Pergamon

Solid State Communications, Vol. 96, No. 9, pp. 665–670, 1995
Elsevier Science Ltd
Printed in Great Britain

0038-1098(95)00505-6

0038-1098/95 $9.50+.00

ZERO FIELD-ODMR AND EMISSION/MICROWAVE DOUBLE RESONANCE ON OPTICALLY EXCITED SILOXENE

H. Pioch, J.-U. von Schütz and H. C. Wolf

3. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany

(*Received* 13 *June* 1995; *accepted* 14 *July* 1995 *by M. Cardona*)

The first zero field optically detected magnetic resonance experiments on siloxene as-prepared (Sx(ap)) and annealed (Sx(an)) revealed a single inhomogeneously broadened signal reaching from 30 up to 1000 MHz. It is attributed to a distribution of triplet states from electron hole pairs (bound excitons?), whose spins are separated between 14 and 4.5 Å. Using emission/microwave double-resonance techniques, a weak emission could be resolved in the long wavelength part of the broad photoluminescence (PL) spectrum of both materials. The maxima of these microwave affected emissions are shifted by 1100 cm^{-1} for Sx(ap) and 1300 cm^{-1} for Sx(an) against the PL maxima, respectively.

Keywords: A. Semiconductors, D. Electronic States, E. Electron paramagnetic resonance, E. Luminescence.

1. INTRODUCTION

The interesting question whether the strong photoluminescence of porous-Si [1] is due to structural properties (disorder or quantum confinement [1, 2, 3]) or due to "chemical effects", e. g. specific Si-O-H compounds (siloxene and its derivatives [4]), is still under controverse discussion.

The striking similarity in both photoluminescence and magnetic resonance data (ESR in X-band [5]) between porous Si and Wöhler siloxene suggested the presence of some siloxene compounds in porous Si. Both, ESR and high field-ODMR clearly revealed magnetic transitions of $S = 1/2$ states (localized defects due to dangling bonds) and of $S = 1$ states, identified as triplets by $\Delta m = 2$ transitions [6].

Their broad, more or less Gaussian shaped ESR-line was correlated to a dipolar interaction (broadening) between the spins of the two species constituting the (bound) excitonic state.

A separation between the spins of the order of 4 Å was evaluated matching the proposed Si-six membered ring structure, isolated by oxygen atoms from the next unit [7, 8, 9].

In order to contribute to the question of the lineshape and linewidth found in high-field ODMR, we decided to perform similar experiments in zero magnetic field.

In zero field (Zf), due to the lack of Zeeman splitting, there are no $S = 1/2$-states detectable. The quantization and energy splitting is given by the fine structure (FS) tensor $\boldsymbol{F}$ only and the hyperfine structure (hfs) is

reduced to second order pertubation.

On the first glance it seems that we loose information in zero field, but there are advantages on the other hand: The $S = 1/2$-signal obscuring partially and interfering with the triplet signal in high field ESR does not appear at all, and in our powdered samples the random orientation of the FS-tensor $\boldsymbol{F}$ (quantized in the symmetry of the molecule) as well as the g-factor anisotropy does not cause any broadening. Both effects lead to a broad powder spectrum in high field.

If we dealt with just one triplet species we would expect three narrow ODMR signals at $\nu_{\text{microwave}} = |D| + |E|$, $|D| - |E|$ and $2|E|$ (figure 1). D and E represent the FS-constants as given in [10].

The authors of the high field ODMR [6] claim to detect the microwave induced changes in the emission directly, i. e. via the triplet state emission. It must be mentioned, however, that microwave induced changes in optical properties can be achieved also indirectly, since the change in the steady state value of the triplet concentration affects that of the ground state population as well; fluorescence-detected [11] or absorption-detected ODMR [11] are best examples for that.

