Formation and characterization of porous silicon films obtained by catalyzed vapor-chemical etching

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Porous silicon films obtained by the metal-assisted vapor-chemical etching technique have been characterized. For the film formation, epitaxial (100) N/P+ , 1–5 Ω cm monocrystalline silicon wafers were used. The vapors of an alcoholic solution of H2O2/HF were drawn towards the silicon surface, which was previously covered with a thin layer of gold (~8 nm) for the catalytic etching. For the optical and morphological characterization of porous films, Raman spectroscopy, Ellipsometry, FTIR spectroscopy and SEM images were used. The films thickness kept a linear relationship with etching time. A porosity gradient from the surface towards the interface (65% to 12%) was observed in the films. A large amount of Si–H bonds as related to O–Si–O bonds were observed and the pore size depends on the HF concentration. Irregular morphology was found in films formed with 50% HF.

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1. Introduction

In the literature there are a large number of papers focused on Porous Silicon (PS) formation and its optical, insulating and chemical sensing applications [1]. The ability of the PS to adsorb gaseous species [2] is due to its high surface chemical activity and a great surface to volume ratio greater than 200 m²/cm³ [3], which is suitable for sensing applications.

Since the PS discovery by Uhlir and the subsequent works of Canham on its properties in 1990 [4,5], the electrochemical etching technique has been used for many applications of PS rather than other methods such as the chemical etching, therefore motivate us to make this work.

In this paper, we use the chemical etching method, particularly the metal-assisted etching technique [6,7]. This technique has the advantage of being easy to implement, requiring neither biasing nor illumination sources, in addition to being able to form PS on N-type and P-type silicon. It is also selective, since it allows etching only on the areas covered by the metallic film, which catalyzes the etching reaction and it can be produced at room temperature. However, some disadvantages of this method are its low reproducibility an irregular PS/Si interface and high formation ratios (about 15 nm/s or greater). This last disadvantage is overcome by performing the etching with the vapors of the solution, rather than immersion, in analogy to the procedure used by Saadoun et al. [8]. As mentioned, this technique uses as a catalyst either a nanometric film (~10 nm), or nanoparticles [9] of Au, Pt, Pd or Ag. These can be deposited by either physical or chemical methods. The silicon surface is then exposed to the vapors of the etching solution, which is composed of Ethanol, Hydrogen peroxide and Hydrofluoric acid. The overall chemical reaction for the formation of the PS is given as [6]:

\[ \text{Si} + \text{H}_2\text{O}_2 + 6\text{HF} \rightarrow 2\text{H}_2\text{O} + \text{H}_2\text{SiF}_6 + \text{H}_2 \uparrow \]  \hspace{1cm} (1)

The presence of PS on the silicon substrate is observed as a color change of its surface, indicating a decrease of the refractive index in contrast to the one of crystalline silicon [10], initially from 3.89 and decreasing down to values close to 1.5 at 632.8 nm, as determined by ellipsometry, allowing also deduc the optical thickness. The thickness of the porous layer is associated with the etching depth, and is equal when the dissolution of a thin surface layer does not occur. Additional studies made to characterize the PS films were: Raman and FTIR spectroscopy in order to determine the chemical composition, and SEM microscopy to study surface morphology. The PS/Si junction can also be electrically characterized, but this will be reported in another work.
tering process under the following conditions: 10 of a thin layer of Au (used for cleaning the substrates. It was followed by the deposition thick and 1 from three different etchant solutions with ratios: acid HF (49% purity) were used for preparing the solutions. 20 ml the solution A with etching times of three and four hours. The samples were mounted 20 cm apart from the solution surface and then exposed to the vapors under a constant N2 flow of 2.3 l/min as carrier gas. The reactor was manufactured with and is similar to that used in reference[8], but in our ver-

