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Unimportance of siloxene in the luminescence of porous silicon

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Near-edge- and extended-x-ray absorption fine structure measurements, as well as luminescence excitation and emission spectra, were obtained from samples of porous Si and siloxene. Combined, these data establish that, contrary to a recently proposed explanation, siloxene is not generally responsible for the observed room-temperature luminescence in porous Si.

Room-temperature luminescence from anodically grown porous silicon (por-Si) is a phenomenon which holds important promise for possible Si-based light emitting devices. Its origin, however, is still currently under debate. The proposed mechanisms for the luminescence include quantum confined structures,[1,2] surface SiH_x,[3] amorphous Si,[4] and siloxene.[5,6] The intriguing suggestion that siloxene, $Si_6O_3H_6$, is responsible for the observed luminescence has only recently appeared and is as yet uncorroborated.

In this letter we report on near-edge- and extended-x-ray absorption fine structure measurements from freshly prepared porous Si grown under different electrolytic conditions. The data show that within the region of porous Si responsible for optical activity, namely the <1000-Å penetration depth of the photoluminescent-exciting radiation,[7] Si is *not* coordinated to oxygen. These results, along with transmission electron microscopy and emission and excitation measurements, definitively rule out the importance of the siloxene hypothesis as being generally responsible for the observed luminescence in porous Si.

The samples were prepared by anodic oxidation of B-doped Si wafers of $>50\ \Omega$ cm resistivity.[8] Aluminum was deposited on the back of the wafers to facilitate electrical contact. The electrolyte was 30% by volume of concentrated HF (49%) in ethanol and the cathode was a Pt stirrer running at about 50 rpm. Two types of por-Si were prepared, one etched at a current density of 25 mA/cm^2 for 12 min and one at 50 mA/cm^2 for 6 min. These are referred to as "red" and "orange", respectively, after their luminescence colors under UV light. Following etching, rinsing, and drying, the samples were transferred to an Ar-filled container in which they were mounted on holders before introduction into the measurement vacuum chamber. Total air exposure of the samples after etching was less than 5 min. Cross-section electron microscopy showed that these samples had porous layers of the order microns thick.

The Si *K*-edge absorption measurements, conducted on the AT&T X-15B beamline[9] at the National Synchrotron Light Source, were obtained using InSb(111) monochromator crystals located downstream from a harmonic-rejecting mirror. Total-electron and *KLL*-Auger-electron yield detection schemes, with effective sampling depths of <1000 and ~ 25 Å,[10,11] respectively, were used to ensure that the measurements correspond to the optically relevant regions of our por-Si samples. No substantive differences in data were observed between these two detection schemes. Reference measurements using total yield were also obtained from crystalline Si, from fused silica, and from annealed[5] and unannealed siloxene prepared according to Wöhler's description.[12]

The features in the x-ray data within ~20 eV from threshold, referred to as the near-edge x-ray absorption fine structure (NEXAFS), are shown for all the samples in Fig. 1.[13] The prominent peak at ~1845 eV in SiO_2 arises primarily from Si $1s \rightarrow O\ 2p^*$ transitions and is shifted ~6 eV to higher energy from the bulk Si edge due to the more positively charged Si in SiO_2. This peak serves as a sensitive fingerprint for identifying and estimating the amount SiO_2-like species present in other samples. As an example, the data in Fig. 1 for bulk Si are seen to show a small peak at ~1845 eV, which is due to the native oxide layer present on the surface of that sample. Coincidentally, at this energy a similar feature is also observed[10] in atomically clean Si, but its integrated intensity is only about half as large as that in Fig. 1 because of the absence of the oxide layer. By subtracting the intensity of this intrinsic Si feature from the 1845-eV peak in the data of the oxide-coated Si sample, and using an effective total-yield detection sampling depth of ~500 Å,[11,12] we obtain a native-oxide layer thickness of $\sim 25 \pm 10$ Å, consistent with typical values.

