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Four-Particle Radiative Transitions of Biexcitons and Multiple Bound Excitons in Si

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In this paper the observation of sharp and very weak emission lines in phosphorous-doped silicon near twice the band-gap energy is reported. The line with the highest energy can be attributed to the total radiative annihilation of a free biexciton. The other three lines originate from the decay of two electron-hole pairs in a multiple bound exciton complex of two, three, and four excitons.

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In recent years there has been a large number of publications dealing with series of sharp excitonic emission lines connected with shallow impurities in the semiconductors with indirect band structure Si,[1] Ge,[2] SiC,[3] and GaP[4] at low temperatures. Originally the lines have been attributed to the radiative decay of multiple bound excitons (MBE). A more detailed model, called the "shell model," has been proposed by Kirczenow[5] and supported experimentally mainly by Thewalt.[1] After considerable controversy it is now generally accepted that the shell model adequately describes most of the experimental properties of the MBE's.[6] Nevertheless, no direct proof of the many-particle nature has been given so far. As a direct proof, in this paper the observation of emission lines at about twice the band-gap energy is reported for the first time. They are ascribed to the simultaneous decay of two excitons bound in a multiple exciton complex.

Some years ago, Betzler, Weller, and Conradt observed a green emission from highly excited silicon at room and liquid-nitrogen[7] as well as at liquid-helium temperatures.[8] The broad emission band which appears at low temperature was explained by the simultaneous radiative recombination of two electrons and two holes within the electron-hole droplets (EHD).

If MBE's really exist, analogous transitions should lead to sharp emission lines near $2E_g$. In order to estimate the expected luminescence intensity, one can compare the transition probability of the MBE's and the EHD. Within a MBE complex the particles have a similar mean particle separation as in the electron-hole droplets. For instance, in the case of the exciton bound to the donor phosphorous in silicon a "density" of 1.2×10^{18} cm^{-3} is estimated[9] in comparison with 3.5×10^{18} cm^{-3} in the case of the EHD.[10]

In principle, one can expect to observe also a simultaneous radiative transition of two electrons and two holes in a MBE complex as the transition probability should be comparable at comparable carrier densities. On the other hand, because of the high reabsorption of the green luminescence, one can estimate that the observable luminescence from the bound excitons is still weaker than the luminescence from the EHD.

The measurements were performed on a P-doped Si sample ($\rho = 10$ Ω cm) exhibiting quite strong α and β lines near the band gap (nomenclature according to Thewalt[1]). The experimental setup was similar to that used by Betzler and Conradt[8] but the overall sensitivity has been substantially improved. The sample was immersed in liquid helium pumped to 1.5 K, and excited by a GaAs laser array consisting of 12 diodes operated at 77 K. The pulse length was 500 ns, the peak power about 10 W. The excitation intensity was chosen such that the sharp exciton lines were strong, but with only very weak emission from the EHD near the band gap E_g. The luminescence near $2E_g$ was dispersed by a grating monochromator and detected by a cooled photomultiplier with S11 characteristic. The photomultiplier pulses were counted by two counters. The first counter was gated for a time interval of 750 ns during the laser pulse. The second counter was gated during ten successive time intervals of 750 ns before the laser pulse. From the difference of the correctly weighted count rates it is possible to detect signals with count rates less than the dark pulse rate of the photomultiplier which was on the order of 1 count/s before the gates. The spectrum was measured several times and averaged.

In Fig. 1 the emission intensity in the region of $2E_g$ is plotted versus photon energy. The error bars denote the resolution of the spectrometer ($\Delta E = 2.2$ meV) and the statistical counting error, respectively. This picture is similar to Fig. 1 of Ref. 8, but it was recorded with much higher spectral resolution. In contrast to the experiments of Ref. 8 which were performed on high-purity samples, there appear in addition to the broad EHD band[8] four new structures beyond the statistical counting error, at about 2.289, 2.294, 2.301, and 2.308 eV. On the other hand, the spectral resolution of this measurement is not good enough to determine the energetic position of sharp lines which should originate from the MBE complexes. For that reason, the energy interval between 2.285 and 2.312 eV was measured with a resolution of $\Delta E = 0.6$ meV. The excitation intensity was chosen weaker to further reduce the EHD emission. The experimental result is given in Fig. 2. In practice, the spectral resolution is limited by the extremely weak signal intensity and the measuring time. It should be noted that the "intensity" of the line ϵ^2 in Fig. 2 corresponds to a net count rate of one photon every three minutes! Although the error bars due to the statistical error of the count rate (mainly given by the dark pulse rate of the photomultiplier) are quite large, one can clearly identify four lines at

