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Alkyl-functionalization of porous silicon via multimode microwave-assisted hydrosilylation

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ABSTRACT

Porous silicon (PSi), with its large surface area-to-volume ratio and tunable surface morphology, remains an attractive substrate for applications ranging from optoelectronics to medical diagnostics. However, one significant obstacle facing the development of specialized PSi devices is the inherent instability of its native, silicon-hydride surface termination. In order to bypass this difficulty, a number of benchtop hydrosilylation reactions have been reported for functionalizing organic groups onto oxide-free, PSi surfaces via Si—C bonds. PSi passivated in this fashion is protected against ambient oxidation and chemical attack. This work describes a facile, efficient, and highly-scalable reaction that results in alkyl-functionalized PSi by way of a multimode microwave reactor. Resultant monolayers were characterized via qualitative and semi-quantitative Fourier transform infrared (FTIR) spectroscopy. The multimode microwave-assisted hydrosilylation reaction described here provides stable monolayers in a fraction of the time required by traditional reflux methods and in greater yield than catalyst-mediated room temperature reactions.

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1. Introduction

Porous silicon (PSi) is a nanostructured variant of elemental silicon that is comprised of a mesoporous network, resulting in a large surface area-to-volume ratio (Fig. 1) [1]. Surface morphology is modulated by etching conditions and can yield samples exhibiting surface areas in excess of 500 m^2/cm^3 [2]. PSi samples contain pore surfaces decorated with nanocrystallites as small as three nanometers, each consisting of only about one thousand silicon atoms each. For features of this size, nearly one-half of the silicon atoms reside at the surface. These samples provide ideal substrates for fundamental studies, owing to the enhanced ratio of surface atoms to those that comprise the bulk, and use in the design of functional interfaces for device applications. PSi has also attracted a great deal of attention due to its unique electro- [3], chemo- [4], and photo-luminescent [2] properties, which may also be tuned by careful modulation of etching conditions.

Thin samples of PSi are prepared on commercially available Si (100) wafers, via a variety of methodologies [5–8]. These include both chemical [9] and electrochemical [10] etching processes, which may be tailored to precisely modulate pore size and morphology of the resulting PSi layer. Furthermore, the preparatory etching protocols allow for the facile incorporation of PSi into well-established VLSI and MEMS fabrication processes [11–13]. These properties make PSi an attractive candidate for use in the fabrication of exotic new devices, ranging from optoelectronics and chemical sensors to biocompatible materials and medical diagnostics [14–22].

One of the most substantial obstacles preventing the widespread application of PSi in specialized devices results from the inherent instability of its native interface. This surface termination, produced in the presence of the hydrofluoric acid etchant, consists exclusively of silicon-hydride bonds. The silicon atoms are bound to one, two, or three hydrogen atoms in order to fulfill their tetravalency (Fig. 1). These ≡SiH, =SiH_2, and —SiH_3 surface moieties exist in a diverse variety of environments and local orientations, resulting from the inherent nature of this porous material [2]. Hydride-terminated PSi is only metastable with respect to oxidation under ambient conditions, thereby limiting its utility over extended periods of time.

However, freshly prepared, hydride-terminated PSi, is virtually "oxide-free" and serves as an attractive precursor to more functional interfaces [23–24]. The surface is stable enough to be manipulated in the presence of air for short periods of time (on the order of tens of minutes), and yet reactive enough to functionalize

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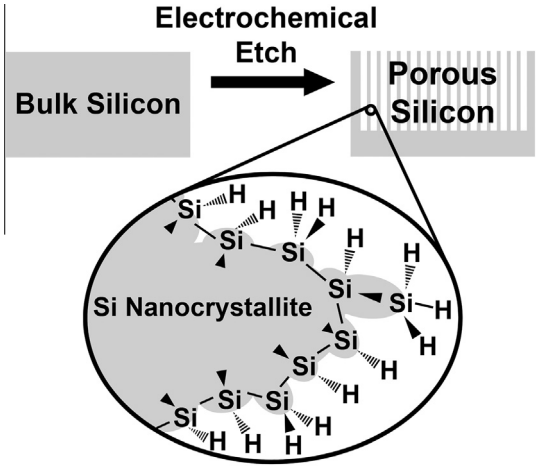


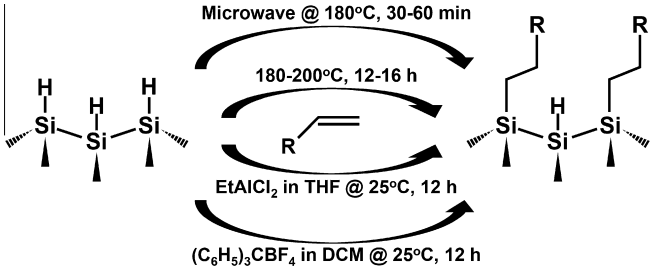
Fig. 1. Cartoon portraying a hydride-terminated PSi nanocrystallite exhibiting ≡SiH, =SiH_2, and —SiH_3 surface moieties.

