

BOUND MULTIPLE-EXCITON COMPLEXES IN SILICON AT HIGH DOPING LEVELS?

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The well known excitonic and condensed electron–hole state emission spectra of silicon are substantially modified in a narrow typical range of higher doping levels. The new spectra and their dependence on excitation level can be interpreted partially by the existence of bound multiple-exciton complexes of predominantly higher order. Some features are not yet understood.

THE EMISSION spectrum of 'pure' silicon at low temperatures and high excitation levels is dominated by the broad luminescence band of the condensed electron–hole state (EHD) and the free exciton (FE) line.¹ Silicon doped with phosphorus or boron up to concentrations of 10^{15} cm^{-3} shows at low excitation levels besides the FE-line the sharp bound exciton (BE) emission. With increasing excitation level, sharp additional lines arise below the BE-line.^{2,3} As previously described in detail, their characteristic properties have induced a model of multiple-excitons bound to the neutral impurities;³ the impurities serve as nucleation centers supporting the phase transition from the FE-gas to the liquid of electron–hole drops.⁴

In this work we report a new type of emission spectrum which is revealed by silicon doped with donors or acceptors at a particular narrow range of high impurity concentrations at medium excitation levels and at low temperatures. The typical doping level where the new features prevail is about $7 \times 10^{16} \text{ cm}^{-3}$ for acceptors and $1.5 \times 10^{17} \text{ cm}^{-3}$ for donors. Typical excitation densities are a few Wcm^{-2} corresponding to an unfocused exciting laser beam of $\approx 400 \text{ mW}$ cw-power. For the case of Si:B, the new spectra are shown in Fig. 1 at low excitation level. The curves at 0.37 or 2.2 Wcm^{-2} for example consist of a slightly structured emission band which is asymmetric with a steep slope on its high energy side and which is

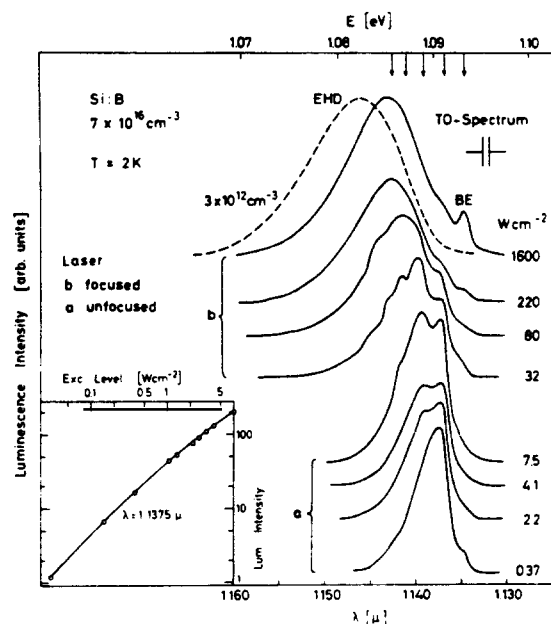


FIG. 1. Emission spectra of Si:B ($7 \times 10^{16} \text{ cm}^{-3}$) dependent on excitation density. The EHD-spectrum of a weakly doped sample is given for comparison (dashed curve). Amplitudes are arbitrary, the intensities of the band at $\lambda = 1.1375 \mu$ versus excitation level are shown in the insert. The arrows mark the experimental positions of the sharp multiple-exciton lines in less doped samples.³

much narrower than the EHD-emission band. The energetic position of its maximum is between the BE-line and the maximum of EHD-luminescence. When lowering the excitation level to 0.03 Wcm^{-2} , this band essentially does not change in lineshape. Its intensity depends roughly linearly on the excitation level which is shown in the insert of Fig. 1. When increasing excitation levels, peaks grow successively from the low energy wing of the band until they finally blur and form a nearly structureless broad band at lower maximum energy (220 or 1600 Wcm^{-2}). This band is probably due to EHD-emission, but its halfwidth is smaller and its maximum energy is higher by about 3 meV than that of the EHD-band from a pure crystal. This is shown in Fig. 1 by comparison with the EHD-spectrum of a weakly doped sample indicating that the condensed electron-hole state is modified by the presence of impurities at high concentrations.⁶ Quite similar spectra as shown in Fig. 1 were obtained from silicon doped with Al ($7 \times 10^{16} \text{ cm}^{-3}$), Sb ($1.5 \times 10^{17} \text{ cm}^{-3}$), As ($1.5 \times 10^{17} \text{ cm}^{-3}$), and P ($1.8 \times 10^{17} \text{ cm}^{-3}$). They are also structured in the case of As, but do not show characteristic structure in the case of Al, Sb and P. This may only depend on the choice of an appropriate doping level in the above mentioned critical range.

To interpret the new spectra we want to point out two features which are in common with the case of Si:B at low doping levels. Firstly, the energies of the peaks which can be distinguished from 0.37 to 32 Wcm^{-2} coincide with the positions of the sharp emission lines in less doped samples of Si:B³ apart from a small shift of $\approx -0.6 \text{ meV}$. Secondly, the peaks of lower energy grow more strongly with increasing excitation level than those of higher energies. We conclude from this that the different bands originate from the same electronic states as in samples of low doping levels. In the latter case, these lines were ascribed to complexes of two or more excitons bound to the impurities. On the other hand, two striking deviations from the spectra of low doping concentrations have to be explained: (1) the broadness of the 'lines' and (2) the absence of the BE-line.

