Elaboration of Self-Organized and Perforated Polymeric Thin Films for Precise Localization of Electrochemical Etching of Silicon

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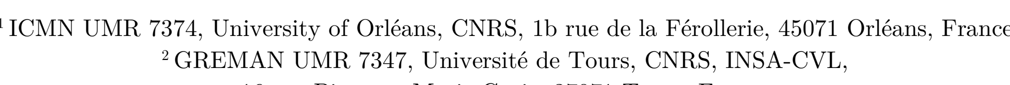

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Abstract. *Porous silicon is a nanostructured material resulting from the partial electrochemical etching of crystalline silicon. Localization of electrochemical silicon etching on a silicon wafer could be achieved without the use of hard mask. For that purpose, a polymer mask, and in particular a polystyrene (PS) mask was prepared using a thin film of polymer blend based on PS, which exhibits a lateral phase separation. After a selective extraction of the other polymer, the polymeric mask exhibits discreet domains of PS of less than 2 µm in diameter. Electrochemical etching through this mask allow to localize porous silicon on a silicon substrate and opens the ways to a large range of localization of porous silicon on a silicon surface.*

Keywords. Polymer blend, thin film, polymer template, electrochemical etching, porous silicon

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1 Context and Motivation

Porosification of silicon enlarges the applications of this semiconductor material. Due to its porosity, this material becomes a thermal and electrical insulator [1], presents a large specific area leading to sensing applications for example [2] or turns biodegradable paving the way for biomedical applications [3].

Porous silicon (PSi) formation is carried out by electrochemical etching in the hydrofluoric acid-based electrolytes and results from the competition between silicon electrochemical oxidation and dissolution of this oxide. It is generally formed in electrochemical cells filled as represented in fig. 1.

For many applications, it is necessary to localize the PSi area on the silicon substrate. Hard masks are generally used for this purpose. It involves a photolithography step followed by a plasma etching to open the mask with the desired forms [4]. This step can be time-consuming, expensive and above all, limits the minimal mask aperture at 2 µm in conventional photolithography step. To override this technological barrier, we propose to localize PSi with a polymeric mask which can present apertures smaller than 2 µm in diameter. Such structured polymeric masks were used to localize plasma etching of silicon in 2015 [5]. This mask must resist to the electrochemical etching conditions, hence resist to highly concentrated hydrofluoric acid. In addition, the mask must be easily deposable on the substrate and removable without damaging the formed PSi.

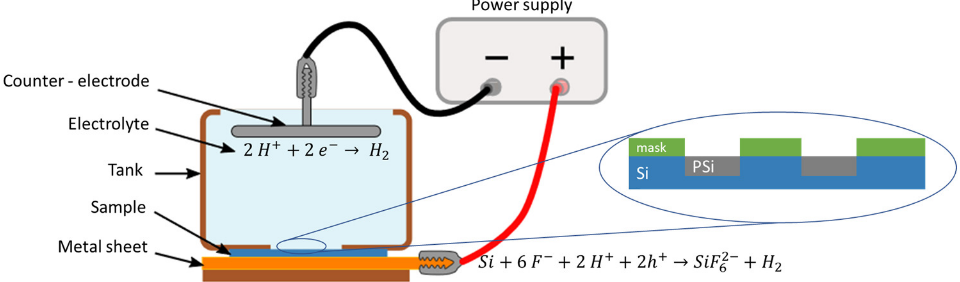

Figure 1. Single tank electrochemical cell typically used to make porous silicon and the half-reactions occurring during the etching [6]

2 Polymeric mask elaboration

2.1 Principle

The principle chosen to elaborate the perforated mask is the phase separation of a polymeric blend (cf. Figure. 2). At first, two non-miscible polymers (A and B) were dissolved in a common solvent (α). During solvent evaporation, the polymers separate and polymer B is selectively dissolved using another solvent (β) and leaving only polymer A at the surface. Polymer blend in thin film can present, after adapted phase separation process, a lateral phase separation with domains of one polymer perpendicular to the substrate embedded in a matrix of the other polymer.

A selective extraction of one polymer leads to a perforated polymeric mask. The general procedure is schematized in Figure 2.

