



Short communication

Porous silicon fabrication by anodisation: Progress towards the realisation of layers and powders with high surface area and micropore content

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ABSTRACT

With a view to producing thick and very high surface area microporous silicon layers (and subsequently powders) by electrochemical anodisation, the incorporation of various types of chemical additives has been investigated, these in combination with hydrofluoric acid electrolyte and high-resistivity p-type parent substrates. Comparison under constant charge conditions shows that anodisation using 50 wt% hydrofluoric acid, or inclusion of the additives hydrochloric acid, sulphuric acid, or ammonium dodecylsulfate with lower concentration hydrofluoric acid, can facilitate powders with internal surface areas of up to 864 m²/g, average pore sizes in the region of 2.8–3.2 nm, and pore volumes in excess of 0.8 cm³/g – all as determined using nitrogen gas adsorption and associated isotherm analysis. Porous silicon powders with appreciable micropore content have thus been achieved, for the first time. Relevant application areas for such material are diverse, and potentially include energetics, impurity gettering, gas sensing microchips, orthopaedic implants, hydrogen storage, and Li-ion battery anodes.

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1. Introduction

Nanoporous materials, typically with pore diameters in the range 1–100 nm [1], are receiving increasing attention by nanotechnologists. According to current definitions from the International Union of Pure and Applied Chemistry (IUPAC) [2], there are three classes of pore that fall into this size regime: micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). Mesoporous and macroporous silicon, created via electrochemical etching techniques, are currently being actively researched for a variety of applications in microelectronics (RF devices, sensors, MEMS, etc...), energy micro-sources (Micro-fuel cells, micro-supercapacitors, Li-ion battery anodes, etc...) or biology (therapy, orthopaedics, etc...) for instance [3]. Mesoporous silicon layers are mainly obtained in highly-doped silicon (either n- or p-type), whereas macropores are observed after lightly-doped silicon electrochemical etching in dilute hydrofluoric acid (HF) [4,5]. As for micropores, these dimensions are only obtained in very specific

conditions, i.e. lightly-doped p-type silicon etched in highly concentrated HF solution [3].

Many of the applications of mesoporous silicon utilise the large internal surface area that is accessible, which, when created via wafer anodisation, typically lies in the range 200–600 m²/g [6,7]. In this study, our objective was to investigate the anodisation conditions that would create surface areas well in excess of 600 m²/g, assessing the potential upper limits for a process that could generate both nominally thick layers and powders. Gas adsorption analysis is an established technique for quantifying mesopore size, pore volume and surface area in silicon [6–9] so we have utilised this characterisation tool exclusively.

2. Experimental

Porous silicon layers were prepared via electrochemical etching of p-type, (100)-oriented silicon substrates. Two different resistivities were utilised in the expectation of achieving small pore diameter: 1–5 Ω.cm [7] and 30–50 Ω.cm [10,11]. Anodisation was possible after rendering the rear sides of these wafers ohmic via boron diffusion at 1050 °C for 1 h. The surface exposed to the electrolyte occupied an area of 3.44 cm².

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Table 1

Processing parameters and nitrogen gas adsorption data of porous silicon powders: AA – acetic acid, HCl – aqueous hydrochloric acid, ADS – ammonium dodecylsulfate, sulphuric acid (H_2SO_4); APD – average pore diameter (anodisation at 65 mA/cm^2 for 2 hr).

Sample	Wafer resistivity ($\Omega\text{ cm}$)	HF:H ₂ O concentrations (wt %)	Additive & concentration (wt %)	BET (m^2/g)	Pore volume (cm^3/g)	APD (nm)
PS0	1–5	30:45	AA (25)	437	0.988	8.9
PS1	30–50	50:50	none	661	0.410	2.8
PS2	30–50	40:52.5	HCl (7.5)	756	0.686	3.0
PS3	30–50	30:55	HCl (15)	796	0.758	3.3
PS4	30–50	20:48	HCl (22)	745	0.741	3.5
PS5	30–50	50:50	ADS	662	0.580	2.9
PS6	30–50	30:55	H_2SO_4 (15)	708	0.782	4.1
PS7	30–50	30:32	H_2SO_4 (38)	640	0.642	3.6
PS8	1–5	30:55	HCl (15)	864	0.806	3.2

