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**LETTER TO THE EDITOR**

# Silicon quantum dot superlattice and metallic conducting behaviour in porous silicon

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**Abstract.** A metallic conducting effect has been observed in a blue emitting porous silicon sample. In the sample, which was prepared using a hydrothermal etching process followed by oxidation treatment at 950 °C for 30 s, it was observed that the resistance decreased linearly with decreasing temperature and became constant near 10 K. A possible mechanism for the observed effect is discussed in view of the silicon quantum dot superlattice structure observed in the sample.

During the past few years, the preparation and characterization of materials on the nanometre scale have provided not only new physics in reduced dimensions, but also the possibility of fabricating novel materials. The quantum structure of semiconductors is an example of this new class of materials. Their crystallites in reduced dimensions generally undergo important reconstruction relative to bulk crystalline fragments, as evidenced by the existence of 'magic number' effects in their physical properties [1]. For example, a silicon semiconductor normally emits only extremely weak infrared photoluminescence because of its relatively small and indirect band gap; recent studies show that very efficient and multicolour (red, orange, yellow, green and blue) visible light emission can be obtained from highly porous etched silicon [2–4]. This phenomenon was attributed to quantum size effects within crystalline material [5, 6]. Nevertheless, the electric properties of small silicon crystallites have never been reported [7]: especially little attention was given to the transport properties of the silicon quantum dot superlattice partially due to the difficulty of sample preparation. In this letter, we report for the first time results on the preparation of porous silicon with silicon quantum dots embedded in an orderly fashion in amorphous silicon oxide columns and on metallic conductivity in this material.

The sample was prepared by hydrothermal etching of a p-type (100) silicon single crystal in a mixture solution of 0.2 mol $l^{-1}$ HF and 4.0 mol $l^{-1}$ $HNO_3$ at 140 °C for 2 h followed by thermal treatment at 950 °C for 30 s.

The surface morphology of the sample, as examined using scanning tunnel microscope (STM) observation [8, 9], was found to be similar to that of electrochemically etched porous silicon which is characterized by an array of free-standing, crystalline silicon columns (about

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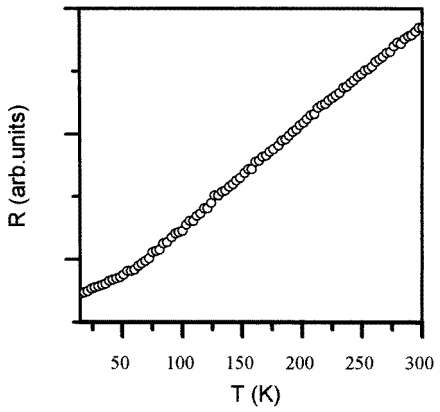


**Figure 1.** Resistance–temperature curve of the as-prepared sample.

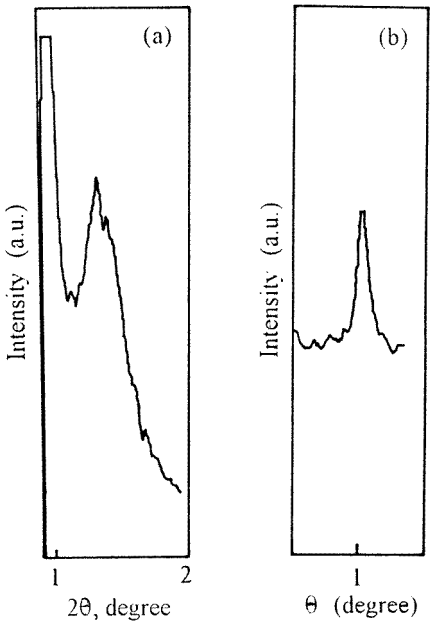


**Figure 2.** Small-angle x-ray scattering (SAXS) pattern of sample hydrothermally etched at 140 °C for 2 h followed by thermal treatment of 950 °C for 30 s (a). (b) is the x-ray rocking curve with a fixed Bragg angle corresponding to the SAXS peak at $2\theta = 1.32^\circ$ in (a).

2–50 nm in diameter) with undulating width [5, 8, 9]. The sample emits blue light peaking at about 430 nm.

The temperature dependence of the electrical resistance was measured by a standard four-probe technique, with a resolution of the voltage measurement of $1 \times 10^{-8}$ V. The resistance, illustrated in figure 1, decreases linearly with temperature from 300 K to 35 K and then remains constant at a temperature as low as about 10 K, displaying a metallic conducting behaviour.

