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Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers

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Indirect evidence is presented that free-standing Si quantum wires can be fabricated without the use of epitaxial deposition or lithography. The novel approach uses electrochemical and chemical dissolution steps to define networks of isolated wires out of bulk wafers. Mesoporous Si layers of high porosity exhibit visible (red) photoluminescence at room temperature, observable with the naked eye under <1 mW unfocused (<0.1 W cm $^{-2}$) green or blue laser line excitation. This is attributed to dramatic two-dimensional quantum size effects which can produce emission far above the band gap of bulk crystalline Si.

Bulk crystalline Si has both a relatively small and indirect energy gap which under normal circumstances prevents efficient interband radiative recombination. At room temperature its near-band-gap luminescence consists of a single weak band at ~ 1.09 eV with a full width at half maximum (FWHM) that varies with excitation conditions but is typically ~ 0.1 eV.¹⁻³

One way to overcome the very low intrinsic radiative recombination probability of Si (Ref. 4) is to introduce specific impurity-activated optical transitions into bulk material. Our work on developing an infrared Si source via this "defect engineering" approach is currently studying isovalent (group IV) dopants. We initially demonstrated that electroluminescence could be attained from a well-known carbon-related complex⁵ and have subsequently developed a technique for incorporating much higher ($>10^{20}$ cm $^{-3}$) levels of the impurity into isovalent solid solutions which is compatible with very-large-scale integrated (VLSI) technology.⁶

Another way is to fabricate Si structures small enough to exploit quantum confinement effects on band structure. The purpose of this letter is to introduce a novel "band-structure engineering" approach that may ultimately lead to the development of a visible Si source.

Despite its discovery as long ago as 1956 by Uhler,⁷ the morphology and structures achievable with partial electrochemical dissolution of Si have only received detailed study over the last decade.⁸⁻¹¹ The anodization of Si wafers at low current densities in HF-based solutions can be used to generate an array of extremely small holes that run orthogonal to the surface. Bulk Si can be made microporous (pore width ≤ 20 Å), mesoporous (pore width 20–500 Å) or macroporous (pore width > 500 Å)¹² depending upon substrate resistivity and anodization conditions.

A demonstration of the shape and size of Si nanostructures left after partial electrochemical dissolution will be made here by highlighting the Euclidean¹⁰ rather than fractal aspects¹¹ of the geometry of porous Si. Figure 1(a) shows an idealized plan view of the anodized (100) face of a layer of relatively low porosity (25%). Both electron microscopy⁸ and gas adsorption data¹³ suggest that mesoporous Si of low porosity can be adequately approximated

by bulk material containing an array of noninteracting cylindrical pores of fixed radius that run perpendicular to the surface. In reality, of course, there is pore branching and variations in pore size, separation, and perhaps even shape. Figures 1(b) and 1(c) show the effect of subsequently increasing the porosity of the layer with an etchant that enlarges each pore by chemical dissolution. For cylindrical pores, porosities greater than 78.5% promote substantial merging of nearest-neighbor pores and consequently the physical isolation of a significant density of Si columns. The width of those columns at a porosity of $\sim 80\%$ is comparable to the average pore radius.

To the author's knowledge there has to date been no detailed high-resolution plan-view analysis of individual

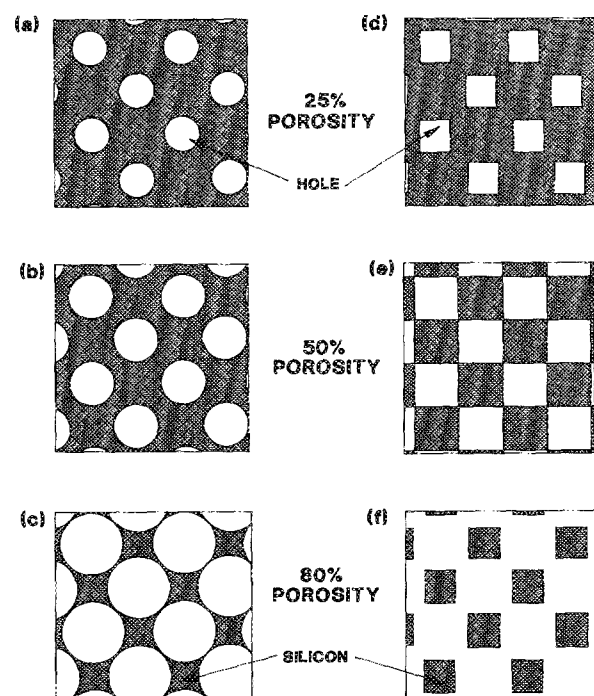


FIG. 1. Idealized plan view of an anodized (100) Si wafer containing (a)–(c) cylindrical holes, (d)–(f) rectangular holes. The indicated changes in porosity are achieved by pore enlargement through chemical dissolution.

