Discovery of Polyexcitons

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We report the first experimental evidence for the existence of free polyexcitons ($n > 2$) in a semiconductor. Resolved polyexciton lines, together with the biexciton line, were observed in the green photoluminescence spectrum of ultrahigh-purity silicon. We propose that the unresolved luminescence of these polyexcitons in the "ordinary" near-infrared photoluminescence process may provide an alternative explanation for a band interpreted by others to be due to a new condensed phase of the electron-hole plasma.

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The analogy between excitons and hydrogenic or positronium systems has been of considerable importance in the development of semiconductor physics and spectroscopy. In 1958, Lampert[1] used these analogies to predict the existence and properties of a number of new excitonic species, including donor- and acceptor-bound excitons (both neutral and charged), trions (free complexes of two holes and one electron, or vice versa), overcharged donors and acceptors (D^- and A^+, respectively), and finally, the (free) excitonic molecule or biexciton.

Wang and Kittel[2] first pointed out in 1972 that the extra band-edge degeneracy of indirect-gap semiconductors allowed for novel excitonic systems considerably more complex than those envisioned in the above analogies, since in these semiconductors more than two electrons (namely, twelve for Si and eight for Ge) could be placed into the same ground-state orbital without violating the exclusion principle. Wang and Kittel[2] were specifically concerned with neutral, free molecular complexes containing more than two electron-hole (eh) pairs, which we shall refer to as polyexcitons (PE). Morgan[3] later gave further theoretical consideration to PE in Si, concluding that PE containing up to at least six eh pairs would be stable.

It is remarkable that no experimental evidence for the existence of these unique excitonic species was obtained in the sixteen years since their first prediction. This is especially true in light of the large body of experimental evidence regarding bound multiexciton complexes (BMEC's), which can be thought of as biexcitons or polyexcitons localized on either neutral donors or neutral acceptors.[4]

We report here the first experimental evidence for the existence of free PE, which is obtained from the green photoluminescence (PL) spectrum of highly excited ultrahigh-purity (UHP) Si over a range of sample temperatures. This process, in which two eh pairs recombine simultaneously to give one photon at almost twice the band-gap energy, has been used previously to study eh plasmas[5] and the "normal" condensed phase of the eh plasma known as the eh droplet (EHD)[6] as well as the biexciton[7,8] and BMEC's[7,9] in Si. In addition to being intrinsically very weak, the green PL is also strongly reabsorbed by the Si, necessitating an extremely sensitive detection apparatus.[8,9]

Our high-sensitivity PL apparatus was as described previously,[8,9] except that excitation was provided by 800 mW of 700-nm dye-laser light. Freshly etched samples of UHP Si were mounted in a strain-free manner on the temperature-controlled stage of a VariTemp Dewar. Sample temperatures were measured with a calibrated Si diode and further verified by monitoring of the near-infrared (NIR) free exciton (FE) line shape. The peak intensity of the green polyexciton PL was $\simeq 4$ counts per channel per minute (10 times the dark count). Even with this high-sensitivity apparatus, each spectrum required $\simeq 20$ h to collect.

In Fig. 1 we summarize the evolution of the green PL spectrum as a function of temperature. Very similar results were observed in a second UHP Si sample obtained from a different source. The 11-K spectrum is dominated by the broad EHD line,[6-9] which can be quite strong for $T < 20$ K. A very weak biexciton (X^2) line can also be seen at 11 K, at the same energy as reported previously.[8]

Upon our increasing the temperature the spectrum changes remarkably, as shown in Fig. 1. At 20 K, the EHD band is weaker and the X^2 line has grown enormously. This reflects the increase in the equilibrium FE density caused by the temperature-induced reduction of the EHD binding energy, which results in a much larger population of molecular species. This at first surprising increase of the X^2 population with increasing T was earlier observed by Hulin *et al.*[10] in AgBr. In retrospect, it is unfortunate that prior studies[7,8] of the green X^2 luminescence in Si were done at $\simeq 2$ K, where the signal is extremely weak.

