

- ing study of aggregate garnets. With the incident laser beam focused to a spot size of 15  $\mu\text{m}$  and a scattering length in the sample of only 15  $\mu\text{m}$  at high pressures, even an average grain size of 2  $\mu\text{m}$  results in several hundred randomly oriented crystallites being probed during the experiment. This ensures that an appropriate orientational average is being sampled.
16. J. P. Watt, G. F. Davies, R. J. O'Connell, *Rev. Geophys. Space Phys.* **14**, 541 (1976).
  17. A. Yeganeh-Haeri, D. J. Weidner, E. Ito, *Geophys. Res. Lett.* **17**, 2453 (1990).
  18. J. Frankel, F. J. Rich, C. G. Homan, *J. Geophys. Res.* **81**, 6357 (1976).
  19. The P-wave velocity data set was obtained independently of earlier results; Frankel *et al.* (18) relied on the isothermal equation of state of NaCl to estimate the sample thickness, a necessary parameter in the data reduction of their ultrasonic technique. Pressures are also measured more precisely with the ruby-fluorescence technique used in our work; Frankel *et al.* (18) estimated an

- error of  $\pm 15\%$  from their resistometric calibration. Birch (8) compared the high-pressure polycrystalline NaCl results of Frankel *et al.* (18) with those of Morris *et al.* (20) (to 9 GPa) and those of Voronov and Goncharova (20) (to 10 GPa) and found very good agreement among these data sets using ultrasonic techniques; this work is further verified by the results of our Brillouin-scattering experiments. However, as Birch (8) pointed out, there remains some discrepancy between the zero-pressure slopes inferred from high-pressure polycrystalline work and low-pressure single crystal work; this issue needs further clarification.
20. C. E. Morris, J. C. Jamieson, F. L. Yarger, *J. Appl. Phys.* **47**, 3979 (1976); F. F. Voronov and V. A. Goncharova, *Soviet Physics JETP* **23**, 777 (1966).
  21. To calculate density as a function of pressure, isothermal equation of state data were taken from Birch (8) for NaCl, Yagi (22) for the low-pressure (B1) phase of KCl, and Campbell and Heinz (22) for the high-pressure (B2) phase of KCl.

22. A. J. Campbell and D. L. Heinz, *J. Phys. Chem. Solids* **52**, 495 (1991); T. Yagi, *ibid.* **39**, 563 (1978).
23. R. C. Liebermann and A. E. Ringwood, *J. Geophys. Res.* **78**, 6926 (1973).
24. R. Jeanloz, in *High-Pressure Research in Geophysics*, S. Akimoto and M. H. Manghnani, Eds. (Center for Academic Publications Japan, Tokyo, 1982), vol. 12, pp. 479–498.
25. D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).
26. Y. Sato-Sorensen, *J. Geophys. Res.* **88**, 3543 (1983).
27. The technical assistance of M. Vaughan and M. Grimsditch is gratefully acknowledged. D. Anderson and two reviewers provided valuable comments on the manuscript. This work was supported by National Science Foundation grant EAR-9104885 and the Materials Science Laboratory at the University of Chicago.

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## Chemiluminescence of Anodized and Etched Silicon: Evidence for a Luminescent Siloxene-Like Layer on Porous Silicon

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Treatment of anodized or chemically etched silicon ("porous silicon") with dilute nitric acid or persulfate solution results in weak chemiluminescence in the visible region. Concentrated nitric acid reacts violently with porous Si produced by anodization with a bright flash of light. The fact that similar reactions occur with siloxene ( $\text{Si}_6\text{H}_6\text{O}_3$ ) prepared from  $\text{CaSi}_2$  suggests that the visible emission seen with porous Si can be attributed to this substance.

Recent interest in porous Si and very small Si particles largely arises from the photoemission in the visible region observed with these materials, indicating a radiative transition well above the indirect band gap of bulk crystalline Si (1–7). This effect has been attributed to the presence of nanometer-size Si structures (Q-particles and quantum dots or wires) in which quantum-size effects (1, 2) occur. However, an alternative explanation for this emission is the alteration of the composition of the Si upon anodization or etching which produces new Si-based compounds that luminesce at visible wavelengths. For example, recent work by Brandt *et al.* (6) has demonstrated that the photoluminescence and vibrational spectra of porous Si can be attributed to siloxene derivatives. In this report we show that treatment of porous Si with nitric acid or persulfate can result in chemiluminescence, as occurs with siloxene prepared from  $\text{CaSi}_2$ . These results strongly suggest that the luminescence of porous Si is attributable mainly to formation of siloxene-like compounds.

