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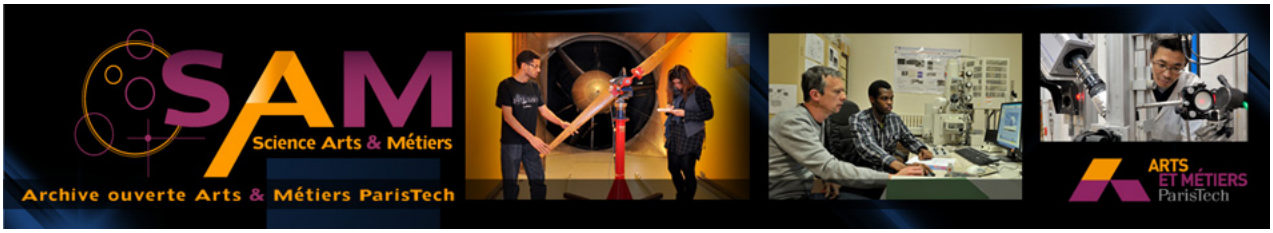

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Vickers Microhardness of Oxidized and Nonoxidized Porous Silicon

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***Abstract*— In this work we present our recent investigation on characterizing mechanical properties of porous silicon (PS) by using instrumented micro-indentation. Hardness and elastic modulus for oxidized and nonoxidized PS were measured. Experimental results revealed that hardness and elastic modulus are significantly lower than that of silicon substrate and decrease with increasing porosities. After oxidation an increase of the hardness and elastic modulus were observed. The task of stabilization of PS mechanical parameters can be solved with the help of oxidation.**

***Keywords*— Vickers indentation, Microhardness, Elastic modulus, Porous silicon, Oxidation**

I. Introduction

The evolution of micro-electronics took place thanks to the development of the semi conductors among which one finds silicon. Silicon quickly was imposed like material impossible to circumvent: it offers many advantages (low costs, good controls), which lead to its use in 95% of modern micro-electronics. Since the discovery of the intense photoluminescence of porous silicon, many studies developed in the world for its use in varied applications. In particular, porous silicon has been investigated extensively as a possible candidate for developing light emitting, photonics, optoelectronics [1-4] and biophotonic [5] devices.

Porous silicon, with its crystalline nanoporous structure, is presented in the form of a material original, able to emit light, but able also to be used as matrix of reception with many liquid materials, amorphous solids or crystalline lens,… a large variety of devices is thus possible to be realized. All these ambitions are of course closely related to problems of structural behavior. The behavior of porous silicon changes according to its conditions of preparation related to its use in various fields.

Freshly made PS is known to be unstable, showing considerable ageing effects that limit its use in practical applications. Porous silicon (PS) layers with high porosity are of great interest; unfortunately, this material was found to be mechanically unstable during drying. Capillary forces have been invoked to explain such cracking [6].

One way to stabilize the PS layers is by thermal oxidation. The common explanation for the improved stability in oxidized PS is a replacement of the hydrogen coverage of the pore walls by more stable layers of silicon dioxide [7]. The study of the mechanical properties of PS is thus very important in order to better apprehend the mechanical resistance of the devices.

In this work we present our recent investigation on characterizing mechanical properties of the (PS) layers. The Hardness and elastic modulus for oxidized and nonoxidized PS were measured.

II. Experimentation

A. Sample preparation

Porous silicon layers were obtained by anodization of a (100) oriented monocristalline p+ silicon wafer with (4- 6 mΩcm) resistivity in a hydrofluoric acid/ethanol electrolyte. The electrolyte was composed of HF (50%): H_2O: ethanol (2:1:2). Anodization was performed at room temperature in the dark and under galvanostatic conditions. The applied current

density was ranging from 50 to100 $mAcm^{-2}$ in order to obtain various porosities. The porosity of the obtained layers was measured from gravimetric measurement [8].
After etching, the samples were cleaned with de-ionized water, dried and stored in ambient air at room temperature.

Some of as prepared samples were oxidized in order to obtain porous silica At first, samples were pre-oxidized at 300°C for one hour following by an oxidation step at 900°C in wet O_2 for one hour . Their morphology was studied by Scanning Electron Microscopy (SEM).

B. Microindentation tests

The microhardness measurements were performed with a micro-indenter Fischerscope H100 XYp (maximum load of 1 N, load resolution of 0.02 mN, depth resolution of 2 nm) at ambient laboratory conditions. Indentation consists in continuously applying a load to a specimen via a sharp Vickers pyramid indenter and to continuously monitor the depth of penetration in the sample. This leads to the following expression for hardness [9]:

$$HV = 1.8544(P_L / d^2) \quad (1)$$

Where d (mm) is the mean diagonal length of the diamond shaped indent and P_L is the applied load.

