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Photoluminescence excitation spectroscopy of porous silicon and siloxene

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We investigate the optical excitation of visible room-temperature luminescence in electrochemically produced porous silicon and in siloxene obtained from the chemical reaction of calcium disilicide with hydrochloric acid. Luminescence and luminescence excitation spectra (2–5 eV) of different porous silicon and siloxene samples are compared. A characteristic feature of luminescence excitation in porous silicon is the appearance of an exponential tail in the low-energy region. As-prepared siloxene has a pronounced peak in the excitation spectrum at 2.5 eV which is attributed to excitons. A close agreement is found between the properties of porous silicon and annealed siloxene, both in photoluminescence and in luminescence excitation.

Strong, visible room-temperature photoluminescence (PL) of porous silicon is a phenomenon of considerable current interest.[1] However, despite a large experimental and theoretical effort, the microscopic origin of this luminescence effect still remains a matter of controversy. Among the different mechanisms discussed in the literature are quantum confinement in small silicon crystallites or wires,[2,3] hydrogen passivated silicon surfaces,[4] and other possibilities such as amorphous silicon, polysilanes, or siloxene.[5–8] In the work described here, we have followed up on the latter hypothesis by comparing the photoluminescence excitation (PLE) spectra of porous silicon samples obtained from various sources to those of siloxene ($Si_6O_3H_6$) prepared and modified in our group in such a way as to produce PL spectra similar to those of porous silicon. In addition, we present PLE spectra of as-prepared siloxene in order to elucidate interband transitions in this material.

The porous silicon samples investigated here have been either obtained from outside sources (samples nos. 1, 2, and 4) or have been prepared by us according to the known procedure.[1] Siloxene has been synthesized from $CaSi_2$ as described previously.[7,8] Prior to the PL and PLE measurements, all samples were characterized by Fourier-transform infrared spectroscopy, which showed hydrogen and oxygen as the main contaminants, being present in the same bonding configurations.[7,9] PL spectra were measured in ambient atmosphere and at 300 K using a double monochromator and standard photon-counting equipment. Excitation in the wavelength range 250 nm< λ_{ex} < 600 nm was carried out with monochromatized and order-filtered light of a Xe arc lamp focused to a spot size of about 2 × 1 mm^2. For the calculation of the relative quantum yield shown below, the PL spectra were corrected for the incident light intensity (measured by a pyroelectric detector equiped with a sapphire window) and for the quantum energy of the exciting photons. Typical excitation powers are of the order of 1 mW/cm^2.

PL spectra of the five porous Si samples used in this study are depicted in Fig. 1. The luminescence was excited at λ_{ex} = 450 nm and the external efficiency of all five samples varied within a factor of 10. The luminescence peak energies lie between 690 and 790 nm for the different samples. The room-temperature PLE spectra for the same samples are shown in Fig. 2, both on a linear scale [Fig. 2(a)] and on a logarithmic scale [Fig. 2(b)]. For each of the excitation spectra in Fig. 2, the luminescence was monitored at the wavelengths indicated in the figure. Arrows show the energy position of the PL monitor on

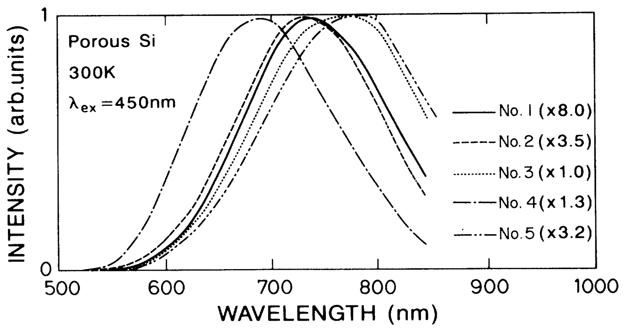

FIG. 1. Normalized luminescence spectra of the five porous silicon samples used in this study. The five samples have been obtained from four different sources. The luminescence was excited at 300 K by 450-nm light from a Xe arc lamp. The various scaling factors are given in the figure. All spectra have been corrected for the spectral response of the luminescence spectrometer.

