PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN 49 (1980) SUPPL. A p. 437-440

HIGH FREQUENCY MODULATION SPECTROSCOPY OF BOUND MULTIEXCITON COMPLEXES

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A high frequency excitation modulation technique has been developed in order to discriminate between luminescence lines in lightly-doped silicon by using the small differences in their decay times. A number of new bound multiexciton complex lines which were predicted by the shell model have been discovered in the spectrum of phosphorus-doped silicon. Also, the pairing between the α and β lines predicted by the shell model has been verified.

It is now generally accepted that Kirczenow's [1] shell model of the structure of bound multiexciton complexes (BMEC's) can account for almost all of the known experimental data concerning the behaviour of these complexes, at least for the case of silicon - by far the most heavily studied host [2]. The studies reported here test further predictions of the shell model which until now had not been investigated. A number of new luminescence lines whose existence is required by the model have been discovered, and these new lines are used to determine ground state binding energies and excited state splittings which were heretofore unknown. These new energies will be useful for comparison with the results of the new and more realistic density-functional calculations of the energy levels of these complexes which are currently being undertaken [3].

We begin by considering the case of complexes associated with substitutional donors, such as phosphorus. In the shell model the number of possible single-electron, single-hole transitions which can originate from a given complex in its lowest energy configuration depends both on the nature of the impurity center and on m, the number of electron-hole pairs in the complex. For substitutional donors there is only one recombination path for ground-state bound excitons (m=1), the α^1 line, since the bound exciton contains electrons in only one shell, Γ_1, and has only one hole in the Γ_8 shell. For $5>m>1$ however, there are two recombination paths from ground-state complexes, since there are now electrons in two shells, Γ_1 and $\Gamma_{3,5}$, the two-fold degenerate Γ_1 shell having been filled at m=1. The recombination of a Γ_1 or $\Gamma_{3,5}$ electron of an m complex with a Γ_8 hole gives rise, respectively, to the well known α^m or β^{m-1} lines.

Since the Γ_8 hole shell can hold only four holes, complexes having m>4 must have holes in a shell above Γ_8, which is currently labelled Γ_χ due to our lack of knowledge of its properties. These BMEC's should therefore have four recombination paths from their ground states, as is outlined in Fig. (1). Kirczenow [1] postulated that the α^5 and α^6 observed by various groups in both the no-phonon (NP) and phonon-assisted luminescence spectra resulted from the

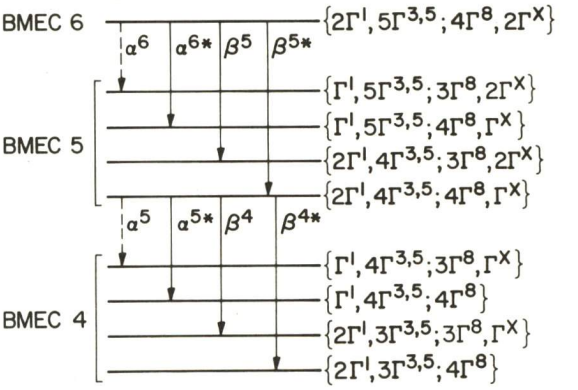

Fig. 1 The shell model level scheme extended for the m=5 and 6 transitions: The well known α^5 and α^6 transitions are shown as dashed lines while the six new transitions are solid lines. For m>4, an asterisk in the transition label indicates that the recombining hole came from the Γ_8 shell. The various configurations are labelled along the right following the method introduced by Kirczenow [1].

recombination of Γ_1 electrons with Γ_8 holes, thus leaving the final state complexes highly excited and explaining the low energies of these lines. The three other possible recombination mechanisms for m=5 or 6 complexes would have to lie at higher energies than α^5 or α^6, respectively, and would therefore be buried under the much stronger luminescence of the smaller complexes. It is for this reason that these transitions have until now not been mentioned in the literature.

In order to reveal these transitions we can make use of the fact that the lifetimes of the complexes are known to decrease somewhat with increasing m [4]. If the excitation beam is chopped at a frequency considerably above the reciprocal of the decay times, the ratio of the A.C. component of the luminescence to the D.C. component will be considerably larger for the higher m lines than for the lower ones. An analytical treatment is not possible due to the non-exponential nature of the initial decays [4].