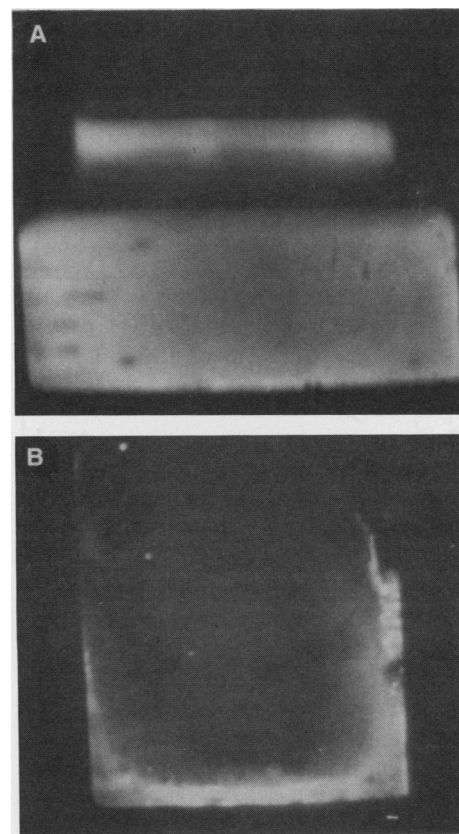
Porous Si was prepared by two different methods. In the first, single-crystal pol-

ished p-type Si (100) wafers (1 ohm-cm) were anodized in a solution of hydrofluoric acid (HF), acetic acid ( $\text{CH}_3\text{COOH}$ ), and ethanol (1:1:1), as previously described (8). In the second, the Si wafer was chemically etched with a solution of HF,  $\text{HNO}_3$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{H}_2\text{O}$  (1:2:1:4) for 5 to 10 min (7). The resulting porous Si, formed by either method, ranged from a dull yellowish-brown to a darker brown in color and showed the characteristic bright orange to red luminescence when illuminated with an ultraviolet (UV) source (Mineralight UVGL-25).

When a piece of porous Si was immersed in an  $\sim 4\text{ M}$   $\text{HNO}_3$  solution, a weak chemiluminescence was observed that could be imaged with a charge-coupled device (CCD) camera (Model CH210, Photometrics, Tucson, Arizona) cooled to  $-113^\circ\text{C}$  (Fig. 1A). Porous Si in contact with  $\text{HNO}_3$  vapor also produced chemiluminescence. Figure 1B is an image of the same piece of porous Si as shown in Fig. 1A but with the sample suspended  $\sim 0.5\text{ cm}$  above the  $\text{HNO}_3$ . This chemiluminescence probably arises from the reaction between the porous Si and the  $\text{NO}_2$  gas present in the vapor phase. Chemiluminescence generated in the vapor phase was passed through a monochromator (Model

100S, American Holographic, Littleton, Massachusetts) and the resulting spectrum (imaged with the CCD) (Fig. 2) also shows the photoluminescence of the same piece of porous Si in air illuminated by a hand-held UV lamp (370-nm excitation).

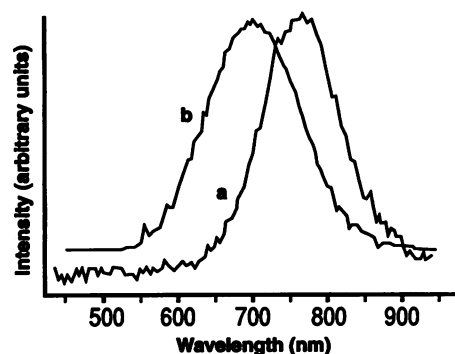
The chemiluminescence obtained from the  $\text{HNO}_3$  solution slowly decayed to about one-half of its original brightness in 10 min. Note that the chemiluminescence in either the liquid or gas phase was very weak and was not visible to the eye in the