The NEXAFS from siloxene[13] shows features at ener-

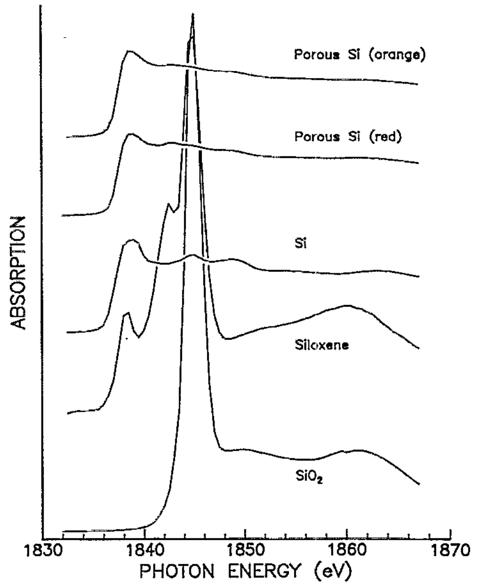

FIG. 1. Si *K*-edge NEXAFS data from three model systems and two different porous Si samples. The large and shifted Si $1s \rightarrow O\ 2p^*$ transitions in SiO_2 and siloxene are very small in the porous Si samples.

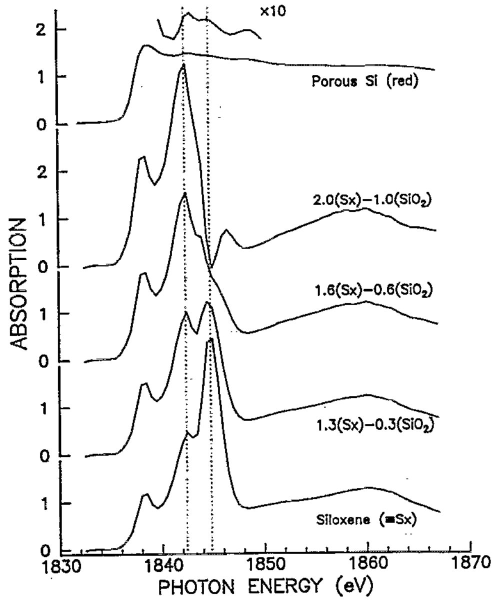

FIG. 2. Analysis using difference spectra to establish upper limit of siloxene (Sx) concentration in porous Si.

gies corresponding to those measured in both the Si and SiO_2 samples. There is also a peak at an intermediate energy of ~1842 eV, indicating that the siloxene sample is not simply a mixture of Si and SiO_2. This peak is likely the Si^{+1} species assigned in earlier photoemission work.[14]

The lack of prominent peaks in the porous-Si data at either ~1845 or ~1842 eV indicate that there is very little siloxene in these samples. To quantify these findings and rule out other possibilities, however, requires a more thorough analysis. We do this in three ways. The first involves the NEXAFS data alone and examines the possibility that our measured siloxene spectrum may contain some (artifactual) amount of SiO_2-like species which, if subtracted from the actual "pure" siloxene spectrum in just the right way, fortuitously mimics the NEXAFS features observed in our por-Si samples. In Fig. 2 we show how this possibility is tested. The bottom spectrum is the siloxene data reproduced from Fig. 1. The next three spectra represent the results of subtracting increasingly larger fractions (~19%, ~27%, and 50%) of SiO_2 from the siloxene data while keeping the overall amount of atomic Si absorption unchanged, i.e., the Si *K*-edge jumps have all been normalized to the same value. Now, looking at the ~1840–1848 eV section of data in red por-Si (the orange por-Si sample is very similar), see ×10 region at the top of Fig. 2, the difference spectrum most closely resembling this region would lie somewhere between 19% and 27% of subtracted SiO_2. Using this result, and the procedure above for estimating the native-oxide layer thickness in bulk Si, we determine that *no more than 5%* siloxene can be present in our por-Si samples. Note that this is an upper limit, because it assumes that all structure in the ~1840–1848 eV region is due solely to a (hypothetical) siloxene species and that none of the observed structure in por-Si is intrinsic to that material.

