

## Invited

**Porous Silicon: A Quantum Sponge Structure?**

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The optical properties of porous silicon and the physical origin of these properties have received considerable attention mainly because of the promise of using porous silicon for silicon based IC compatible optoelectronics. The paper will discuss the formation of porous silicon in terms of a quantum sponge structure as well as various models for the origin of visible photoluminescence at room temperature such as quantum confinement, amorphous silicon or siloxene.

**1. BACKGROUND**

The association of quantum confinement effects with the optical properties of porous silicon<sup>1,2)</sup> and especially the observation of strong room temperature photoluminescence in the visible<sup>1)</sup> has generated an avalanche of follow-up papers<sup>3)</sup>. Electroluminescence under anodic oxidation conditions<sup>4,5)</sup> was observed and shortly afterwards electroluminescence involving solid state contacts was reported in several papers<sup>6-8)</sup> although the efficiency as well as the stability are still far from being satisfactory. For the basic physics community, the possibility that the observed visible photoluminescence might be due to an as yet not understood change-over from an indirect bandgap holding for crystalline bulk silicon to a direct bandgap material in the case of porous silicon induced by quantum confinement effects is a major challenge. For technology, the promise of silicon-based light-emitting diodes for optical on-chip communications or integrated displays has been the reason for the resulting excitement.

Since "optical active" silicon has sometimes been considered as the "holy grail" of silicon research, which has rather unsuccessfully been attempted to be reached by various approaches such as zone folding of strained Si/Ge superlattices or by the incorporation of erbium, the news on the luminescent silicon spilled also over into trade and popular science journals as well as to newspapers. In the meantime, luminescent porous silicon has become an extremely controversial topic, in which it is hotly debated whether the observed luminescence is associated at all with quantum confinement effects. Alternatively, it has been suggested that highly contaminated amorphous silicon<sup>9)</sup> or a molecular Si-H-O compound such as siloxene<sup>10,11)</sup> is actually responsible for the strong

room temperature photoluminescence. The possibility that the whole effect may just be due to unintentionally introduced impurities has even lead to the remark that luminescent silicon appears to be "the cold fusion of semiconductor physics"<sup>12)</sup>.

After some remarks on the history of porous silicon the present paper will try to distinguish between the formation mechanism of porous silicon (which has lead the present authors to suggest a quantum sponge structure) and the controversial physical origin of room temperature photoluminescence of porous silicon. Since the field is moving so rapidly, it can be expected that at the time of the conference the understanding of porous silicon will have moved beyond what is described in this abstract.

**2. HISTORY OF POROUS SILICON**

Porous silicon forms on crystalline silicon substrates in hydrofluoric acid (HF) under anodic bias as first observed by Uhlir<sup>13)</sup> and later investigated in more detail by Turner<sup>14)</sup>. A sketch of a simple setup to produce porous silicon is shown in Fig. 1. As the name porous silicon indicates, the bulk crystalline silicon changes by this etching process into a kind of sponge structure. The pore width and remaining silicon skeleton width strongly depends on the specific doping and etching conditions. Because of its large surface to volume ratio, the associated fast oxidation rate and the adaptable porosity, porous silicon has technologically mainly be used for a specific silicon-on-insulator technology, the so-called FIPOS technology in which the porous silicon is oxidized to form an insulating silicon dioxide layer. In this context porous silicon was well investigated. The pore diameter has been found to be as small as 2 nm. The porosity of the material ranges typically between 20 and 80%. The inner surface

directly after anodic etching is covered with hydrogen.

