Routes of Formation for Porous Silicon

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Abstract

Porous silicon has been fabricated by both "top-down" techniques from solid silicon and "bottom-up" routes from silicon atoms and silicon-based molecules. Over the last 50 years, electrochemical etching has been the most investigated approach for chip-based applications and has been utilized to create highly directional mesoporosity and macroporosity. Chemical conversion of porous or solid silica is now receiving increasing attention for applications that require inexpensive mesoporous silicon in powder form. Very few techniques are currently available for creating wholly microporous silicon with pore size below 2 nm. This review summarizes, from a chronological perspective, how more than 30 fabrication routes have now been developed to create different types of porous silicon.

Introduction

Porous silicon, solid silicon with voids therein, can be generated by diverse means. Although "top-down" techniques utilizing electrochemical etching techniques have dominated the academic literature over the last 50 years, from 1960 to 2010, there

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have since been many other routes demonstrated: both "top-down" routes from solid silicon and "bottom-up" routes from silicon atoms and silicon-based molecules.

The purpose of this review is to capture for the reader, in one brief document, all those fabrication techniques the author is aware of and highlight their potential applicability, depending on desired structures, targeted application area, and acceptable levels of cost. In the following chapters of this handbook, eight of these are then chosen to be reviewed in detail.

Schematic Route Map

Figure 1 illustrates the traditional route whereby porous silicon is created from solid silicon, which itself is derived from solid silica. A number of techniques such as anodization (see handbook chapter "▶ Porous Silicon Formation by Anodization"), vapor etching ("▶ Porous Silicon Formation by HNO_3/HF Vapor Etching"), glancing angle deposition, lithographic etching, and photoetching ("▶ Porous Silicon Formation by Photoetching") are suitable for Si wafer-based processing. Others can be used on both wafer and powder silicon feedstocks, such as stain etching (handbook chapter "▶ Porous Silicon Formation by Stain Etching"), galvanic etching ("▶ Porous Silicon Formation by Galvanic Etching"), and MACE ("▶ Porous Silicon Formation by Metal Nanoparticle-Assisted Etching"and "▶ MACE Silicon Nanostructures"). Most of these techniques create highly directional porosity and therefore properties that can be highly anisotropic (see handbook chapters "▶ Electrical Transport in Porous Silicon"; "▶ Mechanical Properties of Porous Silicon" and "▶ Optical Birefringence of Porous Silicon"). Until quite recently, etching of highly porous structures from solid silicon was reliant on acidic fluoride chemistry; however, alkali-based etches have now been shown to be at least capable of macropore generation under restricted conditions.

Porosifying controlled areas of a silicon wafer enables porous silicon to be integrated with silicon circuitry or MEMS devices within chip-based products. Although porous silicon particles (microparticles and nanoparticles) can be derived from anodized wafers (see handbook chapters "▶ Milling of Porous Silicon Microparticles" and "▶ Photoluminescent Nanoparticle Derivatization Via Porous Silicon"), this route is only viable for low-volume high-value product areas, as in some medical therapy applications (see handbook chapter "▶ Drug Delivery with Porous Silicon").

If highly porous structures are required at high volumes, etching techniques will typically have to remove large quantities of solid silicon as waste, unless recycled. For lower-value, high-volume porous silicon products that are not silicon chip-based (see handbook chapters "▶ Porous Silicon and Functional Foods" and "▶ Porous Silicon for Oral Hygiene and Cosmetics"), there is therefore increasing interest in fabrication routes that utilize existing highly porous feedstocks or silicon-based molecules that are themselves waste products from solid silicon manufacturing. These increasingly use chemical conversion of, for example, silica, silane, or silicon tetrachloride (see Fig. 2). The chemical conversion can be

