gamma_5(1)$ that shifts like $\Delta_1^0+\frac{2}{3}\Delta_c$. The state $\Gamma_1(1)$ which corresponds to the singlet state Γ_1 of the underformed crystal shifts like $\frac{1}{6}\Delta_c+\frac{1}{2}\Delta_2^0-\frac{1}{2}[\Delta_c^2+(\Delta_2^0)^2+\frac{2}{3}\Delta_c\Delta_2^0]^{1/2}$. The singlet states $\Gamma_3(2)$ and $\Gamma_3(1)$, which correspond to the doublet state Γ_3 in the absence of deformation, are shifted like $\Delta_2^0-\frac{1}{3}\Delta_c$ and $\frac{1}{6}\Delta_c+\frac{1}{2}\Delta_2^0+\frac{1}{2}[\Delta_c^2+(\Delta_2^0)^2+\frac{2}{3}\Delta_c\Delta_2^0]^{1/2}$. The wave functions of the states $\Gamma_1(1)$ and $\Gamma_3(1)$ are then linear combinations of the symmetry wave functions of Γ_1 and Γ_3 (Ref. 12). Here Δ_c is the conduction-band splitting and is negative in the case of a compression strain. The value of Δ_c is approximately equal to the shift of the emission line of the free exciton *FE* (Ref. 13) and can be directly determined from Fig. 4. The expressions presented make it possible to calculate the energies of the excited states of the donor under

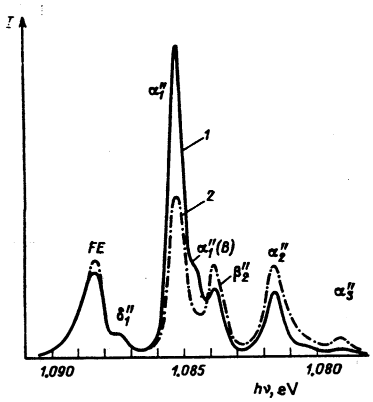

FIG. 2. *TO* component of emission spectrum of phosphorus-doped silicon at 4.2 K and at a pressure $P=1130$ kgf/cm²: 1—recorded without constant additional illumination, 2—with constant illumination.

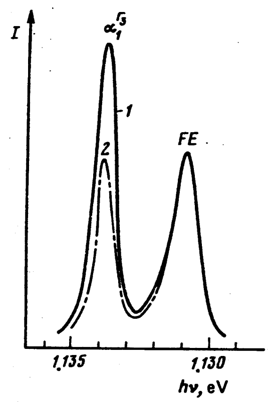

FIG. 3. *NP* emission line $\alpha_1^{\Gamma_3}$ and *TA* component of the emission of a free exciton (*FE*) of silicon doped with phosphorus ([P] = 7×10^{14} cm^{-3}), at 4.2 K and a pressure $P=830$ kgf/cm²: 1—without constant illumination, 2—with constant illumination.

strain.

One can expect the emission spectrum of the bound exciton B_1 to reveal lines corresponding to donor production not only in a ground state but also in excited states. These lines should be shifted relative to the line α_1'' corresponding to production of a donor in the ground state $\Gamma_1(1)$ by an amount equal to the donor excitation energy. For the line $\alpha_1^{\Gamma_5}$, which corresponds to donor production in the state $\Gamma_5(1)$, this shift should be equal to

$$\Delta_1^0(P)=\Delta_1^0-{}^1/_2\Delta_0^2+{}^1/_2\Delta_c+{}^1/_2[\Delta_c^2+(\Delta_2^0)^2+{}^2/_3\Delta_c\Delta_2^0]^{1/2},$$

and for the line $\alpha_1^{\Gamma_3}$ corresponding to production of a donor in the state $\Gamma_3(1)$, it is equal to

$$\Delta_2^0(P)=[\Delta_c^2+(\Delta_2^0)^2+{}^2/_3\Delta_c\Delta_2^0]^{1/2}.$$

The quantities $\Delta_1^0(P)$ and $\Delta_2^0(P)$ calculated in this manner are marked in Fig. 4 by dark circles. It is seen from the figure that the line $\alpha_1^{\Gamma_3}$ is actually observed in the spectrum and its position agrees well with the calculation. This line is excited only under deformation.

