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Triplet states in siloxene and porous silicon

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Abstract

Zero-field optically detected magnetic resonance (Zf-ODMR) investigations have revealed a broad distribution of the fine structure constants in crystalline siloxene and in porous silicon attributed to a broad distribution of triplet states in both materials. By time-resolved ODMR, a triplet emission (phosphorescence) can be identified. The electronic triplet energy and the spin–spin separation distance of the triplet spins are correlated via the decay times of time-resolved optical and ODMR spectroscopy. The light emitting states, the lowest triplet and the associated singlet state, have molecular character. A possible charge transfer character of the triplet state is discussed. © 1997 Elsevier Science B.V.

1. Introduction

Porous silicon shows a strong photoluminescence [1] and there is still a discussion about its origin. Some experimental results suggest a quantum confined state [1–3]. However, a molecular excited state is proposed as the cause of the luminescence [4]. The latter model is derived from investigations of a specific Si-O-H compound, siloxene, which shows very similar properties to porous silicon. It can therefore be used as a model substance.

High-field ODMR investigations on both materials gave evidence for the existence of a triplet state [5,6]. The side bands around the strong resonance signal at a g-value of 2 were interpreted as a triplet powder spectrum. The fine structure value D of this signal, which measures the spin–spin interaction of the two triplet spins was attributed to *one* well-defined triplet state localized on a silicon-6-ring.

To obtain more detailed information we used zero-field optically detected magnetic resonance to investigate powdered siloxene (as-prepared and annealed). By this method the fine structure constants of triplet states can be detected directly. Instead of the three sharp resonances which one expects for one triplet state we observed only one broad signal. We attributed this to a D-value distribution due to the existence of a broad distribution of triplet states. By a simple point-dipole model this distribution is correlated with spin distances of between 4 and 15 Å[7].

In this paper we extend our zero-field ODMR investigations to crystalline siloxene, which forms a well-defined structure of silicon layers terminated by OH-groups and H-atoms [8] and porous silicon. In addition temperature-dependent and time-resolved ODMR experiments are carried out. With these new experimental results we are able to propose a model for the excitation/recombination cycle and also a more specific picture about the nature of the triplet state and its role in the silicon luminescence.

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2. Experimental

In this paper we use the following abbreviations for the samples investigated: **Sx(ap)**: as-prepared siloxene powder, **Sx(an)**: annealed siloxene powder, **Sxcr(ap)**: as-prepared crystalline siloxene, **Sxcr(an)**: annealed crystalline siloxene, **p-Si**: porous silicon.

Powdered samples (Sx(ap) and Sx(an)) were prepared as described in Ref. [7].

The "crystalline" Wöhler siloxene [9] was synthesized from $CaSi_2$ [10]. The crystallinity was checked by X-ray diffraction. Due to the tetragonal conformation of the silicon atoms the Si-layers are not really flat but wavy. Therefore only a mean interlayer distance of 6.0 Å can be defined. Typical variations for this value are ± 0.5 Å with this preparation method and for the samples used in this paper.

Sxcr(an) was annealed for 1 h at 300°C and a pressure of 10^{-2} mbar.

The porous silicon samples were prepared from a highly boron doped (5×10^{18} cm^{-3}) silicon wafer contacting the hydrofluoric acid covered (100)-surface with the positive pole of a voltage supply. A current of 20 mA was applied for 5 min. The formed porous silicon was washed away with water and dried in air. The samples were macroporous with structures larger than 50 nm.

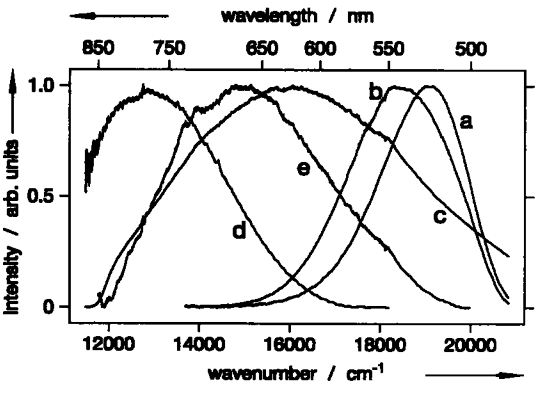

Fig. 1. Comparison of the normalized photoluminescence emission (PL) of the compounds investigated. Scaling factors are given in brackets. (a) Sx (×1) (λ_{exc} = 457.9 nm, 1 mW), (b) Sxcr (×1.2) (λ_{exc} = 457.9 nm, 20 mW), (c) Sx(an) (×35) (λ_{exc} = 363.3 nm, 20 mW), (d) Sxcr(an) (×85) (λ_{exc} = 363.3 nm, 50 mW), (e) p-Si (×60) (λ_{exc} = 363.3 nm, 20 mW). Temperature: 1.3 K.