2. Experimental details

Monocrystalline epitaxial N-type (100) silicon layers on P+ substrate were used to obtain the PS films. Epilayers were 4 μm thick and 1–5 Ω cm resistive. The standard RCA technique was used for cleaning the substrates. It was followed by the deposition of a thin layer of Au (~8 nm), using an Argon plasma DC sputtering process under the following conditions: 10−2 mbar pressure and 10 W power for 30 s. Analytical grade: ethanol C2H5OH (99.9% purity), hydrogen peroxide H2O2 (30% purity), and hydrofluoric acid HF (49% purity) were used for preparing the solutions. 20 ml from three different etchant solutions with ratios: A=(40:50:10), B=(40:35:25) and C=(20:30:50) v% respectively were used in this work. The samples were mounted 20 cm apart from the solution surface and then exposed to the vapors under a constant N2 flow of 2.3 l/min as carrier gas. The reactor was manufactured with Teflon and is similar to that used in reference [8], but in our version the solution was kept at room temperature (20 °C), see Fig. 1. The corresponding concentrations in the vapor phase are shown later in the Table 1 and depend on their vapor pressure. The etching time was set at one and two hours for each of the different etching solutions. In order to stop the etching process, the samples were rinsed in 2-propanol and acetone, and dried with a nitrogen flow. We obtained six types of films, labeled as MR1, MR2, MR3, MR4, MR5 and MR6. Odd-labeled samples set were etched for one hour and pair-labeled samples set were etched for two hours, MR1 and MR2 were formed with 10% HF, MR3 and MR4 were etched with 50% HF, MR5 and MR6 were formed with 25% HF. Two additional PS samples, MR7 and MR8 have been formed using only the solution A with etching times of three and four hours.

3. Characterization and results

3.1. Ellipsometry

The PS films were subjected to optical and morphological analysis. Ellipsometric characterization was performed by means of a variable angle ellipsometer (VAE) Gaertner LZW165366 that uses a 632.8 nm wavelength He–Ne laser. The optical thickness and refractive index were determined by fitting the measured ellipsometry angles Δ and Ψ, to a three-layer model; layer 1 at the surface, layer 2, intermediate and layer 3 at the interface with silicon substrate.

Fig. 2(a) shows the thickness dependence of each layer with the HF concentration in the etchant solution, for the three-layer model of ellipsometry. Layer 1 has a slight variation in thickness between 94 nm and 136 nm, showing scarce dependence with the time at low HF concentrations and it is slightly more dependent with the etching time at highest concentrations. The thickness of the layers 2 and 3 depends much more on the etching time than on the HF concentration.

Fig. 2(b) shows the refractive index values of each layer in the model versus the HF concentration in the solution for both etching times. Small differences between refractive indices corresponding to different times and HF concentrations are observed, except in the cases of layers 1 and 3 corresponding to 50% HF in the solution. A low refractive index at the PS surface (layer 1) and a higher one near the PS/Si interface (layer 3) are observed. This leads us to consider that the PS film refractive index changes gradually with the depth in the film.

The porosity in a film is given by the volume fraction occupied by air. Porosity values were obtained with the help of the Bruggeman effective medium theory [11], using the Eq. (2) and considering mesoporous films, where nSi and nPS are the refractive index of silicon and porous silicon respectively. Table 1 shows the total thickness of the films, dFT, and the porosity of each layer (P) of the model.

\[
P = 1 - \frac{(1 - n^2_{Si})(n^2_{PS} + n^2_{Si})}{2n^2_{PS}(1 - n^2_{Si})}
\]  

The porosity gradually decreases from the surface (~60%), exposed to the constant etching of the HF vapors, towards the interface (less than 12%), which corresponds to the pores bottom. Porosity is not dependent on HF concentration in the etchant solution; this is clearly shown by the values in Table 1. The total thickness keeps an approximate linear relationship with etching time, obtaining an etching rate in the order of 1 μm/h. In Fig. 3 the thickness dependence on the etching time can be seen.