The second way of ruling out the importance of siloxene in our por-Si samples is to look at the region of data >50 eV above threshold, namely the extended x-ray absorption fine structure (EXAFS). This establishes the existence or absence of Si—O bonds which might otherwise go undetected in the NEXAFS region because of conceivably different or unusual Si—O bonding not found in SiO_2 or siloxene (EXAFS measurements[15] are sensitive only to positions of atomic cores, not to details of unfilled valence-derived orbitals). Following standard analysis procedures,[15] Fig. 3 shows the Fourier-transformed EXAFS data from the samples in Fig. 1. The first-neighbor Si—O and Si—Si peaks in SiO_2 and bulk Si, appearing in the raw data (i.e., uncorrected for phase shifts) at ~1.4 and 2.0 Å, respectively, are both present in siloxene, as expected.[5] There is, however, no evidence for Si—O bonds in the por-Si data.[16]

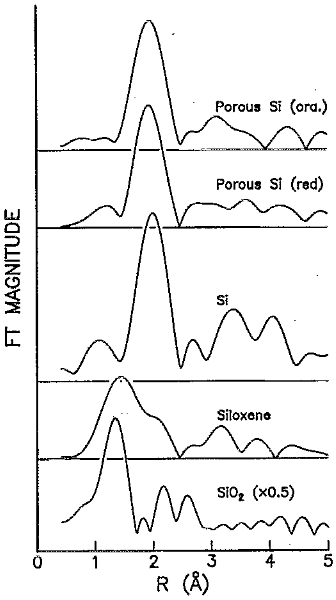

FIG. 3. Fourier-transformed Si *K*-edge EXAFS data from the same systems in Fig. 1. The shorter first-neighbor Si—O bonds in SiO_2 and siloxene, seen as peaks at ~1.4 Å, are not observed in the porous Si data, which exhibit only Si—Si first-neighbor bonds, seen as peaks ~2.0 Å.

The third and final way of testing the importance of siloxene is to measure its quantum efficiency relative to that of our por-Si samples. This procedure is important because siloxene, if much more efficient in luminescing than por-Si, could conceivably account for the reported observations[5] even in very small concentrations. To this end, we have compared the luminescence emission and excitation spectra of ZnS powder, a high efficiency standard, to our por-Si samples and to siloxene, prepared by a variety of methods, including annealing at 400 °C.[5] The data were collected at 10° off normal from samples excited at normal incidence in an optically thick geometry using a commercial xenon lamp fluorometer. All excitation and emission efficiencies were corrected for instrument parameters.

The emission intensities for all the por-Si and siloxene samples were found to be very comparable, with small variations observed depending on sample preparation method. No sample was greater in yield than ~10% of that from

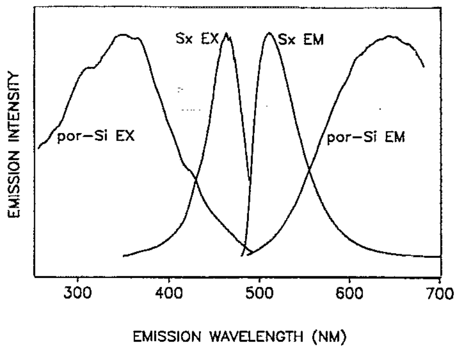

FIG. 4. Excitation (EX) and emission (EM) spectra of porous-Si and siloxene (Sx).

ZnS (the quantum yield of ZnS was >50% relative to a standard Rhodamine-B quantum converter). From this essential equivalence in yield, along with the 5% limit of siloxene determined above, we might conclude that the emission of por-Si cannot arise from the direct optical excitation and subsequent emission of siloxene. However, this does not preclude the possibility of light absorption first by finely divided Si, followed by energy transfer to siloxene and then subsequent emission by siloxene. To assess this possibility, we compare both the emission and excitation spectra of por-Si and siloxene in Fig. 4. The almost mirror-image shapes of the siloxene spectra and the small Stokes shift between them are reminiscent of molecular luminescence for localized excited states.[17] By contrast, the spectral shapes of por-Si are quite different and they exhibit an extremely large Stokes shift, characteristic of absorption by extended states and emission by trap or localized states. While no evidence exists to prove such localized states in por-Si are specifically not due to siloxene, there are numerous documented cases of trap emission spectra from a variety of other Si-containing systems.[18] Therefore, taken separately, either the yield data or the mismatched spectral signatures argue against assigning por-Si emission to siloxene; taken together, they effectively rule out the assignment of por-Si emission to direct absorption and emission from siloxene.

In conclusion, we have shown that the recently proposed explanation of siloxene being responsible for room-temperature luminescence in porous Si is unsupported by our data. Further work is required to decide which of (or whether) the other proposed luminescence hypothesis is (are) appropriate.

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