The ODMR apparatus was a conventional system with direct synthesizers (AILTECH 380), frequency setting by a CPU and power amplification via a travelling wave tube (TWT) and solid state amplifiers. PIN-diodes were used for pulsing/modulation. For details see the block diagram given in Ref. [11]. All experiments were performed in liquid helium at about 1.3 K. The optical excitation was achieved via the UV and visible lines of an argon ion laser, the optical detection via a monochromator (Jobin Yvon HRS 1) followed by a PMT with S20 cathode or by a filter combination and a photodiode in case of the frequency sweeps given in Fig. 2.

The Zf-ODMR signals were obtained sweeping the microwave frequency and detecting the emission using a photodiode combined with a cutoff filter. Lock-in and averaging techniques were applied for the improvement of the signal to noise (S/N) ratio.

3. Results and data evaluation

3.1. Emission spectra

In Fig. 1 the photoluminescence (PL) emission spectra of Sx(ap), Sx(an), Sxcr(ap), Sxcr(an) and p-Si are shown. A significant red-shift and broadening of the emission spectra is found for the annealed samples in comparison to the as-prepared compounds. Additionally, the signal intensity decreases with the red-shift as indicated by the scaling factors. The excitation energy was chosen to obtain maximum absorption for each sample. This was checked by the photoluminescence excitation spectra. To avoid degradation, the excitation power was kept as low as possible for a good S/N ratio. The difference between the spectra of Sx(ap) and Sxcr(ap) might have structural reasons as a consequence of the sample preparation.

With increasing temperature we found a blue-shift for all samples which is consistent with the literature [12].

3.2. Zero-field optically detected magnetic resonance (Zf-ODMR)

Fig. 2 shows the Zf-ODMR signals for all preparations. We always find just one broad signal be-

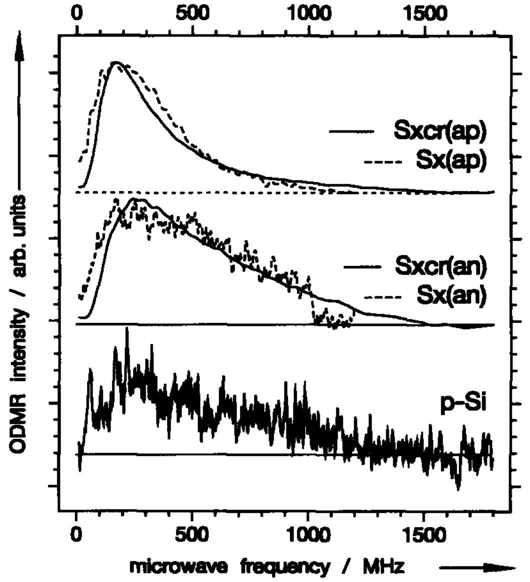

Fig. 2. Comparison of the Zf-ODMR spectra of Sx(ap), Sxcr(ap), Sx(an), Sxcr(an) and p-Si. Sxcr(ap) and Sx(ap) with excitation at 457 nm, 20 mW; Sx(an), Sxcr(an) and p-Si excited at 363 nm with 20 mW. Detection by a photodiode combined with a red glass filter 610. All spectra are normalized at their peak intensity. Temperature: 1.3 K. Microwave power: 800 mW for Sxcr(ap) and Sx(ap); 10 mW for Sxcr(an), 22 mW for Sx(an); 40 mW for p-Si.

tween 10 and 1500 MHz, peaking between 180 and 250 MHz, which is interpreted as a distribution of many different triplet states with different fine structure values *D*. A comparison of the signal shapes shows a higher signal intensity in the frequency range between 400 and 800 MHz for p-Si and the annealed preparations than for the as-prepared samples. This means that there are more triplet states with higher *D*-values. All signals are positive in sign, i.e. the microwave leads to an enhanced emission. The absolute signal intensity decreases by at least a factor of 20 when comparing the as-prepared and annealed samples and again by a factor of 5 when comparing the annealed siloxene and p-Si which means that the absolute number of light emitting excited states decreases. Infrared absorption spectra show changes in O- and H-related stretching modes when comparing the as-prepared and annealed samples so we deduce an increase in structural disorder by temperature treatment [10].