We also measured the Martens hardness, HM by the following equation:

$$HM = \frac{P_{\max}}{26.43\, h^2} \quad (2)$$

Where h is the indentation depth and $P_{\max}$ the maximum applied load.

The hardness is defined as the indentation load divided by the projected contact area and the elastic modulus can be calculated based on the relationship developed by Oliver et Pharr [10]. The so-called reduced modulus (E_r) was derived by:

$$S = 2\beta\sqrt{\frac{A}{\pi}}E_r \quad (3)$$

Where A is the projected contact area of the indenter with the sample surface, $\beta = 1.012$ for Vickers' indenter, S the contact stiffness and E_r is the reduced modulus which is calculated from:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (4)$$

E and ν are the elastic modulus and Poisson's ratio of the sample and E_i (1140 GPa) and ν_i (0.07) are the elastic properties of the diamond indenter, respectively.

III. Results and Discussion

The surface of the PS samples was observed under a Scanning Electron Microscopy (SEM), a JEOL JMS 6500F and a HITACHI 2460N with variable pressure.
For the completely oxidized samples one supposes that the matrix is entirely made up of oxide silicon (SiO_2). Micrographies not having been taken directly after formation of porous film, part of the phase stamps was oxidized with the ambient air.

The etching direction is from top to bottom, PS has been classified depending on the size of micropores as microporous (< 5 nm), mesoporous (5-50 nm) and macroporous (> 50nm) [8]. Figure 1 shows SEM pictures of the top surface of the 60% porosity p+-type PS layer (a) and à 80% porosity (b). These micrographs allowed the size and density of pores to be estimated [11]. It could be seen that the porous layer was composed of a pore network separate by silicon crystallites and pore size varied from 7 to 30 nm revealed mesoporous layers. In figure 2 we can see that after oxidation the pore shape is conserved in spite of size reduction. It shows the SEM pictures of the top surface of the 60% (a) and a 80% (b) porosity of the p+-type oxidized porous silicon layer.

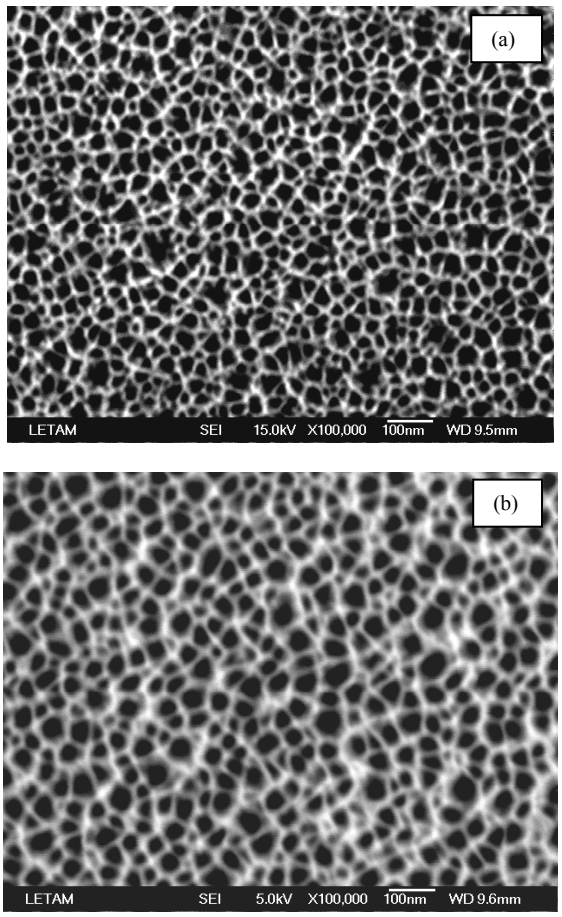


Fig.1 SEM micrographs of the top surface of 60% (a) and 80% (b) the initial porosities, 5 μm thick PS film.

A cross section in figure 3 shows an anisotropic microstructure: the pores are perpendicular to the surface of the silicon substrate and were considered as cylindrical with numerous side branches which have almost the same size as the pore mean diameter. The thickness of the sample can be estimated to 5µm.

