Evidence for Bound Multiple-Exciton Complexes in Silicon

R. Sauer

Physikalisches Institut der Universität, 4. Teilinstitut, D 7 Stuttgart 1, West Germany

At low temperatures and medium excitation levels, a series of emission lines was dis-
covered in silicon slightly doped with phosphorus or boron. Beginning with the bound ex-
citon, the series converges towards the energetic position of the maximum of emission
of the condensed electron-hole state. The sharpness of these lines and the characteristic
dependence of their intensities on doping level and on excitation level suggest a model of
multiple-exciton complexes bound to the impurities.

It is well known that in pure germanium and
silicon a phase transition from an "exciton gas"
of free excitons (FE) to a "condensate" of elec-
tron-hole droplets (EHD) takes place at low tem-
perature and increasing high excitation level.[1-6]
In silicon weakly doped with boron or phosphorus
a few emission lines with energies of some meV
below the bound-exciton (BE) line have been re-
ported.[6] From the idea of a phase transition the
preliminary concept originated that impurities
serve as condensation centers. The first experi-
mental hint for such a concept came from the
interplay of the above mentioned emission lines
with the EHD luminescence depending on excita-
tion level.[6] In this paper a series of bound ex-
citon states is reported suggesting that impurities
can bind a whole series of intermediate "multi-
ple-exciton states" containing the single BE and
the EHD state as the beginning and the end of the
series.

Samples of Si differently doped with B or P
were excited with a krypton ion laser along a lin-
ear crystal edge parallel to the entrance slit of
the monochromator. This technique strongly en-
hanced the luminescence signal and allowed high-
resolution measurements even at low excitation
levels. Highly structured emission spectra were
obtained for Si:B and Si:P, both as TO-phonon
assisted and as no-phonon (NP) spectra. Except
for the absolute magnitude of the luminescence
signal, these spectra from the crystal edge were
identical with those from the center of the crys-
tal surface and they did not vary with different
etching procedures. On the other hand, the lines
of the spectra are closely related to the doping
levels of the samples and to the luminescence of
the bound exciton. Thus surface effects should
be excluded. Since the intensity ratios of the BE
lines in the NP relative to that in the TO spectra
are $\ll 1$ and ≈ 0.4 for boron and phosphorus, re-
spectively,[7] it was convenient to evaluate only the

TO spectra for B and the NP spectra for P. Fig-
ure 1 shows the emission line spectra for the
case of intermediate excitation level, consisting
of six and five lines for phosphorus and boron,
respectively. Beginning with the BE, the lines
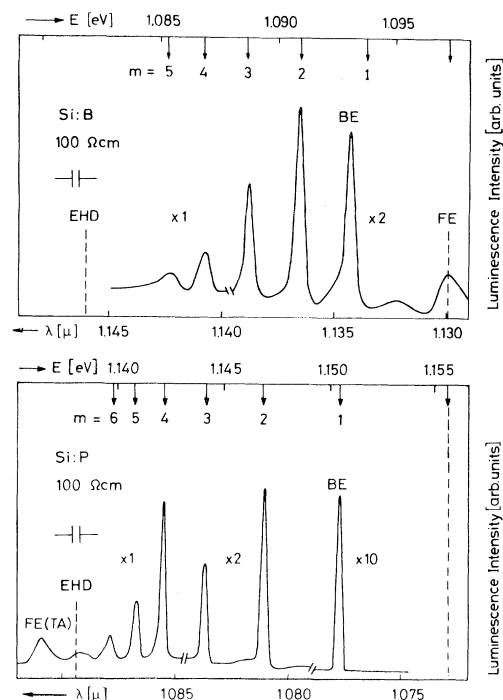are labeled $m = 1, 2, \cdots$. Because of the enlarged

FIG. 1. Emission spectra of Si:B with TO phonon
and of Si:P without phonon assistance. Excitation in-
tensity 7.5 W cm^{-2}, $T = 2$ K. The dashed lines indicate
the positions of the FE's and the maxima of EHD emis-
sion. In Si:P (NP), the FE does not really appear; how-
ever, its position is known from the phonon-assisted
FE spectrum. The EHD emission in the NP spectrum
only appears at higher doping levels and under high ex-
citation (Ref. 8). The arrows mark the calculated val-
ues $h\nu_m^*$ given by $h\nu_m^* = -18.5[1 - \text{expt}(-0.21m)]$ meV
for Si:B and $h\nu_m^* = -18.5[1 - \text{expt}(-0.32m)]$ meV for
Si:P.

