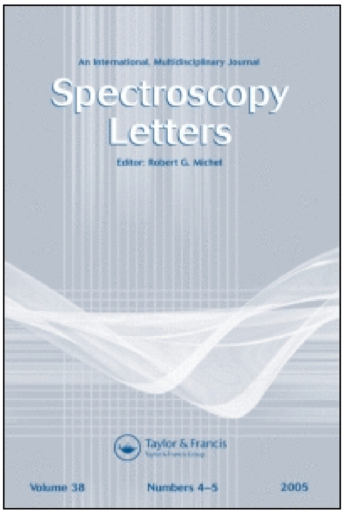

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Investigation of Porous Silicon Wetting by Raman Scattering

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ABSTRACT Wetting phenomena in porous silicon layers are experimentally investigated by Raman scattering. The experimental results show a reversible blue-shift of Raman spectra of wetted porous silicon layers with respect to the unperturbed layers. We ascribe the shift to a compressive stress due to the increased lattice mismatch between the porous silicon layer and the bulk silicon substrate in wetting conditions.

KEYWORDS porous silicon, Raman scattering, wetting phenomena

INTRODUCTION

The behavior of a fluid confined in mesoporous media, which exhibits pore size in the range 2–50 nm, still arouses a great interest because it concerns materials that could have a lot of applications.[1] Besides, from a fundamental point of view, the study of adsorption and condensation processes allow one to get information about the microscopic structure and composition of porous materials.[2,3] Porous silicon (PS) is a material of great interest for the study of fluid–solid interfacial phenomena where the adsorption and wetting phenomena are due to molecular interactions between a fluid and an adsorbent, which is usually considered to be rigid.[4] However, the adsorbent also experiences the action of the molecular forces, causing substrate deformations, as indeed has been revealed by observations of strains induced by adsorption and wetting process [see Ref. 4 and references therein].

For an as-formed PS sample, strain depends on various parameters, the most important being porosity of the PS layer and the type and the level of doping of the silicon substrate. The PS lattice parameter is slightly expanded in a direction perpendicular to the surface, whereas in a direction parallel to the surface, the porous layer has the same lattice parameter as the substrate.[4,5] Because of lattice mismatch with bulk Si, a porous silicon layer is expected to be under compressive stress when attached to Si substrate.[6]

The high specific area and the great reactivity of PS layer allow its use as a basis for the detection of vapors and liquids.[4,7] In fact, because of the large internal surface, the strain is very sensitive to oxidation, to the presence of a fluid, or to impregnation with various substances. Because the pores are in the nanometer range, the presence of any fluid inside the pore network leads to a lattice variation detectable, for example, by X-ray diffraction.[4,5,7]

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A small increase of strain is observed when a p$^+$-type porous silicon layer is filled with a liquid,[7] whereas for vapor adsorption, a small decrease of strain has been observed when capillary condensation occurs in the pores.[4] After evaporation, these effects are usually reversible.

On the other hand, strains and stress produce a modification of the vibrational properties of the materials, which can be observed by Raman scattering. Compressive stress results in the shift of the position of the Raman peak toward higher cm^{-1} (commonly called *blue shift*), whereas tensile stress results in a shift toward lower cm^{-1} (*red shift*). On this line of argument, in this paper the modifications induced in porous silicon by wetting phenomena are investigated by Raman spectroscopy. It is well-known that the position of the Raman peak is the result of a competition between confinement effects,[8,9] which cause a red shift of the peak position with respect to bulk Si, and compressive stress,[6] induced by lattice mismatch with Si substrate, which causes a blue shift of the peak. Top-surfaces Raman studies on porous silicon films have found phonon frequency shift due to strain.[10] Cross-sectional micro-Raman studies report a compressive stress at the interface with the substrate, which can be directly attributed to the lattice mismatch.[11–13] Of course, in order to study wetting phenomena, only top-surfaces Raman studies are feasible. In this paper, several Raman spectra measured on unperturbed PS layers and in PS layers wetted by isopropanol or ethanol have been compared. A reversible blue shift of the PS Raman peak was observed in all spectra measured in wetting conditions, due to compressive stress induced by wetting in porous silicon.

