VISIBLE LUMINESCENCE FROM POROUS SILICON AND SILOXENE: RECENT RESULTS

H.D. FUCHS, M. ROSENBAUER, M.S. BRANDT, S. ERNST, S. FINKBEINER, M. STUTZMANN, K. SYASSEN, J. WEBER, H.J. QUEISSER, AND M. CARDONA
Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-7000 Stuttgart, Germany

ABSTRACT

The optical properties of porous Si (*p*-Si) are compared to those of siloxene and its derivatives in order to gain more insight into the mechanism of the luminescence observed in *p*-Si. We report new results of photoluminescence (PL), photoluminescence excitation (PLE), time-dependent and pressure-dependent photoluminescence, and optically detected magnetic resonance (ODMR). Important information about the structural, electronic, and microscopic nature of the two classes of materials are deduced from these experiments. Annealed siloxene and *p*-Si show very similar properties, suggesting that siloxene-related structures, e.g. electrically isolated Si_6-rings, might be responsible for the luminescence in *p*-Si. The Si-planes in as-prepared siloxene, with their green luminescence, are metastable and are readily oxidized into red-luminescent siloxene configurations.

INTRODUCTION

The strong, visible room-temperature luminescence of porous silicon (*p*-Si) has been reproduced by many groups around the world and has attracted considerable interest, as reflected in the present conference proceedings. There is an increasing effort to utilize the pronounced luminescence properties of *p*-Si in a variety of technological applications. However, the physical mechanism of the luminescence still remains a matter of controversy. The different models proposed in the past include quantum confinement in small silicon crystallites or wires,[1, 2] hydrogen passivated silicon surfaces,[3] amorphous silicon,[4] and siloxene, $Si_6O_3H_6$[5, 6]. A year ago at the 1991 MRS Fall Meeting, we have proposed siloxene and its derivatives to be the origin of the luminescence in *p*-Si.[5] In this paper we follow up on this hypothesis and present a more detailed study of the optical properties of siloxene compared to those of *p*-Si. We investigate, in particular, effects of annealing on siloxene. In all experiments reported here, annealed siloxene is similar to *p*-Si, whereas as-prepared siloxene exhibits properties different from *p*-Si.

SAMPLE PREPARATION

A variety of *p*-Si samples were investigated in this work. Some of the samples originated from other groups (# 1,2, and 4), others (# 3 and 5) were prepared by us according to the procedure described in the literature.[7] Siloxene has been synthesized from $CaSi_2$ powder as described previously.[5, 6] Recently, we used an alternative method to grow a luminescent film of siloxene on a crystalline silicon substrate. This procedure is based on the chemical transformation of a calcium disilicide film deposited on the Si wafer.[8] This approach is promissing because of its possible compatibility with existing silicon technology. Prior to the measurements reported here, all samples were characterized by Raman and Fourier-transform infrared spectroscopy (IR) and TEM.[9, 10, 11]

RESULTS AND DISCUSSION

The PL spectra of three typical *p*-Si samples are compared to as-prepared siloxene and annealed siloxene (at 400°C for 10 min) in Fig. 1. The luminescence wavelength of the *p*-Si samples lies between about 690 nm and 790 nm, and the intensity varies within a factor of 10, depending on the details of the preparation. Freshly prepared siloxene shows

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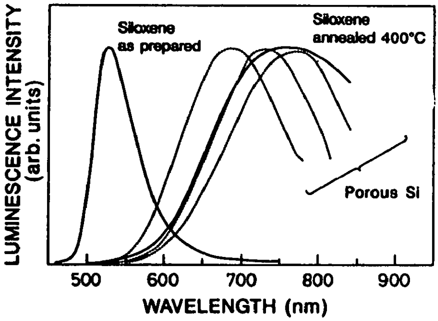

FIG. 1. Normalized photoluminescence spectra of porous silicon samples obtained from different sources. The luminescence was excited at 300 K by 450 nm light from a Xe arc lamp. All spectra are corrected for the spectral response of the detection system.

a bright green luminescence. This green luminescencence, however, is not very stable. Strong laser irradiation or thermal treatment (10 min) between about 100°C and 400°C lead to a red/orange luminescence band around 730 nm.[9] Further annealing of siloxene causes the PL to be quenched due to the over-oxidation of the luminescent material and the creation of defects which act as non-radiative recombination centers. In Fig. 1, the metastable green luminescence from as-prepared siloxene and the red luminescence from the stable, annealed sample seem to be the upper and lower bound in between which the luminescence energy of *p*-Si can vary, depending on the details of the sample preparation.