Holeburning experiments were successful, which prove the inhomogeneity of the signals [7]. This is a clear evidence for a distribution of states. Applying a second (hole burning) microwave source simultaneously (EEDOR), we extended our range of frequency sweeps to up to 3.6 GHz, but no additional signal was found [7]. It is well known, that in case of equal stationary populations of two of the three triplet sublevels, these EEDOR experiments would allow detection of the microwave-transitions between these two levels by lifting the population degeneracy.

The *D*-value roughly measures the distance between the two electrons forming the triplet state. Applying a point-dipole model to calculate the spin distance r_{ij} as a function of the microwave frequency ν results in the relation

$$\frac{r_{ij}}{\text{Å}} = \left(\frac{77.9}{(\nu/\text{GHz})} \right)^{1/3} . \qquad (1)$$

Using Eq. (1), $D_{\max}$ for Sxcr(ap) at a frequency of 175 MHz corresponds to a spin distance of approximately 8 Å. In addition, the number N of triplet spins with a distance r_{12} in a small distance interval $\mathrm{d}r_{12}$ can be calculated. Using the distribution of Fig. 2 we obtained the maximum value for $N(r_{12}r_{12})$ at $r_{12} = 6$ Å in case of Sxcr(ap).

3.3. Time-resolved (optical and ODMR) measurements on Sxcr(ap)

Transient Zf-ODMR measurements have been performed by applying a microwave pulse of 34 ms (see Fig. 3) matching the time constants of the emission. Switching on the microwave power leads to an abrupt increase of the emission intensity. A new equilibrium value is reached after several mil-

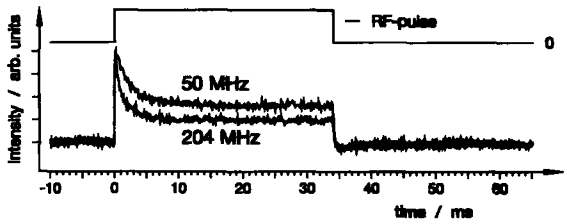

Fig. 3. Time-resolved Zero-field ODMR on crystalline siloxene Sxcr(ap). Microwave pulse: 50 MHz (upper transient) and 204 MHz (lower transient) with 1 W microwave power. Duration: 34 ms. Optical excitation: 457.9 nm, 20 mW. Detection: photodiode with filter combination RG610. Temperature: 1.3 K.

liseconds. Turning off the RF, the emission intensity decreases immediately to a value below the starting point, reaching the base level again after several milliseconds.

This experiment was done in the frequency range shown in Fig. 2. There is a clear indication that a faster accomplishment of the new equilibrium value after pulse excitation is achieved on going to higher frequencies, which continues till the highest frequencies. Between 50 and 1000 MHz the decay rates increase by a factor of 2.5.

Such a variation in decay times is also found in time-resolved photoluminescence emission, if one measures the decay as a function of the wavelength at 1.3 K. In agreement with the literature [13], on going from 15200 cm^{-1} to 19600 cm^{-1} the decay rates of the photoluminescence increase by a factor of 1.7 and are of the same order of magnitude as for the zero-field ODMR transients. This is not accidental as we will see later.

To prove this model, temperature-dependent measurements are performed. On increasing the temperature, the ODMR-signal barely changes the shape but decreases in intensity and the transients become faster. Above 40 K the signal has disappeared. The decay rates for the optical emission increase with temperature from 1.3 to 300 K by a factor of about 100 [12,13].

Time-resolved ODMR on p-Si was not possible just by simple frequency pulses due to S/N problems (see Fig. 2). A fast passage experiment as an integral measurement gives an estimation of the decay time of about 2 ms.

