

Characterisation of the porous silicon layers

Z. Fekih, F. Z. Otmani, N. Ghellai, N. E. Chabanne-Sari

*Unit of research of Materials and renewable Energies (U.R.M.E.R)
University Abou - Baker Belkaid B.p: 119 TLEMCEN 13000 ALGERIA
Tel/Fax: 043. 21. 58. 90 & 89*

Porous silicon (PS) is obtained by anodic attack of single-crystal silicon in concentrated hydrofluoric acid solution. All the properties of the porous silicon layer, such as porosity, the thickness and the diameter of the pores depend in a critical way of the anodization parameters.

This present work aims to study the evolution of the porous silicon various properties according to the anodization parameters. Also we are interested in the various experimental aspects intervening in manufacture and the characterization of the thin layers of porous silicon by gravimetry and ellipsometry.

Key words: Porous silicon, anodization, ellipsometry, porosity.

I. INTRODUCTION

In 1990 it was observed that porous silicon could at ambient temperature emit light in the visible [1]. This discovery has started again the totality of research on this material which is however known for more than 40 years [2].

I.1. How porous silicon is made?

PS is formed by an electrochemical etching of Si in an HF solution. Following an electrochemical reaction occurring at the Si surface a partial dissolution of Si settles in [2]. The simplest electrochemical cell is a Teflon beaker (Fig. 1) [3]. In this cell, the Si wafer is placed on a metal disk and sealed through an O-ring, so that only the front side of the sample is exposed to the electrolyte. When an Si wafer with high resistivity (i.e. more than a few $\text{m}\Omega/\text{cm}$) is used, a high dose implantation on the back surface of the wafer is required to improve the electrical contact between the wafer and the metal disk. This step is crucial to get later homogeneity in the PS layer. This cell is the most widely used because it leads to uniform PS layers, allows an easy control of both porosity and thickness, and it is suitable for front side illumination of the sample during the attach.

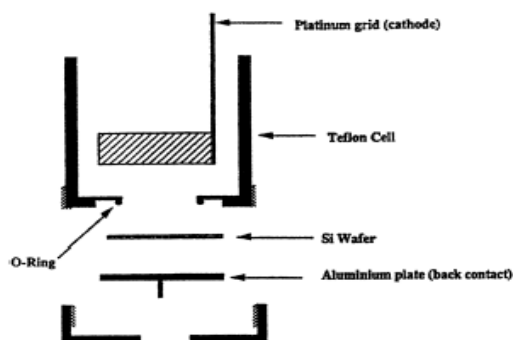


FIGURE. 1: Cross-sectional view of a single-tank anodization cell [3].

I.2. EFFECT OF ANODIZATION CONDITIONS

All the properties of PS, such as porosity, thickness, pore diameter and microstructure, depend on anodization conditions. These conditions include:

- wafer type and resistivity,
- HF concentration,
- current density,
- the illumination,
- the temperature,
- the anodization duration.

II. CHARACTERISTICS OF THE POROUS LAYERS

II.1. Porosity

According to G. Léron del and al. [4], porosity is defined as the fraction of void within the PS layer and can be easily determined by weight measurements.

This macroscopic characteristic can be measured by gravimetry, preferably on thick layers. The accessible porous silicon values typically included between 15 and 90 % [4]. It is significant to note that porosity is an average value and that for the same porosity; various material morphologies can be obtained [5].

We control the porosity of material by the formation parameters of the pores: concentration of hydrofluoric acid, current density, the type and resistivity of silicon [1]. It will be retained that it increases when the density of current increases or when the HF concentration decreases [6, 5]. For a resistivity of silicon ranging between $0,01$ to $1\,\Omega.\text{cm}$, the characteristic current voltage is mainly fixed by the rate of electrolytes in the solution. The characteristic is unstable and depends on the process time. When the resistivity of silicon exceeds $1,5\,\Omega.\text{cm}$, it is mainly the resistance of

the wafer which determines the characteristic current voltage that remains then very stable [6, 7].

Figure (2) shows the variation of porosity according to the current density and the electrolytic concentration for porous silicon samples of type p ($\sim 1 \Omega \cdot \text{cm}$) and type p⁺ ($\sim 0.01 \Omega \cdot \text{cm}$).