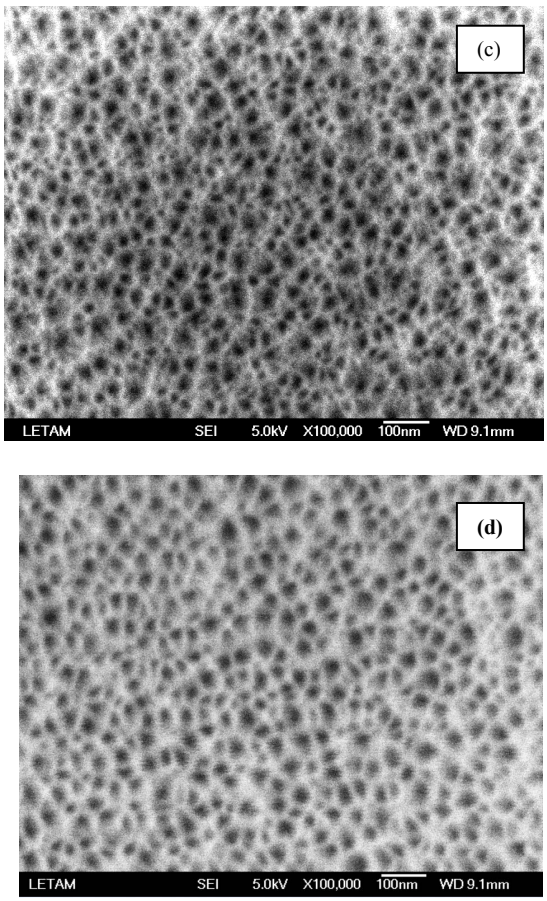


Fig.2 SEM micrographs of the top surface of 60% (c) and 80% (d) initial porosities, 5 µm thick oxidized PS film

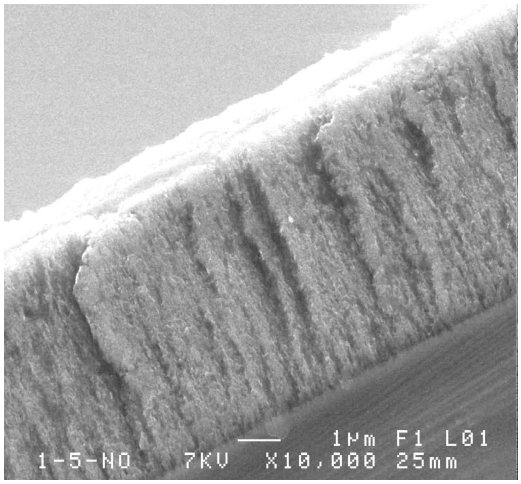


Fig.3 SEM micrograph of the cross section of the 5 µm thick PS film. The porosity was initially about 60%.

Mechanical properties of nonoxidized (NO) and oxidized (O) porous silicon layers 5 µm-thick (t) for an applied load of F=500 nm/20s according to the indentation dept h with $h<t/10$ for ten indentation per sample were summarized in table 1.

A. Elastic modulus

The influence of the substrate is important at penetration depth h > 10% of the film thickness [12]. Elastic modulus changes with the relative penetration depth, indicating that the indenter deforms not only the film but also the substrate, and the substrate influence is more pronounced at higher loads. Fig. 4 shows the influence of the indentation load on the measured elastic moduli for ten indentations.

Reduced modulus of PS5NO was found to be between 15 and 45.50 GPa. The Elastic modulus tends to increase with increasing applied load exhibiting significant dependence on the indentation load. The measures revealed that as the indentation depth (511 nm, 2840 nm and 6728 nm) increases the elastic modulus increases gradually.

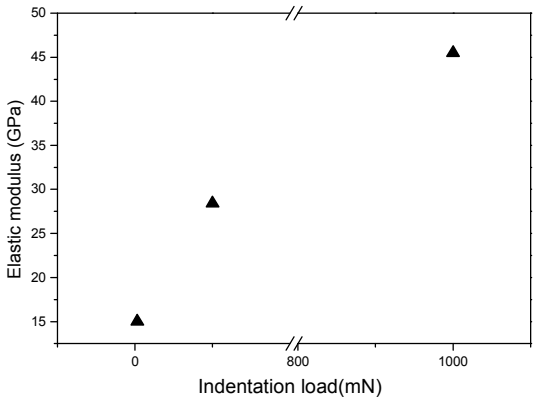


Fig. 4 Elastic modulus as a function of indentation load for PS5NO of 80% porosity.