4. Discussion

4.1. Nature of the triplet state

The experimental results shown above and the corresponding properties allow us to draw a more detailed picture of the triplet state in siloxene and porous silicon. As described earlier [7] we attribute the broad and unstructured Zf-ODMR signal to a distribution of many triplet states, with different spin separation distances.

A g-value of 2 as found by high field ODMR experiments (in porous silicon, siloxene and even in amorphous silicon suboxide alloys [5,6,18]) points to a localized excited triplet state rather than to that of a Wannier state which possesses orbital angular momentum.

The temperature-dependence of the time-resolved optical spectra [12,17] can be explained with a two-level system formed by the singlet and the associated triplet state. Finkbeiner and coworkers estimated from these decay rates a S_1–T_1 separation of between 70 and 640 cm^{-1} depending on the sample/preparation and also on the detection wavelength [12,17]. The latter result is also an indication of a distribution of states.

Finkbeiner and coworkers [13,17] deduced from the analysis of the optical transients a charge separation after optical excitation. Consequently singlet and triplet states can be formed depending on the relative correlation of the two interacting spins. The significant change in the temperature-dependence of the decay rates points strongly to radiative transitions from both excited states to the ground state. Significantly the steep rise of the ODMR-transient is proof for the radiative transition from the triplet to the ground state. This step-like change in the emission intensity and the linear dependence of the delayed emission intensity from excitation power are a clear proof for phosphorescence detection [19,20].

Therefore we can present a general scheme for the excitation/recombination cycle in crystalline siloxene given in Fig. 4 (upper part). By the optical excitation electrons and holes are separated. The next step is a spin-dependent relaxation into a singlet or triplet state. The radiative transitions from singlet states are attributed to fluorescence above 150 K, the low temperature emission is identified as phosphorescence (radiative transitions from triplet states).

The model presented is a molecular model as the nature of the excited states shows typical molecular properties. The facts that the distribution width of singlet and triplet states exceeds the S_1–T_1 energy separation and additionally that there are no changes in the shape of the cw-ODMR signal when varying the detection wavelength, may have their foundations in an energy transfer between different localized excited states.

Therefore not only are a broad distribution of triplet states, with different spin separation and electronic energies, but also a corresponding distribution of singlet states, present.

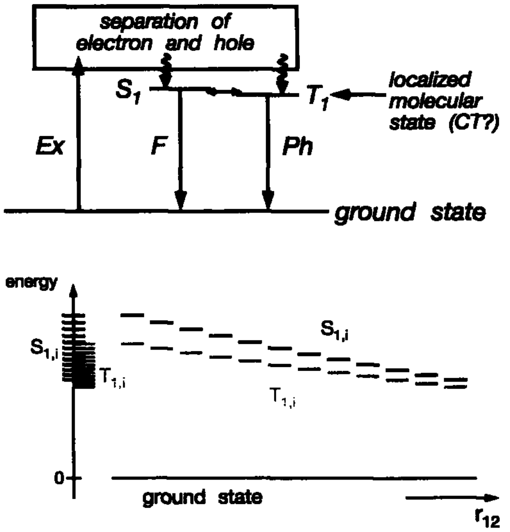

Fig. 4. Upper part: Scheme for the excited states of crystalline siloxene Sxcr(ap): Optical excitation (Ex) from the ground state leads to a spatial separation of electron and hole. Singlet and triplet states are formed by spin-dependent localization. Fluorescence (F) and phosphorescence (Ph) is allowed but temperature-dependent. Lower part: Model for the singlet–triplet separation. The energetic levels of the lowest excited singlet ($S_{1,i}$) and triplet ($T_{1,i}$) states are correlated with the spin distance r_{12} of the triplet state. The width of the singlet and triplet manifold projection on the energy scale is correlated with the fluorescence ($S_{1,i}$) and phosphorescence ($T_{1,i}$) [21].