the photon energy scale. Common to the PLE spectra of all porous Si samples investigated here is a steep rise of the quantum efficiency for photon energies between 2 and 3 eV, followed by a more or less constant response up to $\hbar\omega_{\text{ex}} = 5$ eV. In the range 3 eV $\le \hbar\omega_{\text{ex}} \le$ 5 eV, the normalized PLE spectra show weak, sample-dependent structures at ≈3 eV, ≈3.5 eV, and ≈4.5 eV. The latter two energies correspond approximately to direct optical transition energies of crystalline Si, indicating that Si-Si bonding is important for PLE in this energy range. The detailed shape of the PLE spectra in this high-energy region is influenced by the thickness of the porous silicon layer. We also note that our PLE spectra are quite similar to those reported previously.[10,11] It is important, however, to account correctly for the variation in photon energy and the spectral dependence of the excitation photon flux: uncorrected PLE spectra show a distinct peak around ≈3.5 eV.

A logarithmic plot of the external quantum yield versus photon energy in Fig. 2(b) reveals that the low-energy part of all five PLE spectra follows an exponential dependence, reminiscent of the Urbach tail in disordered semiconductors.[15] In samples nos. 1 and 2, this exponential tail extends over more than two orders of magnitude in quantum yield. The exponential slope parameter $E_0 = \partial\hbar\omega/\partial\ln\eta$ (where η is the quantum efficiency) has a typical value of $E_0 \approx 200$ meV at 300 K.

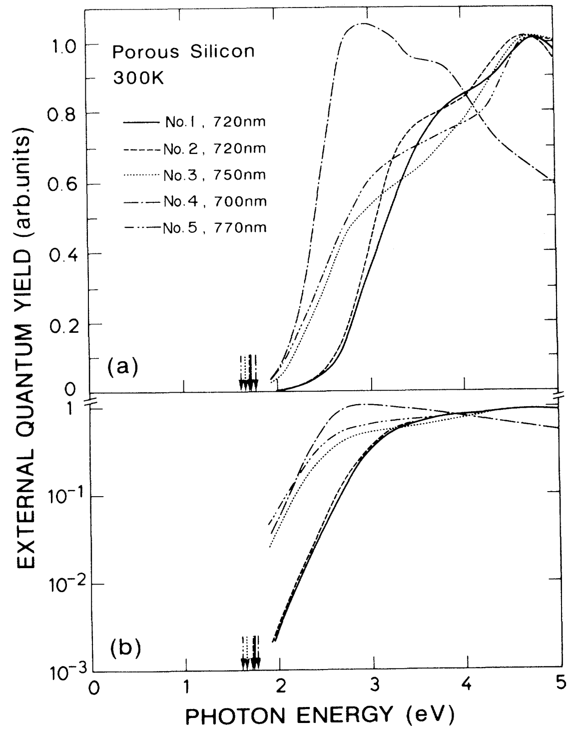

FIG. 2. Luminescence excitation spectra of the samples from Fig. 1. Arrows indicate the energy used to monitor the luminescence intensity for a given sample. The monitor wavelength is also indicated after the corresponding sample number. Excitation spectra have been normalized and are shown with a linear intensity scale (a) and a logarithmic scale (b). All spectra have been normalized by the photon flux of the exciting radiation.

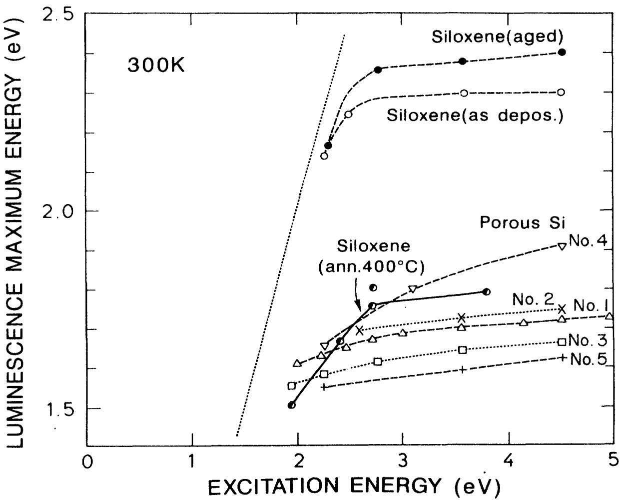

FIG. 3. Dependence of the photoluminescence peak position on excitation energy for porous silicon and siloxene at 300 K. The straight dotted line indicates that the excitation energy is equal to the luminescence maximum.