According to the shell model,[8] the electronic states in multiparticle impurity complexes are analogous to donor states. The electrons fill in succession the shells

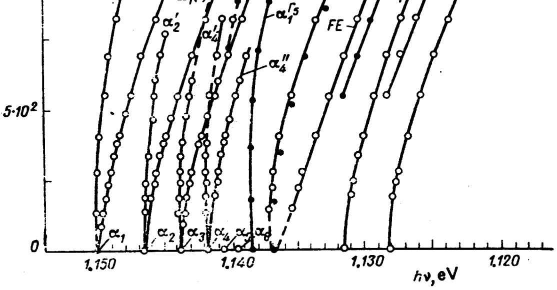

FIG. 4. Dependence of the spectral position of the *NP* and *TA* emission lines of silicon doped with phosphorus ([P] = 7×10^{14} cm^{-3}) on the pressure *P* in the [100] direction. Light circles—experiment, dark—calculation (see the text).

with the symmetry of the wave functions Γ_1 and Γ_3, Γ_5 (the states Γ_3 and Γ_5 in the absence of deformation are assumed to be very little separated and are designated as the state Γ_{35}). The holes occupy primarily the fourfold degenerate shell Γ_8 with the symmetry of the wave functions of the top of the valence band of silicon. Lines of the type α_m appear upon recombination of an electron from shell Γ_1 of the complex B_m with one of the holes of the shell Γ_8 to produce a complex B_{m-1} in the excited state:

$$\{2\Gamma_1, (m-1)\Gamma_{35}; m\Gamma_8\} \to \{\Gamma_1, (m-1)\Gamma_{35}; (m-1)\Gamma_8\}$$

(for $m \geqslant 2$). Because of the strong interaction between the cell Γ_1 and the central cell, these transitions are observed not only in the phonon spectral components, but also in the *NP* ones. Lines of the type β_m appear when the complexes B_m decay to produce complexes B_{m-1} in the ground state

$$\{2\Gamma_1, (m-1)\Gamma_{35}; m\Gamma_8\} \to \{2\Gamma_1, (m-2)\Gamma_{35}; (m-1)\Gamma_8\}.$$

These lines are observed only in phonon components.

It is seen from the presented scheme that within the shell-model approximation the electron and hole configurations of the complex B_m are preserved upon decay for the carriers that remain in the complex B_{m-1}. The emission lines corresponding to transitions with change of symmetry of the carrier wave functions are not observed in experiment, because of the low probability of such transitions.[8,14] One should expect that under uniaxial deformation, just as in the case of a donor, the states $\Gamma_1(1)$ and $\Gamma_3(1)$ of the complexes will correspond to mixed wave functions of symmetry Γ_1 and Γ_3. This can lead to the appearance of new emission lines of the complexes in the deformed silicon. Actually, in the absence of deformation, a decay of the type

$$\{2\Gamma_1; \Gamma_8\} \to \{\Gamma_3\}$$

is possible only with change of the symmetry of the wave function of the remaining electron and has therefore low probability. In the case of deformation, the states $\Gamma_1(1)$ and $\Gamma_3(1)$ correspond to combinations of wave functions of the type Γ_1 and Γ_3, the indicated transition ceases to be forbidden, and this gives rise to excitation of the line $\alpha_1^{\Gamma_3}$. The donor state $\Gamma_5(1)$ corresponds to the wave function of symmetry Γ_5, so that the process

$$\{2\Gamma_1(1); \Gamma_8\} \to \{\Gamma_5(1)\}$$

remains of low probability also in deformed silicon. We assume that this is why we were unable to observe the $\alpha_1^{\Gamma_5}$ emission line corresponding to this transition.

In the absence of deformation the emission line β_2 practically coincides with the more intense line α_1 (Ref. 14), but under sufficiently strong compression the line β_2'' is well resolved both in the *TA* components (Figs. 1 and 4) and in the *TO* components (Fig. 2) of the spectrum. The reason is that the shifts of the lines α_1'' and β_2'' have different dependences on the pressure P in the region of small P. The sublinear dependence of the shift on the pressure in the [100] direction is observed for all the lines of the α series, thus indicating that the shift of the levels $\Gamma_1(1)$ is nonlinear in the pressure for all the complexes B_m. The distance Δ_1^1 between the lines β_2'' and α_2'' corresponds to the difference between the energies of the ground and excited states of the complex B_1. This is precisely the distance also between the lines δ_1'' and α_1'', in both the *TA* (Fig. 4) and *TO* components of the spectrum. It follows therefore that the line δ_1'' appears when the complex B_1 decays from an excited state to produce a donor in the ground state:

$$\{\Gamma_1(1), \Gamma_5(1); \Gamma_8\} \to \{\Gamma_1(1)\}.$$

The population of the level $\Gamma_5(1)$ should not be nonequilibrium in this case and should result, for example, from the decay of the complexes B_2 in transitions of type α_2.

