

Oxidation of Si nanostructures

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The structural information provided by x-ray diffraction is optimized when x-rays scatter from periodic structures—historically the first periodicities in materials to be probed with x-rays were those at the length scale of atomic distances. A vast number of materials, both naturally occurring and synthesized, have been studied in this fashion, but in practically every case the periodicities have been determined by the nature of the chemical interactions at the microscopic level. With the increasing sophistication of lithography for microelectronic circuits, the periodicities of materials can now be determined by the choice of the engineer, within the limits of the available lithographic tools.

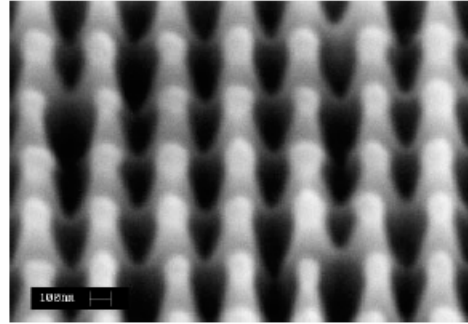
Currently production-line microelectronic circuit elements can be fabricated with periodicities as small as 0.70 μm ; specialized technologies can produce even smaller periodic structures. In order for x-rays to interfere coherently with structures of this size, the coherence width of the radiation must be large

enough to span several repeat distances of the structures. The coherence width of the x-rays at CHES is $\sim 6 \mu\text{m}$ and hence sufficient to detect the periodicities achievable with microfabrication, providing structural information about structures that previously was accessible only to electron microscopy.

Man-made structures with nanometer dimensions (nanostructures) are often fabricated in a periodic fashion because periodicities produce novel electronic or mechanical properties. One exciting application of nanostructures is to produce extremely small, sharp tips that are used as electron emitters for optical display purposes, reproducing on a nanometer scale the electron guns of a standard cathode ray tube. The tips would be produced in large, uniform arrays and the current from each tip could be independently controlled. Extremely fast, high-resolution displays could

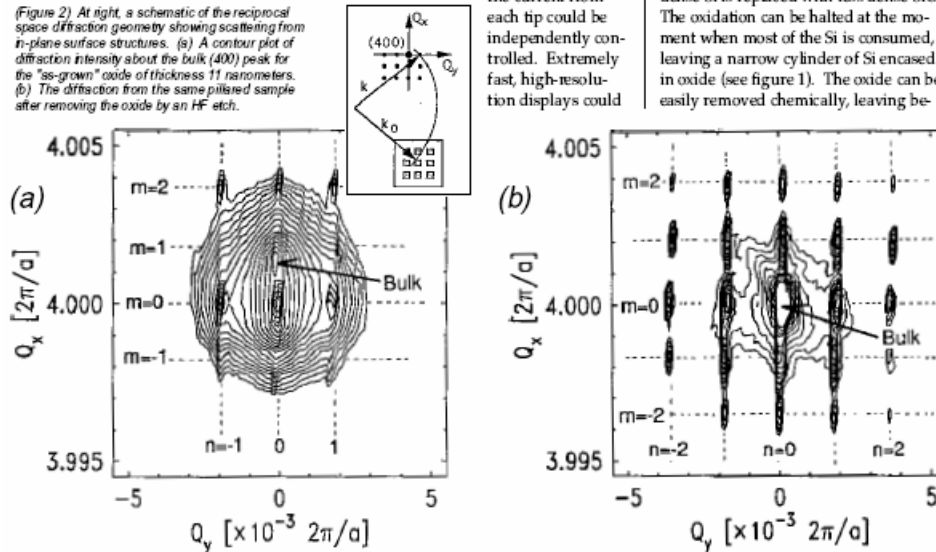
be produced in this fashion.

Synchrotron radiation can be used to probe the regularity of such arrays and also to monitor the processing steps that are used to produce them. As part of an ongoing collaboration between CHES staff scientist Qun Shen and Professor J.M. Blakely's group in Materials Science and Engineering, we have studied the effect of oxidation on periodic arrays of nanometer scale pillars of Si [1-3]. The oxidation of silicon is one step in the process of producing electron emitter tips. When a silicon pillar is oxidized at a high temperature, the oxide-silicon interface moves toward the center of the pillar, as dense Si is replaced with less dense SiO_2 . The oxidation can be halted at the moment when most of the Si is consumed, leaving a narrow cylinder of Si encased in oxide (see figure 1). The oxide can be easily removed chemically, leaving be-



(Figure 1) SEM image of the pillared Silicon surface.