MATERIALS AND METHODS

In our experiments, a porous silicon monolayer obtained by electrochemical etching on p$^+$-type ($\rho = 8$ to $12\,\mathrm{m}\Omega$ cm) standard silicon wafer (001) is used.[14] The PS sample thickness is 20 μm, and its porosity is 70%. The excitation source was a Coherent Innova 70 Ar$^+$ laser, operating at 514.5 nm wavelength.

In order to prevent the laser damaging of the sample, the laser power was maintained at 2 mW at the sample surface. Using a 50× objective having long focal distance, the laser beam was focused to a diameter of a few micrometers. Unpolarized Raman spectra were detected, at room temperature, in back-scattering geomerty using a Jobin Yvon Raman U1000 double monochromator, equippped with an Olympus BX40 microscope for micro-Raman sampling and an electrically cooled Hamamatsu R943-02 photomultiplier for photon-counting detection. As a preliminary measurement, the Raman spectrum of crystalline silicon was recorded. A Lorentzian line centered at 521.4 cm^{-1} having FWHM of approximately 4.4 cm^{-1} was obtained.

RESULTS AND DISCUSSION

In order to investigate wetting phenomena, unperturbed porous silicon layers and porous silicon layers wetted by isopropanol or ethanol were characterized by Raman scattering. We noted that porous silicon layer was closed in a small glass vial, in which a remarkable amount of liquid was added. Therefore, even if a small quantity of liquid evaporated because its vapors quickly saturated the atmosphere surrounding the sample, the porous silicon layer was wetted by immersion during the entire acquisition of Raman spectra. A significant number of measurements was carried out, and the fitting of experimental data was obtained according to the phonon confinement model.[8,9]

For unperturbed porous silicon layers, the mean value of Raman peak is 519.4 cm^{-1} and the standard deviation is approximately 0.1 cm^{-1}. In Fig. 1, an example of experimental data and the result of the fitting procedure for an unperturbed PS layer are shown. According to the model of Campbell and Fauchet, the theoretical value of Raman peak is $\omega_{\mathrm{th}} = 519.8\,\mathrm{cm}^{-1}$ and the estimated dot size L is approximately 6.0 nm.

Yang et al.[10] have shown that experimental results, obtained by Raman scattering study of PS, could only be explained by adding a built-in strain to the phonon confinement effect. In this regard, to estimate the built-in strain in PS, these authors proposed the following relationship, which gives an estimation of the strain by measuring the difference of the Raman peak positions at a specific linewidth:

$$\frac{\omega_{PS} - \omega_{th}}{\omega_0} = -3\rho \frac{a_{PS} - a_0}{a_0} \tag{1}$$

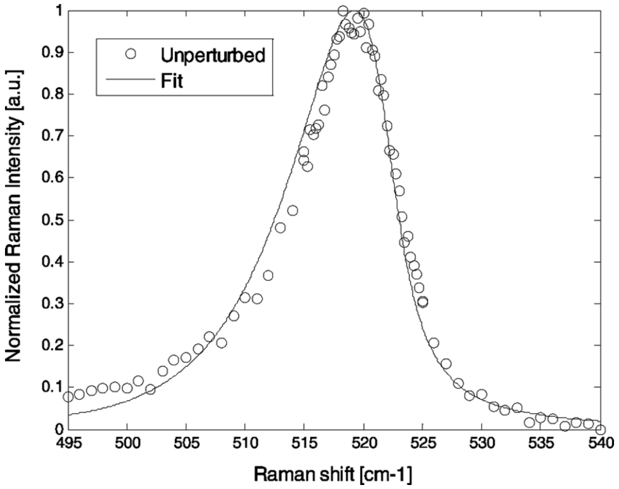

FIGURE 1 Raman spectrum registered on a PS layer in unperturbed conditions (○). The fit of the data is also reported (solid line).