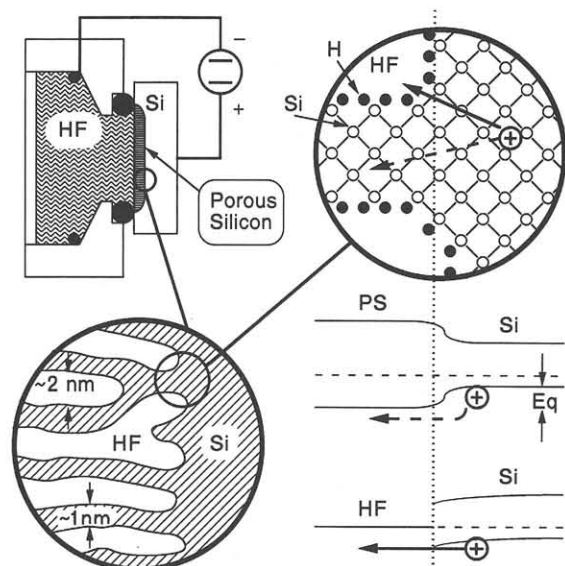


Fig. 1. *Upper left:* Cross-section of the setup used to produce porous silicon. *Lower left:* Enlarged cross section of porous silicon/silicon interface. *Upper right:* Chemical structure of the interface schematically with two possible ways for a hole to cross the interface (arrows). *Lower right:* Corresponding band diagrams indicating the energy barrier due to quantum confinement in the porous silicon columns (dashed arrow).<sup>5)</sup>

Already Uhlir<sup>13)</sup> had noticed that flakes of porous silicon are sometimes red in appearance. In 1984 visible photoluminescence of porous silicon at 4K was reported<sup>15)</sup>. The different optical properties as compared to bulk crystalline silicon were attributed to suboxides, partially amorphized silicon or impurities. In 1990, Canham<sup>1)</sup> found strong visible room temperature photoluminescence in porous silicon which had been etched afterwards chemically in HF. The present authors<sup>2)</sup> observed independently an increase of the absorption edge by about 0.5 eV in porous silicon as compared to bulk crystalline silicon which has a bandgap of 1.1 eV in the infrared range. Both groups attributed the apparent increase in the bandgap of porous silicon to quantum confinement due to remaining thin crystalline silicon columns ("quantum wires"). Initially, Canham had suggested that these remaining columns are free-standing. Our absorption experiments involved pieces of silicon which had been completely transformed to porous silicon but nevertheless behaved as a solid (although showing effects of high internal stresses). Therefore, it has been concluded that porous silicon consists of an interconnected silicon skeleton and should be rather described in terms of a "quantum sponge"<sup>5)</sup> provided the quantum confinement concept is applicable at all.

### 3. POROUS SILICON FORMATION

Various models have been suggested to explain porous silicon formation. For excellent recent reviews see Föll<sup>16)</sup> and Smith and Collins<sup>17)</sup>. It is generally agreed upon that the etching reaction requires electronic holes which have to be supplied by the silicon. In the case of moderately n-doped silicon anodically etched in HF (in the dark) the wall thickness between the pores is governed by the depletion width which is generally too large for noticeable quantum confinement effects, which typically require characteristic lengths below about 3 nm. In the case of p<sup>+</sup> and n<sup>+</sup> material the depletion width is replaced by tunneling distances which allow smaller wall thicknesses between the pores.

The smallest pore sizes and wall thicknesses have been found for anodically etched moderately doped p-type silicon ( $10^{14} - 10^{17} \text{ cm}^{-3}$ ). In this case, neither tunneling nor conventional depletion effects can explain why about 2nm silicon structures remain stable against further anodic etching whereas further vertical etching can proceed over hundreds of micrometers, which corresponds to an etch-ratio of over 100,000. We have suggested that the decreasing thickness of the remaining walls or interconnected columns between the pores leads to an increase of the bandgap due to quantum confinement. This in turn, causes an energy barrier for holes compared to bulk silicon (see Fig. 1) which reduces the availability of holes for the etching reaction. Since the effect increases with decreasing dimensions of the silicon skeleton, this process is self-limiting. Based on these considerations we proceeded to measure the absorption in porous silicon and found an 0.5 eV blue-shift in the absorption edge for moderately doped p-silicon and only a negligible shift for p<sup>+</sup> silicon, as expected. Since within our porous silicon formation mechanism the resulting silicon sponge structure is a self-adjusting process governed by a quantum confinement effect, we have termed the resulting structure a "quantum sponge"<sup>5)</sup>.