3.2. Raman spectroscopy

The measurements were made with a Horiba-Jobin Microprobe Yvon HR800, which uses as excitation source a He–Ne laser.
emitting at 632.8 nm and a 50 × magnification. Fig. 4 shows the Raman spectra for crystalline Silicon and PS films. It is observed a peak centered at 521.8 cm⁻¹ with a full-width at half maximum, FWHM of 3.01 cm⁻¹ for crystalline silicon, 3.13 cm⁻¹ for MR1, 3.24 cm⁻¹ for MR2, 3.35 cm⁻¹ for MR3, 3.57 cm⁻¹ for MR4, 3.18 cm⁻¹ for MR5 and 3.28 cm⁻¹ for MR6. The Raman spectroscopy study revealed a slight peak broadening, according to the values of FWHM. It is also observed an increase of the FWHM with increasing the HF concentration and the etching time, which can be associated with a size decrease of the silicon crystallites of the PS filaments [10,12]. The spectra show also a double peak of lower intensity, for both crystalline Silicon and Porous Silicon films. The left hand-side peak is commonly associated to second order phonons for crystalline silicon and the right hand-side peak to small oxide particles on the surface [13]. The left hand-side peak is located at 950.38 cm⁻¹, which deviates slightly for porous films MR1 to MR6, towards 947.62 cm⁻¹, 947.63 cm⁻¹, 948.16 cm⁻¹, 949.22 cm⁻¹, 950.70 cm⁻¹ and 948.85 cm⁻¹, respectively.
3.3. FTIR spectroscopy

The IR measurements were made with a Thermo Nicolet Nexus 670 Fourier transform infrared spectrometer, by specular reflectance geometry and the spectra were obtained in the absorption mode. There are some chemical species expected to be present on the surface of PS as remnants of the byproducts of the formation reaction, and Si–O bonds formed during and after etching [14]. In Fig. 5 the FTIR spectra of porous films are reported. The absorption peaks commonly present in PS (Si–O and Si–H bonds) are mainly observed. The absorption peaks of Si–O species are not significant; the effect of ambient oxygen is minimal (samples measured 35 days after the formation of the PS).

In contrast, hydrogen bond related peaks arise in the spectra due to the effect of H\(^+\) ions, that did not evolve as H\(_2\) and provide a passivation effect on the surface [10], corresponding to the peak with larger intensity. The films also have Si–OH bonds [15] of the silanol group due to the slow oxidation in the environment. Table 2 shows a summary of the position of the main peaks in the spectra of PS samples. The peaks around 2360 cm\(^{-1}\) are not

![Fig. 6. SEM images of PS films and pore size distribution of different HF concentrations in solution: (a) MR1 (10%), (c) MR3 (50%) and (e) MR5 (25%) for 1 h of etching time.](image-url)
related with the samples, these peaks are due to the CO₂ content in the environment, but such a signal is most probably due to non-accurate compensation from the background during the measurement.

3.4. SEM microscopy

The surface morphology of the films was observed by a Carl Zeiss Auriga 39-16 SEM (Scanning Electron Microscopy). The images are shown in Fig. 6 for the samples MR1, MR3 and MR5 etched for one hour with HF concentrations: (a) 10%, (c) 50% and (e) 25%, respectively, including their corresponding pore size distributions (Fig. 6(b), (d) and (f)). The pore size distributions were automatically calculated using the Image J software and considering circular-shaped pores. Size distributions are close to a normal distribution. The morphologies are slightly similar, as shown in Fig. 6(a) and (e). The sample MR3, etched with solution C (50% HF) Fig. 6(c), is rougher than the others, loses uniformity in its morphology and has narrow pores. As shown in the histograms, the average pore size decreases as the HF concentration increases: for 10% HF the pore size is ~92 nm, for 25% HF the size is ~78 nm and for 50% HF the pore size is of the order of 69 nm.

The cross sectional view for MR7 (Fig. 7(a)) and MR8 (Fig. 7(b)) etched for 3 and 4 hours with solution A (10% HF), respectively, are shown. The thicknesses of 3.10 µm and 4.24 µm are associated to the etching time.

4. Discussion

In general, the films exhibit a gradual porosity, that is, a very porous thin layer at the surface, of the order of 100 nm thick and a thicker layer that reduces its porosity as it penetrates into silicon (intermediate and deep layers). The porosity values obtained in the range of 58–67% are useful for gas sensing applications [16]. Only on the hour range, the PS formation rate keeps a linear behavior, in the order of one micron per hour. The similitude for both the thickness and refractive indices in all samples were associated with the low H₂O₂/HF concentration in vapor phase. These low concentrations are enough to etch the silicon and give rise to similar porosity levels in each layer in agreement with the model.

