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J. D. Moreno, F. Agulló-Rueda, E. Montoya, M. L. Marcos, J. González-Velasco, R. Guerrero-Lemus, and J. M. Martínez-Duart

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J. D. Moreno
Departamento de Física Aplicada C-XII, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

F. Agulló-Rueda[a] and E. Montoya
Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, E-28049 Madrid, Spain

M. L. Marcos and J. González-Velasco
Departamento de Química C-IX, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

R. Guerrero-Lemus and J. M. Martínez-Duart
Departamento de Física Aplicada C-XII, Universidad Autónoma de Madrid, and Instituto de Ciencia de Materiales de Madrid (CSIC), E-28049 Madrid, Spain

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Photoluminescence (PL) and Raman spectra were measured along a cross section of porous silicon films at different oxidation times after application of anodic current transients. The average crystallite size was determined from the Raman spectra with the standard phonon confinement model. Before oxidation, the PL emission energy and crystallite size were found to be independent of the layer depth. Also, the integrated PL emission was larger for the middle layers. The effect of oxidation was a blueshift of the PL band and a decrease in the integrated emission for the outer layers. The crystallite size increases for all layers, particularly the outer ones. © *1997 American Institute of Physics.* [S0003-6951(97)03641-3]

The study of porous silicon (PS) has attracted the attention of many researchers since the discovery in 1990 by Canham[1] of its strong photoluminescence (PL) properties at room temperature. Although many studies have appeared trying to give an interpretation for the PL emission mechanisms, some fundamental questions remain unexplained and the exact origin is still controversial.[2–6]

Porous silicon is currently being considered as a material for Si-based optoelectronics devices.[7–9] However, its extreme reactivity and fragility limit the processing by conventional silicon integration technologies. Recently, it has been shown that partial oxidation enhances its thermal and chemical stability.[10] The interface between silicon and silicon oxide has very few of the undesirable surface states that quench light emission.

Porous silicon has pore diameters varying from a few micrometers to several nanometers depending on the formation conditions,[11–13] as observed by high resolution scanning and transmission electron microscopies.[14] The extreme fragility of porous silicon makes the use of these characterization techniques very complicated, and no information can be gained about PL properties and their relation with crystallite size along the PS cross section. Therefore, Raman spectroscopy has been extensively used to characterize the porous silicon samples. When the crystallite size becomes very small, quantum confinement of phonons inside the particles relax the $q=0$ selection rule, and phonons at $q\neq 0$ become Raman active.[15,16] The phonon peak broadens towards lower energies and shifts slightly. The Raman lineshape and the shift can be related with the average size of nanocrystals within the standard phonon confinement model. However, most studies have limited to the surface. Depth-resolved Raman measurements have been reported only for as-formed n-type porous silicon.[17] In this paper we study depth-resolved micro-Raman and PL spectra along the cross section of p-type porous silicon films at different oxidation states.

Porous silicon structures were obtained by anodization of boron-doped (p-type) (100) silicon wafers with a resistivity of 0.1–0.5 Ω cm. The electrolyte consisted of a 2:1 HF (48% wt)/ethanol (98%) mixture. Samples were etched galvanostatically at a current density of 50 mA/cm^2 for 5 min under illumination, because samples etched in the dark showed no luminescence emission. Porous silicon films were 12 μm thick and had a porosity of ca. 75%. After formation, the samples were rinsed with ethanol and immersed in a 0.1 M Na_2SO_4 aqueous solution. Anodic oxidation of the PS was then carried out under constant current ($I=2$ mA), using a mercurous sulfate reference electrode and a Pt counterelectrode. Electrochemical measurements were made with a computer driven PAR Mo. 273 electrochemistry system. Special care was taken to ensure that the PS remained wet during the transit of solutions. Otherwise, a superficial cracking can be produced.[18]

Three samples have been studied in this work. Sample A consists of fresh PS, i.e., not subjected to anodic oxidation. Sample C was anodically oxidized until a rapid and significant potential increase was observed, indicating that SiO_2 formation had broken the electric contact. Finally, sample B was subjected to a partial oxidation, as the anodic current was stopped when only half the time needed for the electrooxidation of sample C had elapsed.

Raman and PL spectra were measured with a Renishaw Ramascope 2000 spectrometer and an Ar$^+$ laser at different points along a PS cross section, yielding information at different layer depths. The spatial resolution was around 1 μm.

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[a] Electronic mail: far@icmm.csic.es

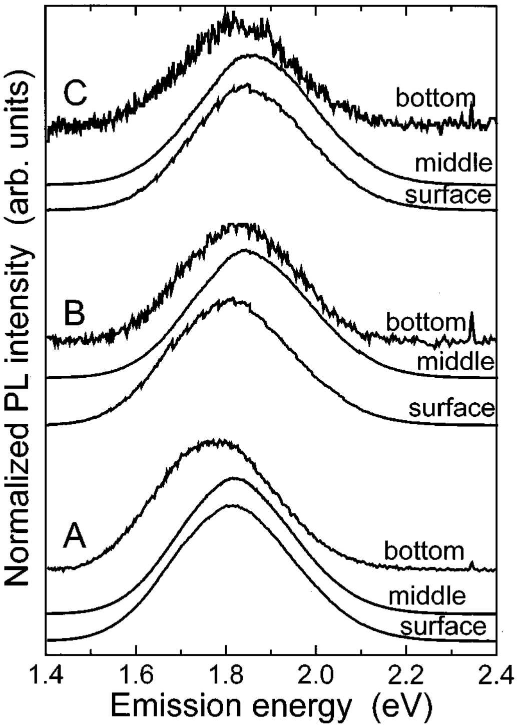

FIG. 1. Photoluminescence (PL) spectra measured along the cross section of the porous silicon film at the bottom (close to the bulk silicon substrate), the middle, and the top surface layers, for a fresh sample (A), a partly oxidized sample (B), and a sample oxidized till electric contact is broken (C).