The shift of the PL maxima upon annealing is accompanied by structural changes of siloxene.[9, 12] Siloxene ($Si_6O_3H_6$) can exist in three different configurations: (i) Two-dimensional Si-planes terminated by hydrogen or OH, (ii) one-dimensional Si-chains, and (iii) Si_6-rings interconnected with oxygen and terminated with hydrogen. Raman, IR, and X-ray spectroscopy indicate that as-prepared siloxene consists mainly of the Si-plane structure.[9, 12] Scanning tunneling microscope topography of as-prepared siloxene also provides evidence for the existence of parallel Si-planes with a basal spacing of about 6 Å.[13] These Si-planes are metastable and easily fragmented by insertion of oxygen. As a result, Raman and IR lines of the Si-planes as well as structures in the X-ray diffraction pattern corresponding to the basal spacing of the planes disappear, and a more amorphous-like behaviour is observed.[9, 12] Ordered insertion of oxygen into the planes leads to the formation of the Si_6-rings which, in the relevant chemistry literature, have always been assumed to be responsible for the luminescence in siloxene. Optical absorption and reflection measurements along with the visible change of the color of the material (from yellow to red) indicate a lowering of the optical gap upon annealing, in agreement with recent quantum chemical calculations.[14] These calculations also support the experimental finding that the Si-plane structure of siloxene is less stable than the Si_6-ring structure.[14]

Drastic changes of siloxene upon annealing can also be seen in the PLE spectra (Fig. 2). The spectra are plotted with a linear intensity scale in (a) and on a logarithmic scale in (b). The corresponding PLE curves for various *p*-Si samples are shown in Fig. 3(a) and (b). Analogous to the PL spectra, the PLE spectra of the annealed siloxene sample and *p*-Si are very similar, whereas the as-prepared siloxene behaves qualitatively different. The room-temperature PLE is monitored at the wavelengths given in the figures (indicated also by the arrows). The excitation wavelength was varied with a monochromatized and order-filtered light of a Xe arc lamp. The spectra have been corrected for the incident light intensity and for the quantum energy of the exciting photons.

Characteristic for the PLE spectra of annealed siloxene and *p*-Si is the steep rise of the quantum efficiency between 2 and 3 eV. The details of the weak structure in the flat region of the spectra above 3 eV depend on the sample preparation and possibly the thickness of

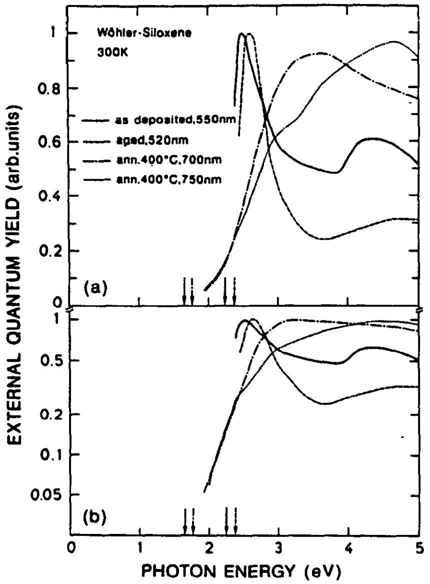

FIG. 2. Luminescence excitation spectra for siloxene (solid curves), aged siloxene (several months at 300 K in air, dashed curves), and annealed siloxene (400°C for 10 minutes, dotted and dash-dotted curves). The wavelengts and the arrows indicate the luminescence energies at which the spectra were recorded. All spectra are normalized to the photon flux and the excitation radiation.

