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TRIPLET EXCITONS IN POROUS SILICON AND SILOXENE

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The microscopic nature of the excited state responsible for the strong visible photoluminescence in porous silicon and siloxene is determined by optically detected magnetic resonance (ODMR). The observation of dipole-forbidden $\Delta m = \pm 2$-transitions proves that this excited state is a triplet exciton. The allowed $\Delta m = \pm 1$-transition has the characteristic shape of a Pake-doublett due to spin-spin interaction, with a linewidth of ≈500 G independent of the photon energy monitored. These results are qualitatively incompatible with geometric quantum confinement, and point to a molecular origin of the radiative center.

I. INTRODUCTION

THE MICROSPOPIC origin of the strong visible luminescence of porous silicon [1,2] is still unclear, despite a large number of experimental and theoretical investigations. The considerable structural inhomogeneity of porous silicon (silicon wires, nano-crystallites, interfacial layers, amorphous matrix) renders a correlation between luminescence and structural properties very ambiguous, since the luminescence could originate from a minority phase not easily identifiable against the background of other structural constituents. Polysilanes, amorphous suboxides, or siloxene have been suggested as such minority phases responsible for the luminescence [3-5]. A more promising approach is to directly analyse the luminescence properties of porous silicon (eg. temperature dependence, excitation spectroscopy etc.) themselves. Thus, phonon structure in the photoluminescence of resonantly exited porous silicon has been taken as evidence for emission from silicon microcrystals with an indirect bandgap [6], although different explanations have been given for this structure [7].

The most direct information about radiative centers in semiconductors and insulators usually comes from optically detected magnetic resonance (ODMR) [8]. In this technique, the luminescence properties (spectral shape, polarisation state, decay time, etc.) are correlated with spin properties of the radiative state and of non-radiative recombination centers. In the following, we will present results of a comprehensive investigation of ODMR in porous silicon and siloxene. Based on these results, we can identify triplet excitons as the initial radiative state. Moreover, we find almost identical ODMR spectra in porous silicon and annealed siloxene, providing conclusive evidence for a common origin of luminescence in these two materials.

A well known problem with porous silicon is the difficulty to obtain samples whose preparation and storage conditions are widely accepted as standard. Therefore, we have investigated and compared samples either prepared by ourselves or obtained from other groups. All samples were different in exact preparation conditions (current density, electrolyte, stain etching), substrate material (p-type, n-type, amorphous [9]), age or degree of oxidation [10], but showed the same strong photoluminescence at around 700 nm whose origin is the subject of the present discussion. Siloxene was obtained by a reaction of $CaSi_2$ with HCl at 0°C with or without subsequent transformation by thermal annealing [11]. ODMR measurements were performed at temperatures between 4.2 K and 100 K using a commercial X-band spectrometer (Bruker ESP 300) with magnetic field modulation and/or microwave chopping. The luminescence was excited by the 457 nm line of an Ar^+-laser with a typical power density of 50 mW/cm^2. For the detection of the luminescence, a silicon photodiode with an integrated amplifier was used. Most spectra were taken by filtering the luminescence light with different edge- or interference filters. Typical modulation frequencies were between 10 Hz and 10 kHz, with the best signal-to-noise ratios obtained around 1kHz, corresponding to the inverse luminescence decay time.

II. TRIPLET STATES IN OPTICALLY DETECTED MAGNETIC RESONANCE

In Fig. 1, we show a schematic view of the different electronic states involved in radiative transitions of a triplet

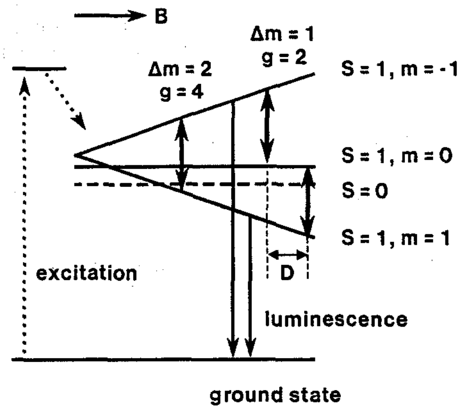

Fig. 1 Term scheme showing the transitions relevant to the detection of luminescence from triplet excitons by optically detected magnetic resonance.