As shown in table 1, all the results confirm a decrease of the elastic properties in function of the porosity for both oxidized and nonoxidized PS layers; 24.68 GPa and 14.98 GPa for a 60% and 80% porosity, 37.56 GPa and 21.39 GPa for oxidized PS. The measured elastic modulus is found to be drastically dependent on the porosity and is lower than those of the Si substrate where the value measured with a maximum load of 1mN is 130.35 GPa ±12.4 %.

For oxidized porous silicon some part of the Si "skeleton'' x has been oxidized and transformed into SiO_2, occupying volume 2.27x [13] (Bonding of silicon with oxygen produces a 2.27 time volume rise of the solid skeleton). Thus, Si volumetric fraction after oxidation will be f- x, and that of pores will be $P = 1-(f-x)-2.27x$, f is considered as the silicon volumetric fraction. For the PS nonoxidized $f = 1-P_{in}$ with P_{in} the initial porosity before oxidation.

TABLE I
Hardness, elastic modulus, and initial porosity for porous silicon

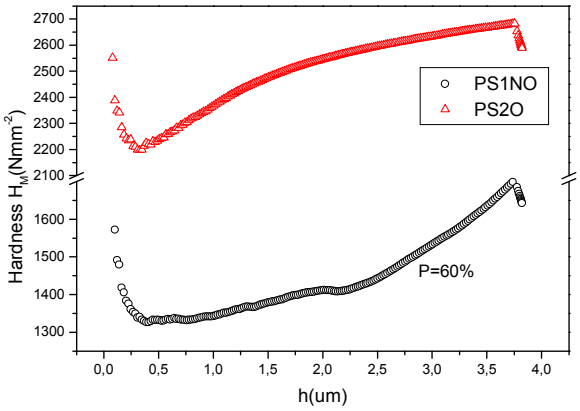
Sample	P_{in} (%)	H_M (GPa)	H_{IT} (GPa)	H_V (Kgfmm^{-2})	$E/(1-\nu^2)$ (GPa)
PS1NO	60	1025.95±2.91	1573.38±4.27	148.68±4.27	24.68±1.23
PS2O	60	2150.99±2.08	4510.19±2.35	426.21±2.35	37.56±2.04
PS5NO	80	448.76±5.13	590.66±6.06	55.82±6.06	14.98±3.49
PS6O	80	913.39±2.19	1404.98±2.76	132.77±2.76	21.39±1.03

It is then clear that elastic modulus for oxidized PS was found to be greater than that of nonoxidized porous silicon. PS is used as a host matrix by infiltrating pores with solids and liquids, as semiconductors, polymers or several organic molecules. S.P. Duttagupta [14] studied microhardness of PS films of different porosities, by infiltrating the pores with polymers. An increase in the hardness was observed without affecting photoluminescence (PL) intensity.
In our case, pores are filled with SiO_2 then, the task of stabilization of PS mechanical parameters can be solved thanks to the oxidation step.

B. Hardness

Fig. 5 shows the influence of the indentation depth on the hardness of oxidized and nonoxidized PS film at higher load (1000 mN) to confirm the ISE.

The measured hardness increases with increasing indentation depth. The "u-shaped" profile observed here is typically observed in the mechanical properties of low-dielectric-constant films [15, 16]. The First region is due probably at a cap layer formed on the surface by the natural oxidation; the second region shows the effect of the Si substrate. Clearly, the Hardness decreases with increasing porosity and an improvement of the mechanical properties is allowed with the oxidation as shown in figure 5. The measured hardness is found to be drastically dependent on the porosity and is lower than those of the Si substrate where the value measured with a maximum load of 1mN is 1374.44 Kgfmm $^{-2}$ ± 25.13% (13.74 GPa).



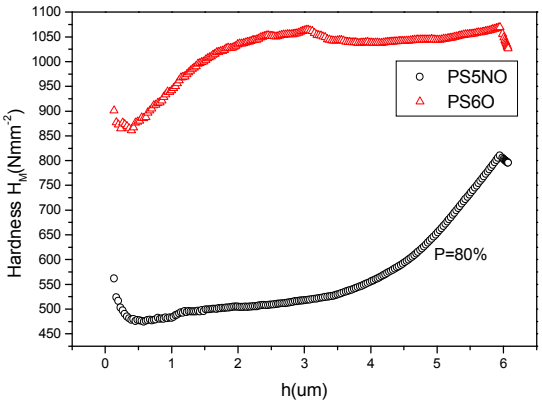
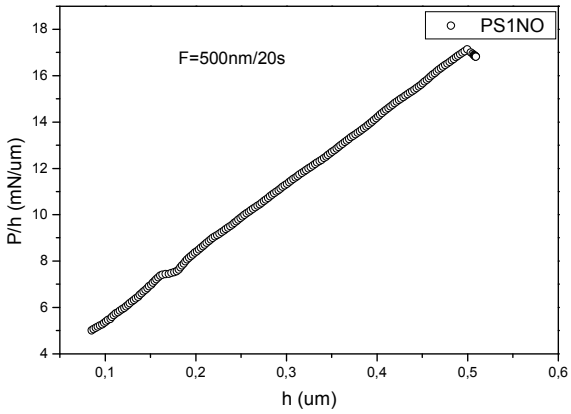


