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X-ray observation of porous-silicon wetting

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High-resolution x-ray-diffraction experiments show that the lattice parameter of porous-silicon layers expands when wetted by an alcohol or an alkane. This phenomenon is nearly reversible when the alkane is removed while there is a time-dependent drift during alcohol wetting. The experimental results obtained for several alkanes and for two types of samples (p and p^+ type) reveal that the magnitude of the lattice-parameter change is correlated with the size of the nanocrystallites rather than with the nature of the alkane. We propose that the lattice expansion is due to a change of the porous-silicon surface stress induced by wetting.

INTRODUCTION

Porous silicon is obtained by electrochemical reaction of a monocrystalline silicon wafer with a concentrated hydrofluoric acid solution. In the last decade, studies on porous silicon were first concentrated on the applications of this material in the field of silicon-on-insulator technology.[1,2] More recently, the discovery of the optical properties[3–5] of porous silicon have stimulated renewed research on this material. Visible photoluminescence[3] and electroluminescence[4,5] were obtained at room temperature, on thin and highly porous-silicon layers with a porosity of 70% or more. The interpretation of these properties is based mainly on the quantum confinement of electrons and holes in nanometric-size silicon crystallites.[3,6,7] However, as this material exhibits a very high surface area (600 m^2/cm^3 for low level doping, p-type samples[2]), the surface state (structure, passivation) also plays a key role.[8,9]

Electron microscopy[10] and x-ray-diffraction experiments[11] have been performed in order to obtain a better knowledge of the structural properties of porous-silicon material. X-ray diffraction has revealed[11] that the porous-silicon layer behaves as a single crystal, in spite of its porous structure, with a small expansion of its lattice parameter with respect to that of the substrate. We have recently shown[12] in an x-ray-diffraction experiment on porous silicon, the coexistence of coherent diffraction with narrow Bragg peaks and of broad diffuse humps at the bottom of the Bragg peaks. The angular position of the former gives the value of the lattice parameter of the porous silicon layer, while from the width of the diffuse scattering pattern the average size of the crystallites can be estimated.

At the present time the most efficient electroluminescence has been obtained with a liquid electrolyte either under anodic[4] or cathodic[13] polarization for p- and n-doped materials, respectively. In such experiments it is necessary to have a complete wetting of the internal surface[14] of porous silicon. Furthermore, there are reports of quenching of the photoluminescence by organic vapor adsorption[15] and of shifts from the usual red luminescence to a green luminescence in the presence of various liquids.[16] Finally, as porous silicon is fabricated in a liquid medium, it is important to have a better knowledge of the interactions of this material with liquids (in particular during drying). In this paper, we report the observation of a reversible increase of the lattice parameter of porous silicon in the presence of various alkanes or alcohols.

EXPERIMENTAL PROCEDURES

Most of our porous-silicon layers were formed in boron-doped (p-type) silicon wafers of (001) orientation and 370-μm thickness, with a resistivity of 5 Ω cm. The electrolyte was a mixture of HF, water, and ethanol (respectively in the following proportion: 1/1/2). The wafers were etched in the dark at a current density of 20 mA/cm^2 for 10 min, which corresponds to a 10-μm thickness and a porosity of 70%. For comparison some p^+-type porous-silicon layers were also fabricated with electrochemical conditions corresponding to the same 70% porosity [resistivity 0.01 Ω cm, electrolyte with HF, water and ethanol (1/1/4), and a current density of 80 mA/cm^2 during 190 sec which also corresponds to a layer of 10-μm thickness].

X-ray-diffraction data were collected on a high-resolution x-ray apparatus (Philips Material Research Diffractometer). The Cu $K\alpha_1$ radiation of an x-ray tube was collimated with a four reflection Ge(220) monochromator. A diffraction rocking curve was obtained by rotating the sample around the ω axis perpendicular to the diffraction plane. In order to avoid the slow oxidation of porous silicon at room temperature,[9] x-ray experiments were performed within a few hours following the formation of the samples. A special cell was built for the present study, allowing *in situ* x-ray experiments to be performed during the wetting.