exciton. Starting from the ground state with total spin $S = 0$, optical excitation and thermalization lead to an excitonic state with one of two possible total spin values, $S = 0$ and $S = 1$ [12]. The $S = 0$ state is singly degenerate and does not couple to an external magnetic field. The $S = 1$ state splits into three Zeeman levels according to the different values of the magnetic quantum number, $m_S = -1, 0, 1$. The four excited states ($S = 0$ and $S = 1$) will be populated with a finite probability, depending on the details of excitation and thermalization (quenching of the orbital momentum by the crystal field followed by a spin transition into the triplet state). Once thermalized, radiative recombination of the exciton can only occur from those substates which are allowed by conservation of total angular momentum. For a localized (Frenkel type) exciton with orbital angular momentum $L = 0$, these are the $m_S = 1$ and $m_S = -1$ Zeeman levels of the triplet state, since the photon carries away a unit angular momentum. Excitons in the $S = 0$ singlet or in the $m_S = 0$-substate of the triplet can only recombine following spin transitions into the $m_S \pm 1$ sublevels caused by spontaneous spin relaxation or by an external resonant microwave field. The last possibility is exploited in the ODMR technique, where one observes an increase of the luminescence intensity I under spin resonance conditions of the luminescent state [8]. In a similar way, the effect of a paramagnetic non-radiative recombination center is a resonant decrease of the luminescence. The relative size $\Delta I/I$ of the observed change depends mainly on the ratio of the spontaneous and the microwave-induced resonant spin-flip rates and on the degree of spin polarization.

III. ODMR OF SILOXENE AND POROUS SILICON

We first present ODMR spectra of siloxene in the as-prepared and annealed state which to our knowledge have not been described in the literature before. Siloxene consists of two-dimensional silicon planes terminated by hydrogen or hydroxyl-radicals. Details of the structure of this material and its electronic properties have been discussed recently [13–15]. The main feature of as-prepared siloxene is its direct bandgap which should give rise to effective generation of excitonic states. Indeed, luminescence occurs as a narrow peak at the bandedge and is most effectively excited for photon energies slightly above the bandgap ($E_{\text{excit}} - E_{\text{lum}} \approx 0.3$ eV). In contrast, the luminescence of annealed siloxene occurs at lower energies, but is best excited in the UV ($E_{\text{excit}} - E_{\text{lum}} \approx 2$ eV), very similar to what is observed in porous silicon [16]. This annealing induced change is due to the destruction of the two-dimensional silicon planes and the crystallinity by the insertion of oxygen, resulting in strongly disordered silicon-oxygen-hydrogen network dominated by localized states [17].

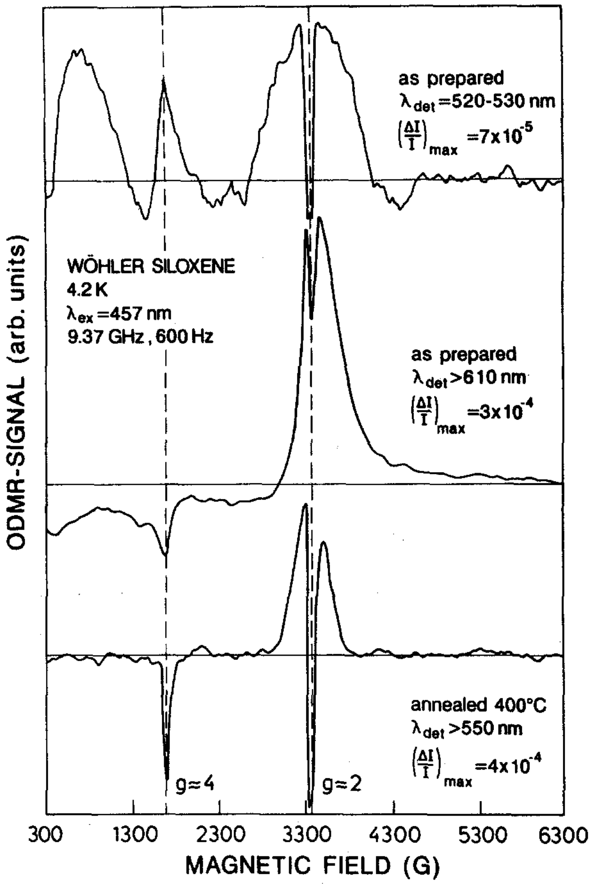

Fig. 2 Comparison of the ODMR spectra of as-prepared and annealed siloxene. λ_{lum} gives the wavelength range used to detect the ODMR. Note the large differences between both ODMR spectra, which correspond to the observed changes of the optical properties in Fig. 1.

ODMR spectra of as-prepared and annealed siloxene are shown in Fig. 2. The main features of all three spectra are: (i) a broad enhancing line around the free-electron g-factor of 2 with a full width at half maximum between 300 G and 1000 G, (ii) a weaker resonance at the position of the forbidden triplet transition $\Delta m_S = \pm 2$ ($g = 4$) and (iii) a narrow strong quenching line at $g = 2.005$ [18]. This latter ODMR signal has already been observed previously and has been assigned to nonradiative recombination at dangling bond-like defects of the siloxene structure which can also be detected in standard ESR [19]. These quenching resonances contain little information about the radiative state and are not of primary interest here. Since distant electron-hole pairs with decoupled spins cannot give rise to $\Delta m = \pm 2$ transitions, the simultaneous observation of the $g = 4$ resonance and of the broad enhancing line at $g = 2$ constitutes direct evidence for the existence of a radiative triplet exciton state.

