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Green and near-infrared luminescence due to the biexcitons in unperturbed silicon

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We have used an ultrasensitive imaging photomultiplier tube to study the green luminescence (caused by the complete no-phonon annihilation of a biexciton to yield one photon) occurring at approximately twice the Si band-gap energy. The binding energy of the biexciton relative to the lowest energy-free exciton edge was found to be 1.36 ± 0.26 meV, in good agreement with an earlier measurement based on the near-infrared biexciton spectrum. Recent attempts to call those earlier results into question are shown to be unfounded.

The near-infrared photoluminescence of biexcitons, which results from the recombination of one electon-hole pair in the biexciton to give a photon, a crystal-momentum conserving phonon, and a free exciton (FE), has been studied in deformed Si by several authors.[1-6] The deformation, which can result either from a uniaxial stress[1-4] or from a Hertzian strain well,[5,6] serves to reduce the stability of the electron-hole droplet (EHD) by lifting some of the band-edge degeneracy. This in turn increases the equilibrium density of FE, leading to large increases in the density of biexcitons, resulting in readily observable luminescence signals.

The near-infrared biexciton luminescence in unperturbed Si is much weaker, and has only been studied in one previous paper,[7] which deduced a binding energy of 1.2 meV for the biexciton. That work has more recently been called into question by Kulakovsky and Timofeev[3] and Timofeev[4] on the basis of their inability to observe the biexciton luminescence at a level purported to be equal to that seen previously.[7] We have repeated these experiments using different samples and a different apparatus and consistently find biexciton luminescence of about the same strength as that seen by Thewalt and Rostworowski[7] when those earlier data are interpreted correctly.

The spectroscopic determination of the biexciton binding energy from the near-infrared transition is complicated by the necessity of doing a fit to the biexciton line shape, which has a high-energy tail due to thermal motion, and a low-energy tail due to the recoil kinetic energy of the remaining FE.[8] Schmid[9] has recently shown that the biexciton in Si can annihilate completely via a no-phonon process which gives a green photon having an energy of roughly twice the Si band gap. The energy of this line, which should be extremely narrow, would exactly equal the total energy of the biexciton, and should thus allow an unambiguous determination of the biexciton binding energy. Unfortunately this luminescence is extremely weak, and even by using prodigious data collection times and a very clever experimental arrangement, Schmid[9] could only obtain results with very marginal signal-to-noise ratio.

We have used a parallel optical multichannel analyzer based upon an imaging photomultiplier tube (ITT Mepsicron) and related position computing electrons (Surface Science Laboratories) interfaced to a computerized data collection system. The extended S-20 tube was operated at $-50\,^{\circ}\mathrm{C}$ and has a resolution of 400 line pairs across its 25-mm face, digitized into 1024 channels. In addition to the parallel collection advantage is the extremely low dark count of about 1 per 5 min per channel resulting from the small photocathode area per channel. The luminescence was dispersed across the detector by a 600-groove/mm grating operated in second order in a 0.75-m spectrometer. Excitation of approximately 1-W total power was supplied by the mixed red lines of a Kr-ion laser, filtered through four Corning 2-67 filters and focused onto a line of area ~ 3 mm^2 on the ultrahigh-purity Si sample. The image of this line was focused onto the spectrometer entrance slits after passing through two Corning 5-56 filters. The sample was immersed in superfluid He at a bath temperature of 1.6 K. The near-infrared luminescence was detected by a Varian VPM159-A3 photomultiplier tube operated in photon counting mode.

The results of a representative eight hour run on the green luminescence are shown in Fig. 1. The biexciton peak

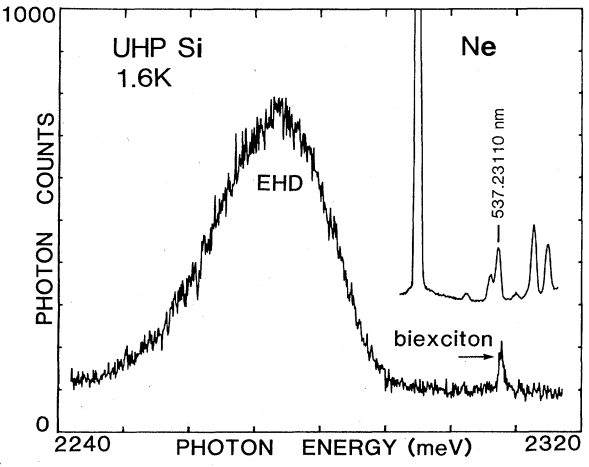

FIG. 1. Green photoluminescence of the biexciton and electron-hole droplet are shown for an eight hour scan on ultrahigh-purity Si at a bath temperature of 1.6 K. A section of the Ne discharge spectrum collected with identical spectrometer settings shows the 537.2311-nm line used to calibrate the biexciton energy. The dark count has not been subtracted.

