Novel fabrication method for nanometer-scale silicon dots and wires

G. S. Chen, C. B. Boothroyd, and C. J. Humphreys
Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, United Kingdom

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We have discovered that a thin film of SiO_2 can be directly reduced to Si under electron beam irradiation. The application of this effect to the fabrication of nanometer-sized Si dots and wires is demonstrated. In particular, if SiO_2 is irradiated with a high intensity 100 keV electron beam of nanometer scale, then a column of Si is formed which can be as small as 2 nm in diameter. If the beam is moved in a straight line, then a very thin wire of Si is formed. These columns and wires are formed directly under electron irradiation with a dose of $\geqslant 3\times 10^9$ C m^{-2} and no resists or chemical development are required.

Self-supporting amorphous 15-nm-thick SiO_2 films were prepared using electron beam evaporation. These were irradiated using a 100 keV electron beam from a field emission gun in a VG HB501 scanning transmission electron microscope. The vacuum in the specimen chamber was 1×10^{-9} Torr. The irradiation process was studied by performing electron energy loss spectroscopy (EELS) of the electrons transmitted by the specimen during irradiation. Figure 1(a) shows a series of low loss spectra taken during the irradiation process, acquired using a stationary probe which had been slightly defocused in order to reduce the damage rate and hence to facilitate the EELS study. The electron beam current was 1 nA in a probe of diameter 15 nm. Initially the SiO_2 volume plasmon peak at 22.9 eV dominates the spectrum, but as the dose increases the position and width of the plasmon peak are shifted continuously toward those of Si. After a dose of 3×10^9 C m^{-2} the plasmon peak is at 16.7 eV, which is the energy of the plasmon loss in pure Si, strongly suggesting that the SiO_2 has been reduced to Si. Figure 1(b) shows a series of spectra at higher energy loss. It is well known that in pure Si the L edge occurs at 99 eV, but in SiO_2 it is chemically shifted to 106 eV, with a large peak at 108 eV. The spectra in Fig. 1(b) demonstrate the reduction of SiO_2 to Si under electron irradiation. The oxygen K edge was also monitored, and its intensity decreases to a level too low to be detected after a dose of 3×10^9 C m^{-2}. Thus the evidence of Figs. 1(a) and 1(b), together with the oxygen spectrum, suggests that the 15-nm-thick SiO_2 is reduced to Si after a dose of 3×10^9 C m^{-2} of 100 keV electrons.

The behavior of amorphous SiO_2 under the electron irradiation described above is very different from the behavior of other materials that have been studied.[1] For example, if amorphous Al_2O_3 is irradiated by an intense focused electron beam a hole is produced surrounded by a sheath of metallic aluminum.[2] Similar effects are observed in amorphous AlF_3.[3] In both of these cases it is believed that the Al ions migrate to the sides of the irradiated area under an intense internal electric field set up in the specimen as a result of irradiation.[4] For the case of SiO_2, the Si clearly stays in the center of the irradiated area rather than moving to the sides.

In Auger electron analysis, it is well known that if SiO_2 is irradiated by a low energy (typically 1–3 keV) electron beam then O is lost from the surface layers[5,6] by a Knotek and Feibelman electron-stimulated desorption mechanism.[7,8] Silicon can also be lost by electron sputtering from the electron exit surface of the specimen.[9,10] The results presented here have demonstrated that if a very high current density 100 keV electron beam is used, then 15-nm-thick SiO_2 can be reduced to Si. Windowless energy dispersive x-ray analysis shows that both O and Si are lost and O is lost faster than Si.[11] It is suggested that O is desorbed from the surface layers by a Knotek and Feibelman mechanism, and also displaced internally with the assistance of the same mechanism. As O is removed or displaced, the Si—O—Si bonds of amorphous SiO_2 are replaced by Si—Si bonds. Thus SiO_2 can be reduced to Si under electron irradiation.

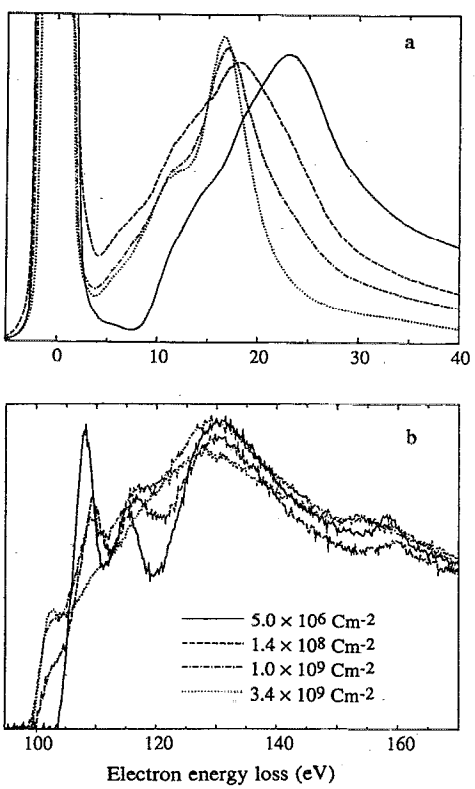

FIG. 1. Energy loss spectra acquired using a slightly defocused probe during irradiation: (a) low loss and (b) Si L edge after background subtraction.

