Investigation of the structure of porous silicon using second harmonic generation and atomic force microscopy

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We have investigated the surface structure and nonlinear-optics properties of porous silicon using second harmonic generation and atomic force microscopy. In a number of cases, we found the second harmonic response to be significantly anisotropic. The data from our nonlinear-optics and atomic force microscopy measurements indicate that samples of porous silicon obtained by short-time anodic etching (up to 10 minutes) of single-crystal silicon substrates with (100) orientation have a structure with a preferred direction that coincides with either the (010) or (001) crystallographic direction. Our studies of porous silicon samples by atomic force microscopy failed to detect any elongated structures perpendicular to the surface with transverse dimensions of a few nanometers, the presence of which is postulated in order to explain the intense photoluminescence of porous silicon through a mechanism connected with size-quantization effects. © *1995 American Institute of Physics.*

I. INTRODUCTION

Recently systems with low dimensionality, including semiconductor nanostructures, have been actively investigated. One system of interest in this context is porous silicon, whose distinguishing property is an intense photoluminescence in the visible range that does not occur in crystalline silicon. A possible mechanism for this photoluminescence is size-quantization in quasi-one-dimensional semiconductor nanostructures (with characteristic dimensions of order several nanometers) that form at the surface of silicon under anodic etching.[1] However, there are a number of alternative mechanisms that could produce this photoluminescence, involving various changes in the porous silicon surface: the generation of an amorphous silicon phase,[2] various silicon compounds with hydrogen and carbon,[3] surface stresses in the porous structure,[4] etc.

Because there are a number of ways to explain the intense photoluminescence in porous silicon, the study of the porous silicon structure is a problem of ongoing interest. Many papers have been devoted to this problem, in which local properties of the surface structure of porous silicon are investigated by x-ray analysis,[5] electron[6] and electrochemical tunneling microscopy,[7] etc.

In this work we have investigated the structural properties of porous silicon on both microscopic scales by the method of atomic force microscopy (with nanometer resolution) and macroscopic scales by the method of second harmonic generation, which is sensitive to anisotropy in the structure of a system.[8] Although a number of papers have been published on second harmonic generation in films,[9,10] up to now no one has dealt with the problem of anisotropy in the nonlinear optical response of a porous layer.

Our porous silicon samples were prepared by the method described, e.g., in Refs. 11, 12. First, metallic contacts were deposited on the back of a p-type silicon wafer with (100) orientation and resistivity $\rho = 1-10\ \Omega\cdot$cm. This wafer was then anodized in a solution of $HF:H_2O:C_2H_5OH$ with proportions 1:1:2 by volume; the current density was varied over the range $5-50$ mA/cm^2. The luminescence properties of the porous silicon were monitored by exciting the porous surface with light from a He–Cd laser at a wavelength of 441.6 nm and recording the photoluminescence spectrum. The maximum photoluminescence intensity occurred for values of the current of $30-40$ mA/cm^2.

In our studies of second harmonic generation, we used p-polarized light pulses from a Nd^{3+}–YAG laser at a wavelength of 1064 nm with pulse durations of 15 ns and powers of 10 MW/cm^2 per pulse. The second harmonic radiation at a wavelength of 532 nm was isolated by a DFS-24 double monochromator and recorded by an electronic gating system. The second harmonic signal had a narrow spectrum (no wider than the spectral resolution of the monochromator, which was 1 nm); furthermore, its intensity was proportional to the square of the power of the probe radiation, which corresponds to a second-order nonlinear process. In order to study the azimuthal angular dependence of the second harmonic intensity $I_{2\omega}(\Psi)$ (where Ψ is the azimuthal angle of rotation of the sample in the laboratory system of coordinates), we rotated the sample about an axis perpendicular to its surface. For $\Psi = 0°$, the field intensity vector of the pump was parallel to the (010) crystallographic direction (or the equivalent (001) direction) in the substrate plane.

The surface structure of samples of porous silicon was investigated by atomic force microscopy in the constant-force regime, with a mean force of $5\cdot 10^{-9}$ N. Reference 13 describes the design of our microscope and the methodology we used in our experimental observations of the surface relief of poorly conducting objects, such as those made of silicon. At the surface of many samples we observed a quasi-ordered structure with characteristic scale 20–50 nm (Fig. 1a). We scanned the surface over sample areas of 1.5×1.5 μm, repeating the scan at several points on the surface so that it encompassed an area of 1×1 mm. The preferred direction, which is clearly evident in the figure, was constant over the full scan area, and did not vary from point