We mention specifically that the above porous silicon formation model does not necessarily imply that the quantum sponge structure would show any room temperature photoluminescence. It turns out that the absorption edge and the maximum of the photoluminescence spectrum are located at about the same position. The self-limiting etching process controlled by the increase in the bandgap could naturally explain the very narrow distribution of crystallite sizes required for the fairly narrow half-width of the observed photoluminescence.

The recent suggestion<sup>10,11)</sup> that the observed photoluminescence is associated with the molecular compound  $\text{Si}_6\text{O}_3\text{H}_6$  does in no way help to explain porous silicon formation unless the presence of siloxene is restricted to an almost monomolecular layer on the surface of the quantum sponge which still essentially consists of crystalline silicon. In this sense we maintain our original model that the formation of porous silicon on moderately doped p-type silicon is an effect controlled by quantum confinement.

#### 4. ORIGIN OF PHOTOLUMINESCENCE

The major models trying to explain the physical origin of the photoluminescence are based on i) quantum confinement<sup>1)</sup>, ii) siloxene<sup>10,11)</sup> or iii) contaminated amorphous silicon<sup>9)</sup>.

Although none of these models have been proved or disproved conclusively, the amorphous silicon model is unlikely to hold in view of x-ray<sup>18)</sup> and Raman<sup>19)</sup> data indicating that the overwhelming percentage of freshly prepared porous silicon is crystalline. Because of the high surface area, porous silicon is oxidizing easily even in high humidity air which might trigger amorphization of small crystallites. Lattice imaging by transmission electron microscopy<sup>20,21)</sup> shows the presence of crystallites in the correct size range but does not allow to estimate the volume percentage of these crystallites because of strong distortions which do not allow to get proper imaging conditions for a large fraction of the crystallites at the same time.

Quantum confinement models claim that the quantum size of the remaining crystalline silicon in porous silicon is closely connected with the observed photoluminescence. Beyond that general statement, many different specific mechanisms have been discussed such as a change-over from an indirect to a direct bandgap material or excitonic effects becoming important at these sizes<sup>22)</sup>. Another possibility is that electron-hole pairs generated in these quantum confined silicon crystallites are fed into surface states (which could somehow resemble siloxene in the case of hydrogen or oxide covered silicon). An interesting suggestion<sup>23)</sup> is to consider the inadvertent atomistic surface roughness as being responsible for momentum conservation similar as in the well established case of optical emission from metal-insulator-metal tunnel junctions.

Within the siloxene model the luminescence of porous silicon is due to the presence of the molecular compound siloxene ( $\text{Si}_6\text{O}_3\text{H}_6$ ) or modifications of it.<sup>10,11)</sup> These compounds can show photoluminescence and vibrational spectra which are strikingly similar to those of porous silicon.

Although the siloxene interpretation of porous silicon is appealing, the present authors consider the model as not satisfactory, especially in view of recent rapid thermal oxidation experiments which show that the photoluminescence which disappears at about 500°C comes back at higher temperature treatments when the surface is again passivated by a high quality thermal oxide<sup>24)</sup>. A detailed discussion of this and other experiments which are difficult to be explained within the siloxene model will be presented at the conference.

#### 5. CONCLUSIONS

The present authors consider the quantum sponge concept as the best one available for explaining the formation of porous silicon on moderately doped p-type silicon. Quantum confinement is probably also closely associated with the observed visible photoluminescence at room temperature although surface states

resembling those of compounds related to siloxene may play a role in the radiative recombination process. Epitaxial films of siloxene should be investigated in their own right for possible applications in a silicon-based optoelectronics independent of porous silicon.

The stability, which presently constitutes a serious problem for both porous silicon and siloxene, the quantum efficiency of light-emitting diodes and the IC process compatibility will finally decide on a possible use of either one of these materials (or some other new materials arrangement or combination) in a silicon-based optoelectronics. There is still a long way to go.

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