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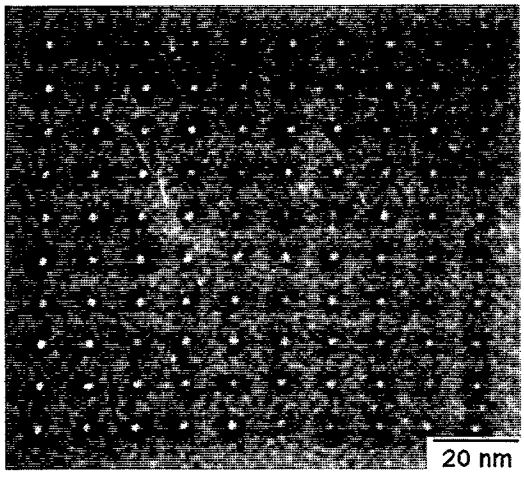

FIG. 2. Si dots produced on a 15-nm-thick SiO_2 film by irradiation with a focused electron beam for 4 s (giving a dose of 5×10^9 C m^{-2}) per spot, and imaged in the scanning transmission microscope using Si plasmon loss electrons.

As an application of this effect we have considered the fabrication of nanometer-diameter columns and wires of Si. It has recently been discovered that porous Si can emit visible light.[12] This is an important discovery since it demonstrates that Si has the potential to be an optoelectronics material. The mechanism of light emission from porous Si is still not understood, but it appears that it may be due to quantum size effects,[12–14] and electron microscopy of light-emitting porous Si reveals that it contains irregular columns of crystalline Si typically 3 nm in diameter.[14] The direct reduction of SiO_2 to Si using electron irradiation reported in this letter may enable the emission of light from nanometer-dimensioned Si to be studied in a controlled manner. The smallest Si features produced using conventional electron beam lithography are 5–7 nm.[15] This size is probably still too large for light emission. As described below, our technique enables Si columns and wires to be produced with diameters as small as 2 nm, thus we may be able to investigate, in a controlled manner, light emission from Si.

Figure 2 shows an array of irradiated areas in 15-nm-thick SiO_2 formed using a 4 s electron beam dwell time, equivalent to a dose of 5×10^9 C m^{-2}, per irradiated spot. The full width at half maximum (FWHM) of the electron beam was 2 nm. Figure 2 is an energy-filtered electron micrograph using electrons which have lost energies in the range 16–17 eV, corresponding to the Si plasmon loss. Bright dots, 2 nm in diameter, appear in the center of each irradiated area. We identify these bright dots as Si since they are present in this Si plasmon energy-filtered image, and are also present in bright-field and annular dark-field images, but are absent from a SiO_2 plasmon energy-filtered image (taken using electrons which have lost energies from 22 to 24 eV). Surrounding each bright 2 nm Si dot in Fig. 2 is a darker annular region which we identify as a thin region of SiO_{2-x}. Eventually after irradiation for 16 s the thinned SiO_{2-x} region is totally cut through. Some Si dots

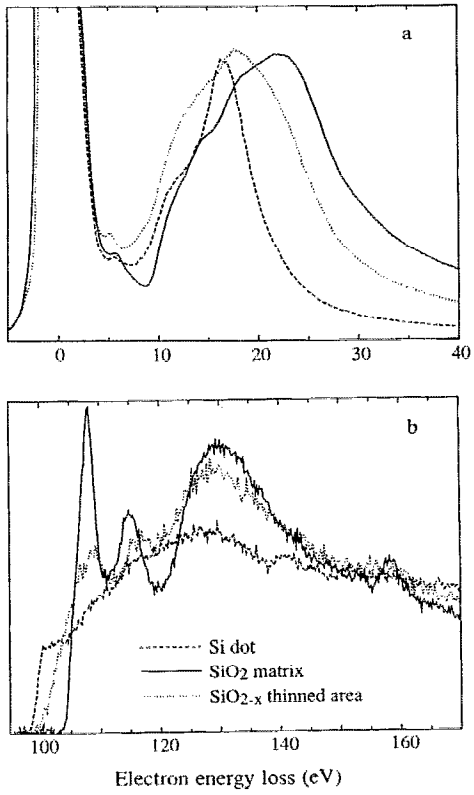

FIG. 3. Low loss (a) and Si L edge (b) spectra from a Si dot, the SiO_2 matrix, and the SiO_{2-x} thinned region surrounding a Si dot, demonstrating the composition of these regions.

are then lost, while others are left attached to the sides of the holes.