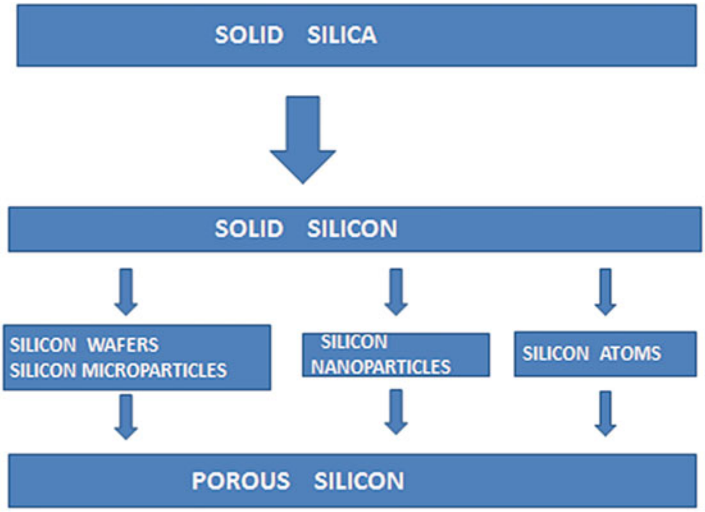

Fig. 1 Routes to porous silicon via solid silicon

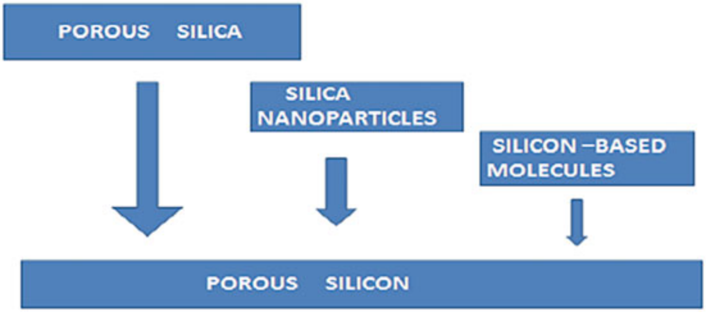

Fig. 2 Routes to porous silicon using chemical conversion

promoted thermally, mechanically, or electrochemically. Here the morphology of porosity can reflect that of the starting solid feedstocks (see handbook chapter "▶ Porous Silicon Formation by Porous Silica Reduction") or how the silicon nanoparticles are assembled into a porous body via sintering (see handbook chapter "▶ Porous Silicon Formation by Mechanical Means").

Specific Fabrication Techniques

Table 1 illustrates the variety of processes (currently more than 30) now available to create porous silicon, arranged in approximately the chronological order they have been introduced. Historically, it was high levels of mesopores (see handbook chapter on "▶ Mesoporous Silicon") that were created first via anodization (1) and stain

Table 1 A multitude of routes to form porous silicon. The techniques highlighted in black are reviewed in detail in the handbook. Also highlighted in black are those techniques reported to generate macroporous and microporous silicon. The literature has to date been dominated by mesoporous silicon fabrication

Fabrication technique	Class of technique	Class of porosity	Early paper on technique	Year
Anodization	Etching (wet)	Mesoporous	Uhlir (1956)	1956
Stain etching	Etching (wet)	Mesoporous	Archer (1960)	1960
Anodization	Etching (wet)	**Macroporous**	Theunissen et al. (1972)	1972
Anodization	Etching (wet)	**Microporous**	Canham and Groszek (1992)	1992
Spark erosion	Etching (dry)	Mesoporous	Hummel and Chang (1992)	1992
Photoetching	Etching (wet)	Mesoporous	Noguchi and Suemune (1993)	1993
Laser ablation	Thermal	Mesoporous	Savin et al. (1996)	1996
Hydrothermal etching	Etching (wet)	Mesoporous	Chen et al. (1996)	1996
Metal ion-assisted chemical etching (MACE)	Etching (wet)	Mesoporous	Dimova-Malinovska et al. (1997)	1997
Galvanic etching	Etching (wet)	Mesoporous	Ashruff et al. (1999)	1999
Plasma deposition	Deposition	Mesoporous	Kalkan et al. (2000)	2000
Vapor etching	Etching (wet)	Mesoporous	Saadoun et al. (2002)	2002
Laser-induced plasma	Etching (dry)	**Macroporous**	Kabashin and Meunier (2002)	2002
Glancing angle deposition	Deposition	Mesoporous	Beydaghan et al. (2004)	2004
Melt gasification	Thermal	**Macroporous**	Nakahata and Nakajima (2004)	2004
Plasma hydrogenation	Deposition	Mesoporous	Abdi et al. (2005)	2005
Dealloying	Etching (wet)	Mesoporous	Fukatani et al. (2005)	2005
Laser-induced silane decomposition	Deposition	Mesoporous	Voigt et al. (2005)	2005
Magnesiothermic reduction of silica	Conversion reaction	Mesoporous **Microporous**	Bao et al. (2007)	2007
Mechanochemical reduction	Conversion reaction	Mesoporous	Zheng et al. (2007)	2007
Milling/sintering	Mechanical	**Macroporous**	Jacubowicz et al. (2007)	2007
DRIE-UV lithography	Etching (dry)	**Macroporous**	Woldering et al. (2008)	2008
Femtosecond laser ablation	Thermal	Mesoporous	Mahmood et al. (2009)	2009
Ultrathin film annealing	Thermal	Mesoporous	Fang et al. (2010)	2010
Anodization (alkali)	Etching (wet)	**Macroporous**	Abburi et al. (2010)	2010
Electrodeposition	Deposition	Mesoporous	Krishnamurthy et al. (2011)	2011

