Supplementary Material (ESI) for Lab on a Chip

Characterization of porous silicon integrated in liquid chromatography chips

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ELECTRONIC SUPPLEMENTARY INFORMATION:

i) Calculation of porosity (ε) and specific surface area

ii) Literature data on pore size, porosity and specific surface area of porous silicon

i) Calculation of porosity (ε) and specific surface area (A_{BET})

From the N_2-isotherms the specific surface area C_{BET} can be estimated via the BET method [1]. Table 1 contains the specific surface area per unit mass of sample, C_{BET}. It has to be mentioned here that the mass of sample includes the mass of the thick solid silicon substrate underneath the porous layer. In order to compare with other, completely porous materials, it would be preferred to have the surface area *per unit mass of porous material*. To determine this, one would need to measure the weight of the porous layer (or the weight change after anodization), however, such a weight measurement turned out to be too inaccurate. The desired parameters can however also be calculated from C_{BET} by taking into account the porosity of the layer (see Table 1), and the measured thickness of the substrate (not in table) and the thickness of the film (see Table 1). This parameter, $C_{BET,por}$, is also show in the table. The porosity values are calculated by multiplying the weight of each sample by the ratio of the total pore volume of each sample (which volume follows from isotherm data, in cm^3/g) to the total geometrical volume of each sample. The latter follows from the known surface area of the sample and the measured thickness of the original substrate. For practical purposes we have also calculated the surface area *per unit volume of porous material*, A_{BET}, shown in the last column of Table 1. This value allows us to estimate the total internal surface area of a porous layer of known volume, e.g., a porous layer on a pillar in a microchannel, see main manuscript.

Galvanostatic formation conditions			**Characteristics porous silicon layer**					
Electrolyte [wt %]	Current [mA]	Process time [min]	Thickness [nm]	Pore size [nm]	$C_{BET,sub}$ [$10^{-3}m^2/g$]	Porosity ε [%]	$C_{BET,por}$ [m^2/g]	A_{BET} [m^2/cm^3]
5% HF	50	5	612 ± 4	4.2 ± 0.2	151	23	170	300
	100		745 ± 7	4.9 ± 0.1	251	36	280	410
	200		1640 ± 10	5.4 ± 0.1	477	55	340	350
15% HF	50	5	890 ± 20	-	-	-	-	-
		10	1485 ± 6	3.2 ± 0.2	209	21	94	170
	100	5	1630 ± 20	-	-	-	-	-
		10	2130 ± 20	3.6 ± 0.3	649	27	220	370
	200	5	2270 ± 20	4.4 ± 0.5	534	47	230	290
20% HF	50	5	950 ± 9	2.1 ± 0.5	112	20	78	140
	100		2164 ± 5	2.5 ± 0.4	231	35	87	130
	200		3201 ± 4	3.5 ± 0.3	511	39	140	200

Table 1: Formation conditions and characteristics of porous silicon on flat substrates

ii) Literature data on pore size, porosity and specific surface area of porous silicon

For comparison with our results, we have collected literature data on properties of porous silicon obtained by anodization. The majority of the data in literature deals with p-type silicon, which is also the substrate material used in our work. Table 2 shows these data, which consist of pore size, crystallite size[1], porosity and specific surface area as a function of galvanostatic formation conditions for moderately and highly doped p-type silicon. Identical porosity values can be obtained for a wide range of dopant levels, acid concentrations and current densities (Table 2). For different dopant levels not only the size of the pores and crystallites fluctuate, but the amount of pores as well. For example, porous silicon layers realized on moderately and highly doped p-type silicon using identical process conditions, have an identical porosity, while the average crystallite size in layers obtained from moderately doped material is *ca.* 5 times smaller than that obtained from highly p-doped silicon [2]. Furthermore, for a wide range of pore sizes a nearly constant specific surface area per volume is measured [3,4]. Although we have found a specific surface area per volume proportional to the pore size, our measured values of A_{BET} are in the same range as the reported specific surface area values given in Table 2.

[1] Porous silicon is a more or less (dis)ordered network of interconnected nano- or microscale crystalline silicon particles with pores in between; the sizes of the pores as well as the crystallites constituting the porous material can be measured.

Original Si wafer	Galvanostatic formation conditions			Porous silicon layer					Ref.
	Current density [mA/cm^2]	Electrolyte composition	Process time [min]	Thickness [µm]	Pore size [nm]	Crystallite size [nm]	Porosity [%]	Specific surface area [m^2/cm^3]	
p+, (111), 10 mΩcm	10 - 240	12.5%HF:EtOH (1:1 vol%)	-	80	2 - 10	-	30 - 70	200 ± 20	3
p, 0.01-1 Ωcm	10	20-48% HF	-	0.25 - 1.2	2.5 - 12	-	-	-	5
p, (100), 1 Ωcm	10 - 240	10-35%HF:EtOH (7:3 vol%)	-	3 - 20	< 2 nm	-	-	*ca.* 600	4
p+, (100), 10 mΩcm	10 - 240	10-35%HF:EtOH (1:1 vol%)	-	3 - 20	1.8 - 7.0	-	36 - 70	215 ± 15	4
p+, (100), 10 mΩcm	10	10% HF	-	-	2 - 10	2 - 10	-	-	6
p, (100), 0.02-33 Ωcm	30 - 100	50% HF:EtOH (1:1 vol%)	-	25 - 200	0.5 - 5	-	58 - 60	230 - 760	7
p+, (111), 10 mΩcm	0.5 - 100	3-48% HF	-	-	1 - 5	20 - 54	-	-	8
p, (100), 0.01-52 Ωcm	30 - 50	25% HF	-	10	-	-	40 - 45	-	9
p+, (100), 10 mΩcm	-	50%HF:EtOH (1:1 vol%)	-	-	-	3 - 8	72 - 79	-	10
p, (100), 0.01-0.2 Ωcm	-	48% HF:EtOH (1:1 vol%)	-	21 - 46	-	1.7 - 9.0	64 - 89	-	2
p+, (111), 10 mΩcm	15	12-20%HF:EtOH (1:1 vol%)	30	10 - 23	-	-	50 - 60	-	11
p+, (100), 20 mΩcm	40 - 70	15-25% HF	-	25 - 30	-	-	55 - 75	-	12,13
p+, (100), 20 mΩcm	20 - 150	25% HF	-	100	-	7.0 - 8.3	38 - 74	-	14
p, (100), 0.01-10 Ωcm	30 - 70	25%HF:EtOH (9:1 vol%)	16 - 62	-	-	1 - 75	-	-	15
p, 0.7-1.3 Ωcm	13.2 - 26.4	70% HF + IPA	20 - 40	19 - 38	-	-	61 - 73	-	16
p+, (100), 10 mΩcm	20	HF:EtOH (3:1 vol%)	20	20	4 - 13	5	50	-	17,18
p+, (100), 10 mΩcm	5 - 80	50% HF:EtOH (3:2 vol%)	4.2 - 8.3	3.2 - 25.1	-	-	28 - 48	-	19

Table 2: Characteristics of porous silicon as reported in literature

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