FTIR and IES Characterization of Fresh and Passivated Macroporous Silicon

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1. Abstract

As-etched and passivated macroporous layers were studied by Fourier Transform Infrared (FTIR) and Impedance Electrochemical Spectroscopy (IES). The results show that IES is highly sensitive to chemical and structural variations of sample/electrolyte interface. Moreover, the presence of SiO_2 within the structure yields the formation of an additional capacitance and also increases the resistance of the system, but it is brought back by the polyaniline presence.

2. Introduction

Porous silicon (PS) is an interesting material because their physical and chemical properties can be tuned during the anodization. Among the different possible applications of PS, one of most promising is the sensor field because of its porous structure [1]. However, for sensor applications, it is necessary to avoid the interaction between the porous matrix and the target species (analytes) and, thus, ensure that any change change in the sensing parameter is solely due to the presence of the analyte. To achieve this aim different strategies have been employed to passivate the porous structure such as oxidation, carbonation and so on [2]. However, because of its relative simplicity, chemical and electrochemical means is preferred and its effect upon the porous matrix was studied by different techniques [2,3]. Here, it is reported the passivation of macroporous silicon (MPS) by oxidation and polymer deposition and its characterization by the IES method.

3. Experimental procedures

For the experience, a set of p-type c-Si (100) with $\rho \approx 10$ Ω.cm was cleaned following the standard CMOS procedure. After, they were immersed into a solution composed by 15 ml of hydrofluoridric acid (HF) mixed with 135 ml of dimethylformamide (DMF). For pores formation, 10 mA/cm^2 of current density was applied during 5 min. For pores passivation by oxidation, the as-etched samples were immersed into aqueous solution composed by 30 ml of H_2SO_4 and 150 ml of distilled water and then 10 mA/cm^2 of current density was applied during 20 min. for oxide growth. After this procedure, polyaniline was deposited upon some oxidized MPS samples by immersing them in solution composed by 1 M HCl, 1M aniline and 0.25 M

of $(HN_4)_2S_2O_8$ during 24 hours in darkness and a room temperature.

The structural characterization of the pristine MPS was made by the scanning electron microscopy (SEM), from which was computed the porosity, hence also its effective refractive index [4], and then it was used as input parameter to compute its thickness by ellipsometry, focusing the incoming light ($\lambda = 632.8$ nm) upon the porous structure Surface. For pore formation, electrochemical passivation, and characterization by IES, the AUTOLAB potenciostatic equipment was employed. The latter procedure was carried out by immersing the samples into 1M KCl diluted in ethanol [3].

The presence of both the SiO_2 and polyaniline phases within the MPS structure was investigated by FTIR spectrometer.

4. Results and discussions

Fig. 1 shows the top-view SEM image of the as-etched MPS, where the effective pore diameter varies from 0.3 to 3 μm (see the inset histogram) and its porosity was estimated to be about 61%, which corresponds to an effective refractive index equal to 1.94 in the infrared region [5]. This value together the ellipsometric measurement reveals that the porous layer thickness is about 5 μm.
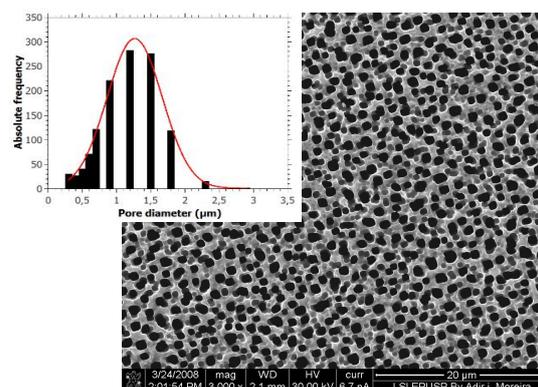

Fig.1. *Top-view SEM image of the as-etched MPS, showing inset the pore diameter distribution.*