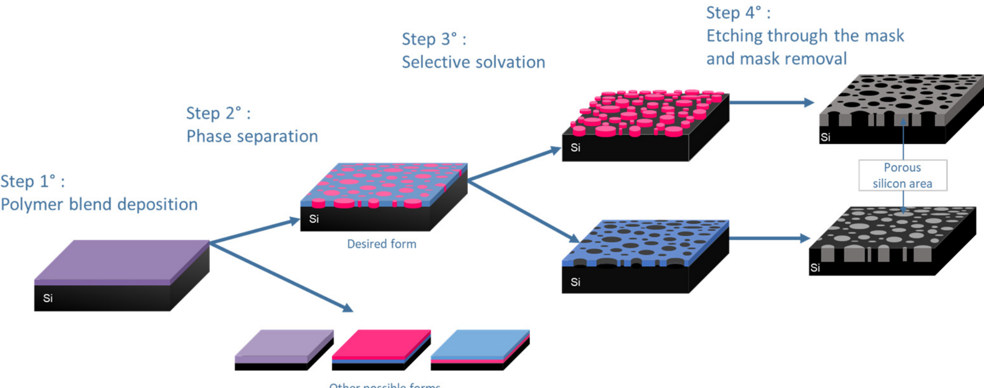

Figure 2. Schematic principle of the polymeric blend and phase separation followed by a selective solvation for localizing silicon etching

The polymers potentially suitable for the mask must be resistant to HF. Polystyrene (PS), THV Dyneon 221, Poly (vinyl chloride) and Poly (vinylidene fluoride-hexafluoropropylene) were selected.

In order to predict the suitable solvent for the blend and the suitable solvent to extract one polymer of the blend, the Flory-Huggins parameter $\chi_{Polymer,Solvent}$ is used. This empirical parameter is related to the Hansen's solubility parameters : the dispersive δ_d, polar δ_p, and hydrogen bond δ_{hb} Hansen's solubility parameters used in equation (1) and gives an indication of miscibility of a polymer and a solvent [7].

$$\chi_{P,S} = 0.6\ \frac{V_{m,S}}{RT}\left[\left(\delta_{P,d} - \delta_{S,d}\right)^2 + 0.25\left(\delta_{P,p} - \delta_{S\,p}\right)^2 + 0.25\left(\delta_{P,hb} - \delta_{S,hb}\right)^2\right] \qquad (1)$$

The lowest the parameter is, the highest is the miscibility. A value of $\chi_{P,S}$ inferior to 0.5 suggests that the studied polymer is soluble in the solvent.

The Hansen's solubility parameters could be also compared to evaluate the affinity of two polymers and their mixing or separation ability. Two polymers with very different solubility parameters will preferably unmix rapidly and will reduce their interface by forming large domains.

The suitable solvents were chosen among the authorized solvent in microelectronics industry (acetic acid, acetone, 2-butanone, ethyl acetate…).

Table 1 and 2 summarize the of Flory Huggins and Hansen solubility parameters to choose an appropriate set of polymers and solvents compatible with the use of PS. Poly vinyl acetate (PVAc) could be selected since Hansen solubility parameters for PS and PVAc are sufficiently different to PS and PVAc being immiscible.

Table 1. Hansen's solubility parameters of the polymers and solvents studied[1] in $MPa^{1/2}$

Polymer	δ_d	δ_p	δ_{hb}	δ_t
Polystyrene (PS)	19.4	4	2.5	20.0
Polyvinyl acetate (PVAc)	18.4	8.7	8.4	22.0
Butan-2-one	16	9	5.1	19.1
Acetic acid	14.5	8	13.5	21.4

Table 2. Flory-Huggins parameter calculated with eq.1

Polymer	$\chi_{\text{polymer, Butan-2-one}}$	$\chi_{\text{polymer, Acetic acid}}$
Polystyrene	0.4	0.8
Polyvinyl acetate	0.2	0.3

In Table 2, the Flory-Huggins parameter inferior to 0.5 for polystyrene, polyvinyl acetate and Butan-2-one indicates the possibility of blending for PS, PVAc in Butan-2-one (solvent α). Flory-Huggins parameter for PS / acetic acid of 0.8 and PVAc / acetic acid of 0.3 predict that the PS is not soluble in acetic acid contrary to the PVAc. It is consequently possible to create a PS mask opened by the selective extraction of PVAc with acetic acid (solvent β).

The structuration of the polymer blends thin films can be tuned by a large array of parameters such as the affinity of the polymers, the affinity with the solvent or the substrate [12]. The features of the polymers such as the their molecular mass and the characteristics of the blend solvent play a major role in mask structuring [13].

2.2 Structuration of polymeric mask and localized etching of silicon

The structuration of a polymer blend thin film and the etching localisation method were tested on a blend of 70:30 PS (Mw = 35 000 g/mol) / and PVAc (Mw = 100 000 g/mol) in Butan-2-one, at 30 mg/mL and is presented *vide infra*.