In Fig. 2 we have determined the PLE spectra of porous silicon by varying the excitation energy while monitoring the luminescence yield at a fixed wavelength. Such a procedure only results in correct PLE data in cases where the luminescence spectrum does not change significantly with excitation energy. As shown in Fig. 3, this is certainly a good approximation for porous Si samples with PL peaks below 2 eV (see Fig. 1). In most samples studied we observed that the shift in luminescence peak position (≈100 meV) is much smaller than the full width at half maximum of the luminescence spectra (≈300 meV) for excitation energies above 2 eV. An exception is sample no. 4, which shows a somewhat larger peak shift of ≈250 meV. The same sample also deviates from the other four in the PLE spectra of Fig. 2. We attribute this to the larger thickness of the porous Si layer in sample no. 4 (≈ 100 μm), which gives rise to a pronounced depth dependence of the luminescence peak position. This depth inhomogeneity was clearly observable by optical microscopy under uv illumination. A similar thickness-dependent inhomogeneity of the PL peak position is also the origin of the strong shift of the PL maximum for annealed siloxene in Fig. 3 for excitation energies below 2.6 eV. For all other porous silicon samples shown in Fig. 3, the layer thickness is much smaller, typically 10 μm.

Also shown in Fig. 3 are luminescence peak positions for siloxene in the as-prepared state, after long storage (months) under ambient conditions, and after annealing at 400 °C for several minutes. The corresponding luminescence peak positions are 2.3 eV, 2.4 eV, and 1.8 eV, respectively.[16] The PLE spectra of these three siloxene samples are shown in Fig. 4. In the as-prepared as well as in the aged state, the most noticeable feature of the PLE data is a pronounced, relatively narrow peak around 2.5 eV, followed by a much weaker response up

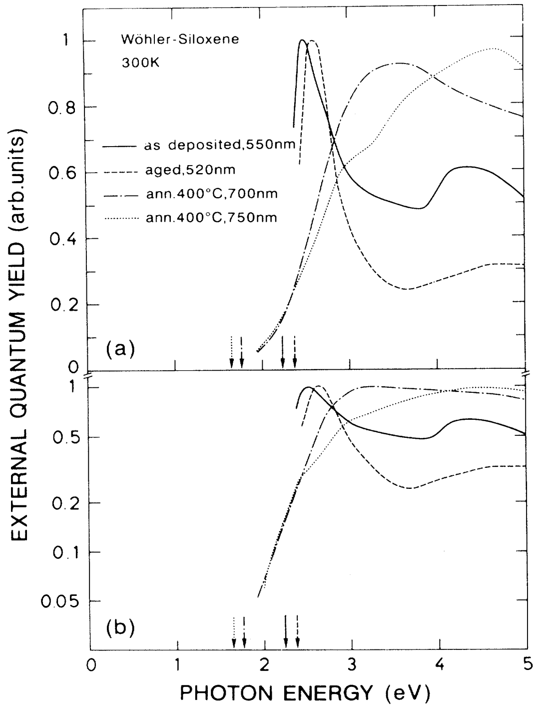

FIG. 4. Luminescence excitation spectra for as-prepared siloxene (solid curves), aged siloxene (several months at 300 K in air, dashed curves), and annealed siloxene (400 °C for 10 min, dotted and dash-dotted curves). (a) and (b) show linear and logarithmic intensity scales, respectively. Arrows indicate the luminescence energies which have been monitored for the different samples.

