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Characterization of photoluminescent porous Si by small-angle scattering of x rays

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A microstructural study of high-porosity porous silicon layers formed on lightly P-doped wafers has been performed by x-ray small-angle scattering (SAXS) using the powerful and parallel beam of the synchrotron radiation. When the porosity of the sample is increased from 55% to 85% there is a continuous modification in the shape of the scattering profiles. The silicon skeleton mass fractal dimension decreases continuously. For porosity around 85%, the value for which the sample starts to display a strong photoluminescence at room temperature, there is a large increase in the pore size. The scattering profiles are characteristic of an isotropic three-dimensional structure.

Electrochemical dissolution of monocrystalline silicon in concentrated hydrofluoric acid solutions can be used to fabricate a silicon microstructure known as porous silicon which consists of a network of extremely small pores. Porosities greater than 70% have so far been considered of little interest because they lead to a poor quality silicon dioxide. This situation has now changed since photoluminescence and electroluminescence phenomena in the visible range and at room temperature have been recently obtained with high-porosity (>80%) PSL.¹⁻³ Canham¹ attributed the photoluminescence of porous silicon to a dramatic two-dimensional quantum size effect in a structure which is an array of free-standing silicon pillars.

More structural characterization of the high-porosity PSL is necessary to improve the understanding of the physics involved in these luminescence phenomena. One characterization technique which can be used is x-ray small-angle scattering (SAXS). In fact, we demonstrated in a previous paper⁴ that this technique is well suited for the investigation of microstructures such as porous silicon. In the present paper we use SAXS to characterize PSL when the porosity is increased from 55% until a porosity value around 80%, for which the luminescence of PSL is observed at room temperature.

The porous silicon samples were prepared on P-type silicon wafers, (100) oriented, boron doped, with a resistivity of 1 Ω cm. In order to minimize the x-ray absorption in the transmission mode, the wafers were chemically thinned down to a uniform thickness of 100 μ m ($\pm 2\%$) prior to porous silicon formation. The porous silicon was formed by electrochemical anodization in solutions containing 10% to 45% of hydrofluoric acid at constant current density in the 10 to 50-mA/cm² range.⁵

The small-angle scattering measurements were performed on a spectrometer⁶ at the French Synchrotron Radiation Source: Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE), Orsay, France, at the D22 station. The sample-to-detector distance can be varied to get information in a wide range of q values, $q = 4\pi \sin \theta /$

λ where 2θ is the scattering angle and λ the x-ray wavelength corresponding to 8041 eV. Two sample-detector distances have been chosen: $D_1 = 540$ mm and $D_2 = 1540$ mm, so the q values range from 3 to 3×10^{-2} nm⁻¹. As the cross section of the x-ray beam is only 1 mm², it is possible to work in point-like collimation. Furthermore, a small area of the samples can be easily analyzed.

In order to get a good signal-to-background ratio during the x-ray experiments, thick PSL (5 μ m) were prepared.

Since the thickness of the porous layer illuminated by the x-ray beam cannot be determined with enough accuracy, it is difficult to convert the experimental intensities into the scattering power $i(q)$ of the samples. As we show below in the text, the scattering being isotropic, one can calculate the total scattered integrated intensity Q'_0 which gives a value close to the one of the invariant Q_0 given by⁷

$$Q_0 = 1/2\pi^2 \int_0^\infty q^2 i(q) dq.$$

Our calculation is achieved as follows: we first calculate the integral in the observed angular range (between $q_1 = 3 \times 10^{-2}$ nm⁻¹ and $q_2 = 3$ nm⁻¹), then we add the contribution from q_2 to infinity because the integral converges when $q \rightarrow \infty$ as we shall see later on [the product $q^4 i(q)$ being a constant K for $q > q_2$]. We neglect the contribution between the angular origin and q_1 because it never exceeds a few percent of the value of Q_0 . Then we have the experimental determination of Q'_0 :

$$Q'_0 = 1/2\pi^2 \int_{q_1}^{q_2} q^2 i(q) dq + K/2\pi^2 q_2.$$

So, it is possible to get quantitative information independently of the PSL thickness by normalizing by Q'_0 and plotting a normalized intensity $I_n(q) = i(q)/Q'_0$ vs q in the usual log-log representation. Consequently, all the scattering curves are directly comparable.