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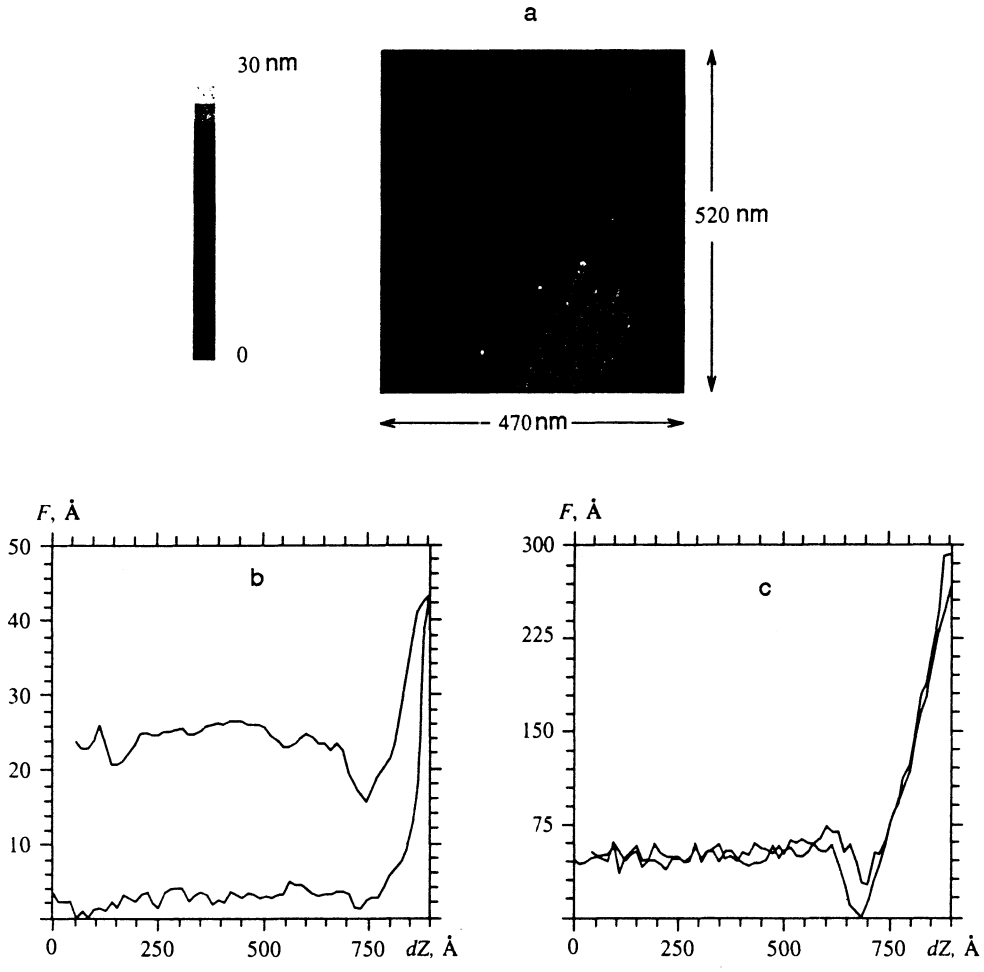

FIG. 1. a) Characteristic structure observed at the surface of porous silicon using atomic force microscopy. The dimensions of a frame were 520 nm×470 nm. The gray scale of the image corresponds to 30 nm. The image was obtained using an average force of $5 \cdot 10^{-9}$ N. The dependence of the tip displacement $F(z)$ on the displacement of the sample is shown for porous silicon samples whose etch times were b) 7 min and c) 10 s. The stiffnesses of the cantilevered recording tips were 0.5 and 0.1 N/m respectively.

to point. To an accuracy of $\pm 5°$, this direction was parallel to the (100) plane of cleavage of the silicon wafer, i.e., it lay in the (010) or (001) direction.

We note that our results matched those of Ref. 14, i.e., for the porous silicon samples we investigated using atomic force microscopy, we observed no elongated surface structures oriented perpendicular to the surface with transverse dimensions of several nanometers (i.e., quantum pillars).

In our experiment we studied the azimuthal anisotropy of the s-polarized component of the second harmonic signal $I_{2\omega}^{p,s}(\Psi)$ reflected from the porous silicon surface. Like the authors of Ref. 9, we found that the second harmonic intensity generated by a porous silicon film was of the same order of magnitude as that of crystalline silicon. For a large number of porous silicon samples made with etch times of 1 to 5 minutes, the functions $I_{2\omega}^{p,s}(\Psi)$ were anisotropic, with a form analogous to that shown in Fig. 2a. However, it is well known that for the smooth surface of a (100) facet of a single crystal with m3m symmetry, $I_{2\omega}^{p,s}(\Psi)$ is proportional to $|\sin 4\Psi|^2$. We observed exactly this dependence in experiments where silicon wafers were used as substrates (Fig. 2b). From the plots it is clear that the number of maxima in $I_{2\omega}^{p,s}(\Psi)$ is only half as large for porous silicon as it is for the analogous function taken from a smooth crystalline silicon surface. This implies that the formation of the porous structure leads to changes in the anisotropy of the nonlinear response of the sample compared with that of a smooth silicon surface.

