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X-ray diffraction and x-ray absorption studies of porous silicon, siloxene, heat-treated siloxene, and layered polysilane

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Several porous silicon, siloxene ($Si_6H_6O_3$), heat-treated siloxene, and layered polysilane (Si_6H_6) samples have been studied with K- and L-edge x-ray photoabsorption, photoemission, and powder x-ray diffraction. The x-ray absorption of layered polysilane and porous-Si are found to be remarkably similar. In particular, the K absorption edges of these samples shift by about 0.4-0.6 eV to higher energy relative to crystalline silicon. Siloxene samples heated to 400 °C in inert gas are best described as a mixture of SiO_2 and amorphous-Si. When heat-treated siloxene is studied by photoelectron spectroscopy (surface sensitive) it resembles SiO_2 , when it is studied by x-ray absorption (bulk and surface) features from both SiO₂ and amorphous-Si are observed and when it is studied by x-ray diffraction (bulk measurement) it resembles amorphous-Si. The SiO₂ is therefore predominantly at the surface and heat-treated siloxene is very small amorphous-Si particles coated with SiO_2 . The Si L edge of heat-treated siloxene is not shifted significantly with respect to crystalline Si, unlike that of porous-Si, as-prepared siloxene, or layered polysilane. Taken together, these results suggest that heat-treated siloxene does not resemble electrochemically prepared porous-Si but that it might resemble rapid thermal annealed porous-Si. On the other hand, we believe that layered polysilane and unheated porous-Si may be related.

I. INTRODUCTION

The discovery of efficient photoluminescence in the visible region for porous-silicon prepared from anodized or chemically etched silicon has stimulated an enormous interest in the properties of this material.^{1,2} The origin of the luminescence phenomenon is generally accepted to be due to the preservation of crystallinity in the columnar microstructure of porous-silicon² resulting in a quantum confinement effect.³ Although the structure of porous silicon has not been fully characterized, this interpretation has received support from a number of experimental and theoretical studies. In a recent report,⁴ it is shown that the reaction of siloxene with concentrated nitric acid can result in chemiluminescence similar to that observed when porous-silicon is similarly treated. These results raise the possibility that the luminescence of porous-silicon may be attributed to the formation of siloxene layers.⁴

The strong photoluminescence of as-prepared siloxene is peaked near 550 nm,^{5,6} while that of siloxene heated to 400 °C in inert gas is much weaker⁶ and is near 700–800 nm.^{5,6} The photoluminescence peak of electrochemically prepared porous-Si can be shifted depending on treatment conditions in approximately the same range as the siloxene and heat-treated siloxene samples. This fact has led to further speculation that surface siloxene may be responsible for the luminescence of porous-Si.⁵

Recently, the crystal structure of siloxene prepared by literature methods⁵ has been determined⁷ and shown to agree with that proposed by Weiss et al.⁸ The structure is shown to consist of Si(111) layers terminated above and below by OH groups and H atoms respectively as shown nicely in Fig. 1(a) of Ref 9. It was also shown that asprepared siloxene has a substantial glassy SiO_x (1 < x < 2) impurity.⁷ Furthermore, siloxene prepared at low temperatures was found to combust spontaneously upon exposure to air and to have an x-ray diffraction pattern consistent with oxygen-free siloxene (Si_6H_6) . The authors of Ref. 7 called Si_6H_6 "layered polysilane." First principles electronic calculations show that Si_6H_6 has a direct band gap of about 3 eV.^{10,11} Conceivably, porous-silicon, which is known to be predominantly oxygen-free, 12,13 could be made up of a small number of Si(111) layers stacked as in crystalline Si and terminated above and below by hydrogen. In view of the possible relationship between poroussilicon, siloxene, or layered polysilane, it is therefore important to characterize the properties of these materials.

The measurement of the core-level absorption spectrum is a powerful and efficient technique for probing the energy distribution of the empty states of a material. For

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example, the blue shift and broadening of the conduction band observed in the Si L-edge absorption spectrum in porous-silicon is consistent with electrons confined within small regions of varying dimension.¹² Here, the Si K- and L-edge absorption spectra for two unheated siloxene samples, one of which has been rinsed in HF (to make layered polysilane) and rigorously excluded from contact with air, are reported. The Si K absorption edge of as-prepared siloxene shows a characteristic blue shift and, more significantly, the absorption features resemble that of a mixture of amorphous-silica and porous-silicon in contrast to the results presented by Friedman et al.¹³ Here we show that the K edge of layered polysilane resembles that of porous-Si without the addition of an amorphous-silica component. These observations clearly demonstrate a close correlation between the electronic properties of layered polysilane and porous-silicon.