RESULTS

Figure 1 shows a typical x-ray rocking curve obtained for the (004) reflection on a p-type porous silicon sample of 70% porosity (plotted on a semilogarithmic scale).

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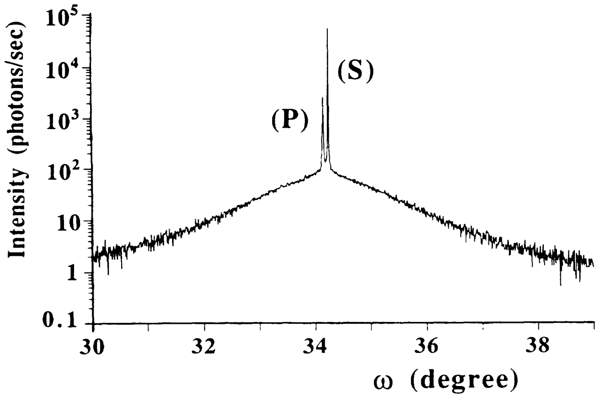

FIG. 1. X-ray rocking curve (on a semilogarithmic scale) obtained by rotation around the ω axis, for the (004) reflection of a p-type porous-silicon sample, with a porosity of 70% and a thickness of 10 μm. (S) is the substrate Bragg peak, and (P) is the porous layer Bragg peak.

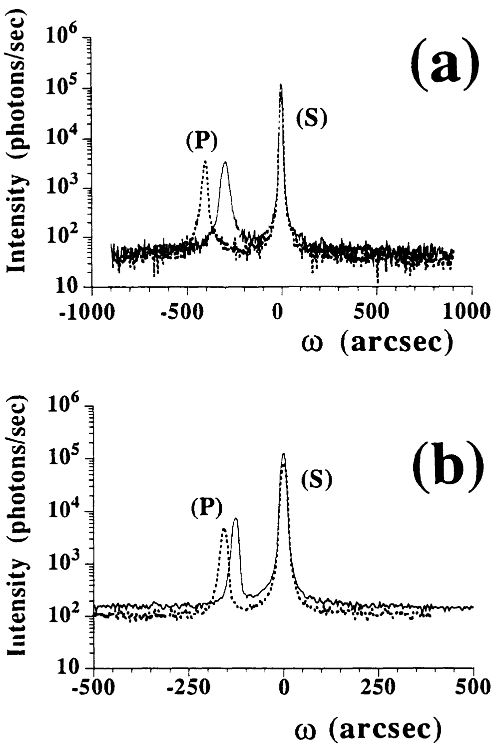

FIG. 2. X-ray rocking curve (on a semilogarithmic scale) of 70% porosity porous-silicon samples, showing lattice parameter expansions due to pentane wetting (dashed line) relative to the dry state (full line). (a) For a p-type sample. (b) For a p^+-type sample. [Note the change by a factor of 2 between ω scales of (a) and (b) figures.]

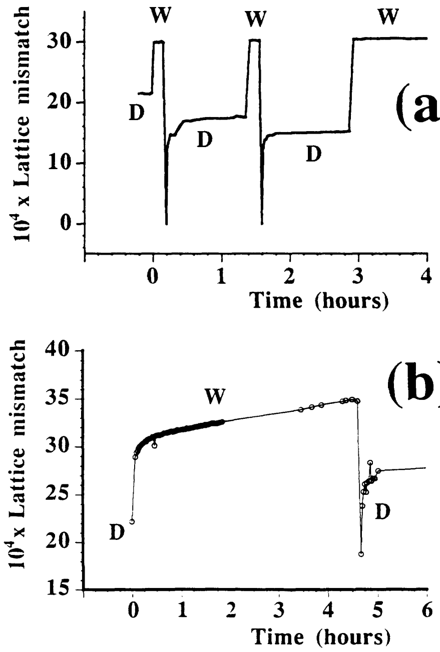

FIG. 3. Time variation of the lattice parameter expansion during wetting experiments on 70% porosity p-type samples. W, during wetting by a liquid; D, during drying; (a) in pentane, (b) in ethanol (with a different time scale).