(Figure 2) At right, a schematic of the reciprocal space diffraction geometry showing scattering from *n*-plane surface structures. (a) A contour plot of diffraction intensity about the bulk (400) peak for the "as-grown" oxide of thickness 11 nanometers. (b) The diffraction from the same pillared sample after removing the oxide by an HF etch.



hind the silicon. When properly executed, extremely sharp Si tips can be produced in this manner [4].

The oxide is expanded in volume relative to the Si and exerts a compressive stress on the Si pillar. However this compressive stress of the oxide is reduced by the tension in the Si that arises because Si contracts more than SiO_2 when cooled down from the oxidation temperature. The state of strain of the pillars before and after the oxide is removed is of interest because it may influence the mechanical and electrical properties of the Si.

For the oxidation experiment, arrays of pillars along the [100] direction with heights of 500 nm and wavelengths of 300 nm were used (Figure 1). These pillars were fabricated from Si wafers at the National Nanofabrication Facility at Cornell using electron beam lithography and reactive ion etching. The pillars are approximately cylindrical in shape, with a width at half-maximum of 140 nm. A SiO_2 layer 11 nm thick was grown in dry O_2 at 850°C, followed by 10 min post-annealing in N_2 .

Figure 2a shows the reciprocal space map near the in-plane (400) reflection from the oxidized pillars. The presence of the regular array of pillars causes superlattice peaks near the Si Bragg peak. The separation of these peaks allows an exact determination of the pillar periodicities. The superlattice reflections are marked as (m,n) and the (m=n=0) peak near $(Q_x, Q_y) = (4,0)$ is surrounded by the higher order superlattice peaks. The zero order superlattice reflection is shifted in the negative Q_x direction relative to the bulk Bragg reflection. Such a

shift indicates that the pillars are strained relative to the bulk. From the peak separation between the bulk reflection and the grating reflection at (m=n=0), a tensile strain of $\Delta a_x/a = 1.5 \times 10^{-4}$ is obtained.

Figure 2b shows the reciprocal space map after removing the SiO_2 with 3% HF. In contrast with Fig. 2a, this intensity contour shows no extra structure in either the Q_x or Q_y direction. This indicates that the strain in the pillars formed by the oxidation is relaxed elastically. The scattering intensity along the surface normal direction (Q_z) was also collected around the (0 0 4) Bragg reflection. A tensile strain of $\Delta a_z/a = 2.0 \times 10^{-4}$ was obtained; its elastic relaxation by removing the oxide was also observed.

Since the x-ray measurement was performed at room temperature, the total strain in the pillars is the sum of at least two contributions: the thermal expansion difference of Si and SiO_2 and the intrinsic stress exerted by the SiO_2 layer. These experiments show that the contribution from the thermal expansion component is larger than that from the compression of the oxide coating because the pillars are observed to be in tension. A simple model of the oxidation of a flat Si plate predicts that the thermal expansion difference produces a tensile strain of 8×10^{-4} in a 75 nm-thick flat Si plate with an 11 nm-thick SiO_2 layer [5]. This plate thickness is approximately half of our pillar width. Our measured strain is smaller than predicted value, but is of the same order of magnitude; the difference may be due to the compressive stress from the oxide. Further experiments and simulations are underway to understand the magnitude of the observed strain.

The time required to produce the mesh scans in reciprocal space such as those shown in Fig. 2 is approximately three hours. It would be desirable to monitor changes due to processing on a time scale on the order of seconds. We are looking forward to the increased brightness that will be available at CHSS in the future that will reduce the time for data acquisition significantly. The diffraction from pillar arrays can also be studied in a method analogous to Laue diffraction, where a polychromatic collimated x-ray beam is incident on the sample [2]. The scattered beams can be measured simultaneously by a detector with spatial resolution, such as a CCD detector. With higher brightness and CCD detectors, real-time monitoring of processing on Si nanostructures will be achievable.

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