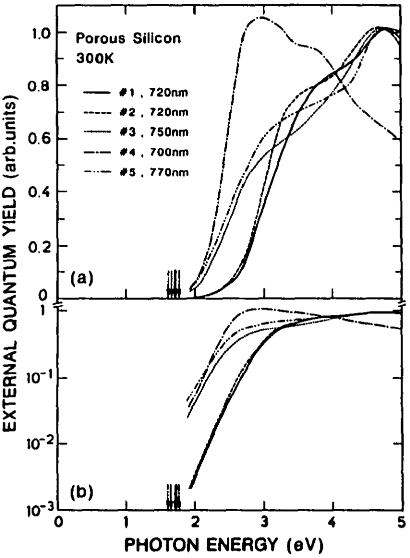

FIG. 3. Luminescence excitation spectra for various porous silicon samples, obtained under identical conditions as those for as-prepared and annealed siloxen in Fig. 2.

the porous layer (inhomogeneity in the depth profile). The logarithmic plots of the PLE curves show that the low-energy part of the spectra follows an exponential dependence, similar to the well-known Urbach tails in disordered semiconductors.[15] The exponential slope parameter $E_0 = \partial\hbar\omega/\partial\ln\eta$ (η is the quantum efficiency) is about 200 meV at 300 K.

As opposed to p-Si and annealed siloxene, the PLE spectra of as-prepared siloxene are dominated by a sharp peak around 2.5 eV. The Si-plane structure of siloxene, which is mainly present in the as-prepared sample, has a direct gap of about 2.8 eV.[14]. In the Si_6-rings, on the other hand, the lowest electronic gap is indirect with an energy of 2.8 eV.[14] Thus, it is likely that the sharp feature of as-prepared siloxene in Fig. 2 arises from excitonic states at the direct gap, and the green luminescence (of the as-prepared siloxene) is mainly caused by optical transitions at this direct gap. The red/orange PL (of annealed siloxene and presumably of p-Si) is caused by indirect optical transitions within the electrically isolated Si_6-rings.

The difference in the nature of the green PL, from the Si-planes, and the red PL, from the Si_6-rings, manifests itself also in the time-dependent PL measurements. The decay of the PL of both siloxene and p-Si is strongly non-exponential (Figs. 4 and 5). The decay is faster the shorter the wavelength of the detected PL. The decay times of annealed siloxene are shorter than the ones of as-prepared siloxene (not shown here) because the defects

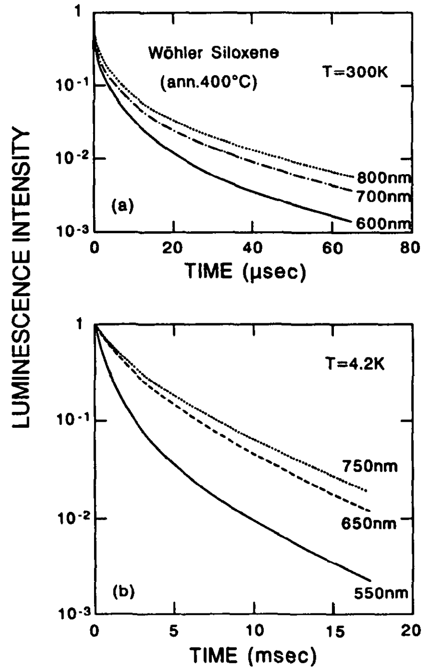

FIG. 4. Luminescence decay in siloxene following pulse excitation with a 458 nm line at 300 K. The different transients correpond to different wavelenghts at which the luminescence was recorded.

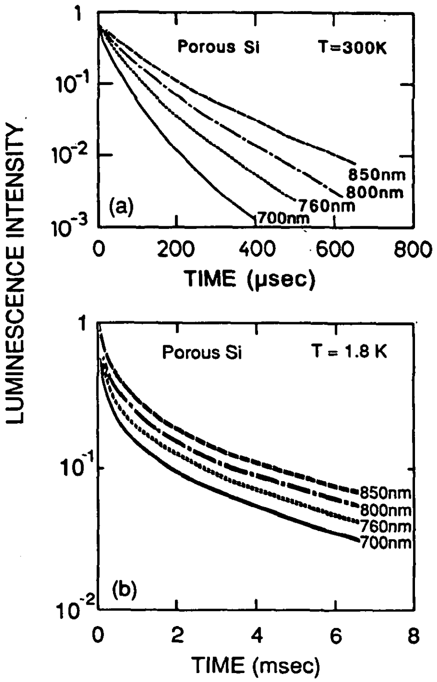

FIG. 5. Luminescence decay in porous silicon, obtained under identical conditions as those of annealed siloxene in Fig. 4. From Ref. [5].

created during annealing (defect density of about 10^{18} cm^{-3}) shorten the lifetime of the PL. The high defect density in the annealed siloxene is also the reason why the PL at 300 K decays about ten times as fast as in *p*-Si. At low temperatures, however, the PL decay times of *p*-Si and annealed siloxene are comparable. A detailed analysis would require the consideration of all possible recombination channels. At this point, we just want to emphasize the similarity of the low-temperature time-resolved luminescence in annealed siloxene and in *p*-Si.