The lattice parameter a of the porous layer, in the [001] direction, is expanded relative to the bulk silicon one, with $\Delta a/a = 21 \times 10^{-4}$. This value is about five times larger than those obtained on p^+-type samples.[11,12] At the bottom of the Bragg peaks, the broad diffuse scattering is due to the nanometric structure of the silicon crystallites.[12] Since the diffuse scattering curve has a smooth decrease, one can assume that there is no interference between the diffuse x-ray scattering from neighboring crystallites. An estimation of the diameter of the spherical crystallites can then be obtained from the value of the FWHM (full width at half maximum), using the approximate formula:[17] $\delta\omega = K\lambda/2L \cos\theta$, where $\delta\omega$ is the width of the pattern (in radian), K is a constant close to 1 (depending on the crystallite shape), $\lambda = 0.154$ nm is the x-ray wavelength, L is the diameter of the crystallites, and $\theta = 34.56°$ the Bragg angle. The width of the diffuse pattern in Fig. 1 (6000 arcsec) corresponds to a diameter of about 3.2 nm (similar to the values obtained by electron microscopy[10] and small angle x-ray scattering[18] for p materials).

When the sample is wetted by heptane, there is a shift of the porous Bragg peak, as shown in Fig. 2(a). The lattice mismatch $\Delta a/a$, for the p-type sample (of 70% porosity), increases from 21×10^{-4} (in air) to 28×10^{-4} (in heptane). A short time after the removal of the alkane (i.e., when the sample is dried), the lattice mismatch parameter is reduced to its initial value, measured before the wetting. Figure 3(a) shows the evolution of $\Delta a/a$ during successive wetting-drying cycles. The same values of lattice expansion as for pentane were observed with different alkanes on similar 70% porosity p-type samples.

Similar wetting experiments were performed on p^+ samples, where the pores have a cylindrical shape with larger diameters around 6 nm.[2,10] As shown in Fig. 2(b), a smaller lattice expansion is observed for the heptane wetting of a 70% porosity p^+-type sample which corresponds to an increase of $\Delta a/a$ from 9×10^{-4} (in air) to 11.1×10^{-4} (in alkane). Therefore the magnitude of the lattice expansion is mostly dependent on the porous silicon structural properties (shape and size of the crystallites, etc.) rather than on the nature of the alkane.

Just after the start of wetting with ethanol, the lattice expansion is the same as with pentane. However, Fig. 3(b) shows clearly that there is a time-dependent drift of $\Delta a/a$ during ethanol wetting. When the ethanol is removed (and when the sample is dried) the lattice mismatch parameter has a larger value than before wetting. This fact has also been observed with other alcohols, and could be attributed to the chemical reaction of the alcohol on the silicon surface.[19]

DISCUSSION

It is well known that the lattice parameter of porous silicon is slightly increased (by a few 10^{-4} for p^+ and a few 10^{-3} for p material) in the direction perpendicular to the substrate surface (parallel to the surface, the porous layer is coherent with the substrate and $\Delta a_{\parallel}=0$). As discussed below, this change of lattice parameter $\Delta a/a$ is probably due to the large effects of surface stress in small crystallites, an effect known to produce a contraction in small metallic particles.[21]

We now discuss the possible origin of the lattice expansion due to the wetting. From the value of the thermal expansion of silicon, an interpretation considering a temperature change of the lattice, when the alkane penetrates the layer, is not plausible. The change of the porous-silicon lattice parameter can be attributed to a modification of the surface stress of porous silicon crystallites due to liquid physisorption. This assumption is consistent with previous observations[19] of reversible changes of the silicon surface electrical resistance on contact with a methanol atmosphere.

