Second harmonic generation and atomic-force microscopy studies of porous silicon

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Structural properties of porous silicon were studied with atomic-force microscopy (AFM) and optical second harmonic generation (SHG). Depending on etching conditions, the SHG response was observed to be either anisotropic, showing C_{2v} symmetry, or isotropic. This correlated with AFM observations of quasi ordered structures in the first case. The Si etching process was studied by *in situ* SHG measurements. © *1995 American Institute of Physics.*

Porous silicon (PS), formed by the anodical etching process of Si in F-containing solutions, is attracting a lot of attention recently. The most striking feature of PS is the observed intense visible photoluminescence (PL)[1] that is absent in the case of crystalline or amorphous silicon. Several mechanisms for this effect have been proposed: quantum confinement effects in silicon nanostructures,[1] the formation of *a*-Si,[2] siloxene derivatives,[3] silicon hydride complexes,[4] surface stresses in porous structures,[5] etc. A lot of effort is devoted now to study the structure of PS using x-ray scattering,[6] Raman scattering,[7] transmission electron microscopy,[8] scanning tunneling,[9] and electrochemical tunneling[10] microscopies, etc.

In the present letter, structural properties of various PS samples are studied both on a microscopic scale, using atomic-force microscopy (AFM), and on a macroscopic scale by means of anisotropic second harmonic generation (SHG). The latter is known as an effective tool for studying the symmetry properties of surfaces.[11] We find a clear correlation between the results obtained by these two techniques.

For the SHG experiments we used the output of a *Q*-switched Nd^{3+}:YAG laser at 1064 nm, a pulse duration of ~15 ns, and a repetition rate of 12.5 Hz, pulse power being ~10 MW/cm^2. The SHG intensity at 532 nm was detected with a photomultiplier and gated electronics, using a double monochromator to isolate the small SHG signal from the spectral background. The anisotropy of the SHG intensity was studied by varying the azimuthal angle Ψ between the optical plane of incidence and a fixed direction in the plane of the surface.

Photoluminescent spectra of all the samples were measured using a He–Cd laser at 441.7 nm, and found to be similar to those obtained in Ref. 12. The PS samples were studied by AFM in the constant force mode; the average value of the force F being $\sim 5\times10^{-9}$ N. The construction of the AFM used in our experiments is described in Ref. 13. The samples were prepared from *p*-type (100) silicon wafers of 1–10 Ω cm resistivity, anodized in a solution of HF: H_2O:C_2H_5OH=1:1:2 for 2 s–10 min.[14] The current density was varied in the interval 5–50 mA/cm^2. One set of specimens was made at the Philips Research Laboratories.

Figure 1 shows an AFM scan, typical for the first kind of PS samples that had been etched for a short time (<5 min) and using a "small" current (<45 mA/cm^2). The scan shows a quasiordered structure, with an approximate C_{2v} symmetry and a lateral period of about 40 nm. The scanning area was 1500 nm×1500 nm, which was repeated at several points at the surface, covering a studied area of 1 mm×1 mm. The ordered structure with the same orientation was consistently observed over the whole area studied. This same structure was observed on all of the more than ten samples produced in this way. The direction of the "trench" structure was always along a main crystallographic axis ([010] or [001]). The samples used were standard wafers, showing no structure prior to the etching procedure. At variance with this, for

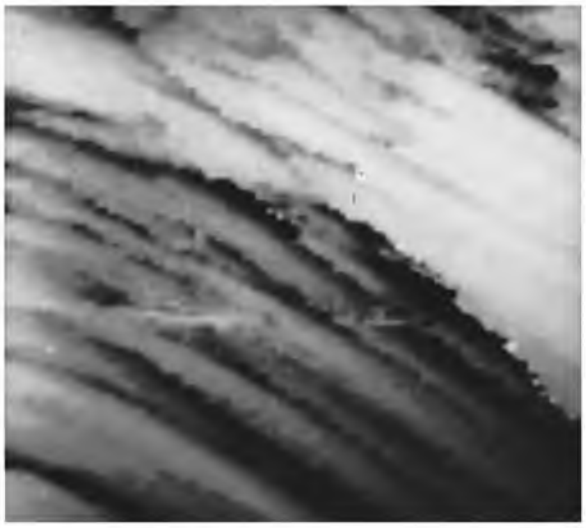

FIG. 1. The typical AFM pattern of a "rigid" PS surface. The size of the scan is 520 nm×470 nm. The grey scale of the picture corresponds to 30 nm. The image was obtained with an average force of 5×10^{-9} N.