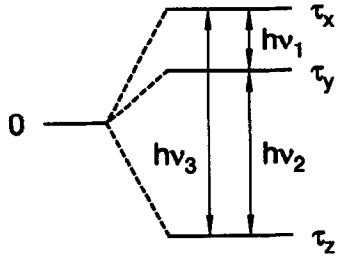

Fig. 1. Zero field splitting of the triplet state (schematically). The indicated transitions between the three possible spinfunctions τ_i have the following energies:

$$h\nu_1 = 2|E|$$
$$h\nu_2 = |D| - |E|$$
$$h\nu_3 = |D| + |E|$$

2. EXPERIMENTAL

In this paper we use the following abbreviations for siloxene:

siloxene as-prepared: Sx(ap)
siloxene annealed: Sx(an)

The preparation of the samples was according to ref. [12, 13] and from the batch used for the high field ODMR [6]. The annealing conditions used for Sx(an) were 2 minutes at 400°C which may have not been entirely sufficient to convert the whole sample as we will see later.

The ODMR set-up was a conventional system with direct synthezisers (AILTECH 380), frequency setting by a CPU and power amplification via TWT and solid state amplifiers. For details see the block diagram given in [11]. All experiments were performed at the temperature of pumped Helium (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. 3 and 4.

The Zf-ODMR signals were obtained sweeping the microwave frequency and detecting the emission using a photodiode combined with a cutoff filter.

The microwave induced emission (MIE) spectra were performed by modulation of a frequency source fixed in frequency while sweeping the wavelength of the monochromator.

Lock-in and averaging techniques were applied for the improvement of the S/N ratio.

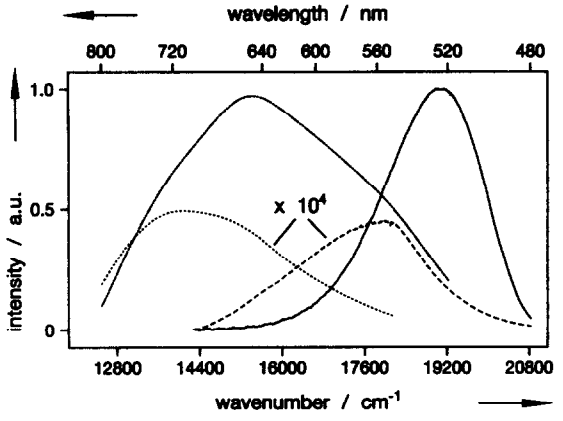

Fig. 2. Photoluminescence (PL) emission of Sx(ap) —, excitation at 457 nm, Sx(an) — · · —, excitation at 360 nm. Both spectra are normalized to 1 at their peak intensity and corrected with the spectral sensitivity of the apparatus. The curves normalized to 0.5 represent the respective MIE spectra (x10^4, see text) of Sx(ap) - - - and Sx(an) · · ·. Excitation conditions as in case of the respective PL.

3. RESULTS

3.1. Emission Spectra

In fig. 2 the PL emission spectra of Sx(ap) and Sx(an) are given, matching with those given in the literature [5]. Only the slightly different shape of the photoluminescence spectra of Sx(an) shows a sizeable contribution of insufficiently annealed siloxene.

3.2. Zero Field Optically Detected Magnetic Resonance (Zf-ODMR)

In fig. 3 and fig. 4 the Zf-ODMR-signals of Sx(ap) and Sx(an) are given. We have just one broad signal starting at about 30 MHz, peaking at about 200 MHz and reaching up to 1000 MHz (Sx(an)). In case of Sx(ap) the asymmetry is more pronounced at higher power levels. All signals are positive in sign, i. e. the microwave leads to an enhanced emission.

The inhomogeneous origin of the signals in fig. 3 and 4 is shown by hole burning attempts. These experiments are performed using a second microwave source, unmodulated and fixed in frequency, in addition to the sweeping frequency source. This microwave-source saturates the transitions in the vicinity of its frequency permanently, resulting in a hole in the Zf-ODMR spectrum. This hole burning attempt is given in the inset at the upper left corner.

If this second microwave-power source is modulated, just the "inverse hole" appears in the sweeps only, as given in expanded frequency scale in the upper right inset. Both widths coincide with each other.

