Ciencia y Tecnología **21** No.1-2(1997) 45-52

# Nanostructure Size Determination in N+-Type Porous Silicon by X-Ray Diffractormetry and Raman Spectroscopy

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**Abstract:** A series of porous silicon surfaces were obstained after different exposition times of electrochemical etching on crystalline n+-type silicon in presence of hydrofluoric acid. These kind of surfaces show photoluminescence when illuminated by UV light. One possible explanation for this is that the treated surface is made up of small crystallites in the nanometer scale that split away the semiconductor band edges up to optical photon energies for the band-to-band recombination processes. In this study, a nanometer size determination of such proposed structures was performed by the use of X-Ray Diffractometry and Raman Spectroscopy. The results suggest a consistency between the so called Quantum Confined Model and the experimental results.

**Subject headings**: Nanoestructure, x-ray diffractormetry, Raman Spectroscopy, porous silicon

**Resumen:** Una serie de superficies prososas se obtuvieron después de varios tiempos de exposisión a un cocinado electroquímico sobre silicio del tipo n+ en presencia de ácido fluorhídrico. Este tipo de superficies al tratadas muestran fotoluminicencia al ser ilumindadas con luz ultravioleta(U.V). Una posible explicación para esto es que la superficie tratada esta formada por pequeños cristales en la escala nanométricas que divide los bordes de la banda semiconductora hasta las energías ópticas del fotón para los procesos de recombinación banda-banda. En este estudio se efectuó una determinación nanométrica de tales estructuras propuestas utilizando difractometría de rayos X y espectroscopía Raman. Los resultados sugieren una consistencia del denominado Modelo Cuántico Confinado y los resultados experimentales.

**Descriptores**: Estructuras nanométricas, difracción de rayos x, espectroscopía de Raman, silicio prososo

## 1. Introduction

The importance of crystalline silicon in our present world cannot be overestimated. Silicon is the building block of modern microelectronics because of its advantages, such as low power consumption, cheapness, etc. However, it is a bad candidate for optoelectronic devices since it is an indirect gap semiconductor(1). This means that if a radiative recombination between an electron in the conduction band and a hole in the valence band takes place, a phonon must participate in order to conserve momentum and energy. A three particle process is a very unusual event, so the radiative spectrum of crystalline silicon is very weak. The quantum efficiency, defined as the ratio of the radiative lifetime over the total lifetime, falls in the order of $10-5\%$ at room temperature(2). There are many attempts to improve this efficiency, creating silicon-based alloys, as Si-Ge for example 3, or implanting isoelectronic impurities(4), among others. The resulting luminescence is good for low temperatures, but unfortunately drops to low values at room temperatures. This is why the discovery of strong luminescence on porous silicon at room temperature when illuminated with UV light(5) received great attention. Porous silicon is known(6) since 1956 as a surface film formed during anodic attack of crystalline silicon. Now, research is focused on distinct aspects of the process, but the mainstream deals with the luminescence mechanism. Many possible scenarios have been proposed(7), the most outstanding being: the quantum confinement within silicon crystallites(8) or wires(7,9), recombination through surface states on the crystallites(10), siloxene compounds(11), amorphous silicon(12) and SiHx complexes(13). From all these explanations, only the first two seem to be plausible(14) because they stand after the very large number of experiments that have been performed to test the hypothesis. Moreover, there is a tendency to synthetize both models in a new one. In this paper, we applied a couple of conventional spectroscopic methods to probe the porous surfaces and determine the existence of theoretically proposed nanostructures according to the quantum confinement model.

## 2. Experimental procedure

The porous silicon films were prepared from a commercially available wafer of 2 inches in diameter. The wafer was n+-type, (111) crystallographic plane, 0.3 mm thick and 0.6 - 1.4 Ohm.cm resistivity. The front face was polished and the back had an ohmic contact which consisted on a sputtered layer of gold on top of a layer of chromium. Passivation was performed by heating to around 400°C for a few minutes. An ultrasonic cuter (SBT SoniCut 380) was employed to take out circular pieces of 0.5 cm2 from the wafer. An arbitrary selected piece was initially etched in dark by putting on the polished side a drop of an aqueous solution of 20% per volume hydrofluoric acid, electronic grade, for 20 minutes to remove the excess of oxide. The sample was then mounted under screw pressure to the bottom of a Teflon cell between a plastic holder and a Kalrez o-ring. The cell had a hole of 0.13 cm2 which exposed the samples polished side. A wire pressuring on the gold side was employed as a back contact. After assembling, another minute of 20% HF solution was applied on the exposed polished side. The anodization solution was a mixture of electronic grade 48% HF solution, ethanol with 90% purity and distilled water. The $HF : EtOH$ proportions were $25 : 12$ or $25 : 25\%$.

