On the Microstructure and Composition of Semi-insulating Polycrystalline Silicon (SIPOS)

Joe Wong,[a,b] John M. Thomas,[a] David A. Jefferson,[a] Timothy G. Sparrow,[a] and Edward F. Koch[b]

[a] *Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, U.K.*
[b] *General Electric Corporate Research and Development, P.O. Box 8, Schenectady, N.Y., 12301, U.S.A.*

Using a range of electron spectroscopic (plasmon, core-electron-edge, *X*-ray emission) and electron microscopic (high-resolution imaging and optical diffractometry) techniques it is established that unannealed SIPOS is non-crystalline $SiO_{0.50 \pm 0.05}$ and that the annealed form contains microcrystallites of elemental silicon (100 Å diameter).

Thin films of the title material grown to a thickness of *ca.* 5000 Å on single crystals of silicon by chemical vapour deposition from mixtures of silane and nitrous oxide, figure eminently in modern high-voltage power devices and in the technology of metal-on-semiconductor integrated circuits (MOS–IC).[1] Little, however, is known about either the composition or the structure of these layers. Here we report the successful use of a combination of electron microscopy and electron spectroscopy for the clarification of these structural and compositional problems.

The composition of the SIPOS films has been determined by electron-energy-loss spectroscopy, utilizing plasmon frequencies[2,3] and K-edge intensities,[3,4] along with *X*-ray emission (O K and Si K) spectroscopy,[5–8] much in the manner employed[3,5,9] by us previously to characterize microcrystalline catalysts and adsorbents. Details of the microstructure have been determined by the use of high-resolution electron microscopy (HREM)[10,11] combined with optical diffractometry, just as in our earlier studies of zeolites[12,13] and other minerals.[14]

Layers of SIPOS were chemically (vapour) deposited from a preset SiH_4–N_2O mixture in N_2 as carrier gas, onto the (111) face of a wafer of single-crystal silicon which had been previously cleaned in HF. The temperature of the Si surface was 625 °C. When required, annealed SIPOS layers were obtained by heating the substratum and its overlayer in N_2 at 900 °C for 30 min. Specimens for microscopy [*i.e.* thin Si(110) cross-sections, showing in elevation the SIPOS deposited on the underlying Si single crystal] were prepared as previously described.[15] Electron-energy-loss spectra were recorded[3,6] in a conventional transmission electron microscope operating at 80 kV (vacuum 10^{-7} Torr) equipped with a magnetic spectrometer having a resolution of *ca.* 4 eV. High-resolution electron micrographs and *X*-ray emission spectra were recorded with a JEOL 200 CX microscope equipped with an ultra-high-resolution polepiece and a special double-tilt goniometer stage. A similar microscope equipped with a windowless Li-drifted Si detector for energy dispersive analysis permitted analytical (*X*-ray emission) studies to be carried out[11] on microregions of the films.

Using the integrated intensities of a 50 eV window above the K-edges of both oxygen at *ca.* 530 eV and silicon at *ca.* 1839 eV in the electron-energy-loss spectrum (Figure 1a), and using the corresponding signals from thin fractured fragments of vitreous silica to calibrate the calculated[3] cross-sections for core-level electron-energy losses, the chemical composition of the SIPOS was determined to be $SiO_{0.50 \pm 0.05}$. This result is very close to that obtained using another electron-probe method, the *X*-ray emission technique. The areas under the O K and Si K peaks generated when the primary electron beam

