

ON THE RELATIONSHIP OF POROUS SILICON AND SILOXENE

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Recently it has been suggested that siloxene is present in porous silicon and that this siloxene is the actual source of the visible luminescence observed in porous silicon.¹. This claim is based on similarities in the infrared and Raman spectra of these materials. In this paper we review the arguments that led to this claim and show that the properties of porous silicon are inconsistent with that conclusion.

As a result of recent observations of efficient visible luminescence from porous silicon, considerable effort has been directed at understanding the fundamental mechanism of luminescence in this material, and, ultimately, its potential for optoelectronic applications²⁻⁴. The optical properties of porous silicon have most frequently been interpreted in terms of a quantum confinement model⁵; however, several groups have also emphasized similarities between porous silicon and other silicon-based materials which emit visible light. These include silicon-rich SiO_2^6 , a-Si:H⁷, silicon nanocrystals⁸, polysilane⁹ and most recently siloxene^{1,10}. In general the photoluminescence (PL) characteristics of these materials are quite similar to porous silicon, i.e. broad (tenths of eV) spectra with peak energies that can be changed, by varying the fabrication process, over a wide range of the visible and infrared spectrum. In addition, many have high external quantum efficiencies, from tenths to a couple percent. Given the overall similarities in optical properties it is quite natural to speculate that there may be a common mechanism that is responsible for the luminescence in porous silicon and some of these materials. Recently, however, this argument has been taken a step further by the claim that a much stronger relationship exits between the polymer siloxene and porous silicon. Brandt et al. argue that siloxene is actually present in porous silicon and that this siloxene is the actual source of the luminescence observed in porous silicon.^{1,10}. In this paper we review the arguments that led to this claim and show that the infrared properties of porous silicon are inconsistent with that conclusion.

The identification of porous silicon as siloxene is based on comparing the physical and electronic properties of these two materials. Central to this is a comparison of the infrared (IR) vibrational spectra of siloxene and porous silicon. Since siloxene has the nominal composition $Si_6O_3H_6$, one expects to observe Si-H, Si-O, and O-H related vibrations. Fig. 1 reproduces the IR spectra of siloxene from reference 10. This spectrum exhibits the expected features including: (1) Si-H modes - the Si-H stretching mode at 2050-2150cm⁻¹, the Si-H scissors mode at about 900 cm⁻¹ and bending/wagging modes near 600-850cm⁻¹, (2) Si-O modes - the Si-O (SiO₂ vibrations) stretch at $\simeq 1100$ cm⁻¹ and O-Si-H modes which occur on the high energy side of the the Si-H stretch band, and (3) O-H stretch modes near 3300cm⁻¹.



1. Infrared transmission spectra for siloxene and porous silicon from Ref. 10 and for freshly prepared and oxidized porous silicon. Oxygen-related vibrations are not detectable in freshly prepared porous silicon, which is inconsistent with the conclusion that siloxene and porous silicon are equivalent.

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In Fig. 1 we have also reproduced the IR spectrum for porous silicon from Ref. 10. It bears a strong resemblance to the siloxene spectrum and Brandt et al, take this as evidence that what is observed in the IR spectrum of porous silicon is actually siloxene. However, it is particularly disconcerting that the IR spectrum for their porous silicon is significantly different from spectra previously reported in the literature^{4,11}. To illustrate this we also show in Fig. 1 an IR spectrum for a freshly prepared porous silicon film which luminesces in the red/infrared at approximately the same wavelength as Brandt et al.'s porous silicon. The sample was prepared as described in reference 4 and all measurements were made with the sample maintained in a non-oxidizing, nitrogen ambient. It is worth mentioning that we obtain the highest quantum efficiency from freshly prepared material treated in this manner. This IR spectra is the result of ratioing the porous silicon spectrum to that of bare silicon from the same wafer. This minimizes substrate-related vibrational features. This spectrum, which is consistent with earlier publications, shows only three basic features, all associated with Si-H bonds. These are the Si-H stretching modes at 2050-2150cm⁻¹, the Si-H scissors modes at about 910 cm⁻¹ and the Si-H wagging mode at 600-750cm⁻¹ (Two phonon Si-Si vibrations probably also contribute to this low frequency peak.) We note in particular that all oxygen related modes are absent in the sample. As we discuss below, this lack of oxygen is inconsistent with the ratio of oxygen to silicon and hydrogen in the chemical formula of siloxene, and thus inconsistent with the idea that these samples contain a large amount of siloxene.

Some insight into the differences between the infrared spectra of Brandt et al. and of the freshly prepared porous silicon shown in Fig. 1 are provided by studies of the oxidation of porous silicon. The IR spectrum of our porous silicon film after it was oxidized at $\simeq 200^{\circ}$ C for 5 minutes is also shown in Fig. 1. As previously discussed, oxidation results in the insertion of oxygen at the Si-Si back bond and a distortion of the Si lattice¹². New peaks appear in the the Si-H stretch band (at $\simeq 2250$ cm⁻¹) which are associated with the presence of second nearest-neighbor oxygen (O-Si-H stretch). In addition, a very large Si-O stretch mode appears centered at about 1100 cm^{-1} which is related to SiO₂. These features, as well as the position of the Si-H stretch band, are indicated by the dotted vertical lines in Fig. 1.