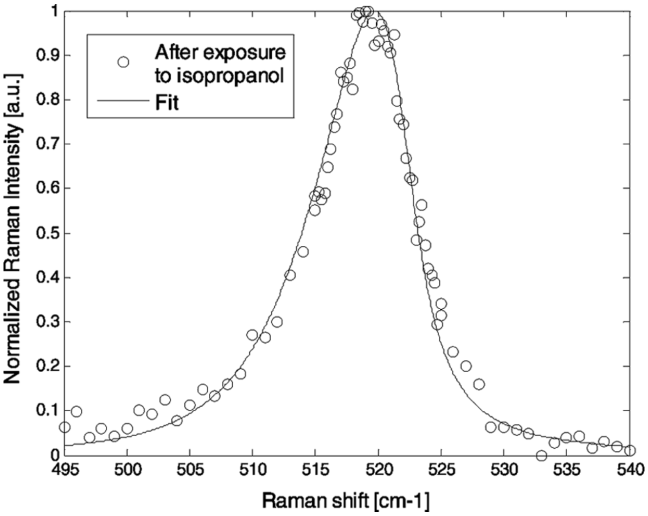

FIGURE 2 Raman spectrum registered on a PS layer after wetting by isopropanol (○). The fit of the data is also reported (solid line).

In this relation, ω_{PS} is the position of the measured porous silicon Raman peak, ω_{th} is the corresponding theoretical value estimated accordingly to the phonon confinement model,[8,9] ω_0 is the Raman peak in c-Si ($\omega_0 = 521.4\,\mathrm{cm}^{-1}$), a_{PS} and a_0 are the lattice constants of PS layer and bulk Si crystal, respectively, and ρ is the Grüneisen constant ($\rho \approx 1$). The built-in strain in PS calculated using Eq. (1) is 2.2×10^{-4}, which is fairly in agreement with literature results.[10]

Afterwards, aiming at studying the influence of wetting, the PS layer was wetted by liquid solutions of isopropanol or ethanol. In the first case, the Raman peak position has showed a mean value of $519.8\,\mathrm{cm}^{-1}$ and a standard deviation of approximately $0.1\,\mathrm{cm}^{-1}$. Therefore, a blue shift of $0.4\,\mathrm{cm}^{-1}$ of the Raman peak with respect to the unperturbed PS layer is observed. This shift disappears when isopropanol completely evaporates and unperturbed conditions are restored. An example of Raman spectrum and fitting of experimental results obtained wetting porous silicon layer by isopropanol are shown in Fig. 2.

Because of similar values of density and surface tension of isopropanol and ethanol, the effect on the porous silicon layer induced by wetting with both liquids is expected to be quite comparable. In fact, the mean value of the Raman peak position obtained in case of wetting with ethanol is $519.9\,\mathrm{cm}^{-1}$ and the standard deviation is $0.2\,\mathrm{cm}^{-1}$. Therefore a blue shift of $0.5\,\mathrm{cm}^{-1}$ with respect to the unperturbed PS layer is obtained and also confirmed the reversible effect. An example of Raman spectrum and fitting of experimental results obtained wetting PS sample by ethanol are shown in Fig. 3. In Table 1, the peak position, the standard deviation, and the shift are reported for each case.

It is worth noting that the analysis of the experimental data presented in this work has been performed not only with the model of Campbell and Fauchet but also with a more common fitting procedure by means of a commercially available software, using two Gaussian curves centered at approximately $514\,\mathrm{cm}^{-1}$ and $519.5\,\mathrm{cm}^{-1}$. The use of two bands is imposed by the asymmetry of the PS Raman peak. Bands at approximately the same wavenumber shifts have already been used by other