The ODMR spectra of as-prepared siloxene show a rather complicated dependence on the wavelength of the luminescence used to detect the magnetic resonance, as indicated in Fig. 2. Most pronounced is a decrease of the full width at half maximum of the broad enhancing line and the change in sign of the $g = 4$ resonance. An additional, about 150 G broad enhancing resonance at $g = 2$ is only visible at the beginning of an ODMR experiment and disappears quickly due to laser-induced degradation. The microscopic information about triplet excitons in the two-dimensional Si layers of as-prepared siloxene contained in the ODMR spectra of Fig. 2 will be discussed in detail elsewhere. In the remainder of this article we will instead concentrate on the remarkable similarities between the ODMR spectra of *annealed* siloxene and porous Si which have previously been shown to exhibit almost identical photoluminescence features.

To this end, we compare in Fig. 3 ODMR spectra and time-resolved ODMR transients of porous Si and annealed siloxene. The resemblence between both materials is striking, both qualitatively and quantitatively. For example, the characteristic lifetime of the ODMR transients is almost the same (1 to 2 ms) in porous silicon and annealed siloxene and, moreover, agrees well with the radiative lifetime in both materials as deduced from time-resolved photoluminescence measurements [20]. This close correspondence leaves little doubt that the triplet exciton states responsible for radiative processes in porous Si and in annealed siloxene have an almost identical microscopic structure. Small differences between the low temperature photoluminescence decay times are due to different defect densities, which are known to act as nonradiative recombination centers also in porous silicon [21].

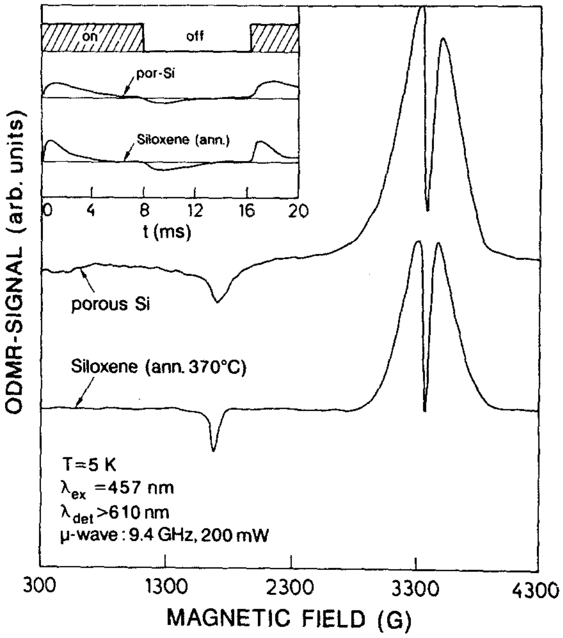

Fig. 3 Comparison of the ODMR spectra of porous silicon and annealed siloxene. The inset shows time-resolved ODMR transients obtained by switching on and off the resonant microwave power.

IV. DISCUSSION

Relevant information concerning the luminescent triplet exciton can be deduced from the broad enhancing line. In a Si-network with long radiative lifetimes and quenched orbital momentum, ODMR linewidths of 500 G can only be due to unresolved fine structure (spin-spin interaction). Thus, dipolar interaction in a disordered solid will give rise to a so-called Pake-doublet with a splitting $\Delta H = \mu_0 g \mu_B / 4\pi r^3$. In this model, the observed ODMR linewidth of $\approx$500 G corresponds to a spin-spin-separation of about 4 Å [22]. However, irrespective of the details of the spin-spin-interaction, Fig. 4 shows that the ODMR linewidth in porous Si and in annealed siloxene does *not* depend on the particular luminescence energy monitored. This behaviour is qualitatively incompatible with a geometric quantum confinement approach, where the luminescence energy is determined by the excitonic radius, $E_{\text{lum}} \propto r^{-2}$. The same confinement should lead to a strong variation of the observed line width as $\Delta H \propto r^{-3}$ (dipolar coupling) or $\Delta H \propto \exp(-r/r_0)$ (exchange coupling), which is clearly not the case.