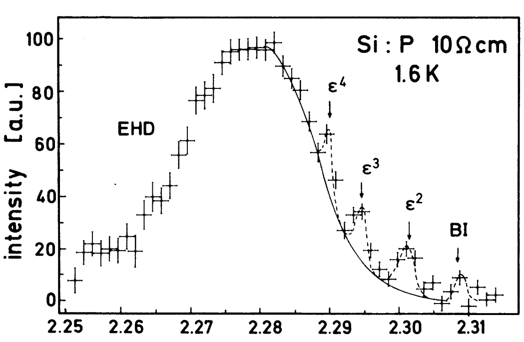

FIG. 1. Emission spectrum near $2E_g$. The broad band comes from two-electron transitions within the EHD. The new additional structures are labeled BI, ϵ^2, ϵ^3, and ϵ^4 and described in the text.

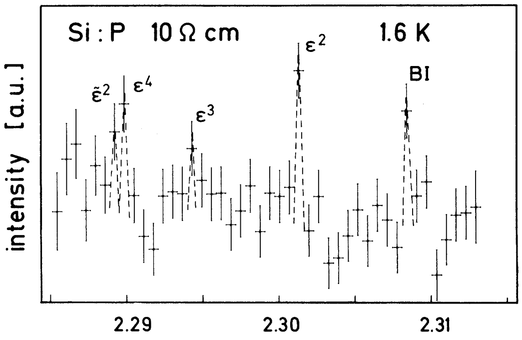

FIG. 2. Emission spectrum with higher spectral resolution in the energy range of 2.285 to 2.312 eV. The excitation intensity was less than in Fig. 1 to reduce the emission from the EHD.

2.2898, 2.2944, 2.3012, and 2.3084 eV, respectively.

We now discuss the interpretation of the new lines. The line labeled BI in Fig. 2 at 2.3084 eV is ascribed to the phononless radiative recombination of a free biexciton. In a recent paper, Thewalt and Rostworowski[11] report on the observation of a biexciton emission in Si which is also seen from the present samples. They give a binding energy of 1.2 meV relative to two free excitons. However, it seems that they have used an energy value for the free exciton gap which is too small. A new interpretation of their data in connection with the present observations in which the free exciton line shape has been calculated including intrinsic line broadening[12] gives a biexciton binding energy of 1.5 meV, so that the total energy of a biexciton is twice the free exciton energy minus 1.5 meV. The most reliable absolute value for the free exciton gap in Si is 1.1551 eV.[13] If the biexciton recombines emitting only one photon, no phonon participation is required as the two electrons can occupy two "opposite" conduction band minima. Moreover, no emission broadening due to recoiling is to be expected as is the case if only one of the two electron-hole pairs recombines.[11] Therefore, a sharp line at 2×1.1551 eV - 1.5 meV = 2.3087 eV is expected. This agrees very well within the experimental resolution with the line BI observed at 2.3084 ± 0.0006 eV. This is the first direct proof of the existence of free biexcitons.

The lines ϵ^2, ϵ^3, and ϵ^4 (Table I) are attributed to the simultaneous phononless recombination of two electrons and two holes within a MBE complex of two, three, and four excitons, respectively, bound to the neutral P impurity. An energy level and transition scheme according to the shell model[5] is given in Fig. 3. The transition energies are summarized in Table I.

First, a complex of two excitons bound to the P donor will be considered. The total binding energy of this complex is not unambiguously known up to now. In the shell model of Kirczenow,[5] the binding energy can be computed from luminescence data. If a MBE(2) in its ground state recombines leaving the neutral donor in its ground state the resulting photon energy is the sum of the β^1 and α^1 line.[14] The total energy of the MBE(2) which is emitted in one photon amounts then to 2.3010 eV in excellent agreement with the line ϵ^2.

TABLE I. No-phonon transition energies in electronvolts of the α, β, and ϵ lines of the multiple bound excitons in P-doped silicon. The experimental error of the ϵ values amounts to ± 0.0006 eV.

i	α^i	β^i	$\alpha^i+\beta^i$	$\epsilon_{\mathrm{exp}}^{i+1}$
1	1.1502	1.1508	2.3010	2.3012
2	1.1465	1.1479	2.2944	2.2944
3	1.1438	1.1457	2.2895	2.2898

In the shell model[5] there is one electron with Γ_1 and one electron with $\Gamma_{3,5}$ symmetry involved in the transition described above. Considering the analogous recombination process in a MBE(3) complex, it turns out that the emitted photon energy should be the sum of the β^2 and α^2 lines, i.e., $h\nu = 2.2944$ eV. This value corresponds again very well with the ϵ^3 line.