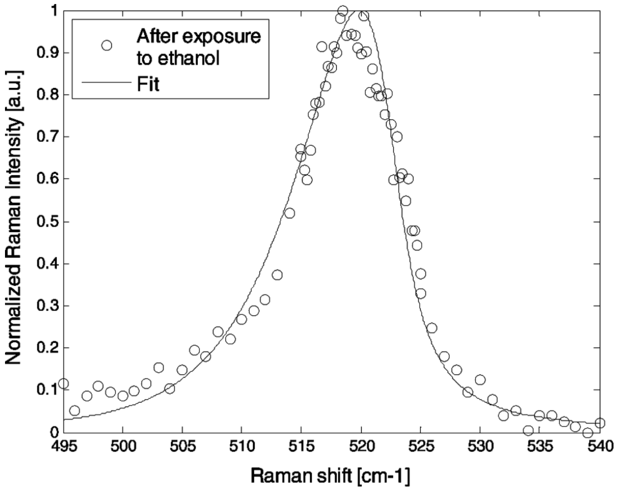

FIGURE 3 Raman spectrum registered on a PS layer after wetting by ethanol (○). The fit of the data is also reported (solid line).

TABLE 1 **Experimental Results in Wetting Conditions**

Case	Mean (cm^{-1})	σ (cm^{-1})	Shift (cm^{-1})
Unperturbed	519.4	0.1	—
After exposure to isopropanol	519.8	0.1	0.4
After exposure to ethanol	519.9	0.2	0.5

authors.[11] We have observed, after the wetting with isopropanol or ethanol, that the component at approximately 519.5 cm^{-1} shows a weak blue shift, whereas the component at approximately 514 cm^{-1} sensitively shifts toward higher wavenumbers. The mean shift of the component at 514 cm^{-1} is approximately 3 cm^{-1}, which is sensitively higher than the global shift obtained with the model of Campbell and Fauchet, which regards the whole lineshape. The blue shift of the 514 cm^{-1} component results in a more symmetric shape of the whole Raman spectrum of porous silicon measured in wetting conditions.

In summary, in the current work, micro-Raman spectroscopy and the spatial correlation model[8,9] were used to observe and separate structural and strain effects in as-formed porous silicon samples and PS layer wetted with isopropanol or ethanol. In as-formed porous silicon samples, as expected, a shift of the Raman peak and a broadening of the Raman spectra with respect to c-Si is obtained. According to the spatial correlation model, we estimated that PS layer could be formed by quantum dots whose size is approximately 6.0 nm. An additional red shift of the Raman peak, obtained by our experimental results with respect to the spatial correlation model, was explained, according to Ref. [10], by adding a built-in strain to the phonon confinement effect. According to previous results reported in literature,[4,5] a reasonable small expansion of the porous layer lattice parameter of a few 10^{-4} was estimated. Regarding wetting, we observed a reversible blue shift when the PS layer was wetted with isopropanol or ethanol, indicating the presence of a compressive stress. The use of two liquids having quite similar density and surface tension, as expected, showed quite comparable blue shift.

Regarding our results, we note that the additional red shift of Raman peak, obtained for as-formed PS layer stored in air with respect to the spatial correlation model, can be attributed to the growth of a native oxide after aging in air at room temperature.[4,5,7] Regarding wetting, the measured compressive strain, according to results obtained by X-ray,[7] can be attributed to lattice expansions due to a change of the porous silicon surface stress induced by wetting. The variation of surface stress can be explained by the liquids confined inside the nanopores and exercising compression of the nanocrystallites. Moreover, we note that our results, obtained by wetting with ethanol, agree with those shown in Ref. 15. However, we provided further information. In fact, in our article, Raman spectra measured on PS layers wetted by isopropanol or ethanol have been compared. We prove that due to similar values of density and surface tension of isopropanol and ethanol, the effects on the porous silicon layer induced by wetting with both liquids are quite comparable.

Before concluding, we point out that the aim of the study was not to give a further contribution to basic physics of wetting phenomena, but rather to elucidate a simple mechanism that could be useful in sensing devices.

CONCLUSIONS

In conclusion, in this article an investigation of wetting phenomena in PS layers is presented. Moreover, a simple method to individuate for example the presence or not of a liquid is also suggested. Unfortunately, the shift of Raman peak is very small, and this could be a disadvantage for sensing application. Work is in progress to try to get a greater shift of Raman peak in wetting phenomena on samples having the same or higher porosity and/or different thickness. Another important aspect for sensing applications is to consider liquid with different surface tension in order to investigate if it could be possible to distinguish different liquids.

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