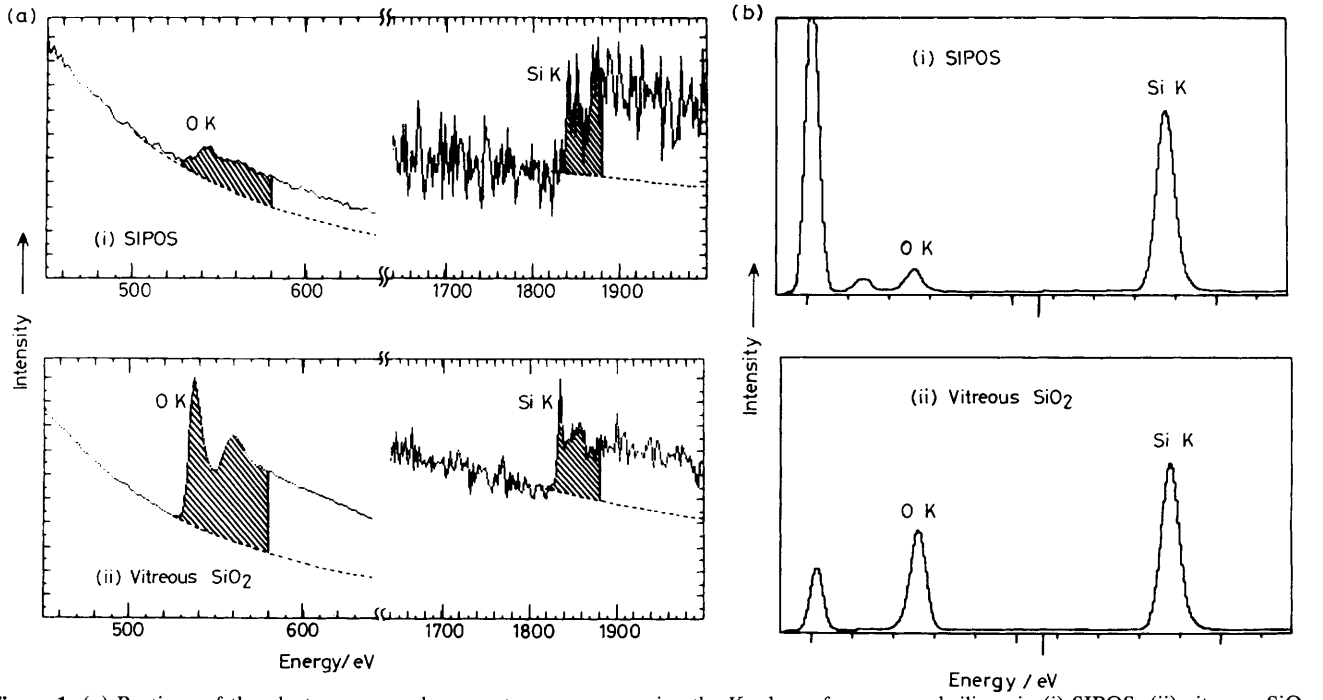
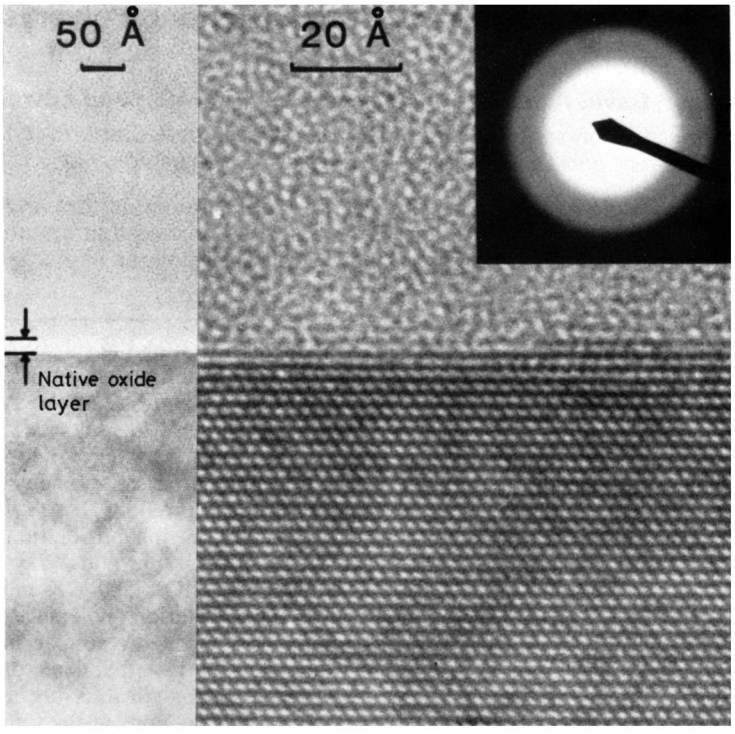
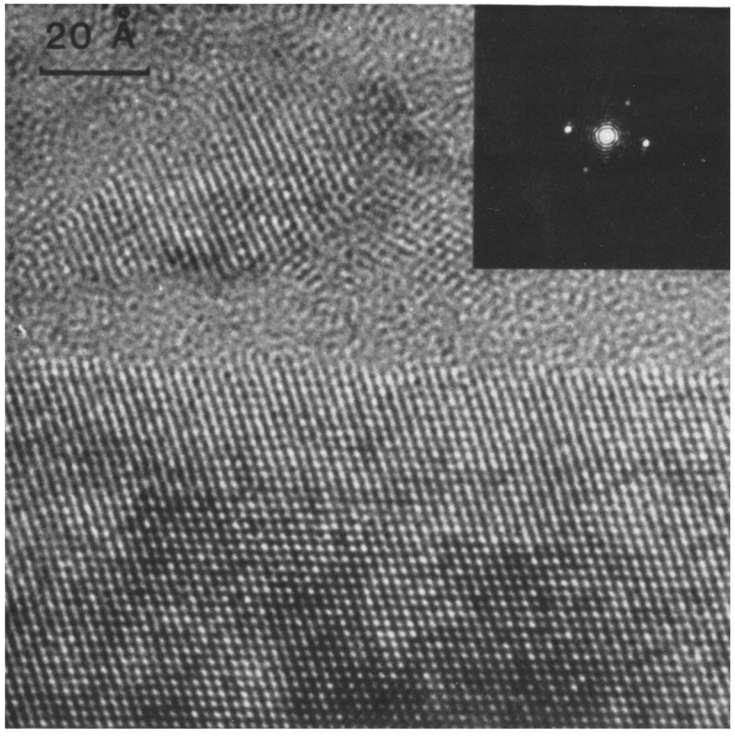