to 5 eV with an additional, less pronounced structure at about 4.5 eV. After annealing at 400 °C, the sharp peak at 2.5 eV disappears and the PLE spectra become very similar to those of our porous silicon samples. In particular, an exponential tail as in Fig. 2 is also observed in the siloxene samples. For a discussion of the experimental results in Fig. 4, we mention briefly some established results concerning the optical properties of as-prepared siloxene. X-ray diffraction shows that to a considerable fraction siloxene consists of two-dimensional Si planes separated from each other by about 6 Å and terminated by H and OH radicals.[9,12,13] The optical gap of these Si layers is direct, with a value around 2.8 eV.[13,14] Higher interband transitions as observed by spectroscopic ellipsometry and reflection measurements occur in the vicinity of 4.5 eV. The PLE spectra for as-prepared siloxene indeed are compatible with these optical properties. Efficient excitation of the green luminescence occurs mainly via optical transitions at the fundamental gap. The existence of a sharp structure in the PLE and reflectivity spectra in this energy range suggests that excitons may play a significant role, in accordance with the direct nature of the siloxene band gap obtained theoretically.[14] During annealing at 400 °C, the two-dimensional Si planes are destroyed by oxygen insertion and cross linking, resulting in an amorphization of the siloxene network and a gap shrinkage.[13] These effects are clearly visible in the PLE spectra of annealed siloxene in Fig. 4: The excitonic peak disappears, an exponential tail appears, and the optical gap decreases. At the same time, the luminescence changes from green to red and becomes similar to that of porous silicon.[7,8]

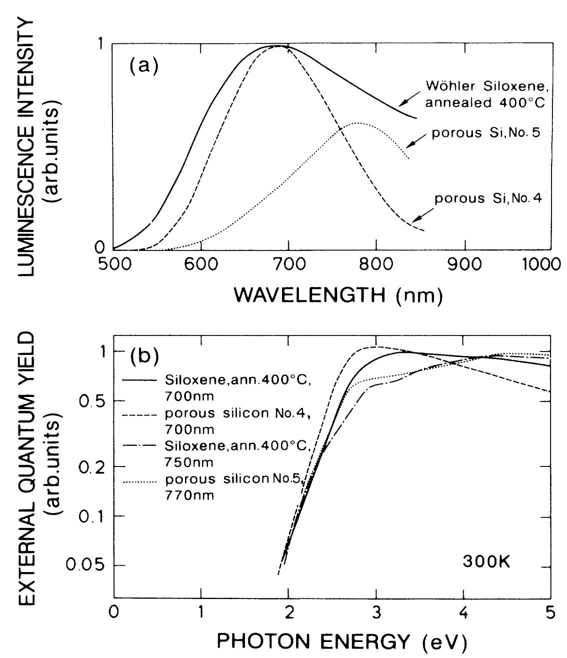

FIG. 5. A comparison of the photoluminescence spectra (a) and the luminescence excitation spectra [logarithmic intensity scale, (b)] of annealed siloxene and two porous silicon samples at 300 K.

The similarity between the optical properties of luminescent porous silicon on one hand and annealed siloxene on the other hand is demonstrated by the PL and PLE spectra in Fig. 5. There, we compare annealed siloxene and two porous silicon samples with overlapping PL spectra [Fig. 5(a)]. The PL spectrum of the annealed siloxene is clearly inhomogeneously broadened, so that for a comparison of the PLE response with that of porous silicon we use three different monitor wavelengths: 700 nm both for porous silicon and for siloxene [solid and dashed curve in Fig. 5(b)], and 770 (750) nm for porous Si and for siloxene with a luminescence maximum somewhat more in the infrared. These values roughly coincide with the PL maxima of the two porous Si samples chosen. As can be seen from Fig. 5(b), the agreement between the corresponding PLE spectra in porous silicon and siloxene is better than 20% over the entire spectral range between 2 and 5 eV. This result provides additional evidence in favor of our model suggesting siloxene derivates as the origin of the strong luminescence in porous Si.

In conclusion, we have presented a detailed study of photoluminescence excitation in porous silicon samples obtained from different groups. The characteristic features of the PLE spectra of all porous silicon samples investigated here are (i) an exponential tail with a slope parameter $E_0 \approx 200$ meV at low excitation energies ($\hbar\omega < 3$ eV), and (ii) an approximately constant external quantum yield for $\hbar\omega > 3$ eV. An important experimental result is that samples with similar luminescence spectra can exhibit quite different PLE spectra, so that there appears to be no unique relationship between optical absorption and emission in porous silicon.

The PLE spectra of as-prepared siloxene exhibit a narrow peak around 2.5 eV, which could be an indication for the formation of excitons in this material. Evidence for a direct optical band gap in siloxene also comes from transmission and reflection spectroscopy and theoretical calculations. After annealing of as-prepared siloxene at 400 °C, a second luminescent phase is formed whose PL and PLE properties are similar to those of porous Si. This provides further evidence for siloxene-derived molecular structures as the origin of the strong luminescence in porous Si.

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