For a given HF concentration the porosity increases with increasing current density. For fixed current density, the porosity decreases with HF concentration (see Fig. 2). [8]

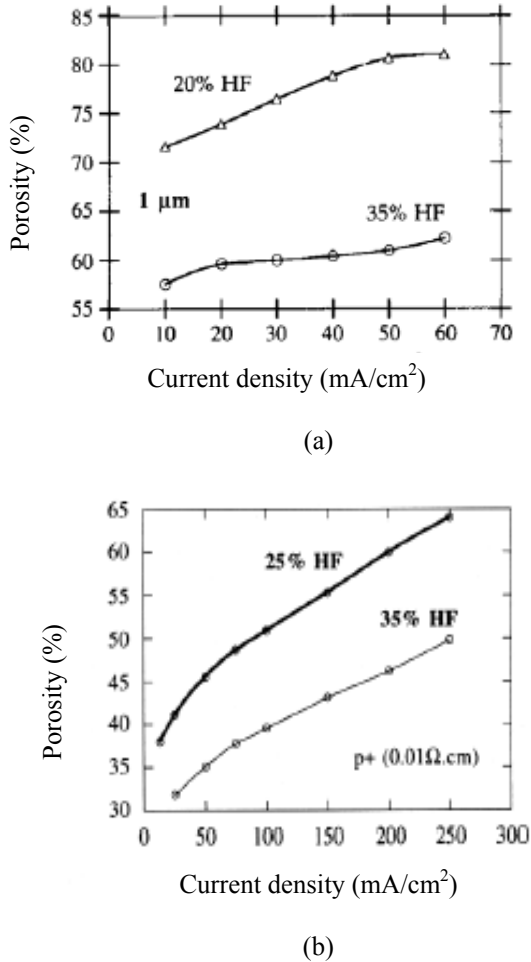


FIGURE. 2: Porosity as a function of current densities for two different types of silicon substrate: p-type (a) and p⁺-type (b) [8].

Thus, for the given anodization conditions (current density, HF concentration) measured porosity is larger for thicker layers. This effect is shown on the Figure (3): the thicker layer has

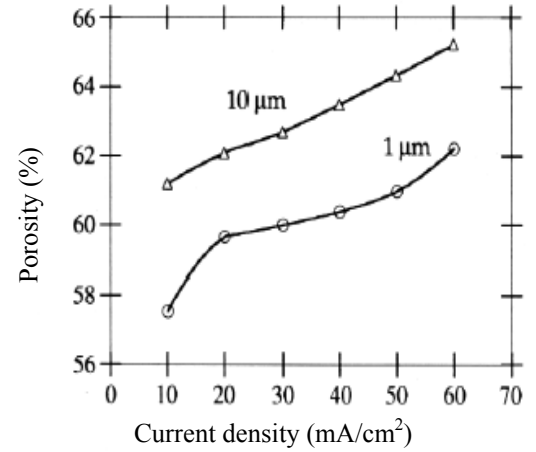


FIGURE. 3: Porosity as a function of current densities for two different thicknesses (1 μm and 10 μm) from the layer, 35 % HF concentration, P-type silicon substrate.

II.1.1. Measure of porosity by gravimetry

The relation (1) makes it possible to obtain porosity knowing the mass of the sample before and after anodization (m_1 and m_2 , respectively) as well as the mass after total dissolution of the porous layer in the weld (m_3)[10]:

$$p = \frac{m_1 - m_2}{m_1 - m_3} \quad (1)$$

It is clear, according to the above formulae, that for having a precise measurement by gravimetry, it is necessary to use the thickest samples possible.

II.1.2. Measure of porosity by ellipsometry

The Bruggman model gives us the relation binding the dielectric function ϵ_i and the percentage in occupied volume p_i by the various constituent bodies' materials:

$$\sum_i p_i \frac{\epsilon_i - \epsilon_{eff}}{\epsilon_i + 2\epsilon_{eff}} = 0 \quad \text{avec} \quad \sum_i p_i = 1 \quad (2)$$

With P_i : average percentage in volume occupied in material by body i

ϵ_i : dielectric function of component i and

ϵ_{eff} : effective dielectric function .

By considering a mixture of component air-silicon we obtain the following relation :

$$(1 - p) \frac{\epsilon_{Si} - \epsilon_p}{\epsilon_{Si} + 2\epsilon_p} + \frac{\epsilon_0 - \epsilon_p}{\epsilon_0 + 2\epsilon_p} = 0 \quad (3)$$

With ϵ_p electric permittivity of porous silicon given using ellipsometric measurements and p : porosity.

II.2. The thickness

The thickness of the layer formed during an anodization in galvanostatic mode (constant current) is proportional to the quantity of exchanged load and consequently to the duration of the anodization time [10]. The depth control is made

by controlling the anodization time and it is thus a priori simple and effective. As we can see in the figure (4), the thickness of the layer increases linearly with the time of anodization in the case of the layers realized with substrates of the p-type (Figure 4.a) and of p⁺-type (Figure 4.b). The determination of the samples thickness is made directly using a profilometer which determines with a point the uneven between the top and the bottom of the porous layer on samples of which the half was dissolved in weld, or indirectly by the simulation of the reflectivity spectra.