Fig. 5 Hardness HM of oxidized and nonoxidized PS film at higher load (1000 mN)

Figure 6 shows the load / indentation depth (*P/h*) versus indentation depth (*h*) curves. The relation between *P/h* and *h* should be linear if the material is homogeneous with a constant slop [17, 18]. However, this linear relation will change if the material under indentation changes.



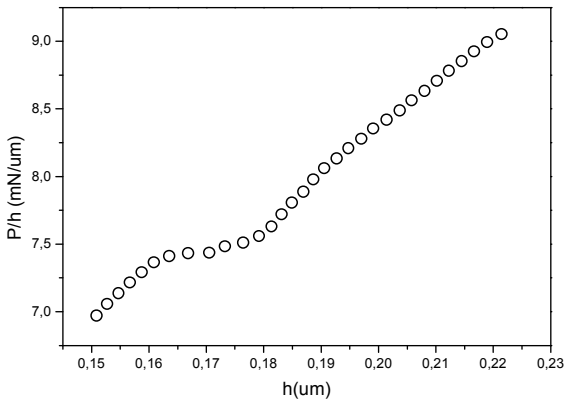
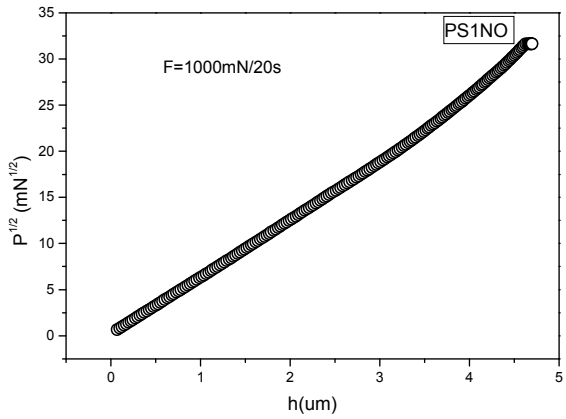


Fig. 6 Load indentation depth (P/h) versus indentation depth of the 5µm thick PS1NO film

In Figure 6 there is a sudden transition of the slop around the change indicating the presence of the contamination with natural oxidation.

Figure 7 reveals a good linearity especially for the oxidized porous film at high load for the square of the load $\sqrt{P}$ [18] versus indentation depth curves. This result proves that the indentation load / size effect on hardness exists in the applied load range [17].



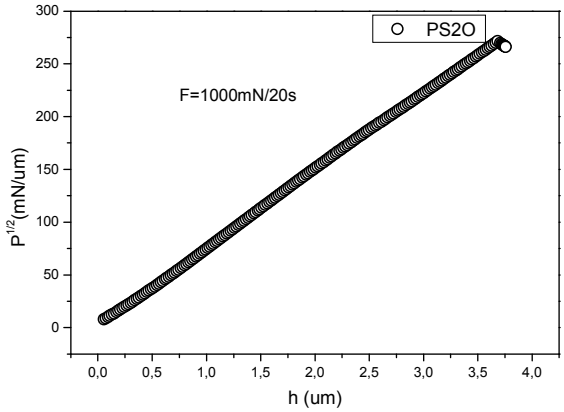


Fig.7 Load indentation depth $\sqrt{P}$ versus indentation depth of the 5µm thick PS1NO and PS2O film

IV. CONCLUSIONS

The mechanical properties of porous silicon of 60% and 80% initial porosities, 5 µm thick oxidized and nonoxidized films are measured.

The porosity plays an important role in affecting the mechanical properties as well as the surface morphology of PS films.

Hardness and elastic modulus changes with the relative penetration depth .

The measured hardness is found to be drastically dependent on the porosity and is lower than those of the nonporous Si.

Elastic modulus and hardness for oxidized PS were found to be greater than that of nonoxidized porous silicon.

The linearity of *P/h* versus *h* can be used as an indication of characterization of the mechanical deformation of the porous film. The task of stabilization of PS mechanical parameters can be solved thanks to the oxidation.

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