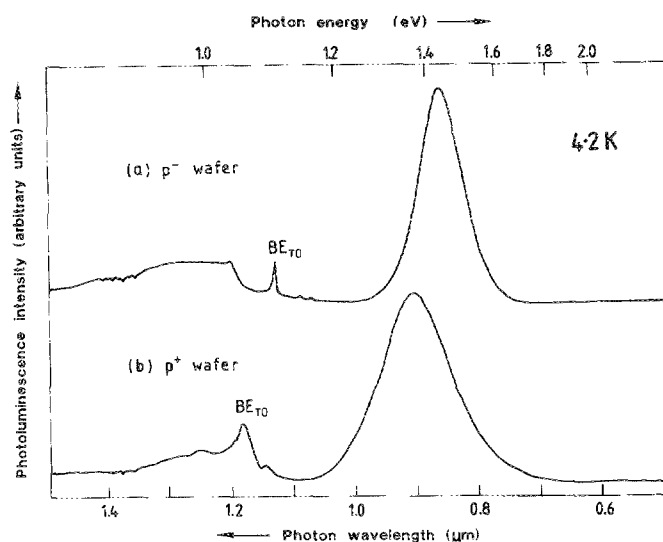


FIG. 2. Low-temperature photoluminescence from freshly anodized Si wafers (a) 10–35 Ω cm p^- wafer anodized at 20 mA cm $^{-2}$ for 5 min in 20% aqueous HF, (b) 0.01–0.04 Ω cm p^+ wafer anodized at 100 mA cm $^{-2}$ for 1 min in 20% aqueous HF. Both wafers have an ~ 5 - μ m-thick layer of $\sim 70\%$ porosity. BE $_{TO}$ indicates the TO phonon-assisted boron luminescence from the underlying bulk substrates. Spectra were taken with ~ 200 mW unfocused 5145 Å excitation incident on the samples in liquid helium.

pore shapes in as-anodized Si by electron microscopy, although there is evidence accumulating for crystallographic effects in mesoporous Si layers.^{14,15} If crystallographic effects do influence micropore and mesopore shapes then for anodized (100) wafers the pores may not be circular as in Figs. 1(a)–1(c) but tend towards the squares of Figs. 1(d)–1(f) [cf. the sirtl etch pits produced by microdefects in the (100) face of dislocation free FZ Si].¹⁶ The lowest porosity at which Si columns becomes physically isolated for a uniform array of rectangular pores is then only $\sim 50\%$ as shown in Fig. 1(e).

In addition, it is unlikely that the etchant would uniformly enlarge the pores as shown in Fig. 1. As-anodized porous Si exhibits an appreciable lattice expansion that increases with increasing porosity.^{17–19} The in-plane strain distribution may lead to preferential dissolution between nearest-neighbor pores, thereby promoting the pore-pore overlap needed to define isolated wires at a still lower average porosity.

To observe dramatic quantum size effects the characteristic widths of the Si skeletons of Fig. 1 need to be significantly less than the dimensions of the free exciton (Bohr radius ~ 50 Å) of bulk Si.²⁰ A suitable etchant is one that will enlarge each pore at an extremely slow but controllable rate and will leave a chemically passivated surface.

Figure 2 shows typical 4.2 K photoluminescence spectra from freshly anodized p^- and p^+ substrates with surface layers of similar thickness and an already high level of porosity. Their front face emission was dispersed with a 3/4 m Spex monochromator and detected with a cooled North Coast Ge photodiode. A 30° optical geometry was employed to minimize self-absorption by the underlying

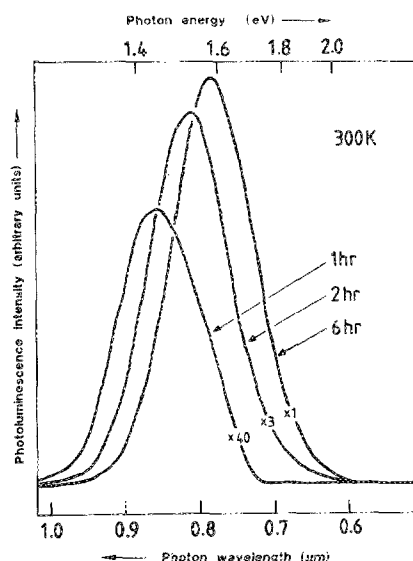


FIG. 3. Room-temperature photoluminescence from the anodized p^- wafer of Fig. 2 after immersion in 40% aqueous HF for the times indicated. Spectra were taken with 200 mW unfocused 5145 Å excitation incident on the sample in air and amplified by the relative gains indicated.