Figure 1 shows three characteristic scattering curves, in a double log₁₀ presentation, relative to three different

porosities: (a) 55%; (b) 68%; and (c) 85% (the photoluminescent sample). First of all we point out that when tilting the sample with respect to the x-ray beam, the scattering profiles remain approximately the same, confirming the isotropic behavior of the PSL even for the highly porous layer. The porous structure of the photoluminescent sample (c) cannot be analyzed in terms of a model consisting of cylindrical holes running perpendicular to the surface of the wafer.¹ Such a morphology should display a strong anisotropy in the scattering profiles as the one we evidenced in P⁺-type samples with a two-dimensional x-ray detector.⁸

The three characteristic curves in Fig. 1 have a general trend that we have already obtained with the P-type samples.⁴ Two linear parts are separated by a curved region which is a shoulder for the (b) and (c) samples and a clearly visible maximum for the (a) sample (porosity 55%). In the curved region an arbitrary q_c value can be defined for each curve in order to make the interpretation of the spectra easy. So a distinction can be made for each side of the q_c value which separates the region of interfaces ($q > q_c$) from the region of the bulk ($q < q_c$).

For $q > q_c$: This is the region linked with small objects and with the interfaces between matter and pores. The log-log plot gives a linear part with a slope of about -4 for the three samples, indicating that the Porod power law⁹ holds in this region. Consequently the boundary between matter and void is sharp (well defined) for the three freshly prepared samples. Let us notice that in our previous study,⁴ dealing with P-type samples having a porosity of 60%–65% and which in fact were aged at room temperature during several weeks, the scattering curves display a q^{-5} slope for high q values; such a behavior was attributed to a fuzzy surface¹⁰ resulting from a partial oxidation of the pores walls, because after an attack of SiO₂ in hydrofluoric acid solution the slope became equal to -4 .

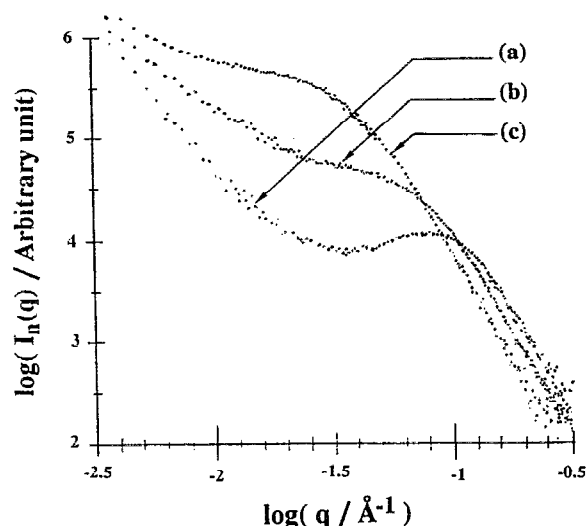


FIG. 1. Log-log representation of the x-ray small-angle scattering curves of porous silicon layers having three different porosities: (a) 55%; (b) 68%; and (c) 85%.

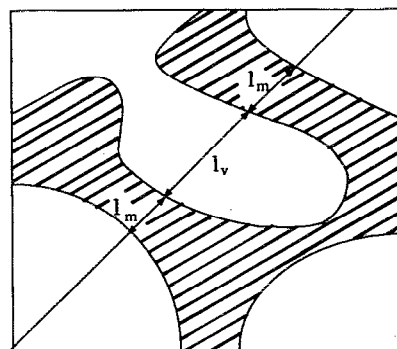


FIG. 2. Schematic drawing of a nonparticulate two-phase system with chords l_m and l_v in matter and voids, respectively.

In the case of high-porosity porous silicon, the volume fraction of pores is large. Moreover, as a result of the open porosity due to their formation by electrochemical dissolution (characteristic of all porous silicon structures), the pores are connected to each other. So, it is not possible to deduce from the small-angle scattering curves a geometrical parameter, such as the electronic radius of gyration,¹¹ which must be associated with a small fraction of isolated and similar particles or pores.

In a nonparticulate two-phase system Porod¹² established the relationship between the outer part of the intensity function, the specific surface, and the concept of chord distribution. Furthermore the chord distribution is very sensitive to the surface structure.¹³ The advantage of such a treatment for porous silicon which is a nonparticulate system is that the concept of size and shape may still be applied, with a different meaning than in particles. According to Porod, a chord is formally an "intersect length" as schematically shown in Fig. 2 for a nonparticulate two-phase system. A line crossing through the system will cut out alternating chords l_m in matter and l_v in voids. An average intersect length $\langle l \rangle$ can be deduced when the classical Porod power law is obeyed. It is given by the following formula:

$$\lim_{q \rightarrow \infty} [q^4 I_n(q)] / 8\pi \simeq 1 / \langle l \rangle.$$

We can distinguish chords in voids $\langle l_v \rangle$ and chords in matter $\langle l_m \rangle$, with $\langle l_v \rangle = \langle l \rangle / (1 - c)$ and $\langle l_m \rangle = \langle l \rangle / c$, where c is the porosity.

