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NEW EXPERIMENTAL RESULTS ON BIEXCITON FORMATION IN SILICON

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The properties of biexcitons in silicon are studied for various band structure configurations by photoluminescence experiments. For the first time, the total radiative annihilation of biexcitons is observed as a weak emission close to $2E_g$ in Si. The formation of biexcitons from electron-hole droplets is investigated and compared with theoretical calculations.

I. Introduction

Biexcitons BI (excitonic molecules EM) in semiconductors have been the subject of intensive study in recent years [1]. Up to now, however, biexcitons have been observed mainly in materials with a small "hydrogen like" electron to hole mass ratio $\sigma = m_e/m_h$. With increasing mass ratio σ the binding energy decreases until the positronium limit is reached. Theoretical calculations of the BI binding energy differ slightly for small σ, but become strongly model dependent in the limit $\sigma \to 1$ [2-5]. Due to the large mass ratio of $\sigma = 0.75$, the binding energy of the BI in Si should provide a clear distinction between different models.

The first observation of BIs in Si has been reported by Kulakovskii and Timofeev [6] for Si[2;1] under high stress along the <100> direction, where the numbers in brackets denote the degeneracies of the conduction and valence bands, respectively. The BI has also been observed in unstressed Si[6;2] [7], and in the stress configurations Si[4;1] (stress // <110>) [8], and Si[2;1] under inhomogenious stress [9].

There is some discrepancy in the experimental values of the binding energy. First, Kulakovskii and Timofeev [6] have found 1.3 meV for Si[2;1], but corrected it later to 0.55 meV [10]. Thewalt and Rostworowski [7] quote 1.2 meV for unstressed Si, Gourley and Wolfe [9] 1.5 meV for nonuniaxially stressed Si. Since the optical masses are nearly independent of the applied stress, the BI binding energy is expected to be about the same in all configurations.

In this paper we present a detailed study of the properties of biexcitons under various band structure configurations. The binding energy, lifetime, and interaction with electron-hole droplets (EHD) and free excitons (FE) are studied. For the first time, we have observed the total radiative recombination of BIs in unstressed Si[6;2] and stressed Si[2;1] giving unambiguous proof of the existence of biexcitons.

II. Experimental

The samples have been cylinders (r = 0.6 mm, l = 10 mm) and kept in liquid He at 1.7K. The stress has been checked to be highly homogenious by linewidth analysis of free excitons. The samples have been excited by a GaAs laser. On the detection side the photomultiplier pulses have been

counted while a quartz clock controlled gate was open immediately before and during the excitation [11]. The difference in count rates gives the luminescence intensity which may be less than 1 photon/min.

III. Biexcitons in Unstressed Si[6;2]

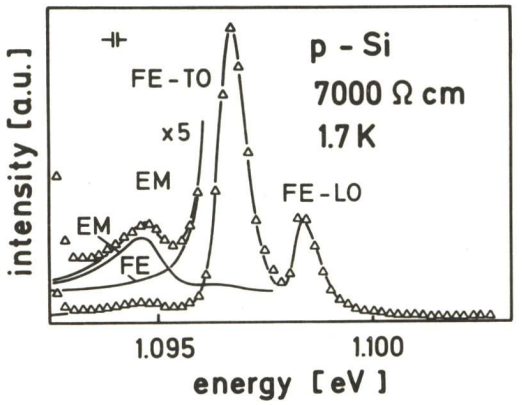

Fig. 1 FE and EM emission near the band gap energy of Si[6;2]: The drawn lines represent calculated line shapes

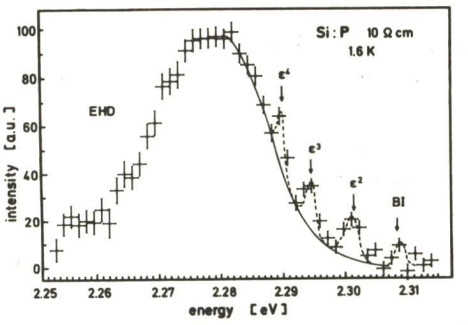

Fig. 2 Emission spectrum of Si[6;2] near $2E_g$: The labels are defined in the text

Figure (1) shows part of the TO/LO phonon assisted emission spectrum of Si[6;2]. Similar to Thewalt and Rostworowski [7] we observe a weak emission below the FE-TO line which can be fitted by a BI line shape according to Cho's theory [12]. We have seen the corresponding emission in the TA phonon assisted spectrum, too. However, as pointed out by Voisin et al. [13] the transition matrix element is not independent of k in this case, which complicates the line shape calculation. From the best fit of the TO/LO line we obtain a binding energy for the BI of 1.40±0.05 meV.

Since the excitonic molecule consists of two electrons and two holes the total momentum may be $K \approx 0$ thus allowing a phononfree total radiative recombination. In this case the photon energy occurring close to $2E_g$ corresponds to the total energy of the BI. Transitions of that kind are well known in the case of the EHD [14]. Fig. (2) shows the luminescence spectrum near $2E_g$ which is dominated by the EHD. The lines labelled ε are due to bound multiexciton complexes [15]. The relevant energy range between 2.285 eV and 2.315 eV has been carefully investigated with higher spectral resolution (0.6 meV) giving a total BI energy of 2.3084±0.0006 eV.

This value yields a binding energy of 1.4 meV which is in excellent agreement with our near band gap data.