(1) At doping levels of about 10^{17} cm^{-3} , the average interimpurity spacing of $\approx 200 \text{ \AA}$ is of the order of the exciton radius. Due to interactions between impurities or excitonic complexes the emission lines should broaden. Even in weakly doped samples of Si:B a line broadening was observed for the BE and the bound biexciton at increasing doping

levels. The BE-line e.g. shows linewidths of 3.7 \AA ($2 \times 10^{13} \text{ cm}^{-3}$), 4.3 \AA ($1.3 \times 10^{14} \text{ cm}^{-3}$), and 6.7 \AA ($2.6 \times 10^{15} \text{ cm}^{-3}$) at an instrumental resolution of 1 \AA . The broadening tends to become asymmetric with higher impurity concentration showing a low energy tail. This could be observed even more pronouncedly in Si:P than in the case of Si:B. In Fig. 2, the spectra of two crystals of Si:P containing different doping concentrations are compared. The high energy side of the BE is identical in both spectra, but the BE-line of the $6 \times 10^{16} \text{ cm}^{-3}$ -crystal shows a low-energy tail extending to the bound biexciton and there overlapping with the tail of the biexciton line. The observed peaks in the spectrum are slightly shifted to lower energies as it was already described for the case of Si:B (Fig. 1). The strongly asymmetric form of the broadening cannot yet be explained.

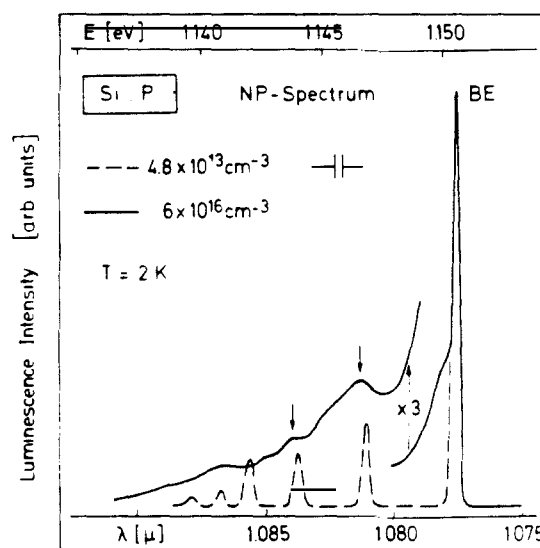


FIG. 2. Emission spectra of Si:P for low and high doping levels. The excitation level is 7.5 Wcm^{-2} .

(2) The absence of the BE-line is not understood. The assumption that the bound exciton may be suppressed at high doping levels e.g. because of its too large 'Bohr radius' does not hold. For with increasing temperatures the BE-line rises, and rapidly growing dominates the spectrum at $T \approx 20 \text{ K}$ together with the FE-line. This is indicated in Fig. 1 where at the extremely high cw-excitation level of 1600 Wcm^{-2} local sample heating causes the BE-line to appear. The model of bound multiple-exciton complexes describes the kinetics of such complexes in terms of a capture

coefficient C of FE's to the complexes, the lifetime τ of excitons in the complex and the density N of FE's.⁸ In the case of high impurity concentration, the diffusion of FE's out of the excited volume is reduced by impurity scattering^{6,7} or capture. Due to this effect, the 'effective' excitation density may be larger in highly doped crystals at given laser power than in less doped samples. Nevertheless, at the lowest excitation levels the number of FE's which are available to be bound should not be large enough as to favour the building up of higher complexes: even neglecting capture processes and using a FE-lifetime of $\approx 3\mu\text{sec}$ ⁸ and a laser penetration depth of $\approx 4\mu\text{m}$, a stationary FE-density of $N \approx 10^{15}\text{ cm}^{-3}$ is obtained for the excitation density of 0.03 W cm^{-2} . This is very small compared with the doping concentration of $7 \times 10^{16}\text{ cm}^{-3}$. By choice of large and individual values of C for the capture

of FE's by neutral impurities and by the BE-complex, one could explain the lack of the BE-line by the model. However, the linear dependence of the 'line' at $\lambda = 1.375\mu$ on the excitation (Fig. 1) is not explained. The physical question remains whether such assumptions about C can be motivated by the depths or the extensions of the binding potentials of the complexes. Eventually, the character of the bound multiple-exciton states changes as well as that of the condensed electron-hole state at high doping levels and modified models have to be applied.

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Die gut bekannten exzitonischen Emissionsspektren und die des kondensierten Elektron-Loch Zustandes in Silizium werden wesentlich modifiziert in einem kleinen typischen Bereich höherer Dotierung. Die neuen Spektren und ihre Abhängigkeit von der Anregung können teilweise durch gebundene Vielfach-Exzitonenzustände vornehmlich höherer Ordnung erklärt werden. Einige Charakteristika der Spektren werden nicht verstanden.