Figure 1. (a) Portions of the electron-energy-loss spectrum encompassing the K-edges of oxygen and silicon in (i) SIPOS, (ii) vitreous SiO_2. Areas containing a 50 eV limit above each 'loss' edge are used (see ref. 4) to compute the Si/O ratio. (b) Electron-induced *X*-ray emission peaks (O K and Si K) from thin sections of (i) SIPOS and (ii) vitreous SiO_2.



SIPOS (as deposited)



SIPOS (annealed)

Figure 2. (Above) High-resolution image of single-crystal silicon and its adjacent non-crystalline, as-prepared, semi-insulating polycrystalline silicon (SIPOS). The low-resolution image (at left) reveals the presence of the non-crystalline native oxide (25 Å thick) more clearly than the high-resolution image (right), and the electron diffraction pattern (top right) generated by the SIPOS reveals the non-crystallinity. (Below) High-resolution image of silicon substratum and of the annealed SIPOS. The microcrystallites visible in the SIPOS were shown to be elemental silicon by diffractometry (refs. 13, 14). The spots in the optical diffractogram (top right) correspond to those obtained from pure, crystalline silicon.

is focused on the SIPOS, compared with the corresponding areas obtained from a vitreous silica sample, yielded the Si/O ratio (Figure 1b). Gratifyingly the results of another independent thin-film analysis, Rutherford back-scattering,[16] using a primary beam of ions indicated that 30 atom % of the SIPOS layer is oxygen. Furthermore, the frequencies of the plasmons[2,3] in Si, SiO_2, and SIPOS were determined to be, respectively, 16.7, 23.2, and 17.6 eV, values that are interpretable in terms of the SIPOS layers being a suboxide.

The ultrastructural details of the interface between silicon and the SIPOS, and the internal features of the latter, are well revealed by HREM (Figure 2). The crystalline Si substrate is seen to possess a thin (25—30 Å) amorphous layer of so-called 'native oxide,' known[17] to form on Si surface upon exposure to air at room temperature. And the non-crystallinity of the contiguous SIPOS is apparent both in the real-space image and in the corresponding electron diffraction pattern. Annealed SIPOS, on the other hand, is seen by optical diffractometry, using He–Ne laser light as a source to consist of islands ($\leq$100 Å in linear dimension) of microcrystalline Si dispersed in the amorphous suboxide.