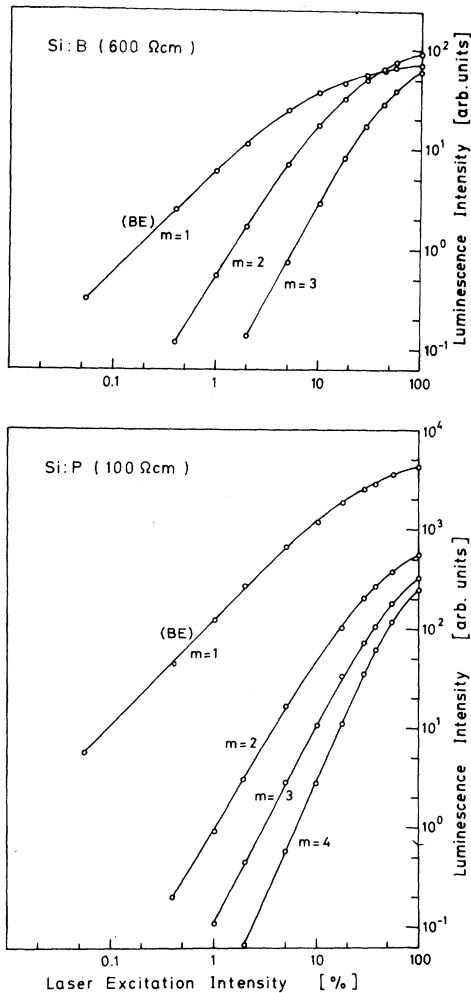FIG. 2. Luminescence intensities of the complexes for Si:B and Si:P at $T = 2$ K versus laser excitation level ($100\% = 5$ W cm^{-2}).

FIG. 3. Luminescence intensities of the complexes for differently doped Si:P and Si:B versus the complex number m. Excitation level 5 W cm^{-2} at $T = 2$ K.

number of observed lines and the high resolution we can establish that the lines form a series in both spectra: The spacings between the lines diminish with lower energy and both spectra converge to an energy not too far from the maximum of the EHD edmission band which emerges at higher excitation (corresponding to focused laser beam) at 15.4 meV below the FE line. The lines of the series are extremely sharp. Their half-widths are comparable to those of the BE's (ΔE < 0.05 meV in Si:P, 100 Ω cm; $\Delta E \approx 0.4$ meV in Si:B, 100 Ω cm), increasing slightly for the lines of lower energy. Therefore the initial and final states corresponding to the observed transitions should be bound states.

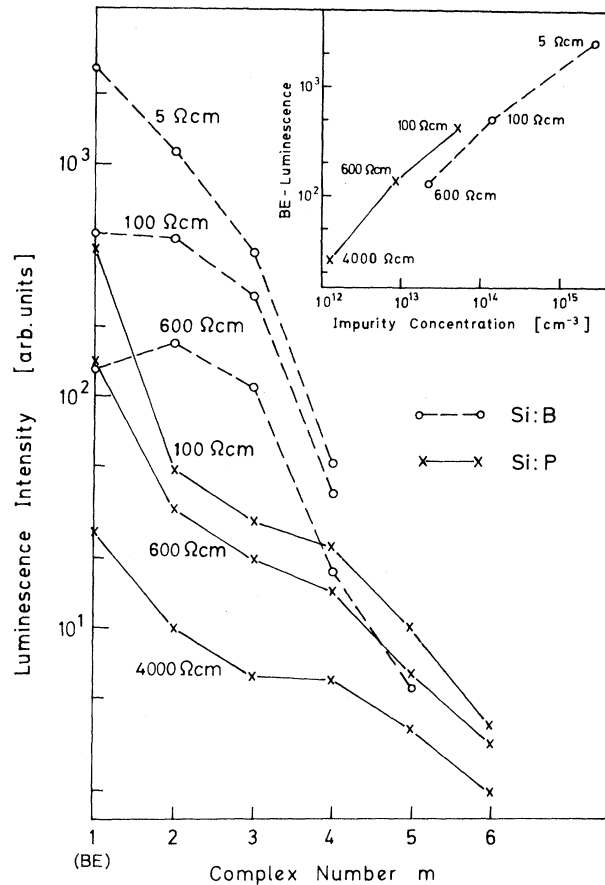Figure 2 shows at constant doping level the dependence of the luminescence intensities of the