Figures 3(a) and 3(b) show energy loss spectra from a Si dot, the SiO_2 matrix, and the SiO_{2-x} thinned region surrounding a Si dot, demonstrating the composition of these regions. It is clear from these spectra that the bright dots in Fig. 2 are indeed images of 2-nm-diam columns of Si, and that the matrix in Fig. 2 is SiO_2 (the matrix appears fairly bright in this Si plasmon energy-filtered image because the broad SiO_2 plasmon peak overlaps the narrower Si plasmon peak). The dark annular region surrounding each bright Si dot in Fig. 2 is produced by the less intense tails of the electron beam, and it has spectra intermediate between Si and SiO_2 (see Fig. 3). We therefore identify this annular region as SiO_{2-x}.

Diffraction patterns from these 2-nm-diam Si columns do not show sharp rings or spots, but consist of diffuse rings characteristic of amorphous Si. We therefore believe that the array in Fig. 2 is composed of amorphous Si nanocolumns.

If a 2-nm-diam (FWHM) electron beam is rastered many times along a line in the SiO_2 specimen, then Si wires can be produced. Figure 4(a) shows that the beam initially creates a damaged area with a width of 30 nm. Presumably the width of this damaged area is mainly due to the tails of the electron beam (the beam shape is non-Gaussian: it has a narrow central peak of 2 nm FWHM, and long extended tails). After rastering for 10 min an 8-nm-wide Si wire is

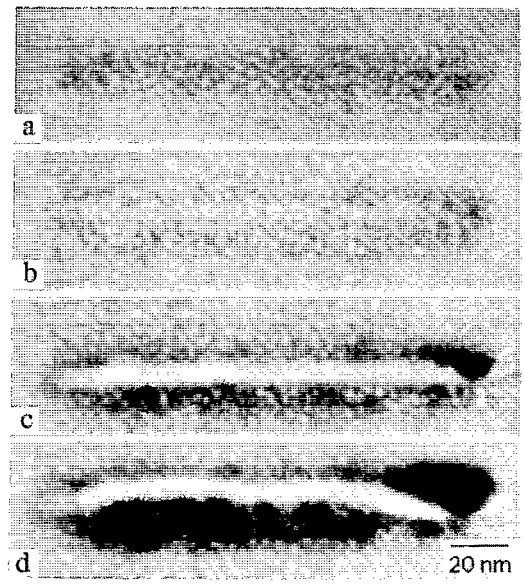

FIG. 4. Si wires fabricated by scanning the electron beam across a 15-nm-thick SiO_2 film and imaged during fabrication, using Si plasmon loss electrons after scanning for period of (a) 1 min, (b) 3 min, (c) 10 min, and (d) 12 min.

formed surrounded by SiO_{2-x}. The width of the wire is mainly due to specimen drift. After prolonged rastering (12 min) the thinned SiO_{2-x} has been completely cut through on one side of the wire, and the wire has been pulled toward the side still attached [Fig. 4(d)]. Diffraction analysis shows that these wires are amorphous. Figure 5 shows an array of several Si wires, each wire being 4–5-nm wide.

In conclusion, we have shown that 15-nm-thick amorphous SiO_2 can be reduced to amorphous Si by electron irradiation. This effect can be used to form nanometer-diameter columns and wires of amorphous Si. We plan to

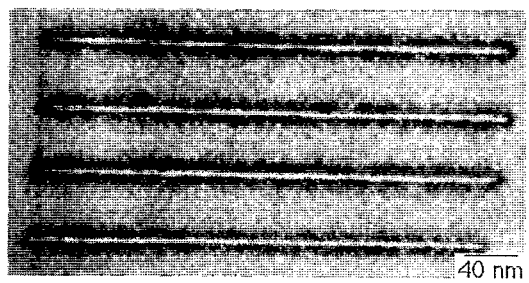

FIG. 5. An array of Si wires, each wire 4–5-nm wide. Each wire was produced by rastering the electron beam for 10 min.

crystallize these structures by annealing them, and to study their electrical and optical properties.

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