The IR spectra of Ref. 10 much more closely resemble that of oxidized porous silicon than of freshly prepared samples, suggesting that the porous silicon in Ref. 10 was inadvertently oxidized prior to making the measurements. In general we have found that oxidation of porous silicon (either thermally at temperatures near 200°C or optically) dramatically reduces its optical efficiency⁴. In addition, removal of the oxide by dipping in HF recovers the as-prepared IR spectrum as well as much of the PL efficiency⁴. Although there are reports of oxidation procedures which do not significantly degrade the optical properties^{3,13}, it is clear that introducing oxygen into the films does not result in large increases in efficiency. We conclude that while oxidation makes the IR spectrum of porous silicon look more like that of siloxene, the presence of oxygen is not essential (and is often detrimental) to obtaining efficient luminescence.

It is not clear why the porous silicon in Ref. 10 shows evidence of substantial oxidation. Oxidation of porous silicon can occur easily in air, particularly during optical excitation^{3,4}. In addition, the authors of Ref. 10 do mention that in in some cases they have used an HF/HCl/ethanol etch instead of the standard HF/ethanol/water²⁻⁴ used here. This might account for some of the differences between their results and others. Another unusual aspect of their infrared spectra is the presence of an additional mode at $\simeq 3500 \text{cm}^{-1}$ which is attributed to an O-H stretch. (This feature is weak in the spectrum in Fig. 1 which was reproduced from Ref. 10.) We do not observe this mode in our samples, nor has it been reported in porous silicon¹⁴ by others.

We have used secondary ion mass spectroscopy to calibrate the oxygen concentration as determined from the O-Si-H (2250cm⁻¹) and Si-O (1100cm⁻¹) stretch modes and are able to place an upper bound on the O/H and O/Si ratios in freshly prepared porous silicon of $\simeq 0.02$. The low value of this ratio demonstrates quite convincingly that the bulk of the material in fresh porous silicon is not siloxene. One could try to argue that a small amount of siloxene present in the porous film is responsible for all of the luminescence, but this seems unreasonable given that freshly prepared material tends to have the highest quantum ef-In addition, other characterization ficiency. techniques also show oxygen to be a very minor impurity in optically efficient porous silicon. Van Buuren et al. have recently reported x-ray absorption



2. Raman spectra for freshly prepared porous silicon, porous silicon from Ref. 10 and crystalline silicon.

measurements on porous silicon after various treatments¹⁵. Fresh or HF-dipped samples show no evidence of oxidation, whereas samples left in air for several days show clear signs of oxidation. Canham et al. reported an oxygen concentration $\simeq 15$ times lower than that for hydrogen in a sample exposed to air for 15 minutes¹⁶. The absence of appreciable amounts of oxygen in fresh porous silicon seems quite reasonable since it is is unlikely that any SiO₂-like material will be stable in the HF-based etchant used to produce porous silicon.

Other properties of porous silicon reported in Ref. 10 also differ from previously published results. For example, Brandt et al. indicate that the Raman spectrum of their porous films is too narrow to be consistent with microcrystalline silicon, but is in good agreement with results from siloxene. In Fig. 2 we have reproduced the Raman spectrum of porous silicon from Ref. 10. We also include the Raman spectrum of a freshly prepared porous silicon film¹⁷ and for a crystalline silicon substrate. The freshly prepared spectrum is much wider than reported by Brandt et al. Similar results have been obtained by Sui et al.¹⁸. The difference between the two Raman spectra undoubtedly arises from differences in preparation. Our results were obtained for a layer prepared on p⁻ Si. Brandt et al. emphasize results on free standing films which it appears have been prepared on p⁺ substrates. The microstructure of p⁺ material is typically reported to consist of long pores running perpendicular to the surface with additional fine structure and branches on the pores¹⁹. p material is often described as having a sponge-like structure in which the characteristic feature size is much smaller than the pore dimension in p^+ samples. As a result, the porosity of the p-material is typically much higher. Thus the Raman spectrum does not provide a unique signature for all types of porous silicon, but instead reflects the microstructure which is dependent on the starting material and fabrication process. Hence, it is not surprising that the Raman spectra look different, with p+ material looking more like crystalline silicon. It is clear from Fig. 2 that the similarity between the Raman spectra of porous silicon and siloxene reported by Brandt et al. should not be taken as evidence that the two materials are the same.

As a final comment we wish to point out that although we do not find porous silicon and siloxene to be chemically equivalent, the fact that many of the optical properties Brandt et al. report for siloxene (e.g. the spectral range of the luminescence, lifetime, degradation effects) are quite similar to those observed in porous silicon is quite intriguing. The notion that the essential physics of the luminescence mechanism in these two materials could be closely related is well worth considering.

To summarize, we have shown that freshly made porous silicon has an IR spectrum which is actually quite different from that of siloxene. In particular, the oxygen content is too low to be consistent with the nominal chemical composition, $Si_6O_3H_6$, of siloxene. Other characterization techniques confirm the low oxygen content of porous silicon. We conclude that the visible luminescence in porous silicon does not arise from the presence of siloxene. At the same time, we find that similarities between the optical characteristics of porous silicon and a number other silicon-based materials including siloxene could point to a common luminescence mechanism in these systems.

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