lines on the excitation level. At small values of excitation, the luminescence of all lines grows linearly in the double-logarithmic diagram but the slopes of the curves increase with growing label number m of the lines. At higher values of excitation, the intensities saturate, first for the BE ($m = 1$) and successively for the following lines. The different slopes of the lines exclude a model with common initial states for the different observed transitions.

At constant excitation level, the intensities of the lines depend on the doping level (Fig. 3); when it is increased the luminescence intensities of all lines of a series become stronger: but those of the low-energy lines grow less strongly than those of the high-energy lines. The intensity of the BE line versus the doping level is shown in the inset of Fig. 3.

The results presented can qualitatively be interpreted by assuming the existence of complexes

which bind one or more FE's. The following model is proposed in detail: Depending on the number of created FE's per unit volume, bound exciton complexes build up by successive capture of FE's at neutral impurities. A complex consisting of m bound excitons and characterized by the complex number m can increase by capture of another FE thus becoming an $m + 1$ complex; it may decrease by the decay of one exciton resulting in a complex with $m - 1$ bound particles. The observed photon energy $h\nu_m$ is the difference between the energies of the initial and final states:

$$h\nu_m = E_g - E_{FE} - E_m = h\nu_{FE} - E_m,$$

where E_{FE} is the binding energy of the FE and E_m that of an exciton in the m complex. Thus, the spacing between the mth line $h\nu_m$ and the FE line directly measures the binding energy E_m. According to the model, the binding energies $E_2, E_3, \ldots$ are astonishingly large. An understanding of this circumstance needs theoretical calculations of these energies.

The experimental values of $h\nu_m$ can excellently be fitted relative to the FE line by the "series formulas" $h\nu_m* = -18.5[1 - \exp(-0.21m)]$ meV for Si:B (except for the BE line) and $h\nu_m* = -18.5 \times [1 - \exp(-0.32m)]$ meV for Si:P (Fig. 1), $h\nu_0*$ $= 0$ corresponds to the FE line.

An increasing excitation levels, the average number m of excitons bound to the complexes will grow, finally resulting in drops of electrons and holes where the influence of the original condensation center becomes negligible. In this case, the connection between E_m and the binding energy per electron-hole pair in the condensate may roughly be the following: For small numbers m of bound excitons, the emission is sharp since the transitions occur between "equilibrium" states without relaxation and thus $h\nu_m* = E_m$. With an increasing number m of bound particles, the emission will broaden because of relaxation of the final state after photon emission (as is the case for radiative recombination in the EHD state) resulting in the inequality $h\nu_m = h\nu_{FE} - h\nu_m*$ $< h\nu_{FE} - E_m$. Simultaneously the interaction of electrons and holes with the impurity averaged over the number m of particles becomes negligible. Thus the values E_m may approach the binding energy per electron-hole pair in the condensate which corresponds to the upper edge of the EHD band. The photon energies $h\nu_m$ on the other hand converge to $h\bar{\nu}$, the average photon energy from the EHD; $h\bar{\nu}$ differs from the upper edge by $\frac{2}{5}E_F$ (E_F is the sum of the Fermi energies of electrons

and holes) and was in the present work obtained to be ≈ 16.7 meV below the FE line which is in sufficient agreement with $h\nu_\infty* = -18.5$ meV. This situation has to be investigated in more detail in the future.