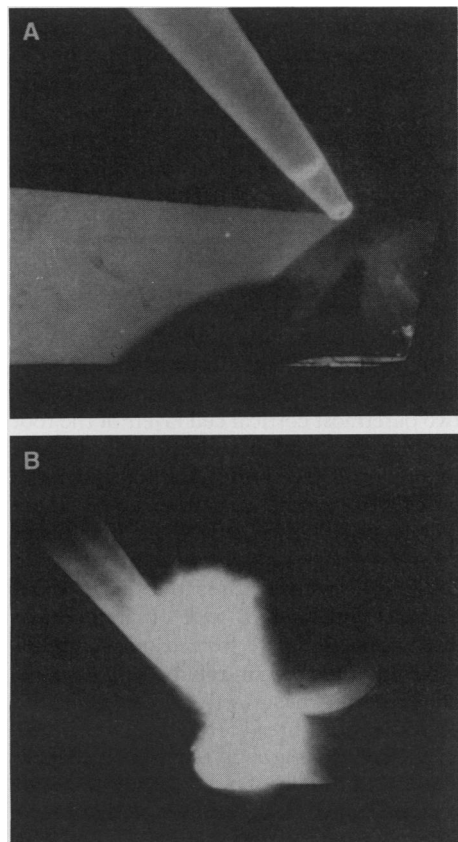
**Fig. 1.** (A) Porous Si immersed in an  $\sim 4\text{ M}$   $\text{HNO}_3$  solution. (B) Porous Si in the vapor phase above a concentrated  $\text{HNO}_3$  solution.

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dark. Similar chemiluminescence was observed when the porous Si was immersed in a solution of ammonium peroxydisulfate, with an intensity about one-half of that found with the  $\text{HNO}_3$  solution. After the chemiluminescence in either of these solutions had decayed to imperceptible levels, photoluminescence of the porous Si surface also disappeared.



**Fig. 2.** Spectra of porous Si during chemiluminescence (a) and photoluminescence (b). Chemiluminescence was from vapor phase above concentrated  $\text{HNO}_3$ . Photoluminescence of porous Si in air excited with a hand-held UV lamp ( $\sim 370$  nm).



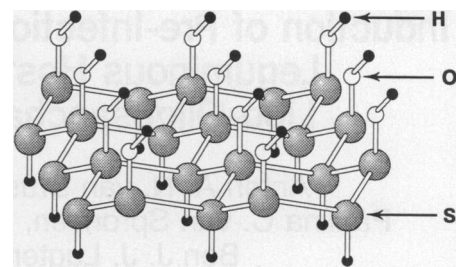
**Fig. 3.** (A) Pipette tip containing concentrated  $\text{HNO}_3$  above porous Si sample. (B) Exposure during the application of a second drop of concentrated  $\text{HNO}_3$ . White residue from the first drop can be seen in the background.

A more dramatic effect was seen when concentrated  $\text{HNO}_3$  was dropped on the surface of dry porous Si. One drop ( $\sim 0.5$  ml) of concentrated  $\text{HNO}_3$  on the surface caused a flash of light with an audible pop. This flash was easily seen, even in a well-lit room. After the flash, a white residue remained on the surface. A photograph before the application of any  $\text{HNO}_3$  is shown in Fig. 3A. The tip of the pipette containing  $\text{HNO}_3$  is directly above the horizontal porous Si sample. Figure 3B is an image of the same arrangement as in Fig. 3A, except that the pipette has been moved slightly down and to the left of its previous position. Figure 3B was taken during the application of a second drop of concentrated  $\text{HNO}_3$  and shows the flash from the reaction. The white residue from the first drop can be seen in the background (where the pipette was located in Fig. 3A). Concentrated  $\text{H}_2\text{SO}_4$  did not induce this reaction or any detectable chemiluminescence. Only the porous Si produced by the anodization method showed this violent reaction. Porous Si produced by chemical etching showed chemiluminescence and photoluminescence but at a lower intensity than that found with the anodized Si. Note also that the Si wafer weakly chemiluminesced during chemical etching in the  $\text{HF-HNO}_3$  etchant.