In addition to the intense, sharp X^2 line, the 20-K spectrum reveals new, resolved structure which we label X^3 and X^4, as well as a shoulder labeled X^5. This same spectrum is shown in more detail in Fig. 2. We interpret the green X^3 (X^4) line as a transition from a ground-

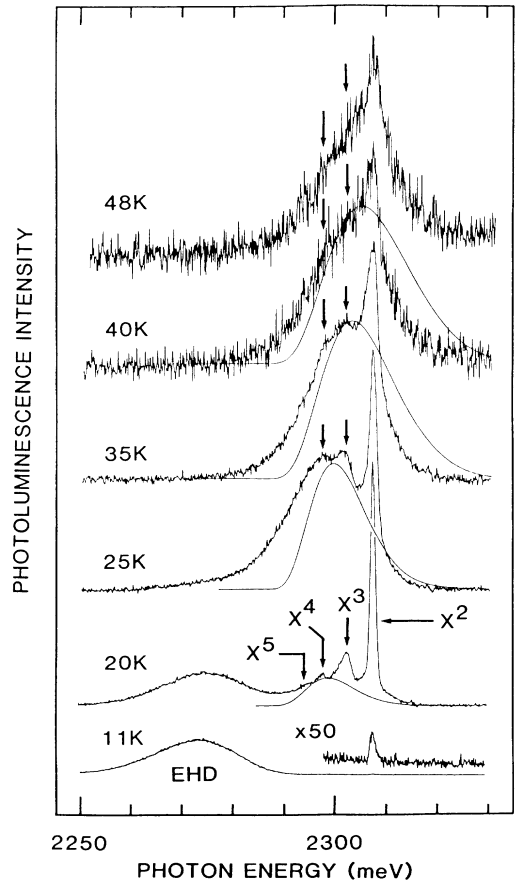

FIG. 1. Green photoluminescence of UHP Si as a function of temperature. The electron-hole-droplet band, which dominates the low-temperature spectra, vanishes near 25 K. The biexciton line (X^2) can be observed at all temperatures, while the X^3-X^5 polyexciton lines appear only at 20 K and above. The calculated line shape of the "condensed plasma" phase is shown between 20 and 40 K. Its high-energy edge is seen to be in poor agreement with that of the observed luminescence. The higher-temperature spectra have been shifted to compensate for the reduction of the band gap with increasing T.

state triexciton (tetraexciton) to a ground state FE (biexciton). As shown in Fig. 1, some resolved structure can be observed in the X^2,X^3,X^4 PL up to at least 40 K. For simplicity we refer only to neutral PE. While charged species larger than X^2 will also be present, their relative concentrations are negligible up to at least 20 K.

Since these lines are observed in two different UHP Si samples, and at temperatures where any localized (bound exciton) states this shallow would be strongly dissociated, an extrinsic explanation can be ruled out. Furthermore, the dependence of X^3-X^5 on FE density is observed to be even more pronounced than that of the biexciton, X^2, as expected for polyexcitons in equilibrium. The strongest support for our PE explanation comes, however, from the luminescence line shapes.

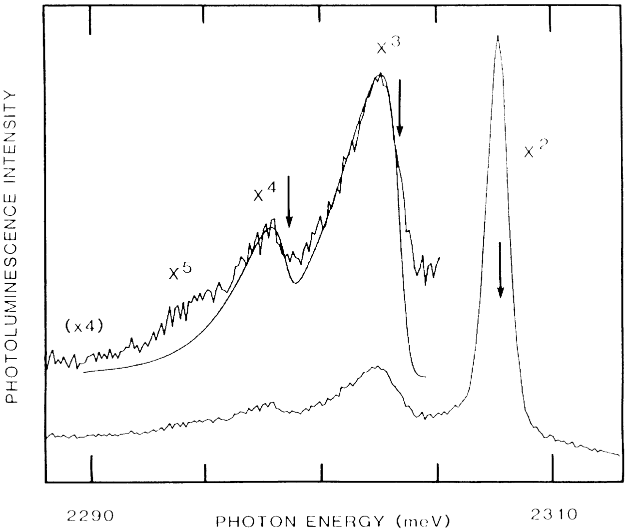

FIG. 2. The 20-K spectrum of Fig. 1 on an expanded scale. The solid curve is a fit to the triexciton and tetraexciton lines as described in the text (the amplitude has been expanded by 4x). The three vertical arrows mark the transition energies of zero kinetic energy biexcitons, triexcitons, and tetraexcitons, respectively.