The pressure-dependence of the luminescence in *p*-Si has been measured by several groups, but so far no results for siloxene have been published. For *p*-Si, the reported shifts induced by hydrostatic pressures up to about 8 GPa are contradictory. Groups using alcohol as the pressure medium report a blue shift,[16] whereas measurements with silicone oil as pressure medium yield a red shift with coefficients between -26 and -33 meV/GPa.[17, 18] Since *p*-Si is known to chemically react with ambient species,[19] this effect has to be considered in the choice of the pressure medium. The present pressure studies of siloxene were performed in non-reactive pressure media (Xenon, CsCl). The shift of the optical gap of siloxene under hydrostatic pressure is demonstrated in Fig. 6(a). With increasing pressure the gap red-shifts, with a coefficient of about -30 meV/GPa (Fig. 6a). Complementary, we measured the pressure-induced shift of the PL maximum (Fig. 6b). The red shift of the PL

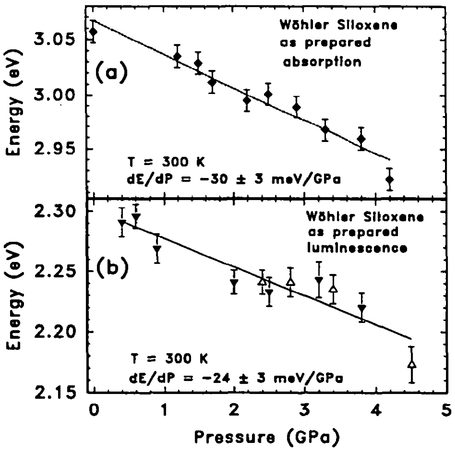

FIG. 6. Pressure-dependence of the optical absorption edge (a), and the PL maximum (b). Xenon was used as the pressure medium for the PL measurements and CsCl for the absorption measurements. The absorption characteristics of CsCl have been taken into account in the analysis of the absorption spectra. The energies of the absorption spectra in (a) correspond to an optical density of 1 (sample thickness ≈ 10μm), where the optical density was normalized to zero below the gap at 2.0 eV.

energy of about -24 meV/GPa is in good agreement with the absorption data (Fig. 6a). A detailed study of the pressure dependence will be published elsewhere[20]

Finally we mention our ODMR measurements which can be used to correlate microscopically the observed luminescence with specific electronic states. Thus, they provide a powerful tool to investigate the origin of the luminescence in *p*-Si. The results obtained at 4 K are summarized in Table I. Characteristic for both annealed siloxene and *p*-Si are the quenching defect with a g-factor of 2.005 due to Si dangling bonds, and two enhancing signals corresponding to the $\Delta m = \pm 1$ and $\Delta m = \pm 2$ transitions of triplet excitons. The details of these experiments will be discussed in a forthcoming publication. The similarity of the ODMR signals between annealed siloxene and *p*-Si also indicates on a microscopic level that the luminescence centers of the two classes of materials are indeed quite similar.

TABLE I. Optically detected magnetic resonance (ODMR): A comparison of siloxene and *p*-Si.

Sample	Defect (quenching)	Exciton, $\Delta m \pm 1$ (enhancing)	Exciton, $\Delta m \pm 2$ (enhancing)
Siloxene, as-prepared	g=2.004	g=1.965, $\Delta H_{1/2}$=400G	coupled mode
Siloxene, annealed	g=2.005	g=2.000, $\Delta H_{1/2}$=400G	g=4
Porous Si	g=2.005	g=2.000, $\Delta H_{1/2}$=300-500G	g=4

CONCLUSIONS

Structural, electronic, and microscopic information about siloxene and its derivatives and *p*-Si were obtained by means of photoluminescence (PL), photoluminescence excitation (PLE), time-dependent and pressure-dependent photoluminescence, and optically detected magnetic reonance (ODMR). The similarity of annealed siloxene and *p*-Si suggests siloxene-derived molecular structures as the origin of the luminescence in *p*-Si.

Irrespective of their role in *p*-Si, siloxene and stucturally related substances could be of great scientific and technological interest.

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