The same concept applies to the MBE(4) complex giving the energy of the β^3 and the α^3 line. This leads to an energy for the emitted photon of 2.2895 eV in agreement with the line ϵ^4.

Although the interpretation of the ϵ lines is con-

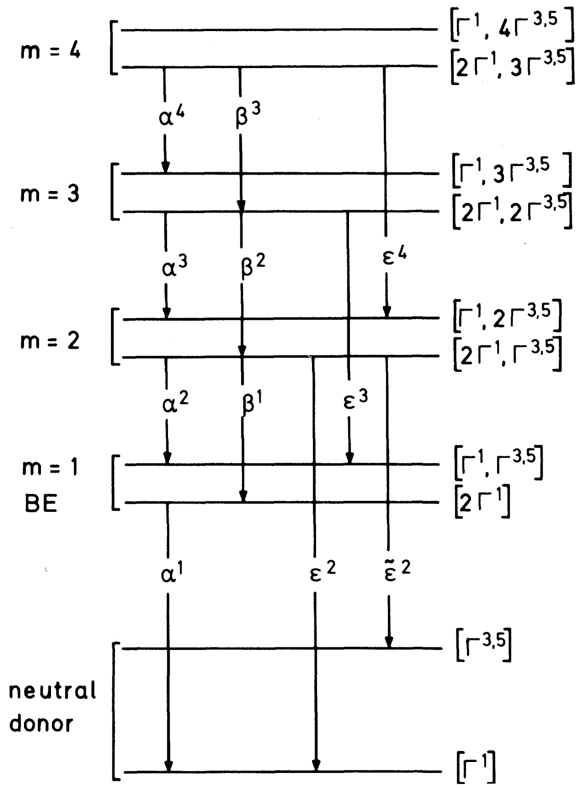

FIG. 3. Energy level scheme of the multiple bound excitons in the "shell model." The new transitions are labeled ϵ^2, ϵ^3, ϵ^4, and $\tilde{\epsilon}^2$ as described in the text.

sistent with the shell model, one should carefully exclude other explanations. In contrast to the case of the two-electron transitions in the EHD, bound states at a substitutional impurity have no inversion symmetry but the symmetry group T_d. Therefore, in principle, frequency doubling is symmetry allowed. However, one would expect in this case the participation of α^1 which is by far the strongest line. But it is not possible to explain the energetic position of the observed lines by mixing α^1 with any of the known sharp α and β lines.

If one accepts the shell model for the MBE's, one may ask why in the transitions described above one Γ_1 and one $\Gamma_{3,5}$ electron is involved. From the group theoretical point of view, transitions including the two Γ_1 electrons, labeled ϵ in Fig. 3, are also allowed. In the case of the MBE(2), the donor would be left in the valley-orbit excited state which lies about 12.9 meV above the ground state.[15] The corresponding transition energy ϵ^2 is the sum of the α^2 and γ^1 lines giving $\epsilon^2 = 2.2893$ eV. This line is also drawn in Fig. 2. However, it is too weak to be definitely distinguished from the noise. But in any case, this transition is weaker than the recombination including one Γ_1 and one $\Gamma_{3,5}$ electron. This may be due to the fact that in the unperturbed crystal with inversion symmetry the ϵ transitions would be forbidden. No transitions including the two Γ_1 electrons are observed for the higher MBE complexes within the resolution of the experiment.

Surprisingly, the ϵ lines and the BI line are comparably intensive although the BI is much weaker than the MBE's in the near-infrared spectrum. This is due to the high reabsorption of the $2E_g$ luminescence. Very close to the excited surface of the sample the absolute number of BI is comparable with that of the MBE's. However, in the average over the volume which is observed in the near band gap spectrum the number of BI's is much smaller than that of the MBE's.

To summarize, in this paper some new and extremely weak luminescence lines at about twice the energy of the band gap in Si are reported. One of the lines with the highest photon energy is consistent with the total energy of a free biexciton in Si. The other three lines can be explained by the simultaneous recombination of two electrons and two holes in a multiple bound exciton complex at the donor P. They confirm the concept of multiple bound excitons, because only in this case sharp lines at about twice the band-gap energy are expected. The results are consistent with the energy-level scheme of the shell model, although they do not prove the shell-model classification of the electrons in terms of Γ_1 and $\Gamma_{3,5}$ symmetries.

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