X-ray absorption, x-ray diffraction, and photoemission results for a siloxene sample heated to 400 °C in argon are also presented. These results show that heated siloxene is best described as small particles of amorphous-Si coated with amorphous-SiO₂.

II. EXPERIMENTAL

The siloxene and layered polysilane samples were prepared from the reaction of powdered CaSi₂ (Aldrich) with aqueous hydrochloric acid.^{7,8} The freshly prepared samples were yellow. One sample was prepared at room temperature and vacuum dried-we call this as-prepared siloxene. The second siloxene sample was prepared at 0 °C under nitrogen, recovered by filtering, rinsed in concentrated HF, and then vacuum dried. This is layered polysilane. Layered polysilane combusts spontaneously upon contact with air, so it must be handled without air exposure. After the drying step, the samples were either directly transferred to an argon-filled glove box or to the UHV chamber for analysis. The powder diffraction pattern of layered polysilane was measured using a sample holder with a beryllium window which makes an air-tight seal. The sample was loaded into the holder in the argon-filled glove box. The diffraction pattern of layered polysilane is shown in Fig. 1 and its interpretation is described in Ref. 7. After the diffraction measurement, the beryllium window was lifted and the sample spontaneously burst into flame upon exposure to air as reported in Ref. 7.

Another siloxene sample was prepared at 0 $^{\circ}$ C (without the HF rinsing step) as above and was transferred while damp to a stainless-steel furnace tube which was connected both to a roughing pump and to an argon line. The sample was first vacuum dried and then heated to 400 $^{\circ}$ C for 90 min then cooled to room temperature both under flowing argon. We call this sample heat-treated siloxene. The sample was red-brown in color and was air-stable at this stage.

One porous silicon sample was prepared by electrochemically etching an *n*-type (100)Si wafer followed by an HF soak as previously described in Ref. 12 while the second was prepared by the "stain-etch" technique.¹⁴ These porous-silicon samples will be referred to as electrochemi-



FIG. 1. The x-ray diffraction pattern of layered polysilane. Miller indices corresponding to the Bragg peaks of layered polysilane are indicated. Silicon is an impurity in our $CaSi_2$ starting material. The Bragg peaks from the Be window are indicated. The solid line is a simulated pattern from Ref. 7.

cal and chemical porous-silicon respectively. For a reference sample of crystalline silicon, a silicon (100) wafer was dipped in concentrated HF and dried with flowing nitrogen just prior to loading into the UHV chamber. Crystalline quartz (c-SiO₂) and amorphous-silica (a-SiO₂) were obtained from Baker Chemicals.

Si K-edge absorption spectra were measured at the double-crystal monochromator (DCM) beamline of the Canadian Synchrotron Radiation Facility (CSRF) at the Synchrotron Radiation Center, University of Wisconsin-Madison. Details of the DCM monochromator have been described elsewhere.¹⁵ In essence, white light from the storage ring is monochromatized by reflection from two asymmetrically mounted InSb(111) crystals. The energy resolution at the Si K edge is about 0.9 eV. Total electron yield¹⁶ was employed to record the spectrum. The Si L-edge absorption spectra were measured using the Grasshopper monochromator beamline at CSRF as in Ref. 12. The energy resolution at the L edge is about 80 meV. This chamber also contained a hemispherical electron energy analyzer so that we were able to measure the photoemission from the same samples. In photoemission, the combined resolution of the monochromator and electron energy analyzer at 80 eV photon energy was 0.5 eV.

III. RESULTS

The Si K-edge absorption spectra for electrochemical and chemical porous-silicon are compared with crystalline Si in Fig. 2. The absorption edge of both porous-silicon samples are shifted to higher energy with respect to crystalline Si although details of their absorption features are quite different. The absorption edge for the electrochemical porous-silicon sample is about 0.4 eV above that of crystalline Si and the shift is about 0.5 eV for the chemical sample. As discussed earlier, a blue shift in the absorption edge is indicative of quantum confinement where the bot-



FIG. 2. Si K-edge absorption spectra for crystalline Si (solid), electrochemical porous-Si (short dash), and chemical porous-silicon (long dash) as indicated in the figure.

tom of the conduction band is raised relative to the 1s core level. A similar observation has been reported in studies of porous-silicon samples at the Si L-edge.¹²