One can expect the spectrum to contain, besides the δ_1'' line, also the γ_1'' line which is produced when B_1 decays from an excited state to produce a donor in an excited state:

$$\{\Gamma_1(1), \Gamma_5(1); \Gamma_8\} \to \{\Gamma_5(1)\}.$$

The distance between lines γ_1'' and $\alpha_1^{\Gamma_5}$ should also be equal to Δ_1^1. This line is indeed well observed in the *NP* component of the spectrum (Figs. 1 and 4). The correctness of this interpretation is confirmed by the fact that the line γ_1'' is not suppressed by the constant additional illumination and is excited when the temperature is increased. The last circumstance is due to the additional thermal population of the $\Gamma_5(1)$ level of the complex B_1. At an approximate temperature 15 K the dominant lines in the emission spectrum of deformed silicon are α_1'' and γ_1'' (Fig. 5).

We have so far taken into account only the splitting of the electronic levels of the complexes. Unaxial deformation leads to a splitting of the fourfold degenerate hole level Γ_8 into two doubly degenerate levels Γ_6 and Γ_7, in each of which it is possible to place two holes. For this reason, each of the emission lines of the complexes should, generally speaking, split into two. Since the complexes B_1 and B_2 contain respectively one and two holes, these holes can be placed on the upper level Γ_7, and the population of the lower hole level Γ_6 is possible only on account of thermal excitation.[10] In fact the intensity of the emission lines α_1' and α_2' decreases rapidly with increasing pressure or with decreasing tempera-

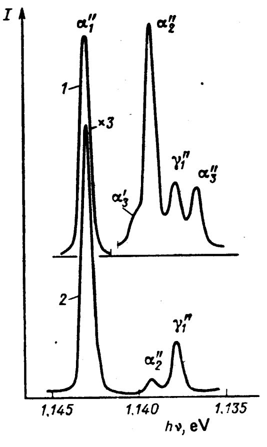

FIG. 5. *NP* component of emission of silicon doped with phosphorus at pressure $P = 1200$ kgf/cm^2 and at temperatures $T \approx 1$ K (1) and ≈ 15 K (2).

ture. Since the emission line β_2 is resolved at relatively high pressures, we succeeded in observing only its β_2'' component, corresponding to recombination of a hole on the Γ_7 level.

The complexes B_3 and B_4 contain respectively 3 and 4 holes, of which only two can be located on the Γ_7 level. The ratio of the populations of the levels Γ_7 and Γ_6 should be 2 : 1 and 1 : 1 and should depend little on temperature. Actually, it is seen from Fig. 4 that in the region of low pressure there are observed in the *NP* components the doublets α_3'', α_3' and α_4'', α_4' with an intensity ratio close to those indicated above. Just as under compression in the [111] direction,[10,16] the splitting of the α-series lines is proportional to the pressure and corresponds approximately to the splitting of the valence band of silicon. At high pressures the intensity of the α_4 lines, and later also of the α_3 lines, decreases strongly. The reason is that if the hole level Γ_8 is subjected to strong splitting (4–5 meV) the existence of the complexes B_4 and B_3 becomes energywise unfavored.[10] We note that the intensity of the α_1'' line also is decreased by deformation, possibly as a result of the opening of the aforementioned new channels of recombination of the complexes B_1.

We were unable to establish a pressure dependence of the positions and splittings of the lines β_3 and β_4. These lines are well observed in phosphorus-doped silicon only in the absence of deformation.[10,14] Since the β-series lines appear only in the phonon components of the spectrum, they have a larger natural width, and at low pressures the splitting of these lines cannot be resolved. At high pressures the lines β_3 and β_4 begin to overlap the strong lines β_2 and β_3.

We note in conclusion that the deduction that the experimental data contradict the results[6,7] of the shell model of multiparticle impurity complexes is unfounded. First, the splitting of the emission lines of the complexes, both in the [111] direction[10,16] and in the [100] direction, obtained in Refs. 15 and 16 as well as in the present study, is much simpler (doublets) than in Ref. 6 (quartets). Therefore the results given in Ref. 6 are doubtful. Further, as already noted, one can hardly establish reliably the character of the splitting of the lines β_3 and β_4 against the background of the strong α-series lines and, at any rate, observed all the components that occur under deformation. For the same reason, a comparison of the kinetics of the relaxation of the emission of the lines of the α and β series is hardly advisable all the more because the difference between the relaxation times of the lines with $m \geq 2$ is negligible [105–158 nsec (Ref. 7)]. Moreover, the relatively weak lines of the β series are registered against the background of the emission of the electron-hole drops,[1] whose lifetimes are of the same order (141 nsec according to Ref. 17). It is quite probable that this circumstance determines to a considerable degree the experimentally measured relaxation time of the emission lines of multiparticle complexes in phonon components of the spectrum.

[1)] The subscript corresponds to the number of the decaying complex m, including also the case of the β-series lines, whereas in Refs. 7 and 8 the β-series lines are labeled $m-1$.

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