The power was furnished by a constant current generator (HP model 6186c) with its anode applied to the ohmic contact of the sample and the cathode to a piece of inert, high purity platinum of about 2 cm2 immersed in the electrolyte. The current density was set to 100 mA/cm2. A tungsten lamp was set at 30 cm above the sample to provide a constant illumination of 100 mW/cm2 during the anodization process. The current was applied for periods of time from 1 to 12 minutes.

After the anodization process, the sample was washed a few times with ethanol, rinsed with abundant distilled water and dried with a flow of pressured nitrogen without dismounting from the cell. Luminescence spectra could be recorded with the aid of a He-Cd 442 nm line, 10 mW laser. The beam was guided through fiber optics to the porous surface and the light emission was collected with fiber optics also and sent to a computer resident CCD-based spectrophotometer.

Two characterization methods were employed. Firstly, X-Rays K( 1.54 o$A$ Cu-radiation was used for diffractiometry using a SIEMENS D5000 Powder diffractometer. Focusing slits and a Ni filter to eliminate ( radiation were employed. The detector was a scintillation crystal counter coupled to a photomultiplier tube. The resolution in the double angle was 0.002 degrees. The sample was kept at room temperature.

Secondly, Raman spectroscopy was performed with the use of a Coherent Innova 99 $Ar+$ laser, 2 mW power provided a 514.5 nm excitation wavelength. The sample was kept also at room temperature. The beam diameter on the sample was less than 2 microns obtained by the use of a 80X eyepiece in the microprobe. Jobin-Yvon T64000 Spectrophotometer with substractive pre-monochromators coupled to a third spectrograph/monochromator grating was employed for spectra recording using a $\sim$ 180° backscattering geometry. The system used a liquid nitrogen cooled CCD detector.

## 3. Results and Discussion

Figure 1 shows the luminescence spectra obtained from the samples after different anodization times. We can notice a raise in the maximum peak which is higher for an anodization time of 4 minutes. The corresponding wavelength associated with this peak is near 700 nm. The behavior of this sample resembles those previously studied and reported in the literature(15,16). Figure 2 shows the X-Ray spectra of a non-anodized sample (reference) and a sample with 12 minutes of anodization, restricted to the range where there was a good signal. In (a) we show the typical crystalline silicon peak, centered around 28.6 degrees, whereas in (b) we found a broader peak made up of two other peaks slightly shifted upwards and downwards with respect to the crystalline peak. All the peaks were fitted using a spectroscopic Pearson distribution curve whose expression is:

$$y = \frac{a_0}{\left[1 + 4\left(\frac{x-a_1}{a_2}\right)^2\left(2^{\frac{1}{a_3}} - 1\right)\right]^{a_3}}$$