Some other properties of the porous silicon are also of interest. A piece of porous Si immersed in an alkaline solution (1 M NaOH) immediately evolved gaseous hydrogen. The surface of porous Si could be scraped off of the treated wafer to yield an insoluble yellow powder that photoluminesces. Porous Si profiled by atomic force microscopy (AFM) revealed surface features of the order of 400 to 600 Å, which is about one order of magnitude larger than that expected for quantum effects (7).

These reactions of porous Si can be compared to those of siloxene, a substance first obtained by Wöhler (9) by treating  $\text{CaSi}_2$  with concentrated HCl. A number of investigations of this material have been reported (9–14). Siloxene (empirical formula  $\text{Si}_6\text{H}_6\text{O}_3$ ) has been described (10) as consisting of Si layers with substituent -H or -OH groups (Fig. 4). A more disordered structure with O-substitution within the Si layer and oxygen cross-linking between the layers has also been proposed (11). This material is known to chemiluminesce upon treatment with strong oxidants (12) and to evolve  $\text{H}_2$  and turn white when exposed to sunlight (13). Treatment of siloxene with fuming  $\text{HNO}_3$  produces incandescence, but concentrated  $\text{H}_2\text{SO}_4$  has no effect (13). On heating siloxene in air, it bursts into flame (9).

In order to confirm the similarity of



**Fig. 4.** Proposed structure (10) for siloxene depicting a layer of hexagonal silicon rings with -H and -OH groups as substituents.

siloxene to that of porous Si, this material was synthesized from  $\text{CaSi}_2$  (Johnson & Matthey, Ward Hill, Massachusetts) by treatment with dilute HCl (12). The siloxene obtained was a greenish-yellow powder that showed a yellow luminescence when irradiated with a UV mineral light. Under a microscope this powder revealed small platelets similar to those observed on the surface of porous Si. Reaction of  $\sim 100$  mg of this siloxene with a drop of concentrated  $\text{HNO}_3$  caused a bright flash and sparks. When the siloxene was stirred into a dilute  $\text{HNO}_3$  solution, the entire solution luminesced a bright orange color. After the siloxene was exposed to air for 2 days, these effects were less pronounced.

It is unlikely that Si alone, even in finely divided form, would undergo the chemiluminescent reactions shown here. Rather, they suggest that "porous Si" consists, at least in part, of a siloxene layer produced by anodic or chemical etching.

## REFERENCES AND NOTES

1. L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
2. V. Lehmann and U. Gösele, *ibid.* **58**, 856 (1991).
3. I. Amato, *Science* **252**, 922 (1991).
4. J. L. Heinrich, C. L. Curtis, G. M. Credo, K. L. Kavanagh, M. J. Sailor, *ibid.* **255**, 66 (1992).
5. H. Takagi, H. Ogawa, Y. Yamazaki, A. Ishizaki, T. Nakagiri, *Appl. Phys. Lett.* **56**, 2379 (1990).
6. I. Amato, *Science* **254**, 1730 (1991); M. S. Brandt, H. D. Fuchs, M. Stutzmann, J. Weber, M. Cardona, *Solid State Commun.* **81**, 307 (1992).
7. J. Sarathy *et al.*, *Appl. Phys. Lett.* **60**, 1532 (1992).
8. C. Tsai *et al.*, *ibid.* **59**, 2814 (1991).
9. F. Wöhler, *Liebigs Ann. Chem.* **127**, 256 (1863).
10. A. Weiss, G. Beil, H. Meyer, *Z. Naturforsch.* **35B**, 25 (1980).
11. I. Hirabayashi, K. Morigaki, S. Yamanaka, *J. Phys. Soc. Jpn.* **52**, 671 (1983).
12. F. Kenny and R. B. Kurtz, *Anal. Chem.* **22**, 693 (1950).
13. O. Honigschmid, *Monatsh. Chem.* **30**, 509 (1909).
14. H. Kautsky, *Z. Anorg. Allg. Chem.* **117**, 209 (1921); *Z. Naturforsch.* **7b**, 174 (1951); *Kolloid-Z.* **102**, 1 (1943).
15. The support of this research by grants from the National Science Foundation and the Office of Naval Research is gratefully acknowledged. We thank F. Zhou for his assistance. We also thank C. Tsai, J. Sarathy, and J. C. Campbell of the Microelectronics Research Center of the University of Texas at Austin for the generous donation of Si wafers.

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