After depositing this blend by spin-coating on a silicon substrate, the blend thin film (Figures 3.a) exhibited a lateral phase separation with discrete domains of PS (bumps in the AFM image) and a matrix of PVAc. After dissolving the PVAc fraction in acetic acid, the PS mask is obtained and structured as cylindrical domains with a population of 1 to 1.5 µm in diameter, a thickness of 220 nm and a second population of smaller domains of 100nm in diameter as shown in AFM and SEM image Figure 3. AFM measurements are performed with a partial polymer strip confirming that there is no wetting layer of PS and the silicon surface is available for electrochemical etching (Figure 3.a). SEM images were then performed to get a scope of the sample (Figure 3.b).

The electrochemical etching was then performed in a tank filled with an electrolyte containing 30%wt. HF and 25 %wt. acetic acid and by applying 15 $mA.cm^{-2}$ during 15 sec. This electrochemical etching was followed by the dissolution of the PSi in a diluted solution of 5 %wt. potassium hydroxide (KOH) [14].

[1] The polymers Hansen's solubility values are the average of different sources [8], [9], [10], [11] and the values for solvents come from [11]. Those values are empirical and don't take into account the molar masse of the polymer neither the terminal functions, for this reason, we averaged the values found. The molar volumes are respectively 90.1 cm^3/mol and 57.1cm^3/mol for the butan-2-one and the acetic acid.

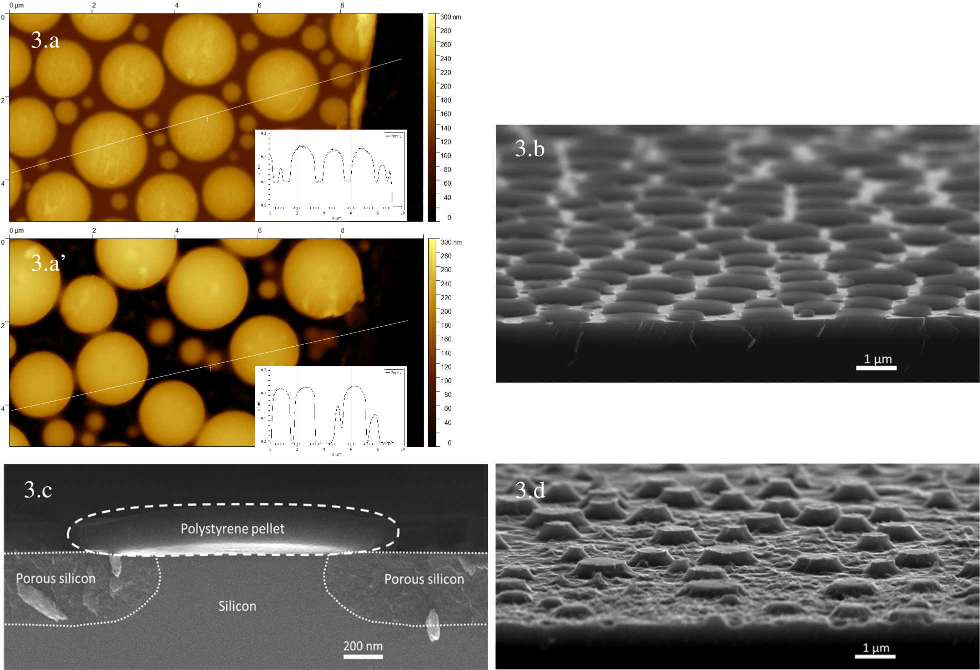

Figure 3. a) AFM images before and after a specific solvation of polyvinyl acetate with acetic acid and associated profiles, **b)** SEM image of the polystyrene mask after polyvinyl acetate removal, **c)** SEM image of silicon after the electrochemical etching through the polystyrene mask, **d)** SEM image of silicon after PSi dissolution by a KOH solution

The Figure 3.c shows the sample after the etching through the mask. It shows one PS domain. Below this domain, the silicon is not porous while the open areas on either side are porous up to a depth of about 350 nm. Figure 3.d presents the sample after dissolution of the porous silicon by the KOH solution. Small plateaus of non-porous silicon are visible. Figure 3.c and 3.d demonstrate that the silicon substrate could be protected from the electrochemical etching with a polystyrene mask.

3 Conclusion

Porous silicon area was localized on a silicon substrate using a polymeric mask composed of discreet domains of polystyrene. This mask was obtained from a structured PS : PVAc polymer blend thin film structuration due to lateral phase separation followed by a selective extraction of PVAc. This method enables to obtain a large variety of morphologies by optimizing several parameters of the blend such as the blend composition, solvent and the features of polymers. This method allows to avoid the use of hard masks structured by photolithography by an "all chemical way" which is cheaper, faster and enables smaller mask pattern.

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