There are various phenomena that can bring about this change in the behavior of $I_{2\omega}^{p,s}(\Psi)$. It would seem that the function shown in Fig. 2a indicates a lowering of the symmetry of the porous silicon layer compared to the substrate; the structure of the porous silicon is close to C_{2V} symmetry, and is described by the second azimuthal Fourier harmonic (for the field).[8] Making the corresponding approximation (Fig. 2a, solid curve) results in a satisfactory description of the experimental functions within the framework of this model. This assumption is confirmed by the atomic force microscopy data for the surface of the porous layer (Fig. 1a). Starting from the fact that the second harmonic signal is collected from a thick near-surface layer consistent with the penetration depth of the second harmonic field into the porous silicon, we may infer that the porous layer is quasi-ordered in structure to this depth, with symmetry close to C_{2V}. By way of comparison, we find the penetration depth of the second harmonic field into crystalline silicon to be 50–100 nm, while is it considerably larger for porous silicon.

On the other hand, it may be that the functional behavior is the result of a coherent sum of nonlinear responses from the porous layer and the porous silicon/crystalline-silicon boundary. Suppose that the symmetry of the crystalline-silicon/porous silicon boundary is same as that of the (100)

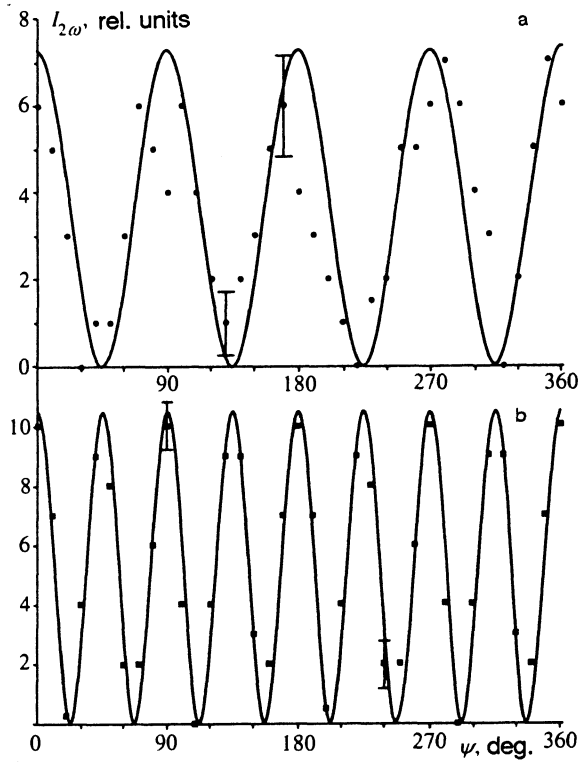

FIG. 2. Dependence of the second harmonic intensity on the azimuthal angle Ψ. a) Porous silicon; b) silicon substrate. The solid curve is the result of approximating (a) with the second azimuthal Fourier harmonic, and (b) with the fourth azimuthal Fourier harmonic (for the field).

surface of crystalline silicon, while the porous structure is isotropic on macroscopic scales. Then $I_{2\omega}^{p,s}(\Psi)$ will be proportional to $|a+b\sin 4\Psi|^2$, and there will be a certain ratio of the coefficients a and b for which four maxima can occur (as the angle Ψ varies from 0 to 2π). However, anisotropy of $I_{2\omega}^{p,s}(\Psi)$ (Fig. 2a) was a typical feature of a large number of our samples, for which the parameters of the preparation procedure differed, implying that the ratio of a and b should, in general, differ from sample to sample. Therefore, our hypothesis would appear to be implausible.

In this study we also investigated the dependence of the reflected second harmonic intensity on the etching time τ used to obtain the porous silicon samples from the silicon wafer (Fig. 3). At 40 mA/cm^2, the anodic current density was the same for all samples. The measurements were made using the same orientation of the samples in the laboratory system of coordinates at $\Psi=0°$. For all samples, the measured photoluminescence spectra were typical of porous silicon,[15] exhibiting a broad (100 nm) maximum in the neighborhood of 700 nm (Fig. 3, inset).

The oscillatory character of the function $I_{2\omega}(\tau)$ is probably due to interference effects in the thin porous layer. We believe that the observed behavior results from linear interference in both the pump radiation and the second harmonic generated in the crystalline silicon. The constancy of the oscillation period indicates that the rate at which the thickness h of the porous silicon layer $\nu \equiv \partial h/\partial \tau$ increases is constant,[16] and in the linear interference model we can set $\nu \approx 100$ Å/sec. However, the authors of Ref. 16 found that ν was 300−−350 Å/sec for samples similar to those investigated in this paper. This sizable discrepancy between our estimate of the rate of growth of the porous silicon layer thickness and theirs suggests that the interference mechanism is probably not fundamental.