bulk substrate. Spectra have not been corrected for apparatus response. Barrett–Joyner–Halenda (BJH) analysis of their nitrogen desorption isotherms¹² indicate that the p^+ substrate's porous layer has a distribution of pore widths varying from 30 to 60 Å with a peak at 50 Å; the p^- substrate's layer has all pores < 40 Å in width.²¹ Both layers exhibit a luminescence band above the band-gap energy of bulk crystalline Si. Note that its FWHM is significantly narrower, and it lies to higher energy, for the layer with smaller pores.

Figure 3 shows the effect on the room-temperature photoluminescence from the p^- substrate's porous layer of extended chemical dissolution in concentrated (40%) aqueous HF. As the porosity of the layer gradually increases from 70 to 80% its color changes from dark golden brown through gold to yellow. This change can be effected by ~ 6 h quiescent immersion in the dark in concentrated (40%) HF. The photoluminescence band becomes significantly more intense as it shifts into the visible from the near infrared. After 6 h immersion the resultant yellow layer glows bright red at room temperature under < 1 mW excitation with the 488 or 514.5 nm Ar laser lines.

Many workers^{8,10} have interpreted data on as-anodized Si in terms of a "crystallinity" that deteriorates with increasing porosity and is superior in mesoporous p^+ substrates to microporous p^- substrates. However, in the author's opinion and that of other workers,¹³ there is as yet no definitive evidence for an amorphous phase in freshly anodized Si. The above band-gap luminescence is attributed, not to an alloying effect in an amorphous phase as has been previously suggested,²² but to a quantum size effect for the following reasons.

First, above band-gap luminescence is observed from all types of freshly anodized Si substrate (p^- , p^+ , n^+ , n^-)

produced in aqueous or ethanoic HF, provided the porosity is high enough.²¹ It is not observed from a macroporous layer in an n^- substrate which has Si skeleton dimensions too large to expect quantum size effects.²¹ It is also not observed from a highly porous layer made completely amorphous by ion implantation prior to anodization.²¹

Second, as Fig. 3 demonstrates, the luminescence gets appreciably stronger during simple chemical dissolution in aqueous HF. Concentrated (48%) HF has been reported to attack bulk Si at an extremely slow but measurable rate. Hu and Kerr²³ reported an etch rate of $18 \text{ \AA h}^{-1}$ for the $\langle 111 \rangle$ face of n -type Si. Its rate of attack on amorphous Si is significantly higher viz. $\approx 100 \text{ \AA h}^{-1}$ for unannealed films, $\sim 40 \text{ \AA h}^{-1}$ for partially annealed films.²⁴ There is currently much interest in the remarkable surface passivation achieved by HF treating Si surfaces which exhibit the lowest surface recombination velocities ever measured.²⁵ Multiple internal reflection spectra have established that HF-treated surfaces, whilst microscopically rough are nevertheless well ordered.²⁶ The internal surface of porous Si has a similar hydride termination^{27,28} and the HF-leached Si skeleton is expected to have a chemically passivated surface with no amorphous hydride lining.

Third, the half width of the luminescence band can be appreciably narrower than the 0.3 eV wide band of device quality a -Si:H at 1.3 eV²⁹ and much narrower than the bands from polysilane alloys (FWHM 0.6–0.7 eV) that also emit in the visible region.³⁰

Finally, Furukawa and Mijasato³¹ have recently reported the fabrication of Si "quantum dots" by a hydrogen plasma sputtering technique. Their crystallites (av. diameter 20–50 Å) also have hydrogen-passivated surfaces and have the appearance of a pale yellow powder. They have not published any photoluminescence spectra to date but have shown a photograph of bright red emission at room temperature.

In conclusion, we have demonstrated that Si wafers subjected to combined electrochemical and chemical dissolution can emit visible photoluminescence at room temperature. This has been interpreted as arising from free-standing Si quantum wires wherein two-dimensional quantum confinement of carriers has appreciably widened the Si band gap.

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