(*continued*)

Table 1 (continued)

Fabrication technique	Class of technique	Class of porosity	Early paper on technique	Year
Carbothermal reduction of silica	Conversion reaction	**Macroporous**	Yang et al. (2012)	2012
Sacrificial template	Deposition	Mesoporous	Huang et al. (2013)	2013
Sodiothermic reduction of silica	Conversion reaction	Mesoporous	Wang et al. (2013)	2013
Magnetron sputtering	Deposition	Mesoporous	Godhino et al. (2013)	2013
Micromachining and wet etching	Etching (wet)	**Macroporous**	Deng et al. (2013)	2013
Platinum NP-assisted etching (PaCE)	Etching (wet)	Mesoporous	Li et al. (2013)	2013
Ion implantation	Irradiation	**Macroporous**	Stepanov et al. (2013)	2013
Templated silicon tetrachloride reduction	Conversion reaction	Mesoporous	Dai et al. (2014)	2014
Rochow reaction-based etching	Etching (dry)	**Macroporous**	Zhang et al. (2014)	2014

etching (2) of electronic-grade crystalline silicon. Depending on wafer resistivity and anodization conditions, it was subsequently shown that both macropores (see chapter "▶ Macroporous Silicon") and micropores (see chapter "▶ Microporous Silicon") could also be realized via the anodization route. In the 1990s a multitude of different techniques for creating mesoporous luminescent silicon were identified. All the etching techniques tend to create "open" porosity where pores are accessible from the external surfaces of the structure. Specific techniques to create "closed" porosity include melt gasification (Nakahata and Nakajima 2004) and milling/sintering (Jakubowicz et al. 2007).

The most popular conversion reaction is currently the magnesiothermic reduction of porous silica, as introduced by Sandhage and co-workers in 2007 (Bao et al. 2007). This has been utilized with both synthetic silicas and biogenic silicas extracted from plants (see handbook chapter "▶ Porous Silicon Formation by Porous Silica Reduction"). The major challenge in scalability for mesoporous silicon via this route is control of the strong exothermic nature of the reaction to avoid sintering. Indeed, carbothermal reduction (Yang et al. 2012) requires much higher temperatures and is more amenable to macroporous silicon fabrication. Sodiothermic reduction (Wang et al. 2013) can be carried out at very low temperatures but is probably less scalable because of the high cost and reactive nature of sodium metal. Similar restrictions are also applicable to the recent study using NaK alloy (Dai et al. 2014). Aluminothermic reduction (Zheng et al. 2007) looks much more attractive in this regard since aluminum is a very inexpensive metal.

Note that there are currently very few techniques to make wholly microporous silicon (see handbook chapter "▶ Microporous Silicon") where the average pore diameter is under 2 nm. For virtually all top-down techniques, the porous silicon created is polycrystalline. For some bottom-up techniques such as sputtering/

dealloying (Fukatani et al. 2005), electrodeposition (Krishnamurthy et al. 2011), or sodiothermic reduction (Wang et al. 2013), it is reported to be amorphous. Choice of fabrication technique for both mesoporous and macroporous silicon is very much dictated by application area, which in turn has differing requirements on porosity levels, pore morphology, skeleton purity, physical form, cost, and volume.

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