Interference between the nonlinear polarizations of the substrate and porous layer must be added to the list of possible mechanisms that might explain the observed behavior of $I_{2\omega}(\tau)$, i.e., $P^{2\omega}=P_{Si}^{2\omega}+P_{PSi}^{2\omega}$. In this case the polarization of the porous silicon layer may be a function of its thickness,[17] which can probably lead to the oscillatory etch-time dependence of the reflected intensity of the second harmonic.

Note that for high anodic etching current density (i.e.,

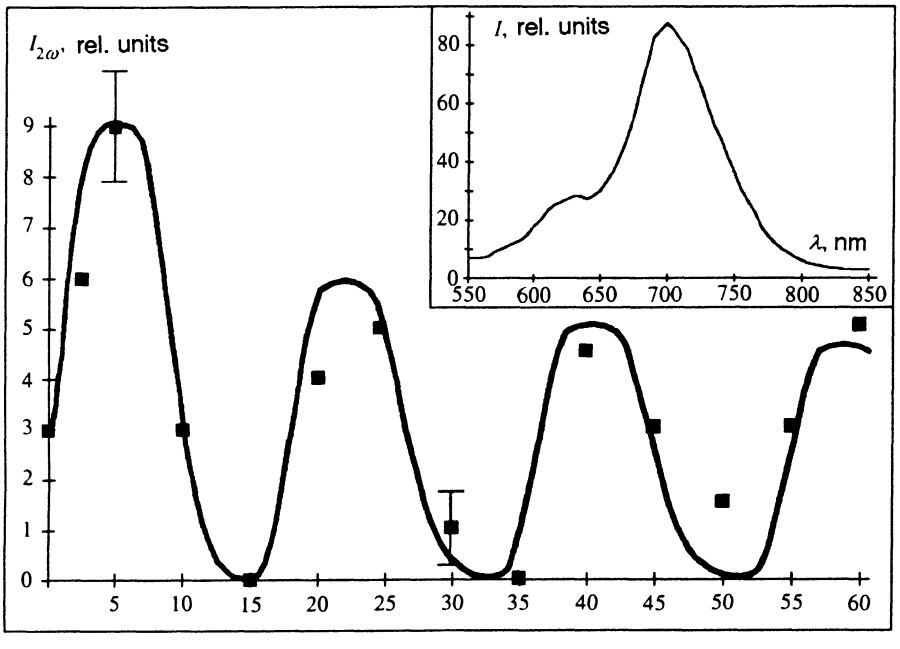

FIG. 3. Second harmonic intensity as a function of anodic etch time for porous silicon samples: the squares are experimental points, the solid curve is the result of graphical interpolation. In the inset, we show typical photoluminescence spectra of porous silicon samples (the current density for anodic etching was 30 mA/cm^2 under excitation by a He–Cd laser ($\lambda=441.6$ nm).

above 45 mA/cm^2), as well as for small currents but long etch times $\tau > 5$ min, the porous silicon surfaces under study become "friable" (on nanometer scales). Figure 1b shows the dependence of the force acting between the microscope tip and the surface on the distance z between them for this type of sample (since the force is proportional to the displacement of the microscope tip, in Figs. 1b and 1c we plot the displacement of the tip $F(z)$ as a function of the displacement of the sample in angstroms). The mean value of the derivative $\partial F(z)/\partial z$ for repulsive regions is considerably smaller than unity, which suggests a low value of the local surface stiffness (lower than the stiffness of the cantilevered recording tip), while hysteresis is observed as the device approaches and recedes from the sample, suggesting that there is local surface damage. At the same time, samples obtained with anodic etch current densities lower than 40 mA/cm^2 were fairly "rigid" in this sense (the average value of $\partial F(z)/\partial z$ in repulsive regions was ~ 1), while the functions $F(z)$ observed in this case were invertible (Fig. 1c).

We point out that in the first case (i.e., for the "friable" samples), the functions $I_{2\omega}^{p,s}(\Psi)$ were isotropic to within the measurement errors, whereas the anisotropies described above in the dependence of the second harmonic intensity were exhibited by samples with "rigid" structure. Thus, our experimental results suggest an interrelationship between the "stiffness" and the degree of order of the structure. However, the question of the mechanism that produces the quasi-ordered structure remains open.

In this paper, we have thus investigated the nonlinear optical properties and structure of porous silicon by means of reflected second harmonic generation and atomic force microscopy. Our experimental data suggest that for silicon substrates with (100) orientation, anodic etch current densities of 40 mA/cm^2, and small etch times (up to 5 min), the structure of porous silicon is close to C_{2v} symmetric and has a preferred direction corresponding to the (010) or (001) crystallographic directions in the plane of the substrate.

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