On the other hand, the ODMR spectra and the small exciton diameter of 4 Å which can be deduced from these data in the dipole-interaction limit are compatible with a molecular type luminescence center. Due to symmetry arguments and similarities to the changes in the photoluminescence of benzene under substitution of ligands it was originally suggested that the luminescence of annealed siloxene originates in six-fold silicon rings, which are isolated from each other by oxygen bridges. It is thus tempting to associate the broad $\Delta m = 1$ ODMR transition in Fig. 3 with excitonic states localized on such rings. In particular,

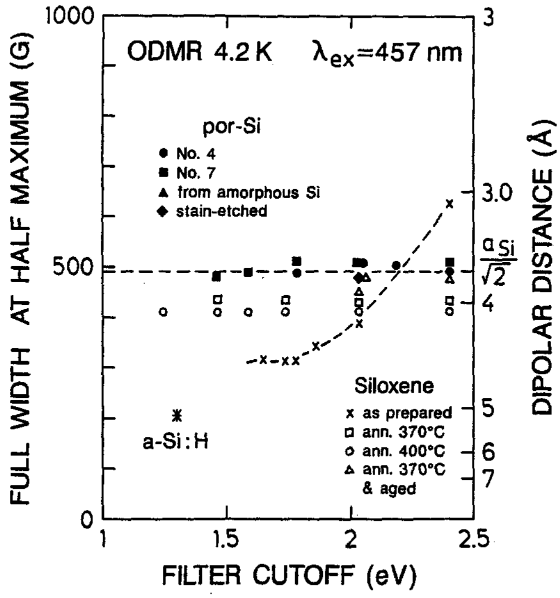

Fig. 4 Linewidth of the $\Delta m = \pm 1$-transitions and the corresponding dipolar distance as a function of the cutoff energy of the filters used for various porous silicon and siloxene samples. With the exception of as prepared siloxene, the broadening caused by spin-spin interaction is independent of the particular luminescence wavelength used in the ODMR measurements.

the exciton diameter of $\approx$ 4 Å agrees well with the geometric diameter of a Si_6 ring. Moreover, the exact energy of the radiative transition will depend strongly on the type of nearest neighbours or ligands at such a Si_6 ring. Although the diameter of the ring will not change accordingly, the exact position of the electron or hole wavefunctions on the ring could very well be influenced by the neighours, although the relative effect on the electron-hole-distance is expected to be much smaller than the effect on the energy. This explains the observed independence of the linewidth from the luminescence energy in Fig. 4. Note that Pake doublets corresponding to exciton diameters of several Å are readily observed in the ODMR of carbon-based materials such as naphtalene, polymers or C_{60} [23-25].

Finally, it is interesting to mention that ODMR spectra very similar to the ones described for porous Si and annealed siloxene have also been observed in amorphous silicon and substoichiometric alloys of silicon with oxygen, nitrogen, and carbon, when the stoichiometry of the alloys is such as to produce a red, visible luminescence. All of these materials exhibit a radiative triplet state with a broad $\Delta m = 1$ transition around $g = 2$, in addition to a narrow quenching line associated with defects. As shown in Tab. I, the width of the $\Delta m = 1$ transition reaches a limiting value of $\approx$ 500 G when the luminescence is shifted to the visible [4,30]. Again, this would point to Si_6 rings as a likely radiative center. Based on statistical arguments, in substoichiometric Si-alloys such rings are expected to form in significant numbers when the concentration of O, N, or C is of the order of 20-40 at.%. Indeed, SiO-, SiN-, and SiC-alloys with such a composition usually exhibit a quite pronounced visible luminescence of yet unknown microscopic origin.

Tab. 1 Luminescence energies $\hbar\omega_{lum}$ and full-width at half-maximum of the main ODMR transition in various silicon-based luminescent materials. A width of 500 G correponds to a dipolar distance of 4 Å.

material	$\hbar\omega_{lum}$ (eV)	ODMR-FWHM (G)	Ref.
μc-Si	0.7	100	[26]
a-Si:H	1.3	200	[27]
a-$SiN_{0.3}$:H	1.5	350	[28]
a-$SiN_{1.1}$:H	2.0	480	[28]
a-SiC_x:H	2	510	[29]
a-$SiO_{0.5}$:H	1.8	490	[30]
ann. siloxene	1.7 - 1.9	390 - 490	
porous Si	1.7 - 1.9	480 - 520	

V. CONCLUSION

We have studied porous silicon and two modifications of siloxene with the help of optically detected magnetic resonance (ODMR). We found that triplet excitons are the radiative states in all these materials. In particular, all porous silicon samples studied and annealed siloxene exhibit almost identical ODMR signatures. The observed independence of the ODMR spectra from luminescence energy is qualitatively incompatible with geometric quantum confinement. Instead, the ODMR data suggest a molecular-type radiative center which we associate with six-fold silicon rings.

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