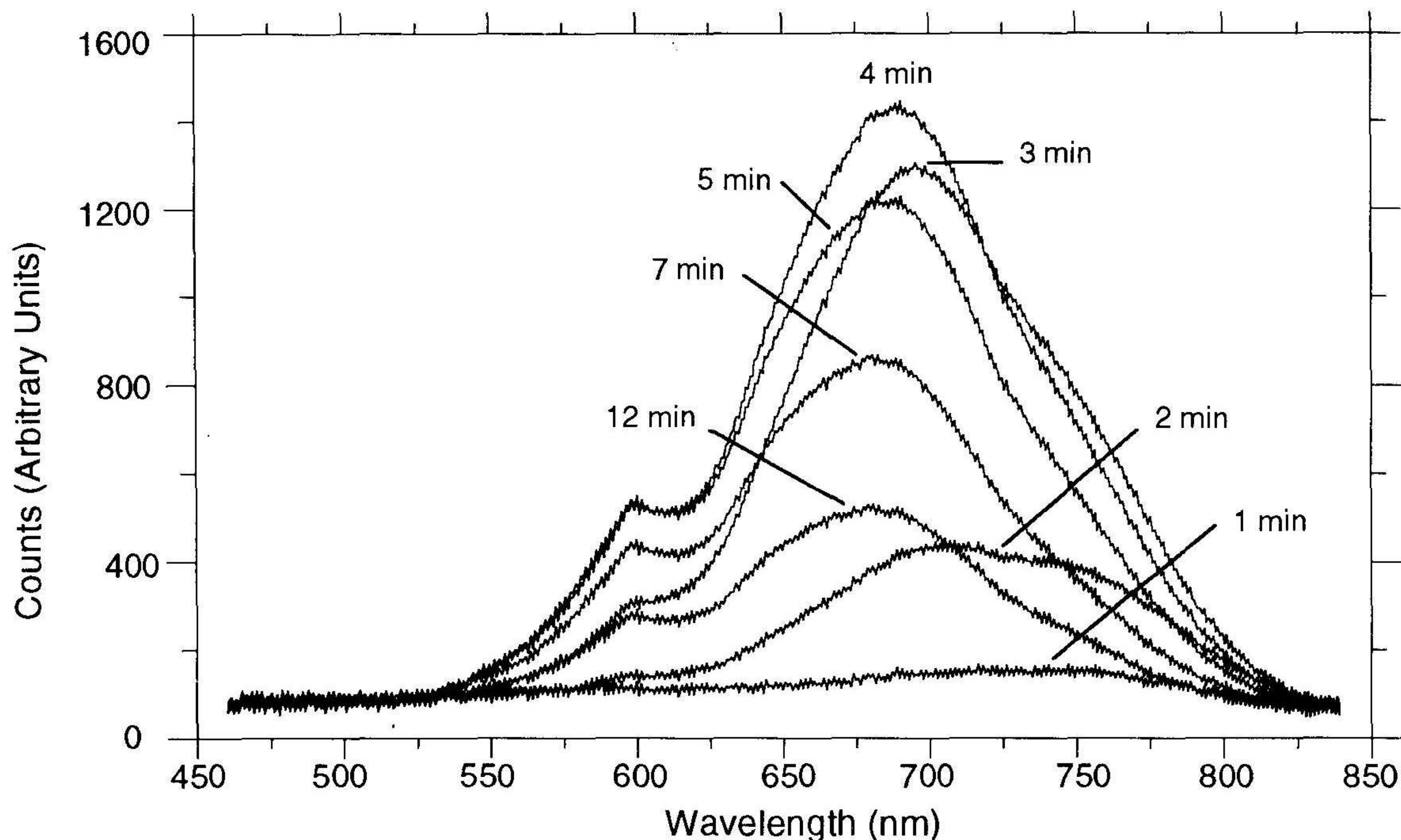


**Figure 1**

where $a_0$ is the amplitude, $a_1$ is the center and $a_{2,3}$ are the widths. With the use of the Scherrer equation(17), which relates the line width (the intensity at the half of its maximum value) with the crystallite size L in the form $\Delta'(2\theta) = \frac{0.9\lambda}{L \cos\theta_0}$ one can estimate the sizes of the structures. Here, $\Delta'(2\theta)$ is the line width (or width at half maximum), $\lambda$ ( the X-Ray wavelength (1.54 $\AA$) and $\theta_0$ the center of the peak. The results for the two peripheral peaks gave a structure size of 6.1 nm for peak 1 and 4.1 nm for peak 2. These sizes agree with the estimated values of crystallites obtained from theoretical calculations(18).

The Raman spectra for different samples are shown in figure 3. Again, crystalline silicon has been taken as reference, where the characteristic peak at 521.5 wavenumbers is observed. The other spectra correspond to 4 minutes (maximum in luminescence) and 12 minutes anodization time. The Raman shift is stronger for longer anodization times. There is no appreciable peak around 150 wavenumbers which is typica(19) of hydrogenated amorphous silicon (a-Si:H) networks. We also note a broadening in the porous peak, particularly visible in the upper graph. This has been attributed(20) as a slight distortion in the tetrahedral network, a process that is different from the one that generates a-Si:H, as stated in some studies(21).