For samples (a), (b), and (c) the variations with the porosity are the following: 25 Å, 29 and 40 Å for $\langle l_m \rangle$; 22 Å, 63 and 227 Å for $\langle l_v \rangle$. This indicates a large increase of the size of voids for the porosity 85%. In fact the structure of the photoluminescent sample seems to correspond to a porous structure which is very open probably due to a coalescence of the pores. A proposed explanation is the following: the pore enlargement through the dissolution of silicon leads to a progressive disappearance of the smallest segments in matter (and consequently a progressive increase of $\langle l_m \rangle$), while at the same time there are communications between nearest-neighbor pores leading to a large increase of $\langle l_v \rangle$ when the pores coalesce.

For $q < q_c$: For the small q regime there is an upturn in the scattering curves shown in Fig. 1. This upturn is obviously due to the existence of much larger objects than those which contribute to the observation of the Porod power law. In fact the small q regime is related to the bulk which, in the present case, is the silicon skeleton.

The log-log plot in Fig. 1 indicates a linear part, at least for the (a) and (b) samples. Taking into account the high value of the porosity of the samples, such a slope could be interpreted as being a mass fractal dimension D_m which would characterize the structure of the Si skeleton.¹⁴ The value of the slope decreases from -3 for curve (a) to about -2 for curve (b) and still less (around -1) for curve (c). According to Schaeffer¹⁵ such an evolution of the slope means that the mass fractal dimension of silicon skeleton diminishes from a structure having three dimensions (when the volume of matter as compared with void is still important) to another one which tends to be linear when the volume of matter is very low (noodle-like structure). A possible explanation of our results is that the porosity increase is associated with an electrochemical dissolution of silicon "walls" separating nearest-neighbor pores. Such a dissolution would lead to a pore-pore overlap and dramatic thinning of the silicon crystallites. This is in agreement with the evolution of $\langle l_m \rangle$ and $\langle l_v \rangle$ with the porosity as shown above. However, another explanation can be given. This second explanation is similar to the one deduced from silica gels data:¹⁶ the upturn in the small q regime is associated with long distance fluctuations within the sample which is not homogeneous on a large scale.

The q_c region: This region of the shoulder is more complicated to understand because it may have different possible explanations.

For the (a) sample, a well-defined peak is observed. It is clear that the angular position of this maximum in intensity could be interpreted as a diffuse interference effect, in the same manner as for liquids or Guinier-Preston zones¹⁷ or small precipitates¹⁸ in alloys. Furthermore, TEM observations¹⁹ of P-type porous silicon samples having a porosity of about 50% show an isotropic network of small size pores. Thus, a rough value of space correlation length, which is the mean distance L between the scattering centers, is deduced from the observed position q_M of the maximum in intensity by $L = 2\pi/q_M$. We found $L = 60$ Å for the (a) sample (porosity 55%). This value is similar to the sum $\langle l_v \rangle + \langle l_m \rangle = 47$ Å.

For the (b) and (c) samples, the shoulder can be interpreted either by the same interference effect as just seen before or by units of diameter $2\pi/q_c$ in a fractal system.¹⁴ We are inclined to believe the first explanation because of the continuous evolution of the scattering curves with the increasing porosity. For example, the scattering curve of a sample having a porosity of 62% is plateau-like in the intermediate q_c region. So, when the porosity increases, the continuous evolution of the shape of the scattering curves would correspond to a continuous dissolution of the silicon and by that way a continuous increase of the pore size. The values of L for the (b) and (c) samples are 100 and 250 Å, respectively, in agreement with the sums $\langle l_v \rangle + \langle l_m \rangle$ which

are 92 and 267 Å, respectively. This agreement is, in our opinion, a confirmation of the interference effect that we have associated with the shoulder in the scattering curves.

In conclusion, a small-angle scattering study has been performed on porous silicon layers when the porosity of the samples is increased from 55% to 85% for which a strong photoluminescent phenomenon is observed at room temperature. Although a continuous evolution of the scattering curves is observed, there is a large increase of the pore size when the porosity reaches a value of about 85%. At the same time the silicon skeleton becomes thinner and thinner, while keeping an isotropic morphology.

Our results suggest that the appearance of the photoluminescent phenomenon is in fact due to three-dimensional structure because of the isotropic behavior of the scattering curves. Considering that the phenomenon has been associated with quantum size effects in the silicon skeleton it would be more appropriate to describe the microstructure of the high-porosity luminescent porous silicon by a 3D network of quantum segments in a "noodle-like" or "wool-ball" structure.

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