height is about 10 counts per hour, while the EHD is much stronger even under these moderate excitation conditions. The energy of the biexciton line was determined by comparison to Ne spectra collected immediately before and after the biexciton run without changing in any way the spectrometer settings. A section of the Ne spectrum is also shown in Fig. 1. The Ne line at 537.2311 nm (Ref. 10) was used as a calibration point since it lies very near the biexciton line. We obtain an energy of 2307.72 ± 0.12 meV for the biexciton line, compared to the previous estimate[9] of 2308.4 ± 0.6 meV. Our data show no indication that the biexciton line is wider than the instrumental resolution, so we can set an upper limit ~ 0.3 meV on its intrinsic width.

The determination of the biexciton binding energy also requires an accurate value of the FE edge energy. Schmid[9] provides an energy of 1155.1 meV for the no-phonon FE edge, as determined from a fit to the TO phonon FE replica after Hammond and Silver,[11] but provides no error estimate. Hence, his biexciton binding energy is $1.8 \pm (0.6 + X)$ meV, where X is the unstated error in the no-phonon FE edge. We have in fact arrived at a considerably different value of the no-phonon FE edge energy by doing a careful least-squares fit to the TA phonon FE replica, as shown in Fig. 2. The second order 546.074-nm line of a low-pressure Hg lamp lies very near the FE TA line, and it was collected simultaneously with the Si luminescence to give both an accurate energy reference and an accurate instrumental response function. In order to fit the FE data, the Hg line was first convolved with a variable Gaussian broadening, and then with a theoretical expression for the FE line shape consisting of an energy shift, an effective temperature, and a splitting between the Δ_7 and Δ_6 FE states, which were assumed to have parabolic densities of states.

Even though the TA replica is much weaker than TO and LO phonon replicas, we have used it to do our fits since it suffers from less phonon broadening.[12] The effects of the Δ_6–Δ_7 splitting are clearly seen in Fig. 2, but cannot be observed in the optical-phonon replicas. Our least-squares fit converged to the values of 1135.82 ± 0.02 meV for the FE TA edge, 0.29 ± 0.06 meV for the Δ_6–Δ_7 splitting, 1.8 K for the effective temperature (slightly above the 1.6 K bath temperature), and a broadening full width at half maximum (FWHM) of 0.14 meV. The optimum χ^2 was 2.24, considerably better than the value of five obtained[11] for the TO and LO replicas. The quoted error limits in our parameters correspond to a doubling of χ^2 when all other parameters are allowed to adjust. The Δ_6–Δ_7 FE splitting obtained here is in excellent agreement with the best previous results.[11,12] We note that the FE TA edge energy obtained here is in exact agreement with that used previously by Thewalt and Rostworowski,[7] but when transformed into a no-phonon FE edge by adding the 18.72 ± 0.05-meV TA phonon energy gives 1154.54 ± 0.07 meV, in considerable disagreement with the value provided by Schmid.[9] When our FE edge energy is doubled and the biexciton green line energy is subtracted we obtain a biexciton binding energy of 1.36 ± 0.26 meV.

We have also double checked our value of the biexciton binding energy using a method which does not require the explicit inclusion of the TA phonon energy. The near-infrared TA replicas of the FE, the boron bound exciton (BE) and the $m = 2$ boron bound multiexciton complex were recorded simultaneously and the energy shifts from the two boron lines to the FE edge were accurately determined. The sum of these two shifts, when added to the energy of the green luminescence line resulting from the annihilation of $m = 2$ boron BMEC[13] gives the expected position of the FE edge in terms of the green spectrum. The green biexciton line occurs 1.33 ± 0.28 meV below this energy, in excellent agreement with our previous value for the biexciton binding energy.