The Si K-edge spectra for the siloxene and layered polysilane samples are shown in Fig. 3. Once again, the absorption edges of these two samples are compared to that of crystalline Si and are found to be blue shifted. The absorption edge of both of these samples is about 0.5-0.6 eV higher than crystalline Si and is similar to the shift shown in Fig. 2 for the porous-silicon samples. A large absorption peak is observed in the as-prepared siloxene sample at 1847 eV which is due to the presence of a-SiO₂ as will be shown below. The magnitude of the a-SiO₂ peak varies from sample to sample and is absent, as expected, in the layered polysilane sample. The x-ray diffraction measurements reported in Ref. 7 also show that as-prepared siloxene has a



FIG. 3. Si K-edge absorption spectra for crystalline Si (solid), asprepared siloxene (small dash), layered polysilane (medium dash), and electrochemical porous-Si (long dash) as indicated in the figure.



FIG. 4. Si K edge for as-prepared siloxene compared to a synthetic spectrum made up of a 8:2 mixture of the spectra for electrochemical porous-Si and amorphous-SiO₂.

glassy SiO_x impurity phase and are consistent with the results presented here.

The absorption spectra for the layered polysilane and the electrochemical porous-Si sample in Fig. 3 are similar. This has been previously reported.¹⁷ The as-prepared siloxene spectrum also resembles that of layered polysilane apart from the peak due to a-SiO₂. Following Friedman et al.¹³ it is also tempting to simulate the as-prepared siloxene spectrum by the superposition of the absorption spectra of porous-silicon and silica. To this end, a simulated spectrum obtained from a 8:2 mixture of the electrochemical porous silicon spectrum with the a-SiO₂ spectrum is compared with the freshly prepared siloxene spectrum in Fig. 4. The resemblance of the two spectra is striking. All dominant absorption features observed in as-prepared siloxene are reproduced approximately in both relative intensities and peak positions. This is in contrast to the results of Friedman et al.¹³ Details of siloxene preparation conditions were not described in Ref. 13, so it is possible that our samples differ from those of Friedman et al.

Figure 5 shows the L-edge absorption spectra for crystalline Si, as prepared siloxene, chemical porous-silicon and amorphous-SiO₂. The dominant features present in the K edge shown in Figs. 2, 3, and 4 are mirrored in the L-edge data. The absorption edges of siloxene and poroussilicon are blue shifted relative to c-Si, and the siloxene sample contains substantial a-SiO₂ as evidenced by the absorption peaks near 105 and 107 eV.

Close examination of the absorption edge in the insets of Figs. 2 and 3, suggests that the K-edges of siloxene and porous-Si are actually *sharper* than that of crystalline silicon. Figure 6(a) shows the derivative of the K-edge absorption data (dI/dE) for crystalline Si, as-prepared siloxene, layered polysilane, and the electrochemical porous-Si sample. These data have all been collected at the same resolution. The full width at half maximum of the crystalline Si edge is about 0.8 eV wider than all of the other samples, which show similar behavior. At the L edge,



FIG. 5. Si *L*-edge absorption spectra for crystalline Si (solid), asprepared siloxene (small dash), chemical porous-silicon (long dash), and amorphous-SiO₂ (medium dash).



FIG. 6. (a) The derivative (dI/dE) of the K-edge absorption (I) with respect to photon energy (E) for crystalline silicon (solid), as-prepared siloxene (small dash), layered polysilane (medium dash), and electrochemical porous-Si (long dash). (b) (dI/dE) of the L-edge absorption for crystalline silicon (solid) electrochemical porous-Si (small dash) and chemical porous-silicon (long dash).



FIG. 7. Powder x-ray diffraction profiles (Cu $K\alpha$ radiation) for amorphous-SiO₂, amorphous-Si, and heat-treated siloxene as indicated in the figure. The curves have been offset vertically for clarity.

shown in Fig. 6(b), the behavior is reversed, that is, the crystalline Si sample shows the sharpest edge. Noise-free L-edge derivatives for the siloxene, and layered polysilane samples are not available. The L-edge results for crystalline Si and the electrochemical porous-Si sample show the doublet expected due to the spin-orbit splitting of the 2p core level. As the L edge shifts become larger, so does the width of the peaks in dI/dE, consistent with the presence of a range in quantum confining sizes as proposed in Ref. 12. The width of dI/dE for the chemical porous-Si sample is still consistent with two broad peaks separated by the 0.62 eV spin-orbit splitting. We do not understand why the Kedges for the quantum confined samples should be sharper than that of crystalline Si. Presumably, this indicates a difference in the nature of the excitonic states near the conduction band minimum for crystalline Si compared to the other materials.