The picture that emerges from our direct study of composition and structure by a variety of electron microscopic and electron spectroscopic techniques leaves little doubt that as-prepared SIPOS itself is a non-crystalline suboxide of silicon, but that the annealed form contains both crystalline elemental silicon and non-crystalline suboxide. These conclusions are in line with, and extend, the views recently expressed by Hitchman.[18] These results are further corroborated by scanning transmission electron microscopy,[19] where an electron beam of cross-section *ca.* 10 Å may be used, and by earlier *X*-ray photoelectron spectroscopic studies.[20]

We thank the S.E.R.C. and the University of Cambridge for support and General Electric Corporate Research and Development for granting research leave to J. W.

Received, 19th September 1985; Com. 1373

References

1 H. Mochizuki, T. Aoki, H. Yamato, M. Okayama, M. Abe, and T. Ando, *Jpn. J. Appl. Phys. Suppl.*, 1976, **15**, 35.
2 T. G. Sparrow, B. G. Williams, J. M. Thomas, W. Jones, P. J. Herley, and D. A. Jefferson, *J. Chem. Soc., Chem. Commun.*, 1983, 1432.
3 J. M. Thomas, B. G. Williams, and T. G. Sparrow, *Acc. Chem. Res.*, 1985, **18**, 324.
4 R. F. Egerton, *Philos. Trans. Roy. Soc. London, Ser. A*, 1982, **305**, 421; J. M. Thomas in 'Inorganic Chemistry towards the 21st Century,' ed. M. H. Chisholm, ACS Series No. 211, 1983, p. 445.
5 D. A. Jefferson, J. M. Thomas, and R. K. Grasselli, *J. Chem. Soc., Chem. Commun.*, 1983, 594.
6 M. Beer, R. W. Carpenter, L. Eyring, C. E. Lyman, and J. M. Thomas, *Chem. Eng. News*, 1981, **59**, 40.
7 A. K. Cheetham and A. J. Skarnulis, *Anal. Chem.*, 1981, **53**, 1060.
8 A. K. Cheetham, A. J. Skarnulis, D. M. Thomas, and K. Ibe, *J. Chem. Soc., Chem. Commun.*, 1984, 1603.
9 T. G. Sparrow, B. G. Williams, J. M. Thomas, and C. N. R. Rao, *J. Phys. Chem.*, 1984, **88**, 5759.
10 J. M. Thomas, D. A. Jefferson, and G. R. Millward, *J. Microsc. et Spect. Electron*, 1982, **7**, 315.
11 J. M. Thomas, D. A. Jefferson, and G. R. Millward, *JEOL News*, 1985, **23E**, 7.
12 J. M. Thomas and G. R. Millward, *J. Chem. Soc., Chem. Commun.*, 1982, 1380.
13 G. R. Millward and J. M. Thomas, 'Proc. Carbon & Graphite Conf.,' London, 1974, Soc. Chem. Ind., 1974, p. 492.
14 J. M. Thomas, G. R. Millward, S. Ramdas, and M. Barlow, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 1075.
15 J. C. Bravman and R. Sinclair, *J. Electron Microsc. Tech.*, 1984, **1**, 53.
16 J. A. Cairns, in 'Characterisaton of Catalysts,' eds. J. M. Thomas and R. M. Lambert, Wiley, New York, 1980, p. 185.
17 H. R. Philipp and E. A. Taft, *J. Appl. Phys.*, 1982, **53**, 5224.
18 M. L. Hitchman, *Vacuum*, 1984, **34**, 377.
19 J. Wong, D. A. Jefferson, T. G. Sparrow, J. M. Thomas, R. H. Milne, A. Howie, and E. F. Koch, *Appl. Phys. Lett.*, 1986, **7**, Jan.
20 J. H. Thomas, III, and A. M. Goodman, *J. Electrochem. Soc.*, 1979, **126**, 1766.