The laser power density on the sample was kept below 24 W cm^2 to avoid excessive heating.

Photoluminescence spectra were taken at three different locations for each sample: at the top (external surface), at the middle and at the bottom (close to the bulk Si) of the porous layer (Fig. 1). For sample A, the wavelength of the PL maximum is the same at the top and at the middle, but shifts towards the red at the bottom. For sample B, a blueshift with respect to sample A takes place at the middle and at the bottom. Finally, for sample C, the blueshift is observed at the three locations.

Figure 2 shows the normalized integrated PL intensity throughout the cross section of the PS layer. As the oxidation state progresses, the intensity maximum moves to deeper layers. The bottom layer does not show any PL in sample A; however, as samples are oxidized (samples B and C), a weak PL emission can be noticed.

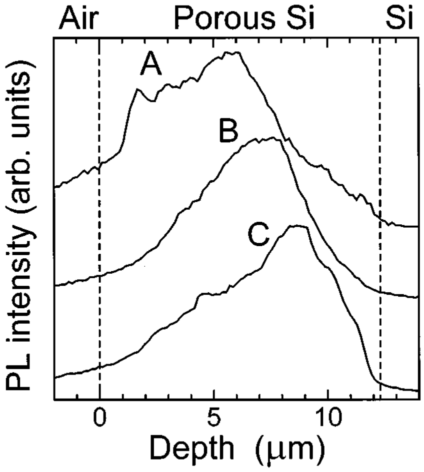

FIG. 2. PL integrated intensity vs depth for samples A, B, and C.

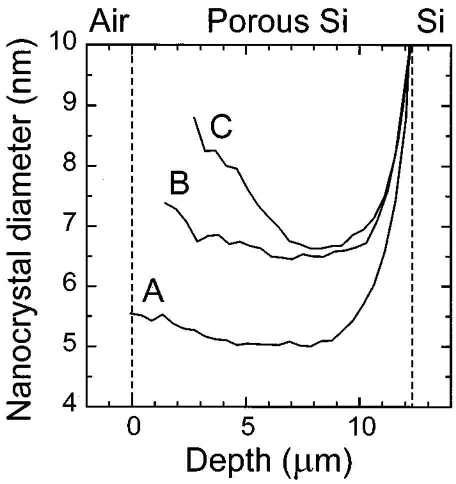

FIG. 3. Average silicon nanocrystal diameter vs depth for samples A, B, and C. Sizes were obtained with the standard phonon confinement model from the Raman spectra, measured at different points along the cross section of the porous silicon films.

Figure 3 shows the average size of silicon nanocrystals versus depth, obtained from the Raman lineshape with the standard phonon confinement model.[16] The crystallite diameter in sample A is about 5 nm throughout the porous layers, except for the lowest 3 μm where it increases gradually. In accordance, the PL intensity is nearly constant for the top 8 μm, and drastically decreases in the lowermost 4 μm. On the other hand, in sample A (Fig. 1) the PL spectra obtained at the top and at the middle are similar, but the intensity maximum shifts to the red close to the bulk, where the crystallite size increases. All these data are in agreement with the quantum confinement model for the PL.

In sample B (Fig. 3) the Raman signal disappeared for the top 1.5-μm-wide layer. Thus, we assume that most of the Si crystallites in this region have been removed during oxidation. However, a small amount must remain, as a very weak PL is still observed. In sample C the top layer in which the Raman signal disappears is wider, ca. 3 μm. As the oxidation state of the PS increases, the crystallite size also increases, and it is ca. 9 nm for sample C at the uppermost site where size can still be determined. Deeper inside the porous layer, the size diminishes, but it is always greater than for sample A.

At first sight, the average crystallite size and the PL spectra seem to be in disagreement in the case of the oxidized samples (B and C). A size decrease would be expected due to silicon oxidation, with a corresponding blueshift in the PL emission. However, although such blueshift is actually observed (Fig. 1, samples B and C), the average crystallite size is larger (Fig. 3). This fact could be explained if we take into account that samples were formed under illumination. Photoetching results in the formation of an additional population of small size crystallites.[19,20] Thus two different size ranges of crystallites are expected. As the oxidation increases, the smaller size nanocrystals are almost completely replaced by silicon oxide, leaving only the larger ones, and the average size increases, as observed by Raman scattering. However, the PL is only emitted by the smallest crystallites. This is in agreement with the weaker PL observed in oxidized samples with respect to fresh PS at the top layer, where smaller size crystallites have been removed by oxidation. This decrease in the PL intensity with anodic oxidation contrasts with previous results.[21] This is probably due to the fact that the size of crystallites responsible for the PL is smaller in this work, as evidenced by the maximum emission wavelength; therefore, they are more easily replaced by oxide. Finally, the density of small size nanocrystals in sample A must be lower in the top layer, because there is where the average size more drastically increases with the oxidation state in samples B and C.

In summary, in fresh porous silicon samples the average size of crystallites, determined from the Raman lineshape, is quite homogeneous throughout the porous layer. The density of small nanocrystals is lower at the top layer. In oxidized samples, the crystallite size depends strongly on the oxidation stage and the layer depth. Anodic oxidation diminishes the number of small size crystallites at all sites of the porous layer, as well as the size of the remaining crystallites. Correspondingly, the maximum PL intensity shifts to the layers that retain a greater density of small size crystallites, i.e., the middle layers. Finally, the intensity maximum shifts to the red close to the bulk, where the average crystallite size increases.

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