4.2. *Correlation of electronic energy and spin separation distance*

The fact that the decay rates of the transient optical and the ODMR measurements are of the same order of magnitude within the experimental accuracy, is not accidental, as we deal at low temperature with transient phosphorescence measurements in both cases. This allows a correlation of electronic energy and spin separation. The optical decay rates increase with higher energies and the ODMR decay rates increase with higher frequencies (smaller spin separation). As a consequence we attribute larger spin separation distances to triplet states lower in electronic energy. This is shown in the lower part of Fig. 4. Furthermore the singlet–triplet separation decreases with increasing spin distance and decreasing electronic energy of the states [12]. The manifold of triplet states gives rise to the emission spectra (phosphorescence) at helium temperature and the manifold of singlet states is responsible for the fluorescence spectra above 150 K. This is indicated by the projected energy levels on the energy axis.

4.3. *Correlation of the triplet state and the structural properties*

The broad distribution of triplet states found even in crystalline siloxene, the sample with the highest structural order, leads to the conclusion that even minor changes in the structural environments of the light emitting states have significant effects on electronic energy and spin separation distance.

For a correlation of the extension of the triplet state with the microscopic structure of crystalline siloxene we calculated the number of triplet states as a function of the spin separation distance using the *D*-value distribution of Fig. 2. This results in a spin–spin distance of about 6 Å at the maximum of the calculated distribution. This can be due to intralayer but also to interlayer spin pairs constituting the triplet. It should be mentioned, however, that the mean Si-interlayer distance of 6 Å for our preparations varies only by about ± 0.5 Å. The possibly accidental correspondence of the Si-interlayer distance and the most probable spin–spin distance might be further clarified by varying the constituents.

However, earlier investigations show the same correlation of electronic triplet energy and spin separation distance [6]: triplet states higher in energy have smaller spin–spin distances. But the spin–spin separations of between 3 and 4.5 Å for as-prepared siloxene calculated in Ref. [6] are probably too small. As described in the introduction the reason can be found in the (mis-)interpretation of the high-field ODMR spectum as only *one* well-defined triplet state.

4.4. *Comparison with other systems*

The large spin separation distances found for the triplet states raise the question of whether the spin separation is connected to a charge separation or not. Broad structureless ODMR signals at low frequencies were observed and discussed for completely different systems. Examples are conducting polymers (Zf-ODMR on poly-para-phenylene-vinylene (PPV) films [14]) and non-emitting reduced reaction centers of photosynthetic bacteria [15,16]. This comparison would point to a triplet state with charge transfer (CT) character in our system, which is also supported by the time-resolved optical and ODMR experiments. They clearly exhibit lifetimes in the order of ms, much too long for lifetime broadening.

Small singlet–triplet separation automatically is a consequence of low overlap-integrals of the orbital wavefunctions which arise if the electrons, constituting the triplet are localized far away from each other e.g. on separate molecules. A systematic correlation of $\Delta E(S_1-T_1)$ and the charge transfer character of the excited triplet state is given in Ref. [11]. The comparison of our singlet–triplet separation with these values allows to estimate the CT-character of our localized triplet states nearly 100%.

4.5. Porous silicon

Although less pronounced than in crystalline siloxene due to the smaller S/N ratio of the signal, qualitatively similar optical and ODMR results are obtained in p-Si. Therefore it seems probable that our model and the interpretations are also valid for p-Si. For a more precise statement the microscopic structure of p-Si should be better clarified.

5. Summary and conclusions

The rather tentative interpretation of our first ODMR-attempts [7] on powdered siloxene can be confirmed and extended by the optical and ODMR-experiments on crystalline siloxene and porous silicon.

Our model: charge separation after optical excitation, spin-dependent localization in singlet and triplet states which both decay radiatively can explain the optical properties. The triplet state is formed by separated electrons (spins) and the associated singlet state can be described as a molecular excited state. A comparison with well-known systems points to a rather strong CT character. We learn from the correlation of the optical and ODMR decay rates, that $\Delta E(S_1-T_1)$ is smaller, the more red the emission and the slower the decay. Due to structural disorder there is a broad distribution in the spin distances (Zf-splittings) and huge site effects governing the width of the optical spectra.

In both the crystalline samples and the porous silicon we found a distribution of triplet states rather different in electronic energy and spin distance for all preparations. The distributions of the spin distances show weakly pronounced differences: the better defined the sample in structure the larger is the mean distance between the two spins forming the triplet state.

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