Therefore, it is concluded that the catalyzed vapor-chemical etching technique allows to control the porous layer thickness and to obtain reproducible samples.

Raman spectroscopy shows a broadening of the peak corresponding to Si–Si bonds due to the size decrease of small silicon crystals in the regions that constitute the filaments [17]. The deviation of the peaks and their asymmetry with respect to that in crystalline silicon are minimal (0.5%). It is known that residual stress is produced by lattice mismatch, which is located near the interface PS/Si when samples have high porosities. The slight shift at lower frequencies is mainly attributed to porosity gradient observed; because in the interface PS/Si there is a low porosity level that maintains relaxed the structure. There is no presence of the silicon amorphous phase, which should be seen, around 480 cm⁻¹. The bands at 950 cm⁻¹ are attributed to silicon lattice second order phonon contributions and the mainly to the agglomeration of small regions of Si–O bonds. The bulk silicon dioxide characteristic band does not correspond to this frequency [13].

As a result of the intense chemical activity on the PS, some chemical species are present on its surface, particularly Si–O–Si. However, in our FTIR spectra the corresponding absorption peak is not strong, possibly due to poor residual oxide formation during the etching and native oxide. We can consider that our samples have a low oxidation rate and that, rather than having a continuous film; there are small oxide particles on the filaments surface [13].

The PS surface is initially passivated by Si–H bonds, showing a peak of greater intensity in the spectra, located at 667 cm⁻¹ [18]. Other species that gradually decrease the chemical activity of the PS is the Si–OH group, as in the case of long etching times with the solution C, constituting an aging effect. This can be critical in chemical sensing and optoelectronic applications [15]. Its origin, as mentioned before, takes place during the formation process, where H⁺ ions arise from the dissolution of silicon with HF. The OH⁻ ions originate from the binding of the surface with O₂ molecules and water vapor from the environment.

The morphology of the samples depends on the HF concentration. From the SEM images, we observed a decrease of the pore size (MR1: D = 92.33 nm, MR5: D = 78.45 and MR3: D = 68.62 nm) and a filament widening, as the HF percentage increases. High HF concentrations produced films with an irregular...
surface, narrow and deeper pores, separated from each other. This agrees with the Raman spectra. The fact that the surface texture is different in MR3 can be attributed to H₂ formed by the reaction, which prevents a more homogeneous distribution of the vapors that etch the Silicon surface or the filaments. The thickness values of the samples MR7 and MR8 obtained by SEM allowed us to confirm the thicknesses measured by ellipsometry and the validity of the three-layer model, as well as the presence of the porosity gradient in all samples. It is possible to see a non-uniform PS/Si interface in both samples, the deviation was found to be ~ 130 nm. This non-uniform interface affects slightly the porosity results, as indicated in Table 1 the porosity depends on the depth in the layer. If the thickness deviation is at most 140 nm, the thickness of the layer 3 in the model is affected too. For samples etched for 1 h the thickness could be less than expected, resulting in similar and highest porosity levels (in agreement with Table 1). For thicker samples with etching time of 2 h or more, the thickness could be higher than expected; in this case, the porosity level would be different of each sample forming a non-uniform interface, as was observed for MR2, MR4 and MR6.

5. Conclusions

In this work, PS films were successfully obtained by the metal-assisted chemical etching in vapor phase technique. A three-layer model applied to the measured ellipsometric angles was useful to evaluate the thickness and refractive indices of films. Based on the Bruggeman’s effective medium theory the porosity decreases when going from the surface towards the crystalline silicon interface. Despite this porosity gradient, the films thickness varies linearly with the etching time. As expected, the largest thickness variations occur in the most internal layers. The HF concentration in the etchant solutions in general, turned out not to be a critical parameter, however, was seen certain influence on the pore size and surface morphology in this vapor-based chemical etching technique. Experimental measurements indicate only decreasing size of crystalline silicon domains, without appearance of amorphous regions, as the etching time increases. The existence of a large number H⁺ and OH⁻ chemical species on the PS surface was observed. Although some chemical instability of these films might be expected, their porosity, morphology and structure are suitable for gas sensing applications. This part of the work will be reported elsewhere.

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