IV. Biexcitons in Stressed Si[2;1]

The luminescence intensity of the BI is drastically increased by applying uniaxial stress along the <100> direction as demonstrated in sec. VI. In Fig. (3) a spectrum is shown for Si under high uniaxial stress ($s \approx 3$ kbar). The experimental data have been fitted by the sum of FE, BI, and EHD line shapes. The BI binding energy is found to be 1.4±0.1 meV which is indistinguishable from our result for unstressed Si.

In Fig. (4) the corresponding spectrum near $2E_g$ is displayed. It consists of the EHD and the BI emission. As expected the BI luminescence is largely increased compared to the case of unstressed Si. The BI line shape has been fitted assuming a parabolic dispersion relation and a Boltzmann

distribution. The $2E_g$ emission from the EHD has been calculated for T = 0K by a Monte Carlo k-space integration.

The bottom of the BI band gap derived from this figure is E_{BI} = 2.2493 ±0.0002 eV. The corresponding FE energy obtained from Fig. (3) amounts to E_{FE} = 1.0681±0.0001 eV thus giving a BI binding energy of 3.0±0.3 meV. This value is about 1.6 meV larger than the spectroscopic value obtained from the line shape fit in Fig. (3).

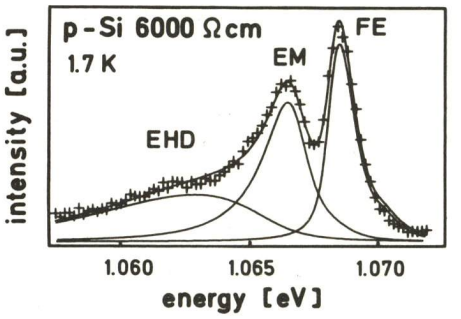

Fig. 3 Luminescence spectrum of Si[2;1] in the high stress limit: The drawn line shape is composed of EHD, EM, and FE

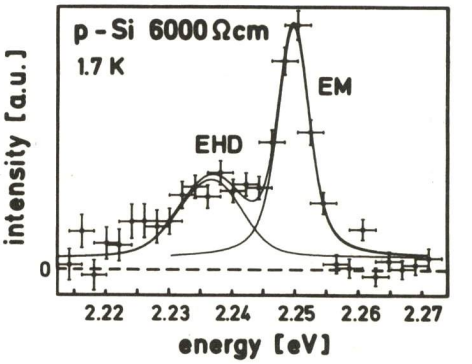

Fig. 4 Emission spectrum of Si[2;1] near $2E_g$: The EM line is much stronger than in Fig. (2)

The discrepancy is not clear up to now. We have verified that the TO phonon energy which enters the calculation is not dependent on stress in this region. Possibly it is caused by the inadequate treatment of the $2E_g$ EHD emission for T = 0K. However, a calculation of the $2E_g$ EHD line shape for finite temperature and finite intraband relaxation time is very complicated and has not been done.

V. Biexciton Lifetime

The FE and BI lifetimes have been measured in Si[2;1] and Si[4;1]. It has been found that the lifetimes are the same in both configurations, i.e., independent of bandstructure. The BI lifetime is about half the FE lifetime indicating that both are in thermal equilibrium. The values for the lifetimes are given in Table I.

Table I. Lifetimes of the FE and BI in stressed Si

	τ_{FE}	τ_{BI}
Si[4;1]	620 ns	320 ns
Si[2;1]	650 ns	300 ns

VI. "Biexciton Pocket"

If the sample is highly excited so that EHD are formed, the chemical potentials of the EHD, BI, and FE must be equal in thermodynamical equilibrium. In this case the density ratio of BI and FE can easily be computed [17]:

$$R = \frac{n_{BI}}{n_{FE}} = \frac{g_{BI}}{g_{EX}} \cdot \left(\frac{m_{BI}}{m_{EX}}\right)^{3/2} \cdot \exp\{-(\Phi - E_{BI})/kT\},$$

where g_i are the degeneracy and m_i the effective mass of the BI and FE.

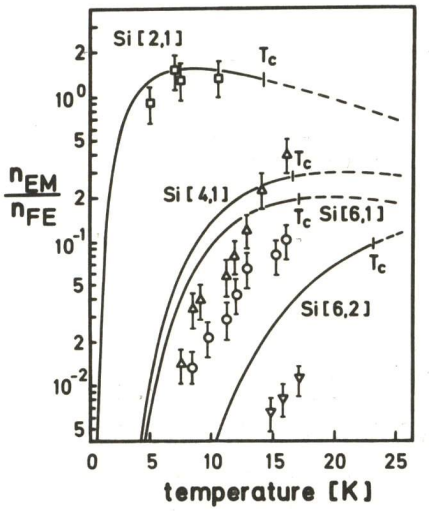

Fig. 5 Ratio of EM and FE densities in equilibrium with the EHD as a function of temperature

Assuming $\Phi(T) = \Phi_0 + \delta\Phi T^2$ this equation leads to the so called "biexciton pocket" [16]. The dependence of this ratio on temperature has been calculated based on theoretical values for the temperature dependent exciton work function [18]. The result is shown in Fig. (5). Experimentally the work function Φ^{exp} has been obtained from line shape fits of the near band gap spectrum.

The points in Figure (5) represent average values over many experiments. The error bars characterize typical scattering of these data. The agreement with theory is quite good for Si[2;1] whereas there is a significant deviation for Si[4;1], Si[6;1], and Si[6;2]. This is due to the fact that for the latter configurations the theoretical values for the ground state density and energy do not agree as well with experiment as in the case of Si[2;1] [10]. Also in the region of very low temperatures, this model does not apply because the assumption of thermodynamic equilibrium is not justified due to supersaturation effects.

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