In the adopted model and at steady-state conditions, the equilibrium between the concentration of the m complexes, the density N, and the generation rate g of FE's is described by the rate equations

$$0 = \partial n_m / \partial t = CNn_{m-1} - CNn_m + (1/\tau_2)(m+1)n_{m+1}$$
$$- (1/\tau_2)mn_m,$$

$$0 = \partial N/\partial t = g - (1/\tau_1)N - \sum_m CNn_m.$$

C is the capture probability of FE's and τ_2 the lifetime of the excitons bound to the complexes: for simplicity, C and τ_2 are adopted to be independent of the complex number. τ_1 is the lifetime of FE's. Using the normalizing condition $\sum_m n_m$ $= N_d$ (N_d is the impurity concentration), the solutions are $n_m = (N_d/m!)\exp(-C\tau_2N)(C\tau_2N)^m$ and N $= (1/\tau_1 + CN_d)^{-1}g$. The luminescence intensities I_m are assumed to be $I_m \sim mn_m$. The expressions for I_m can qualitatively account for the experimental data: At constant doping level and as a function of excitation level g, they typically show the character of the curves in Fig. 2. At constant excitation intensity and as a function of complex number m, they reproduce curves of the type shown in Fig. 3, where the characteristic variation from "boronlike" to "phosphoruslike" curves at similar doping levels is governed by the magnitude of $C\tau_2$. The step of the curves for Si:P in Fig. 3 at $m = 3, 4$ cannot be explained by the model.

Finally, alternative models are considered. The binding of FE's to clusters of one, two, or more impurities is excluded: Isolated impurites should be favored at low impurity concentrations, whereas at increasing concentrations pairs of impurities, etc. should become more probable. This is contradictory to the measured dependence of the luminescence intensity on the doping level. To our knowledge, experimental evidence for clusters of impurities has never been reported at the small impurity concentrations discussed. The decay of excitons bound to excited or valley-orbit–split impurity states is also excluded for energetic reasons and since in this case the well-known structure of boron and phosphorus states should be discernible in the observed spectra. This argument is also true for a model where one of two excitons bound to the same impurity

decays, lifting the residual exciton to a valley-orbit—split impurity state. The decay of BE's where the impurities are left in an excited state cannot account for the lines as the observed photon energies would be considerably lower. The participation of additional impurities such as isoelectronic centers is improbable since the luminescence of all lines is closely related to that of the excitons bound to boron or phosphorus.

In conclusion, the model of bound multiple-exciton complexes in silicon is in qualitative agreement with the experimental data of the new lines. Obvious alternative models are contradictory to the experiments. The model proposed does not contain microscopic details of the binding mechanism. With increasing complex number m the physical concept will gradually change from that of an excitonic state to that of a condensed electron-hole plasma

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Observation of an Underdamped "Soft" Mode in Potassium Dihydrogen Phosphate*

P. S. Peercy
Sandia Laboratories, Albuquerque, New Mexico 87115
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The pressure dependence of the coupled-mode spectra in potassium dihydrogen phosphase (KDP) was measured at room temperature for hydrostatic pressures from 0 to 9.3 kbar. The soft mode, which is overdamped for all temperatures at atmospheric pressure, becomes underdamped for pressures $\gtrsim$ 6 kbar. This is the first observation of an underdamped soft mode for a crystal of the KDP class and resolves the question of whether the excitation should be considered as diffusive or oscillatory in nature.

We report the observation of an underdamped "soft" mode in potassium dihydrogen phosphate (KDP). The mode was made underdamped by the application of hydrostatic pressure ($\gtrsim$ 6 kbar) at room temperature. This is the first observation of an actual peak in the spectral response of the soft mode for any member of the KDP class of ferroelectrics and reveals important information concerning the nature of this excitation. A brief discussion of the previous work relevant to this work is given before presenting the results of these measurements.

Since the original observation of Raman scattering from the soft ("proton") mode in KDP by Kaminow and Damen,[1] several authors have investigated this mode in KDP, as well as in many of its isomorphs. Wilson[2] and Wilson and Cummins[3]

made detailed measurements of the temperature and electric field dependences of the Raman spectra of KDP in an attempt to find conditions for which this mode is underdamped. Their measurements showed the mode to be overdamped at all temperatures; furthermore, these measurements suggested that, at least near the transition temperature, the response of this mode might be relaxational rather than oscillatory in nature. More recently, Reese, Fritz, and Cummins[4] measured the soft-optic—acoustic mode interactions in deuterated KDP (KD*P) and concluded that the soft mode response in KD*P corresponds to a diffusive excitation rather than a propageting mode.

An important aspect of the soft mode for the KDP crystal class is the coupling of this mode with another optic mode of the same symmetry.