Anodisation was performed under constant charge conditions by varying both current density and etching duration. Different etching parameters were tested, including varying the HF concentration in the electrolyte and incorporating, singly, the following additives at various concentrations: acetic acid (AA),

hydrochloric acid (HCl), sulphuric acid (H_2SO_4), and ammonium dodecylsulfate (ADS) wetting agent. After anodisation, the samples were rinsed in de-ionised water and dried in air on a hot-plate ($80\text{--}100\text{ }^\circ\text{C}$, 10 min), to minimise residual electrolyte within the pores. Each porous layer was then mechanically

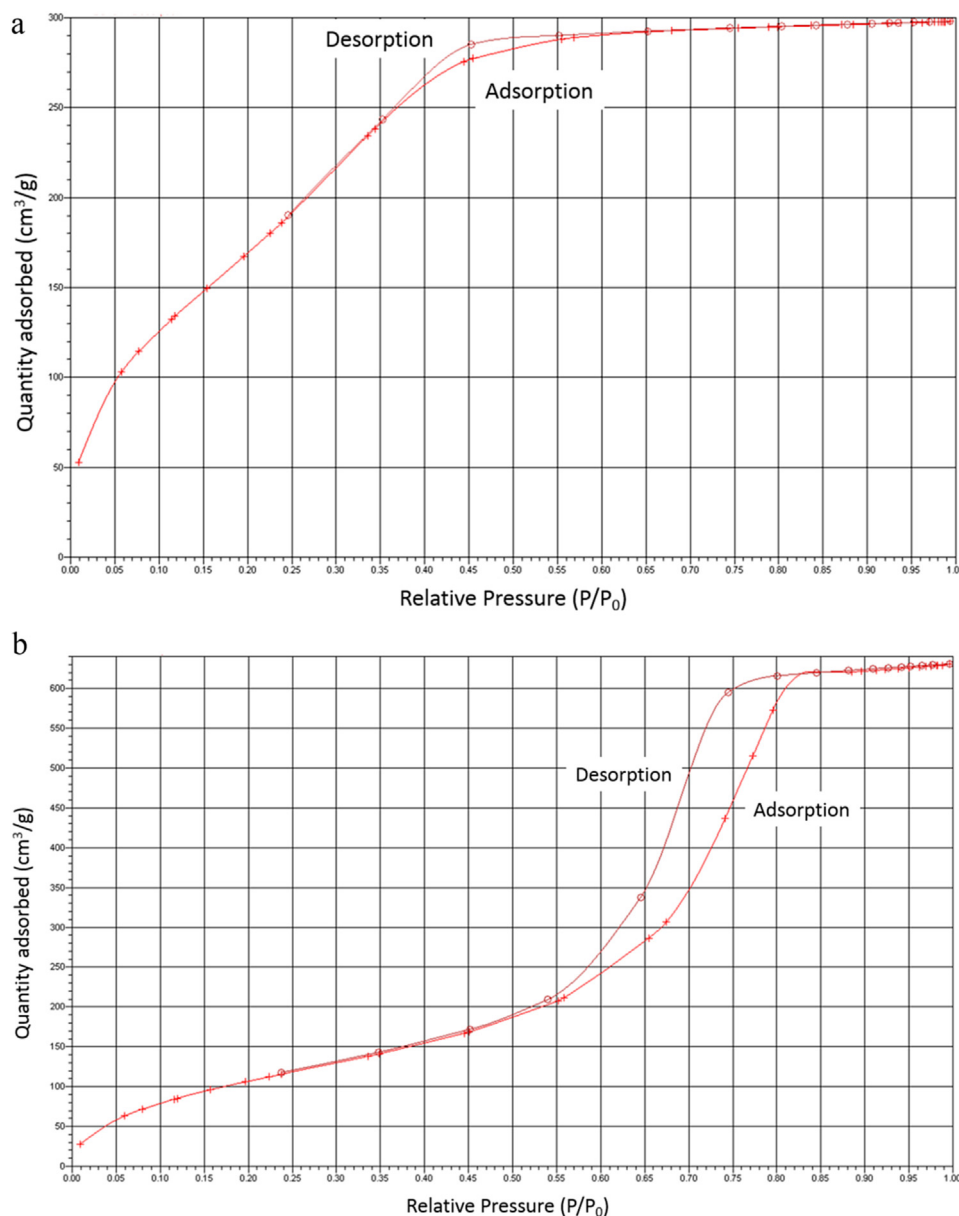


Fig. 1. Adsorption/desorption isotherm for sample produced using (a) 50 wt% HF electrolyte, sample PS1, and comparison with (b) a typical mesoporous sample, PS0.

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