The green process is fundamentally different from the usual NIR PL in two ways. First, since it involves the simultaneous recombination of *two* eh pairs, species such as the FE cannot contribute to the green PL. Second, it is an intrinsic no-phonon process, in which crystal momentum is conserved by having the two recombining electrons in opposite conduction-band valleys. The total momentum of the final state must therefore equal the total momentum of the initial state. Since the final state of the X^2 transition is simply the crystal ground state, only biexcitons which are at rest can contribute to the green X^2 PL, resulting in a narrow, symmetrical line. The X^2 line can be broadened by collisions, but not directly by the thermal kinetic energy of the X^2 distribution.[7,8]

The situation is more complicated for the PE, since in this case both the initial and final states can have momentum and kinetic energy. When X^3 decays to a FE, the recoil FE have the same momentum as that of the initial X^3, but since the FE is 3 times lighter it must carry away 3 times the initial kinetic energy. Thus the X^3 PL photon of a triexciton with initial thermal kinetic energy E_k will occur at an energy $2E_k$ *below* that of the recombination of an X^3 at rest. Since the initial polyexciton distribution will be a Maxwell-Boltzmann (with T's very near the lattice temperature), the X^n $(n>2)$ lines should resemble *inverted* Maxwell-Boltzmann line shapes, with thermal tails towards lower energy, as is observed in Figs. 1 and 2.

A more detailed calculation of the line shapes must take into consideration a momentum-dependent matrix element reflecting the overlap of the momenta of the particles in the recoiling final state with those in the initial state. We have adapted a simple model of the NIR biexciton line shape given by Cho[11] to calculate the green PE line shapes. The best-fit results for the X^3 and X^4 lines are shown in Fig. 2, where T was taken as the lattice temperature, while the zero-kinetic-energy transition energies (arrows) and the linewidth parameters Γ_m[11] were optimized. The resultant binding energies, defined in terms of removal of one FE ($X^n \rightarrow X^{n-1} + \mathrm{FE}$), were 1.36, 3.83, and 6.34 meV for X^2, X^3, and X^4, respectively. There are as yet no reliable theoretical estimates of PE binding energies for comparison. The "radii", as determined from the Γ_m, were 100 and 130 Å for X^3 and X^4, as compared to 100 Å obtained earlier[12] for X^2, but these should not be taken rigorously, considering the approximations contained in the theory.[11]

The binding energy of the pentaexciton (X^5) cannot be obtained from the observed X^5 line, since in analogy to the shell model[13] used to describe BMEC's[4] X^5 must have holes in two different shells (the valence-band edge is only fourfold degenerate). Thus the lowest-energy X^5 transition, which is the one observed by us, leaves the final X^3 in an electronic excited state (two holes in the ground shell, one in the upper shell). Just as for BMEC's,[4,14] there must be a second (weaker) X^5 ground-state to ground-state transition, but it is hidden under the stronger X^2-X^4 lines.

Smith and Wolfe[15-17] have recently interpreted a band seen in time-resolved NIR PL of UHP Si as a new (and unexpected) condensed phase of the eh plasma (CP), having a density $\simeq 10$ times lower than that of the EHD, and a critical temperature of $\simeq 45$ K. The basis for this was the observed independence of the line shape of this band on FE density. Hernandez[18] has recently questioned the CP model, and proposed that the band may originate from excitonic complexes.