We consider an approximate calculation of the order of magnitude of such a change of the surface stress using macroscopic thermodynamics. For a liquid, the surface stress σ is equal to the surface energy γ, and a small liquid drop of radius r is submitted to a compressive pressure ΔP given by the Laplace equation,[22] $\Delta P=2\sigma/r$. For a crystal the surface stress is a tensor σ_{ij} which is related to the (anisotropic) surface energy γ by the Shuttleworth relation[23] $\sigma_{ij}=\gamma\delta_{ij}+\partial\gamma/\partial\varepsilon_{ij}$, where δ_{ij} is the Kroneker symbol and ε_{ij} the strain tensor. As the sign and magnitude of $\partial\gamma/\partial\varepsilon_{ij}$ is arbitrary, the surface stress can be either increased or decreased and can even become negative, leading to an expansion strain. Neglecting the anisotropy for a free silicon sphere of bulk modulus $K, \delta a/a=-2\sigma/3Kr$, where $\delta a/a$ is the isotropic lattice mismatch variation due to a surface stress σ.[21] Indeed, a smaller lattice expansion is found in p^+-type porous silicon (2×10^{-4}) than in p type (7×10^{-4}), consistent with the decreasing crystallite size observed by electron microscopy[10] (assuming that the pore diameter and the crystallite size are similar, 6 nm for p^+-type and 3 nm for p-type materials). If the strain occurs only along the direction perpendicular to the layer surface (with $\delta a/a_x=\delta a/a_y=0$), one obtains $(\delta a/a)_z=(1+\nu)/(1-\nu)\delta a/a$, where ν is the Poisson coefficient.[11]

Taking the elastic constants of bulk silicon ($K=98$ GPa and $\nu=0.28$), a lattice expansion $(\delta a/a)_z=7\times10^{-4}$ would correspond (for a mean radius of silicon crystallite $r=1.6$ nm) to a surface stress value $\sigma=95$ dyn/cm. This value is intermediate between the surface stress (equal to the surface energy) of a liquid (30 dyn/cm for ethanol) and the surface stress of a crystal (in general of the order of 1000 dyn/cm).[22] Porous-silicon crystallites can be in a strain state going from completely anisotropic strains to isotropic. For low porosity materials, the porous layer is coherent with the substrate and the Bragg peak is narrow, so that the value of strain in a silicon crystallite is close to the macroscopic mean value. On the other hand, for highly porous materials (or after oxidation[20]) inhomogeneous strains are observed. In the limit of highly porous materials coherent stress will be reduced, and the strain will be more isotropic.

Although of the correct order of magnitude, the surface stress of porous silicon must be negative to give an expansion, a feature which can be attributed to the presence of SiH_x on the internal surface. The calculations of Ito *et al.*[24] show that the Si-Si distance of the H-covered silicon cluster is increased relative to the bulk value. Indeed after heating to 400 °C, which produces hydrogen desorption, a contraction of the lattice parameter is observed.[25] On the other hand, silicon surface oxidation produces the expansion observed during the growth of native or anodic oxides.[20] Clearly more studies are needed to understand the microscopic origin of porous-silicon lattice parameter variations. One can recall that volume expansion of other porous materials (charcoal, porous silica) has been observed after vapor adsorptions.[26] To go further with porous silicon, a better knowledge of the geometry and surface properties of the pores would be necessary.

Finally, during the removal of the alkane (or alcohol), the lattice mismatch during a few minutes shows a transient with lower values of $\Delta a/a$ (Fig. 3). This evolution is observed for a shorter time when the sample is heated. This can be attributed to the presence of capillary forces during the drying of the porous silicon samples, which leads to a breaking of highly porous samples.[27]

CONCLUSION

With high-resolution x-ray-diffraction experiments, a stable increase of the lattice parameter of porous silicon has been observed when the sample is immersed in an alkane. This phenomenon is reversible when the alkane is removed, and further wetting leads to the same effect. Our interpretation is based on a change of the surface stress of silicon crystallites in contact with the alkane, probably due to the physisorption of alkane at the porous-silicon surface. The magnitude of the lattice change is mostly due to a size effect of the nanocrystallites (as shown by the difference between p- and p^+-type samples) rather than to the composition of the alkane. For wetting with an alcohol, a time-dependent drift of the lattice parameter is observed during wetting. While for a short time the lattice expansion is the same as with an alkane, for longer time in the alcohol an irreversible increase of the lattice is observed probably due to a chemisorption. A correlation between lattice variations and optical properties has been observed for alkane and alcohol wetting.[28]

These observations lead to the conclusion that high-resolution x-ray diffraction is a very accurate and suitable *in situ* technique to investigate the variations of the structural properties of porous silicon.

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