These results are also in agreement with the near-infrared value of 1.2 meV, which was based on the implicit assumption that the biexciton decayed into the lowest (Δ_7) FE branch.[7] If in fact the biexciton decayed predominantly into the Δ_6 FE then the near-infrared binding energy would be ~ 1.5 meV. The near-infrared biexciton results have been

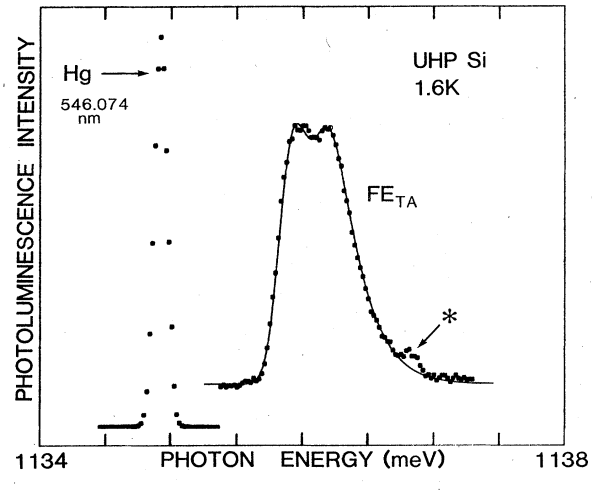

FIG. 2. Dots show a TA phonon replica spectrum of the FE collected simultaneously with the Hg line at 546.074 nm in second order. The instrumental FWHM is 0.12 meV. The solid line is the best least-squares fit to the FE data using the Hg line data as the instrumental response. The bump labeled * is a no-phonon luminescence component which was excluded from the fit.

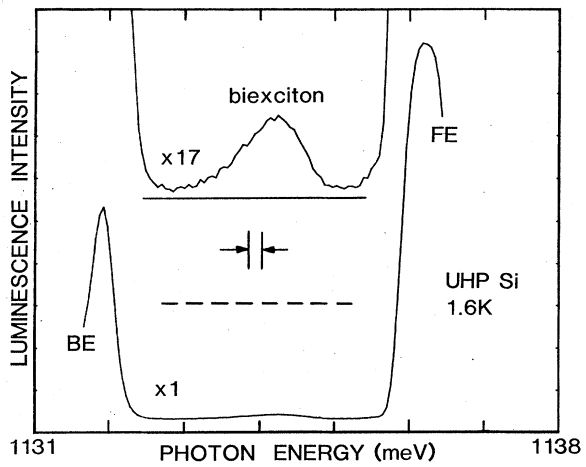

FIG. 3. TA phonon replica of the biexciton is flanked by the FE and boron BE lines. The solid black line is an estimated background level on the ×17 scale which was measured at 1.0848 μm, while the dashed line is the system dark count on the same scale. The bottom edge of the box represents zero signal for both scales.

questioned by Kulakovsky and Timofeev[3] and Timofeev[4] on the basis of their inability to observe the biexciton at a level of $\frac{1}{40}$ the FE intensity. They claimed this was inconsistent with the value of $\frac{1}{20}$ the FE intensity deduced by them from the work of Thewalt and Rostworowski.[7] In fact, there is no inconsistency since the true biexciton strength observed by Thewalt and Rostworowski was $\sim\frac{1}{45}$ the FE intensity. Kulakovsky and Timofeev[3] and Timofeev[4] have simply overestimated the biexciton intensity by including what was clearly considered to be a background level as shown by Fig. 2 of Ref. 7.

In order to verify this we have studied the near-infrared biexciton signal using both different apparatus and samples. We have no difficulty in observing the biexciton line, although never at intensities over $\frac{1}{40}$ the FE intensity. A typical spectrum is shown in Fig. 3, where the intensity ratio is $\sim\frac{1}{85}$. Although the background level under the biexciton line is difficult to determine, we have used a value measured at 1.0848 μm to obtain the solid line shown in Fig. 3. The background likely arises from no-phonon transitions of small EHD localized on P impurities. The dashed line in Fig. 3 indicates the system dark count level. We have not redone the fitting to the near-infrared biexciton line shape since in our estimation the previous result[7] is perfectly valid, given the proviso regarding the uncertainty of the FE final state.

In conclusion, we have accurately determined the binding energy of the biexciton in unperturbed Si by observing its green luminescence, and have also verified the previous results from near-infrared spectroscopy. The biexciton binding energy was found to be 0.093 ± 0.02 of the FE Rydberg (14.7 meV), in close agreement with the best results[5,6] available for stressed Si. The result is also in reasonable agreement with the most recent calculation[14] of the biexciton binding energy, which seems to represent a considerable improvement over an earlier[15] variational calculation.

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