As shown in figure 2, small-angle x-ray scattering (SAXS) studies show that there exists a one-dimensional superlattice with a length of about 7.0 nm in the sample. The rocking curve of the peak at a fixed $2\theta$ value of $1.31^\circ$ is shown in figure 2(b). The full width at half-

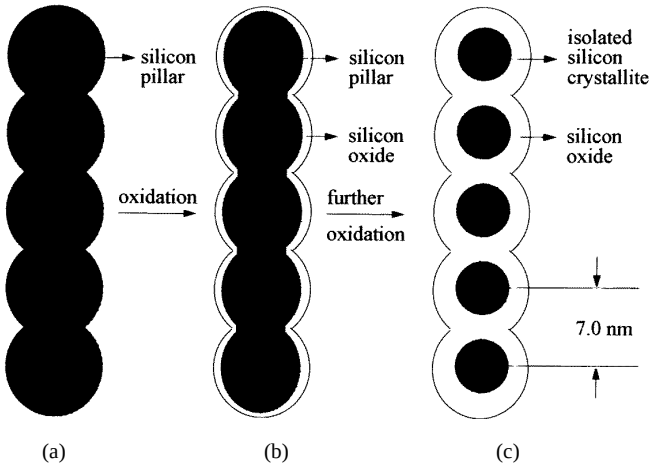


**Figure 3.** Model for the formation process of the silicon quantum dot superlattice. The undulating width of the initial formed silicon pillar and appropriate oxidation are two important factors determining the formation of the structures.

maximum (FWHM) is less than $0.1^\circ$ indicating some degree of structure perfection. It is now quite widely accepted that the microstructure of highly porous silicon can be characterized by an array of tiny columns in which the crystalline order is preserved [10], and there exist undulations in width for silicon columns. From these results the possible formation mechanism for the superlattice, shown in figure 3, was proposed. Figure 3(a) shows the initial silicon column formed by hydrothermal etching; subsequent oxidation treatment leads to the formation of silicon oxide on its surface (figure 3(b)) and reduction of silicon crystal size. Appropriate oxidation treatment would cause the formation of isolated silicon nanocrystallites dispersed in an orderly fashion in the silicon oxide column (figure 3(c)) due to the orderly undulations in width of the initial Si columns. The distance between two nearest neighbours may be the one-dimensional superlattice observed in the SAXS pattern. The local high-resolution transmission electron microscopy (HREM) image of a column observed in STM is shown in figure 4: it reveals isolated individual silicon nanocrystallites of several nanometres embedded in an amorphous matrix. Amorphous silicon oxide was detected by thin-film x-ray diffraction studies which were carried out by fixing the $\theta$ angle at $3^\circ$ with $2\theta$ scanning. Combined with the HREM results, it is reasonable to assume that the matrix covering the silicon nanocrystallites is amorphous silicon oxide.

SAXS measurements have been reported for PS several times [11–14]. However, no superlattice result was reported. Part of the reason is that the authors of these works gave emphasis to the microstructure and silicon size distribution; the main reason is that the superlattice formation needs harsh conditions as discussed above. Actually, in our case, this structure is not always obtained.

Silicon is a semiconductor with a relatively small and indirect band gap of about 1 eV [15]. It has recently been suggested that certain types of porous silicon can show two- or three-dimensional carrier confinement and result in an enlargement of the energy gap, which is suggested to be responsible for the visible emission observed [5, 6]. It is not clearly understood why the as-prepared sample displays metallic conductivity. A possible mechanism is due to the formation of a silicon quantum dot superlattice. The superlattice potential may result in a series of narrow subbands permitted in the basic conduction band,

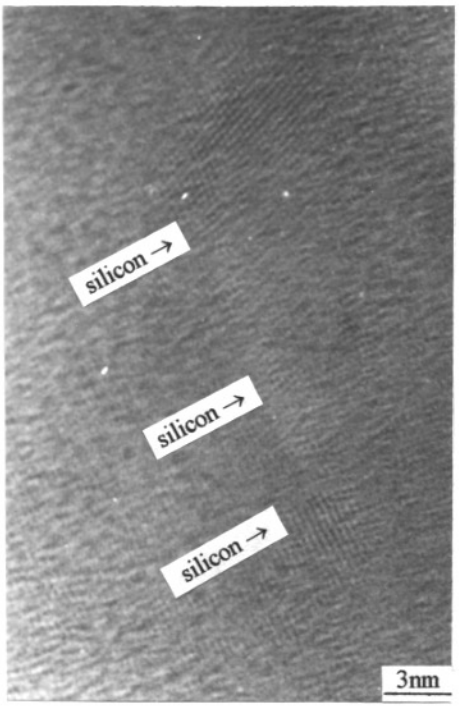


**Figure 4.** Local HREM image of a column observed in an STM micrograph of the as-prepared sample showing localized silicon nanocrystallites.

and then affect the chromatic dispersion relationship of the transport electrons. These electrons can tunnel through the potential energy gap without energy loss. Future work should strive to establish the mechanism of metallic conductivity in PS firmly.

In conclusion, a silicon quantum dot superlattice was observed in blue emitting porous silicon prepared hydrothermally: this structure was suggested to be responsible for the metallic conductivity observed. Such a phenomenon would open up a new field in basic study and optoelectronic device applications of silicon semiconductor materials if the observed effects of material processing are optimized.

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