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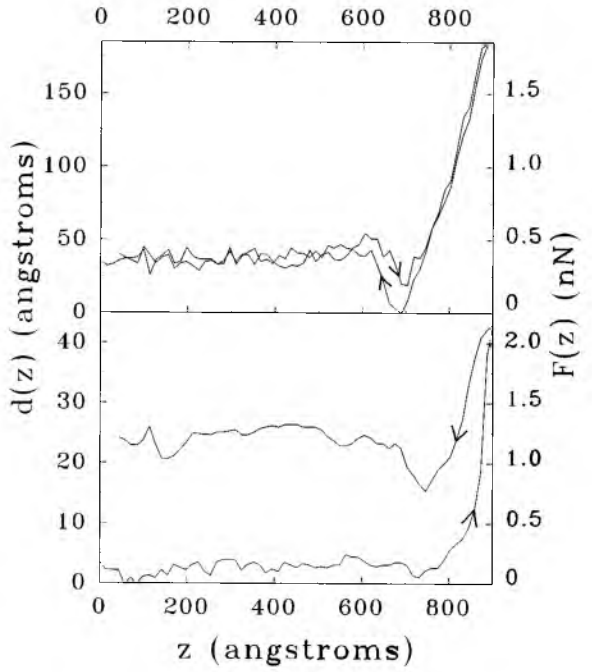

FIG. 2. The force curves for the PS samples with the "rigid" (a) and "soft" (b) surfaces.

the second kind of PS samples that had been etched for a longer time (~5–10 min) or with a larger current (~50 mA/cm^2), the AFM scan only showed pictures with no observable or reproducible structure at all. This was consistently found for all of the more than ten samples produced in this way.

These two kinds of samples reveal completely different force curves. Figures 2(a) and 2(b) show the typical force curves (the force F or cantilever displacement d versus sample displacement $-z$), obtained for the two kinds of surfaces. For the samples with an ordered structure, the force curve $F(z)$ [Fig. 2(a)] is reversible and shows hardly any hysteresis. This, and the observed derivative in the repulsion region ($z>750$ Å) $\partial d(z)/\partial z \cong 1$, indicate the presence of a rather "rigid" surface. For the second kind of sample [for longer etching times or higher currents—Fig. 2(b)], the average derivative in the repulsion region $\partial d(z)/\partial z \ll 1$, indicating an essentially "soft" surface. This is also consistent with the apparent nonreversibility, as observed in Fig. 2(b).

These AFM observations can directly be correlated with the SHG measurements. Figure 3 shows the SHG intensity measured as a function of the azimuthal angle Ψ, for a rigid PS surface as displayed in Fig. 1. The observed dependence of the SHG intensity on Ψ is well described by

$$I_{2\omega} = C|\cos 2\Psi|^2, \tag{1}$$

i.e., the SHG anisotropy is consistent with a C_{2v} symmetry of the nonlinear tensor $\chi^{(2)}$.[11] This symmetry of the macroscopic nonlinear response is the same as the approximate microscopic symmetry observed with AFM.

This correlation between macroscopic and microscopic symmetry was also observed for the "soft" surface: the measured SHG response from these surfaces was essentially isotropic, just as there was also no observable structure in the

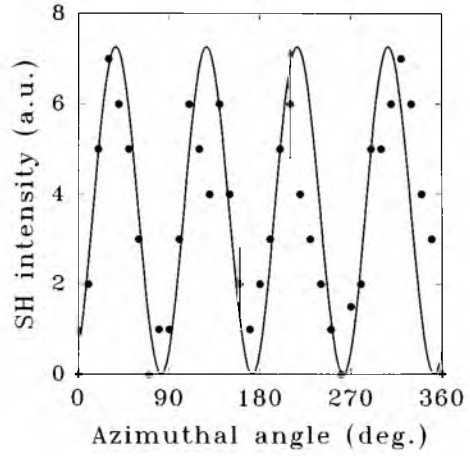

FIG. 3. The experimental dependence of the SHG intensity on the azimuthal angle Ψ (squares). The solid curve corresponds to a fit according to Eq. (1).

AFM scans. Note that the SHG response of a crystalline Si(100) substrate is expected to show a fourfold symmetry: $I_{2\omega} \sim |\cos 4\Psi|^2$.[11] This means that for both the "rigid" and "soft" surfaces, the SHG response is dominated by the PS layer, with no observable contribution from the underlying crystalline substrate.