It should be mentioned, that hole burning, i. e. an enforced reduction of the emission intensity by a second

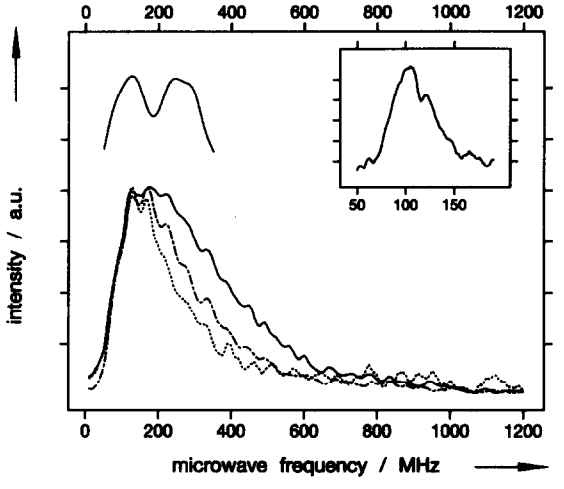

Fig. 3. Main figure: Zf-ODMR-signal of S(ap) at 3 power levels (100 mW: —; 10 mW: - - - -; 1 mW: · · ·), modulation frequency: 1030 Hz. Upper part left: sweep with holeburning cw power at 200 MHz, 100 mW. Upper part right: sweep while hole burning at 100 MHz, now modulated with 1030 Hz, sweep power unmodulated. Optical excitation as given in fig. 2. Detection with a photodiode and $\lambda_{det} > 610$ nm.

microwave power source, is one of the most significant proofs for a "real signal". All artificial features, e. g. heating effects or pseudo resonances in broadband microwave systems, would lead to an enhancement of the emission intensity by the second power source rather than to a reduction.

3.3. Electron-Electron DOuble Resonance - Attempts (EEDOR)

Applying this second (hole burning) microwave source simultaneously (EEDOR) we extended our range of frequency sweeps up to 3.6 GHz, but no further signal was found. It is well known, that in case of equal stationary population of two of the three triplet sublevels, these EEDOR-experiments would allow to detect the microwave-transitions between the two levels by lifting the population degeneracy.

3.4. Microwave Induced Changes in the Emission (MIE-Spectra)

Modulation of the microwave-power at a fixed frequency value within the frequency range of our signal (e.g. at the hole burning frequency) results in an modulation-response of the emission of those states which are coupled to the microwave-induced magnetic transitions. Slowly scanning the monochromator results in the MIE-spectrum given in fig. 2 which is shifted to the red with respect to the PL (total emission) and appears much weaker in amplitude: I(MIE)/I(PL) $\sim 10^{-4}$! The values for the maxima in the spectra are as follows:

Sx(ap):	$\bar{\nu}_{max}$(PL) = 19080 cm^{-1}	(524 nm)
	$\bar{\nu}_{max}$(MIE) = 17990 cm^{-1}	(556 nm)
Sx(an):	$\bar{\nu}_{max}$(PL) = 15430 cm^{-1}	(648 nm)
	$\bar{\nu}_{max}$(MIE) = 14100 cm^{-1}	(709 nm)

This red shift is in accordance to the qualitative findings of [6], that the relative (absolute) amplitude change of the microwave induced emission intensity by microwave increases with increasing detection wavelength within the broad emission. If it holds that we directly change the triplet emission resulting from the T_1-S_0-transition by microwave, this MIE-spectrum would represent the phosphorescence. Time resolved emission spectra may result in similar findings as the PL decay becomes slower with increasing wavelength [14].