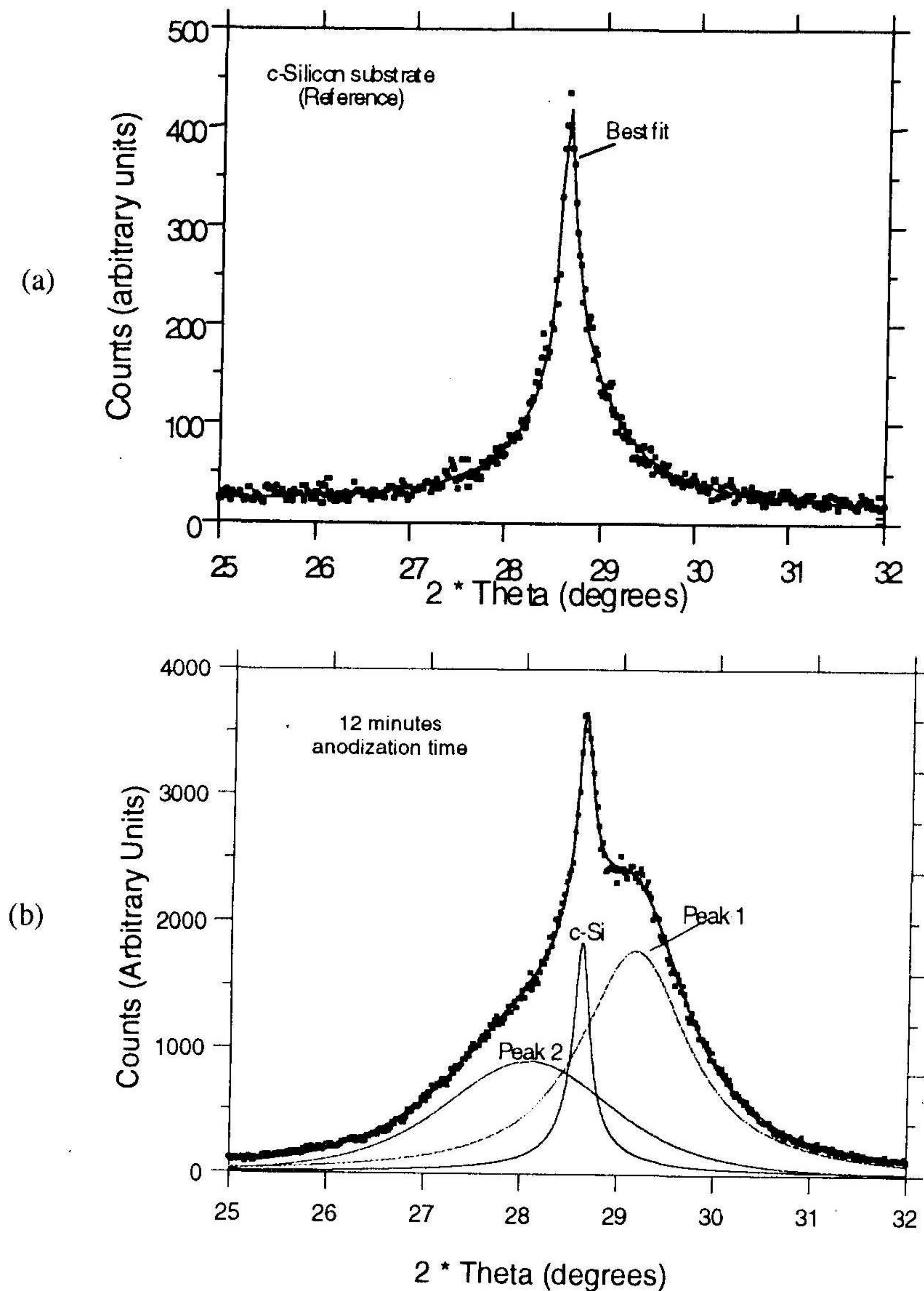


**Figure 2**

As in the case of X-Rays, the width of the Raman peak serves as an indicator for the average diameter of the nanostructures. These can be computed by the use of a spatial correlation model(22,23) which considers the peak width and the peak shift with respect to that of crystalline silicon. After performing the same kind of fittings as previously, the obtained structures sizes lay in the 2 - 4 nm range, which is consistent with the X-Rays results. The peak broadening in the