This alternative explanation is made more compelling by our discovery of the existence of PE, which are seen to have quite large binding energies and to be present in considerable quantities in the same T and FE-density regimes where the "CP" band is observed. The PE observed by us in the green PL would have a broad, unresolved, NIR PL line shape very similar to that of the CP band of Smith and Wolfe.[15-17] The NIR PE line shapes are determined only by T and the momentum matrix elements, and would thus also be independent of the time-varying FE density, as observed. We should point out that we have observed the CP band in the NIR PL of our samples under exactly the same conditions which produce resolved PE structure in the green PL.

Furthermore, the green PL shows little evidence of a CP component, the expected line shape of which has been indicated on the 20-40-K spectra of Fig. 1. Of course this does not prove that the CP does not exist, since one could argue either that its green PL is very weak, or that it does not exist near enough to the surface to be observed under our excitation conditions.

Nevertheless, since we have demonstrated that the PE exist, they must surely contribute some intensity to the NIR CP PL band. The question then is whether the NIR PE PL can account for the entire CP band. Smith and Wolfe[16,17] have argued that it cannot, on the basis of thermodynamic calculations of the populations of the various species. However, these calculations[16,17] were based upon a uniform, *average* FE density, which is not a good description of the spatial distributions present in their experiments. The use of an average FE density, rather than the true spatially varying distribution, can lead to a serious underestimate of the net concentration of the larger complexes, which are strongly enhanced by small increases in FE density.

We have applied the same Richardson-type equations used by Smith and Wolfe[16] to a radially decaying, hemispherically symmetric FE distribution, which is a more accurate description of the true experimental[15,16] situation. The FE density at the origin of this distribution was then adjusted so that the calculated X^2 to FE PL ratio matched that observed by Smith and Wolfe.[16] Under these conditions, our calculated total relative PE PL intensity was in fact very close to that of the observed[16] CP band.

In conclusion, we have reported the first observation of free polyexcitons in a semiconductor, and measured the binding energy of triexcitons and tetraexcitons in Si. We have also demonstrated that polyexcitons can provide an alternative explanation for the new condensed plasma phase reported by Smith and Wolfe.[15-17]

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[1] M. A. Lampert, Phys. Rev. Lett. **1**, 450 (1958).

[2] J. S. Wang and C. Kittel, Phys Lett. **42A**, 189 (1972).

[3] T. N. Morgan, Nuovo Cimento Soc. Ital. Fis. B **39**, 602 (1977).

[4] M. L. W. Thewalt, in *Excitons*, edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982), p. 394.

[5] K. Betzler, T. Weller, and R. Conradt, Phys. Rev. B **6**, 1394 (1972).

[6] K. Betzler and R. Conradt, Phys. Rev. Lett. **28**, 1562 (1972).

[7] W. Schmid, Phys. Rev. Lett. **45**, 1726 (1980).

[8] M. L. W. Thewalt and W. G. McMullan, Phys. Rev. B **30**, 6232 (1984).

[9] M. L. W. Thewalt and W. G. McMullan, in *Proceedings of the Seventeenth International Conference on the Physics of Semiconductors,* edited by J. D. Chadi and W. A. Harrison

(Springer-Verlag, New York, 1985), p. 1243.

[10] D. Hulin, A. Mysyrowicz, M. Combescot, I. Pelant, and C. Benoît à la Guillaume, Phys. Rev. Lett. **39**, 1169 (1977).

[11] K. Cho, Opt. Commun. **8**, 412 (1973).

[12] M. L. W. Thewalt and J. A. Rostworowski, Solid State Commun. **25**, 991 (1977).

[13] G. Kirczenow, Can. J. Phys. **55**, 1787 (1977).

[14] M. L. W. Thewalt, J. Phys. Soc. Jpn. **49A**, 437 (1980).

[15] L. M. Smith and J. P. Wolfe, Phys. Rev. Lett. **57**, 2314 (1986).

[16] L. M. Smith and J. P. Wolfe, to be published.

[17] L. M. Smith and J. P. Wolfe, Phys. Rev. Lett **58**, 2823 (1986).

[18] J. P. Hernandez, Phys. Rev. Lett. **58**, 2822 (1987).