The samples were immersed in superfluid liquid helium and excited by the 514.5 nm beam of an Ar-ion laser chopped at between 10 and 50 MHz by an acousto-optic modulator. The luminescence was detected by a photomultiplier and processed in the photon-counting mode using a digital phase sensitive detector. By changing the duty factor of the integrating period of the phase sensitive detector from the 50% value corresponding to "normal" lock-in-amplifier operation, luminescence processes having any given ratio of A.C. to D.C. intensity could be nulled from the output. Luminescence lines decaying more slowly than the nulled line become negative signals, while those decaying more quickly remain positive. The nulling process of course entails a loss in signal-to-noise ratio, which becomes more serious as the higher frequency lines are nulled.

Of the six new lines expected on the basis of Fig. (1), five have been discovered and are shown in Fig. (2). The α^{5*} and α^{6*} lines have been previously observed in conventional spectra (they are labelled with *'s in Fig. (13) of [5]) but their origin was never understood. Since none of the new lines were observed in the NP replica it is unlikely that they could be due to contaminants, since such deeper states usually have strong NP replicas.

Since the m=5 and 6 complexes have very similar lifetimes, the modulation technique cannot be used to discriminate between them. Thus the assignment of the five lines in Fig. (2) to the transitions

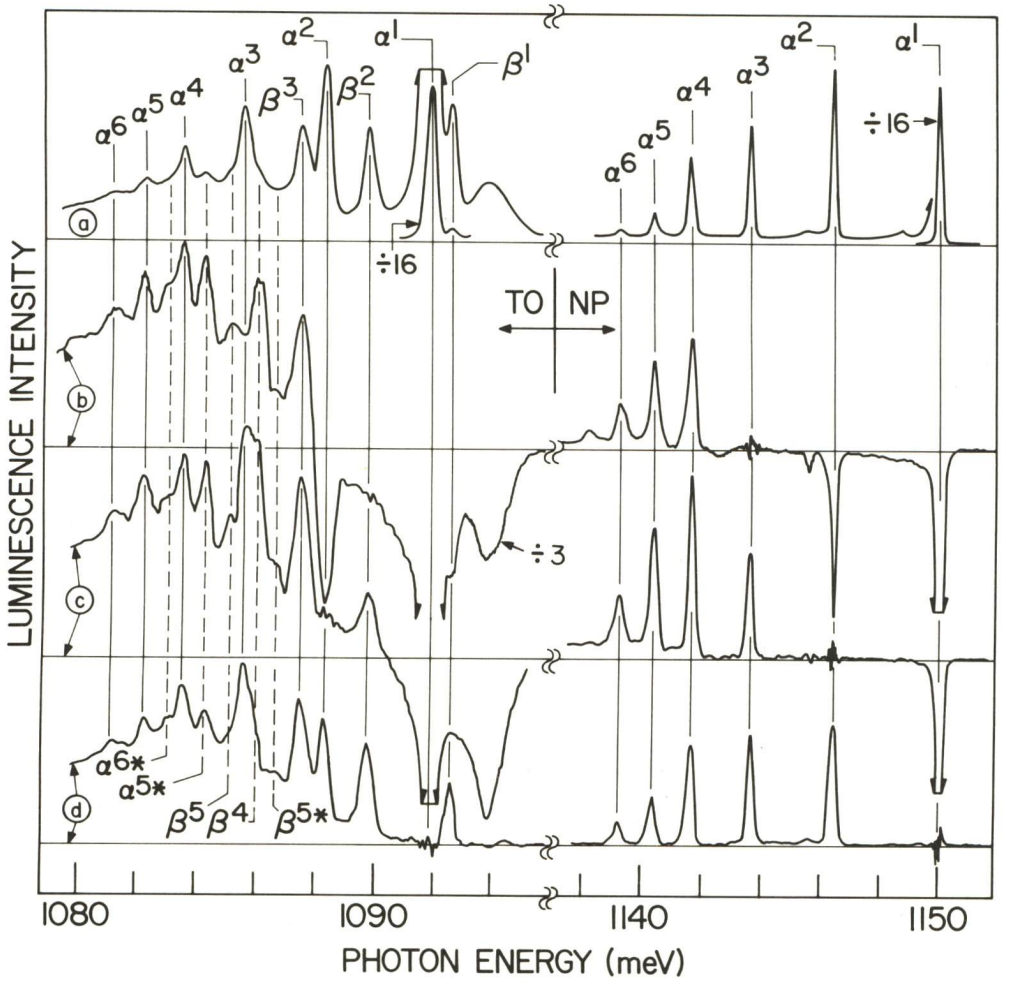

Fig. 2 No-phonon (NP) and TO phonon-assisted photoluminescence spectra of silicon doped with $1x10^{15}$ cm^{-3} of phosphorus taken at a temperature of 2K: A conventional spectrum is shown at a), while b), c) and d) are modulation spectra adjusted for nulls of the luminescence originating from m=3,2 and 1 complexes, respectively. The previously known lines are all labelled across the top of the figure, while the new lines are labelled at the bottom. The weak, broad line seen at the extreme right of the TO replica spectra is the LO phonon-assisted bound exciton (m=1) line. Note that the bound exciton α^1 line has been scaled down by a factor of 16 in a), and that the segment of b) between the high energy edge of the α^1 line and the high energy end of the TO replica spectrum has been scaled down by a factor of 3. The negative-going α^1 lines in b) and c) have been truncated. The intensity scale factors between a), b), c) and d) are arbitrary. The detection circuitry is adjusted to null all luminescence originating from complexes having a given number of electron-hole pairs, m, by monitoring the signal of the NP α^m line. The broad, fast-decaying luminescence background which underlies the lower energy portion of the TO replica is most likely a mixture of electron-hole-droplet and unresolved m>6 BMEC luminescence.

Table 1 Energies of some of the TO replica luminescence lines observed in phosphorus-doped silicon (in meV)

β^{5*}	1086.74 ± 0.25
β^{4}	1086.02 ± 0.1
β^{5}	1085.22 ± 0.2
α^{5*}	1084.38 ± 0.15
α^{6*}	1083.22 ± 0.2