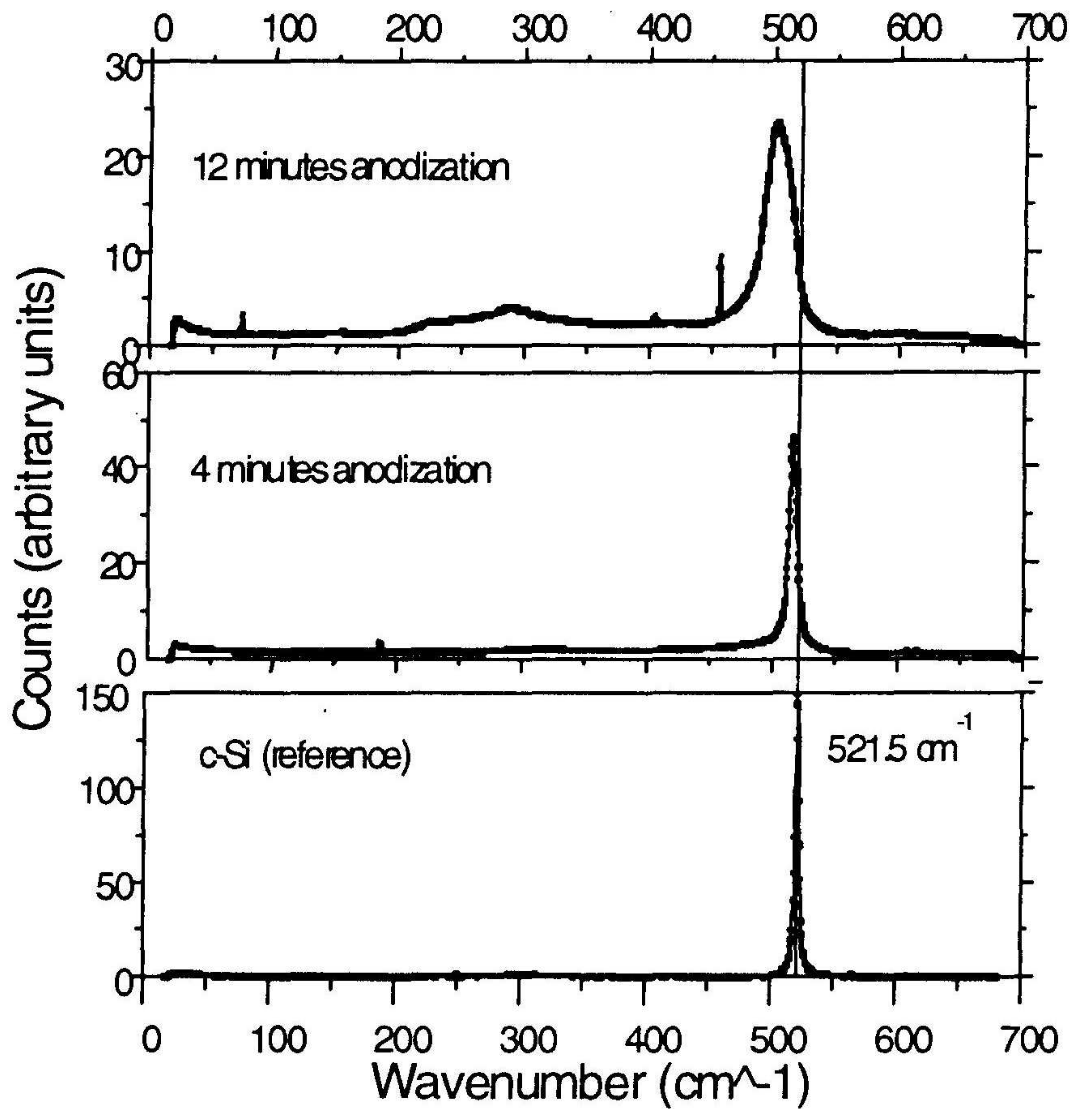


**Figure 3**

Raman spectra as we go from 4 to 12 minutes anodization time corresponds to a shortening in the nanostructure sizes. This result suggests a blue shift in the luminescence peak as predicted by the quantum confinement model(8,18) and actually observed in figure 1.

## 4. Conclusion

Both X-Rays and Raman analyses of anodically etched n+-type silicon showed that the nanostructures sizes are in the order of 2 to 6 nm, which are in the same order of magnitude as the ones predicted from theoretical calculations using the quantum confinement approach. In addition, Raman data suggest a shortening in the nanostructrure sizes with increasing anodization time. This is consistent with the observed blue shift in the luminescence spectra These results therefore support the quantum confinement model.

## 5. Acknowledgments

The author wish to acknowledge Dr. Z. Weisz from the University of Puerto Rico, Dr. Y. Goldstein and Dr. A. Many from the Hebrew University of Jerusalem, for their supervision throughout this study. The x-Ray analyses were performed with the help of Dr. A. Martinez and Dr. V. Pantojas, and the Raman spectra with the aid of Dr. R. Katiyar and Mr. B. Kumar Rai. This work has been supported by NSF grant number OSR 94-52893 and NASA grant project number NCCW-0088.

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