The FTIR analysis after chemical oxidation and polymer deposition is shown in Fig. 2, revealing the typical peaks localized at 455, 804, 920, and 1074 cm^{-1} which correspond to the Si-O-Si bonds, along with other secondary ones [5]. The spectrum from the oxidized MPS in which polyaniline was deposited exhibits the two typical main peaks at 1504 and 1584 cm^{-1}which

correspond to the C-C stretching of the benzenoid and quinoid rings, respectively of the emeraldine base state. The additional peaks at 1240 and 1312 cm^{-1} are linked to the C-N stretching bonds of the benzenoid ring, while that placed at 802.5 cm^{-1} is associated to the plane out deformation of C-H in benzenoid ring. The peak at 1144 cm^{-1} is typical in polymers deposited via HCl solution [6].
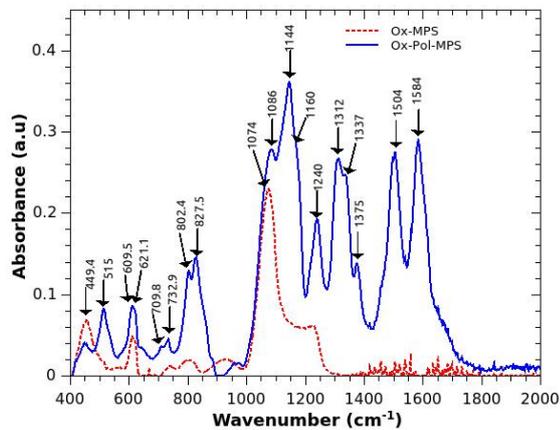

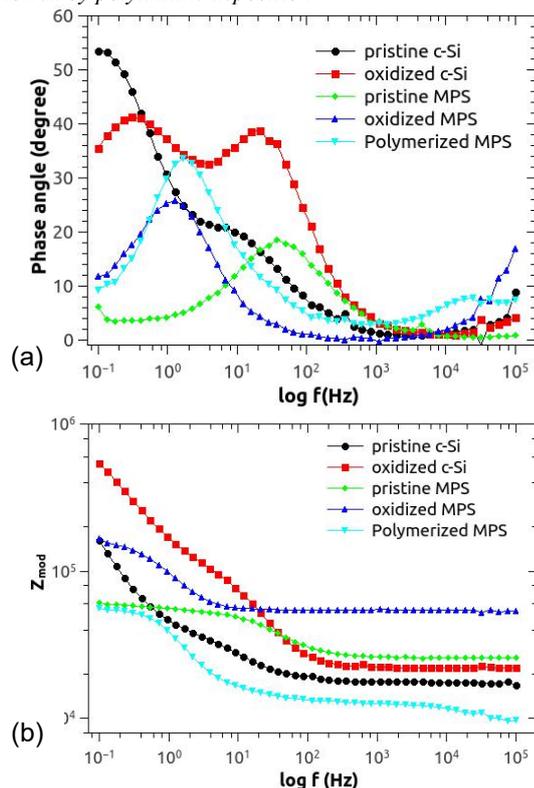*Fig.2. FTIR spectra from samples passivated by SiO$_2$ and SiO$_2$ followed by polyaniline deposition*

Fig.3. (a) phase angle vs log f , and (b) modulus vs log f plots for the pristine and oxidized c-Si, and passivated macroporous silicon.

In Fig. 3 is shown the bode plot of the IES analysis of the samples. The peaks at high frequency regions corresponds to the depletion layer capacitance (C_{si}), while those in the low frequency region is linked to the effect of the double layer capacitance (C_{dl}) [3]. The presence of peaks at intermediate region is associated to the presence of additional layer, as in the case of the oxidized c-Si. However, the peak observed in the bode plot of c-Si could be attributed to the presence of interface states or to the SiO$_2$ growth during the experience, but in the case of the oxidized one, certainly, it is due to the presence of SiO$_2$ layer (C_{ox}). The bode plot of the as-etched MPS shows solely a broad peak, suggesting that in this case the capacitance of the porous layer (C_{PS}) predominates to the other or even the superposition of them. After oxidation, the C_{si} effect appears again, whereas the second peak is shifted to low regions. Since in this case the structure is composed by c-Si and SiO$_2$, this latter peak could contain the superposition of C_{dl}, C_{ox}, and C_{PS}. Similar behavior is observed for the polymer deposited structure, but in this case an additional peak appears at high region and seems to be associated to the polymer layer. According to the Fig. 3b, the resistance of the systems changes after each treatment, so that is larger for the oxidized MPS and becomes lowest after polymer deposition because polyaniline is a conducting polymer.

5. Conclusions

Passivated MPS was investigated by IES method and was shown the accuracy of it for study porous structures. The results show that IES is method sensitive to geometrical and chemical features of the solid/electrolyte interface. The presence of an additional interface is revealed by an additional peak in the bode plot. The oxidation not only introduce and additional capacitance associated to its interfaces,but also shifts the resistance of systems to high values. In counterpart, the polyaniline presence decreases the resistance. It was shown that electrochemical method is an excellent alternative route to passivate the porous structure.

References

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