α^{5}	1082.41 ± 0.05
α^{6}	1081.26 ± 0.05

shown in Fig. (1) might appear arbitrary, but it is the only one satisfying the reasonable requirement that neither the splittings between the electron nor the hole shells should change rapidly with increasing m. The energies of some of the lines are given in Table 1, the others have been tabulated elsewhere [5]. The Γ_1 to $\Gamma_{3,5}$ splittings for the m=4 and 5 complexes measured here are equal within experimental error, and also agree with the previously determined [5] m=3 splitting. The three values of the Γ_8 to Γ_χ splittings which can be obtained from the present results also all agree within experimental error. These values for the m=4 and 5 hole shell splittings are however somewhat smaller than the separation between the α^1 and δ' lines, which has been suggested [6] as the value of the hole shell splitting for the bound exciton. The binding energy of the m=6 BMEC as determined by β^{5*} is 9.8 ± 0.4 meV, slightly larger than the 9.0 ± 0.3 meV binding energy of the m=4 complex. The m=5 binding energy cannot be determined since β^{4*} was not observed, presumably because it was lost under the α^2-β^3 doublet. An attempt was made to observe it by nulling α^4 (and therefore β^3), but it was not succesful due to the large decrease in the signal-to-noise ratio as well as the large negative tail of α^2.

The results shown in Fig. (2) also support the shell model pairing of α^m and β^{m-1} for 5>m>1. Transient studies of this pairing have been the subject of some dispute, with the latest results [4] favouring the shell model, but not conclusively. The results shown here, and also the m=4 nulled spectra, indicate that the only possible pairing for the three previously observed β lines is the one predicted by the shell model.

As expected from the model [1], neither the newly discovered β lines nor the three previously known ones appear in the NP spectra. The absence of the α^{m*} lines from the NP spectra, on the other hand, may tell us something new about the properties of Γ_χ. If a selection rule is involved, two candidates for Γ_χ would be either Γ_6 or a j=5/2 Γ_8 state formed from Γ_8 Bloch states and a p-like envelope.

The excitation modulation transient luminescence technique described here has also been used to verify a previous conjecture [6] that the A and B lines seen in the spectrum of lithium-doped silicon were the ground state to ground state transitions of m=6 and 5 complexes. These results will be described in more detail elsewhere.

Acknowledgment - many thanks to G. Kirczenow and R. R. Parsons for several illuminating discussions.

1) G. Kirczenow: Canad. J. Phys. 55 (1977) 1787.
2) see for example M. L. W. Thewalt: Proc. 14th Int. Conf. Phys. Semicond., Edinburgh 1978 (Institute of Physics and Physical Society, London, 1979) 605.
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4) A. T. Hunter, S. A. Lyon, D. L. Smith and T. C. McGill: Phys. Rev. B 20 (1979) 2431.
5) M. L. W. Thewalt: Canad. J. Phys. 55 (1977) 1463.
6) M. L. W. Thewalt: Solid State Commun. 28 (1978) 361.