4. DISCUSSION

The Zf-ODMR spectra fig. 3, 4 do not reveal one well defined triplet state. Instead of 3 signals we just have one broad line, asymmetrically shaped and inhomogenously broadened in an unusual manner. Such broad signals can be obtained, if we assume a wide distribution of triplet states with different fine structure values. This may be due to a distribution of the distances between

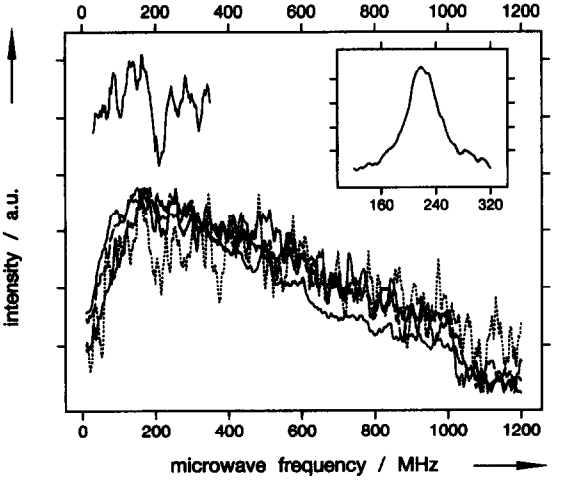

Fig. 4. Main figure: Zf-ODMR-signal of Sx(an) at 4 power levels (2200 mW: —; 220 mW: – – ; 22 mW: ·· — ··; 2 mW: · · ·), modulation frequency: 1030 Hz. Upper part left: sweep while hole burning cw power at 200 MHz, 100 mW. Upper part right: sweep with hole burning at 200 MHz, modulated with 1030 Hz, sweep power unmodulated. Optical excitation as given in fig. 2. Detection with a photodiode and $\lambda_{det} > 550$ nm.

electron and hole in the bound exciton. Assuming the point-dipole model (with $E = 0$) used for the interpretation of the high field-ODMR [9], the onset of our signal at 30 MHz corresponds to a spin-spin separation of 14 Å, the peak intensity at 200 MHz to about 7 Å, and the upper most detected value of 1000 MHz to a separation of 4.5 Å. Taking into account that our Sx(an) sample is not entirely annealed, the upper most correction — the whole low frequency part of fig. 4 is due to Sx(ap) — still results in a broad frequency distribution with its onset at about 200 MHz, peaking at 400 MHz and the upper most detected value of 1000 MHz. This expresses that the mean dipolar distance shifts from about 7 Å to 5.8 Å from Sx(ap) to Sx(an) respectively. In spite of the subtraction of the Sx(ap) frequency profile from the Sx(an)-ODMR-signal (fig. 4) we still see that we do not deal with one well defined triplet state but with a wide distribution of states for both samples.

Our estimated spin-spin seperations are generally somehow larger than that reported from the high field-ODMR [6]. These authors deduced their value from the width of their ESR-signal. One reason for an additional broadening in high field experiments — in addition to the proposed distribution of triplet states — could be a g-factor anisotropy leading to an artificially enhanced D-value.

It is obvious, that there is a rather sharp limit to lower frequencies (largest radii) which in principle tells us that at distances larger than 14 Å there is no long living bound state between the two spins. Correlations to structural properties are lacking until now, but just one dominant structure, e. g. a Si-sixring as assumed from [6], cannot be supported by our results because there is still the contradiction between the three expected Zf-ODMR signals (according to the high field-ODMR) and the actually found broad Zf-ODMR signals. In the high field-ODMR, these "low frequency states" are obscured totally by the $s = 1/2$, $g = 2$ signal originating from the dangling bonds.

Obviously, there are more closely bound excitonic states (higher frequencies) in Sx(an), pointing that the high frequency states seen at high power levels in the Sx(ap)-Zf-ODMR are due to some Sx(an) structure in the original material (and vice versa). An inhomogeneity of Sx(ap)-material was clearly demonstrated by the high field-ODMR line width as a function of the detection wavelength [6]. Such experiments in zero field suffer from the low S/N ratio, and may even be hidden in the large distribution of states.

In the point dipole model used, the asymmetry of the fine structure tensor is dropped by setting E to zero. This rather crude approximation may be justified by a circle like spin distribution on a sixfold Si-ring as assumed to be the structure for the triplet state. This well defined structure, however, would not result in such a broad distribution of frequencies. Therefore microwave transitions involving splittings caused by an asymmetric spin distribution ($E \neq 0$) may be hidden under the broad Zf-ODMR (and high field-ODMR) signal. Evaluating the width and shape of the burnt holes would therefore be ambiguous.