The nonlinear optical probe can also be used to study the dynamics of the etching process, leading to the porous structure. Figure 4 shows the measured SHG intensity as a function of the etching time τ for an anodization current density of 40 mA/cm^2 (i.e., leading to a "rigid" surface). The observed slowly decaying pattern can be fitted with

$$I_{2\omega} = Ae^{-\alpha\tau} \sin^2(w\tau + \varphi), \tag{2}$$

where A, α, w and φ are fitting parameters (solid line in Fig. 4). Equation (2) suggests that the oscillatory behavior in the observed time dependence is the result of an interference effect. This can be attributed to the fact that due to the growth of the PS layer, the SHG intensity shows interference maxima and minima due to multiple reflections between the air-PS and the PS-Si interfaces. From the period of the ob-

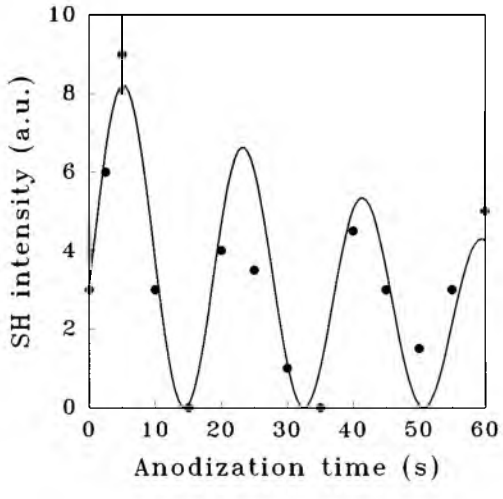

FIG. 4. The experimental dependence of SH intensity on the anodization time τ (squares). The solid curve corresponds to a fit according to Eq. (2).

served oscillations we can deduce an etching rate of $\nu \approx 150$ Å/s, assuming a three layered system (silicon substrate-PS-air), with multiple reflections of the fundamental and SH beam generated at the silicon-PS interface. This value is a factor of 2 smaller than that obtained from other measurements ($\nu \approx 300-350$ Å/s) for similar conditions.[15] The reason for this discrepancy is unclear thus far.

In conclusion, structural properties of porous silicon were studied by means of AFM and anisotropic second harmonic generation. It was shown both with AFM and SHG that for certain conditions of anodical etching (current density about 40 mA/cm^2 and time of anodical etching up to ~5 min) the PS structure is close to a C_{2v}-symmetrical structure, i.e., there is a distinct direction in the porous layer that appears to be along one of the major crystallographic directions. The reason for this is unclear thus far. The oscillatory dependence of the SH intensity on the anodization time yields information about the growth speed of the porous layer.

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[1] A. G. Cullis and L. T. Canham, Nature **353**, 335 (1991).
[2] R. P. Vasquez, R. W. Fathauer, T. George, A. Ksendzov, and T. L. Lin, Appl. Phys. Lett. **60**, 1064 (1992).
[3] P. Deak, M. Rosenbauer, M. Stutzmann, J. Weber, and M. S. Brandt, Phys. Rev. Lett. **69**, 2531 (1992).
[4] S. M. Prokes, O. J. Glembocki, V. M. Bermudez, R. Kaplan, L. E. Friedersdorf, and P. C. Searson, Proc. Mater. Soc. **256**, 107 (1992).
[5] L. E. Friedersdorf, P. C. Searson, S. M. Proces, O. J. Glembocki, and J. M. Macaulay, Appl. Phys. Lett. **60**, 2285 (1992).
[6] V. Vezin, P. Goudeau, A. Naudon, A. Halimaoui, and G. Bomchil, Appl. Phys. Lett. **60**, 2625 (1992).
[7] Zh. Sui, P. P. Leong, I. P. Herman, G. S. Higashi, and H. Temkin, Appl. Phys. Lett. **60**, 2086 (1992).
[8] I. Berbezier and A. Halimaoui, J. Appl. Phys. **74**, 5421 (1993).
[9] M. Enachescu, E. Hartmann, and F. Koch, Appl. Phys. Lett. **64**, 1365 (1994).
[10] S. L. Yau *et al.*, J. Electrochem. Soc. **141**, 402 (1994).
[11] O. A. Aktsipetrov, I. M. Baranova, and Yu. A. Il'inskii, Zh. Eksp. Teor. Fiz. **91**, 287 (1986) [Sov. Phys. JETP **64**, 167 (1986)]; C. W. van Hasselt, M. A. Verheijen, and Th. Rasing, Phys. Rev. B **42**, 9263 (1990).
[12] Y. Q. Jia, L. Z. Zhang, J. S. Fu, B. R. Zhang, J. C. Mao, and G. G. Qin, J. Appl. Phys. **74**, 7615 (1993).
[13] Yu. N. Moiseev, V. I. Panov, S. V. Savinov, and I. V. Yaminsky, J. Vac. Sci. Technol. B **12**, 1690 (1994).
[14] Y. Kanemitsu, K. Suzuki, H. Uto, Y. Masumoto, K. Higughi, S. Kyushin, and H. Matsumoto, J. Appl. Phys. **32**, 408 (1993).
[15] Y. Arita and Y. Sunohara, J. Electrochem. Soc. **124**, 285 (1977).