Figure (5) represents an observation of the porous silicon layers cut thickness by electronic scan microscopy.

The thickness can be also measured by gravimetry;

$$e = \frac{m_1 - m_3}{S \cdot \rho_{Si}} \quad (4)$$

Where ρ_{Si} is the density of massive silicon ($\rho_{Si} = \text{g.cm}^{-3}$) and S surface having been anodic

III. CONCLUSION

In this work we made a study on the characterization of the thin PS layers by using experimental techniques which we will describe as standards. This one made it possible to show that porosity increases according to the current density, this being able to be explained by a privileged dissolution in volume rather than in thickness. Thus, for a given anodization conditions (current density, HF concentration) measured porosity is larger for thicker layers.

We as could show as the thickness of the layer increases linearly with the anodization time. The depth control is made by controlling the time of anodization and it is thus a priori simple and effective.

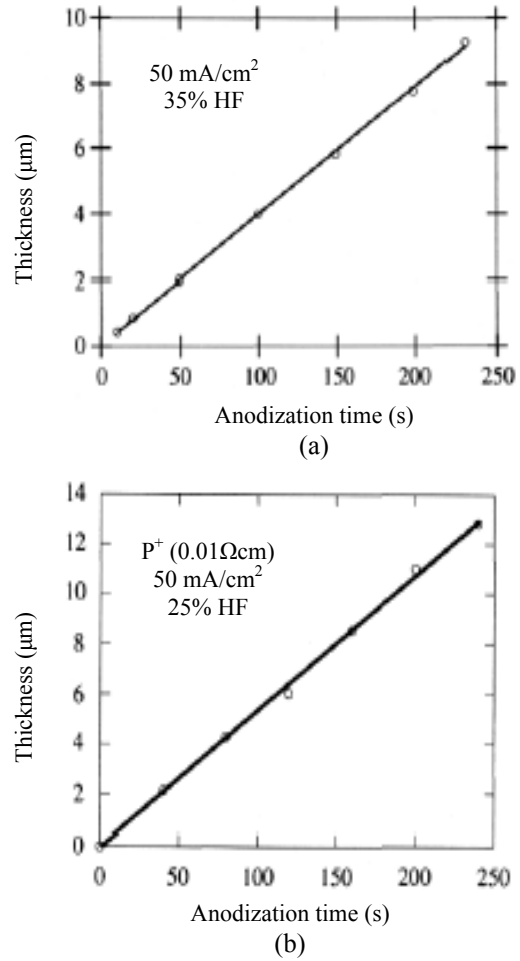


FIGURE. 4: Variation of the PS layer thickness with the anodization time, in the case of p-type silicon (1 Ωm) (a)

The anodization conditions are indicated in the figures [10].

[1] L. T. Canham, Appl. Phys. Lett. 57 (1990), pp. 1046.
 [2] F. Edelberg, S. J. Appl. Phys., vol. 81 (1997), pp. 2410.
 [3] S. Berger, S. Quoizola, A. Fave and al, Journal of Crystal research and technology, Vol.8 (2001), pp.1005.
 [4] G. Léron del, P. Ferrand, R. Romestain, Materials Research Society symposium proceedings, 452 (1996), pp. 711.
 [5] G. Panzarini, L. C. Andreani, A. Armitage, D. Baxter, M. S. Skolnick, V. N. Astratov, J. S. Roberts, A. V. Kavokin, M. R. Vladimirova, M. A. Kaliteevski, Physical Review, Vol. 59 (1999), pp. 5082.

[6] I. Sagnes, A. Halimaoui, G. Vincent, P. Abadoz, Applied Physics Letters, Vol. 62 (1993), pp. 1155
 [7] F. Koch, V. Petrova-koch, Journal of non-crystalline Solids. Vol. 198 (1996), pp.840.
 [8] S. Setzu, S. Letant, P. Solsona, R. Romestain, J.C. Vial, J. Lumin. Solid State Physics, Vol. 80 (1999), p. 129.
 [9] S. Charvet, R. Madelon, F. Goubilleau et R. Rizk, J. Appl. Phys. Vol. 85(1999), pp. 4032.
 [10] M. Stuzmann, J. Weber, M.S. Brandt, H.D. Fuchs, M. Rosenbauer, P. Deak, A. Hopner, A. Breitschwerdt, Solid State Physics, Vol. 32 (1992), p. 179.
 [11] V. Lysenko, PH. Roussel, B. Remaki, G. Delhomme, V. Strikha, C. Martelet, D. Barbier, A. Dittmar, J. Porous Mat., Vol. 7 (2000), pp.177.