It should be mentioned, that Zf-ODMR experiments in GaP:Cu [15] have resulted in a similar distribution of states (frequencies) spread over 1000 MHz, having a quite comparable profile to our signal. The signals, however, are shifted to higher Zf-splitting values as expected for the tight binding between the spins constituting the bound triplet exciton in GaP:Cu.

Further experiments on single crystalline Sx are in preparation [16].

5. SUMMARY

The wide, inhomogeneously broadened Zf-ODMR

spectrum of Sx(ap) and Sx(an) is attributed to a distribution of excitonic states having different distances between the two spins of the exciton and therefore different fine structure splittings. Such a distribution is consistent with the distribution of the decay times of the PL found by Finkbeiner et al. [14]. With our microwave induced emission (MIE) experiment we were able to reveal a weak, red shifted emission. It is hidden below the total PL emission and may be attributed to the phosphorescence of our triplet states. The highest microwave frequencies (strongest bound excitons) belong to the most redshifted states. A correlation to structural properties is not possible yet. Comparison of the frequency profiles of Sx(ap) and Sx(an) shows, that in the latter case only an amount of 20 % of the triplet states have Sx(ap) character.

Acknowledgements — We thank M. Rosenbauer (Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany) for the kind gift of the samples used, H.-J. Qucisser and J. Weber for stimulating discussions.

REFERENCES

[1] L. T. Canham. *Appl. Phys. Lett.*, **57**, 1046 (1990).

[2] P. Deák, M. Rosenbauer, M. Stutzmann, J. Weber, and M. S. Brandt. *Phys.l Rev. Lett.*, **69**, 2531 (1992).

[3] V. Lehmann and U. Gösele. *Appl. Phys. Lett.*, **58**, 856 (1991).

[4] M. S. Brandt, H. D. Fuchs, M. Stutzmann,J. Weber, and M. Cardona. *Solid State Commun.*, **81**, 307 (1992).

[5] M. Stutzmann, M. S. Brandt, M. Rosenbauer, H. D. Fuchs, S. Finkbeiner, J. Weber, and P. Deák. *J. Lumin.*, **57**, 321 (1993).

[6] M. S. Brandt and M. Stutzmann. *Solid State Commun.*, **93**, 473 (1995).

[7] M. Stutzmann, M. S. Brandt, E. Bustarret, H. D. Fuchs, M. Rosenbauer, A. Höppner, and J. Weber. *J. Non-Cryst. Solids*, **164-168**, 931 (1993).

[8] H. D. Fuchs, M. Stutzmann, M. S. Brandt, M. Rosenbauer, J. Weber, A. Breitschwerdt, P. Deák, and M. Cardona. *Phys. Rev. B*, **48**, 8172 (1993).

[9] M. S. Brandt, M. Rosenbauer, and M. Stutzmann. *Mat. Res. Soc. Symp. Proc.*, **298**, 301 (1993).

[10] S. P. McGlynn, T. Azumi, and M. Kinoshita. *Molecular Spectroscopy of the Triplet State.* (1969).

[11] J. Krzystek and J. U. von Schütz. *Triplet Excitons in weak organic Charge-Transfer Crystals*, volume LXXXVI of *Adv. Chem. Phys.*, 167 (1993).

[12] F. Wöhler. *Lieb. Ann.*, **127**, 275 (1863).

[13] H. Kautsky and H. Zocher. *Z. Phys.*, **9**, 267 (1922).

[14] S. Finkbeiner, J. Weber, M. Rosenbauer, and M. Stutzmann. *J. Lumin.*, **57**, 231 (1993).

[15] E. H. Salib and B. C. Cavenett. *J. Phys. C: Solid State Phys.*, **17**, L251 (1984).

[16] In collaboration with J. Weber.