Figure 7 shows the powder x-ray diffraction patterns of the heat treated siloxene sample, amorphous-SiO₂, and a thin film of amorphous-Si deposited on a silicon wafer. The latter sample was measured using grazing incidence geometry leading to the large increase in background counts at small scattering angle. The diffraction pattern of the heat treated siloxene sample closely resembles that of amorphous-Si and no longer bears any resemblance to the original layered polysilane (Fig. 1) or siloxene (Ref. 7) patterns.

Figure 8 shows the Si *L*-edge absorption spectra for crystalline silicon, amorphous-SiO₂, and the heat-treated siloxene sample. The heat-treated siloxene sample shows features in the absorption spectrum which can be associated with both silicon and SiO₂. The sharp edge near 99.5 eV in the heat-treated siloxene sample is not shifted with respect to crystalline silicon, shows the spin-orbit splitting, but does not show a peak after the edge like the crystalline Si sample does. These are exactly the characteristics of the *L*-edge absorption of amorphous-Si.¹⁸

Finally, Fig. 9 shows the valence band photoemission

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FIG. 8. L-edge x-ray absorption spectra for crystalline silicon, heat-treated siloxene, and amorphous-SiO₂ as indicated in the figure. The curves have been offset vertically for clarity.

spectra for the heat-treated siloxene sample and for amorphous-SiO₂ collected with 80 eV photon energy. The spectra are basically identical within the noise. (The binding energy scale assumes an analyzer work function of 4.5 eV.)

The results in Figs. 7, 8, and 9 show that in a bulk measurement (diffraction) heat-treated siloxene resembles amorphous-Si, in a surface sensitive measurement (photoemission) it resembles amorphous-SiO₂, and in a probe of intermediate depth it shows characteristics of both. This proves that the heat-treated siloxene sample must be considered to be small amorphous-Si particles coated with amorphous-SiO₂. Presumably, if the amorphous-Si particles are small enough, they will show quantum confinement effects, and this could explain why heat-treated siloxene is commonly believed to take a stoichiometry of Si₆H₆O₃. As it is heated to near 250 °C, the layered structure collapses and hydro-



FIG. 9. Photoelectron spectra of amorphous-SiO₂ and heat-treated siloxene collected using a photon energy of 80 eV. The binding energy scale assumes a 4.5 eV analyzer work function.

gen is evolved.¹⁹ Our results suggest that the silicon and oxygen arrange into clusters of amorphous-Si which are coated by SiO_2 once the hydrogen is released.

The similarity in the photoluminescence spectra between siloxene and porous silicon has been noted in several recent reports.^{4,5,10,17} It should be emphasized that in spite of similar optical properties, it does not necessarily mean that siloxene and porous-silicon are identical materials. Siloxene prepared with the standard technique as employed here is believed to be composed of a mixed structure with both H and OH terminating Si(111) sheets.^{7,8} However, in Ref. 7, predominantly oxygen-free siloxene derivatives (layered polysilane) were proposed and were prepared by HF rinsing. These have a chemical behavior akin to silanes.⁷ This layered polysilane is composed of single Si(111) puckered honeycomb layers terminated by hydrogen atoms.⁷ These Si_6H_6 layers are then stacked in a roughly parallel fashion. In principle, a silicon-like structure of small dimension perpendicular to the layers can be constructed by stacking several Si(111) puckered honeycomb layers as in crystalline silicon followed by hydrogen termination of the exposed layer surfaces to make $Si_{6n}H_6$ layers. Porous silicon could be such $Si_{6n}H_6$ structures since it is known to be H passivated. In this description, layered polysilane is found when n=1. If this hypothesis is proven to be correct, then the close similarity between the optical properties of these materials follows.

Heat-treated siloxene has been shown to be small amorphous-Si particles coated by SiO_2 . This may bear some relevance to porous-silicon which has been rapidly thermally oxidized.²⁰

In conclusion, we have shown that the K- and L-edge x-ray absorption of porous-Si and layered polysilane are remarkably similar. All of the porous-Si, siloxene, and layered polysilane absorption edges are blue shifted by about 0.4–0.6 eV with respect to crystalline silicon. Layered polysilane (Si₆H₆) may be quite similar to porous-silicon. Our model supporting this argument assumes that porous-Si is composed of Si_{6n}H₆ silicon layer sandwich structures with small *n*. Heat-treated siloxene is small particles of amorphous-Si coated with amorphous-SiO₂ and may be similar to rapid thermal oxidized porous-Si. Heat-treated siloxene or layered polysilane.

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