through hydrosilylation chemistry (Scheme 1) [25–30]. This short term inertia allows utilization of well-established Schlenk and glove box handling methods [31]. Contemporary PSi surface chemistry revolves around formation of silicon-carbon bonds, with no concomitant oxidation. These organic monolayers, bound through Si—C linkages, avoid the insulating and defective oxide monolayer, and allow for good control over interfacial properties. In addition, these PSi substrates offer large surface areas and infrared permeability, thus providing access to conventional characterization methods such as transmission-mode Fourier transform infrared (FTIR) spectroscopy.

This work reports a facile, efficient, and highly-scalable reaction that results in alkyl-functionalized PSi by way of a multimode microwave reactor. While microwave-assisted reactions have demonstrated utility in organic synthesis [32–34], microwave applications to materials synthesis and modification are also gaining prominence [35]. The use of research-grade microwave reactors often yields reactions that are fast, simple, and energy-efficient. In contrast to traditional heating methods, the oscillating electric field of microwave radiation interacts directly with reactant and solvent species via dipolar polarization and conduction mechanisms [35]. These interactions are optimized to enhance reaction rates, improve yields, or enhance selectivity.

To date, the majority of microwave-assisted materials synthesis and modification work has been conducted employing instruments that contain a single-mode, or monomode, reactor cavity. The bulk of these reactors operate by producing a standing wave pattern of microwave radiation within the reactor cavity. While this design is highly effective for orienting a single reaction vessel within the field to maximize absorbed radiation, it prevents any significant scaling to high-throughput, batch processing [36,37]. For a monomode reactor cavity, the reaction vessel must be carefully placed in the region of highest amplitude, thereby limiting the physical dimensions of the reactor vessel. Furthermore, the placement of additional reactor vessels in the cavity disrupts the standing wave pattern, thereby reducing the efficiency of microwave absorption.

Multimode reactor instruments have recently become commercially available and circumvent many of the limitations inherent to the monomode design. In this mode of operation, standing waves of microwave radiation are deliberately avoided though the periodic motion of a metallic vane. This serves to homogenize the field intensity throughout the reactor cavity [38,39]. Field homogeneity allows for reactor vessels of any size that will physically fit within the cavity to be used. Furthermore, numerous reaction vessels may be employed simultaneously for batch processing applications. Field disruption is of minimal consequence due to the fact that the field is continually homogenized throughout the reaction run.



Scheme 1. (top to bottom) Microwave, thermal, Lewis acid, and carbocation hydrosilylation routes to alkyl-functionalized porous silicon.

2. Experimental

2.1. Materials

The following were purchased from the indicated suppliers and used without modification: silicon wafers (Addison Engineering, Inc., San Jose, CA), hydrofluoric acid (Mallinckrodt, 48%), triphenylcarbenium tetrafluroborate (Sigma–Aldrich), ethylaluminum dichloride (1.0 M in hexanes, Sigma–Aldrich). The subsequent reagents were acquired from Sigma–Aldrich and used after distillation, degassing with argon, and passing through dried alumina: 1-dodecene (95%), 1-dodecyne (98%), mesitylene (98%). Finally, HPLC grade solvents were obtained from Sigma-Aldrich and used directly: dichloromethane (DCM), ethanol, acetone, tetrahydrofuran (THF), and pentane.

2.2. Preparation of hydride-terminated PSi

Unfunctionalized, hydride-terminated PSi samples were prepared via anodic electrochemical etching under ambient conditions [40]. Note: HF is extremely hazardous and appropriate safety precautions must be observed. Polished, cleaned, and degreased silicon wafer fragments (B-doped, prime grade, (100) orientation, 1.0–5.0 Ω-cm, 575–650 μm thickness, 1.1 cm^2 exposed area) were secured in a customized Teflon cell and etched with 1:1 (v:v) 48% HF (aq)/ethanol in the absence of light under galvanostatic conditions of 7.1 mA/cm^2 for 30 min. Immediately after etching, samples were washed with copious amounts of ethanol, followed by pentane. Finally, samples were quickly transferred to a vacuum desiccator attached to a Teflon membrane pump and dried prior to characterization via FTIR.

2.3. Alkyl-functionalization of hydride-terminated PSi

Microwave-assisted hydrosilylation was accomplished using a multimode Milestone START Labstation reactor operating at 2.450 GHz [41]. In an inert atmosphere glove box, two PSi samples and ~10 mL of 1:2 (v:v) neat terminal alkene (or alkyne)/mesitylene were loaded into a Pyrex pressure vessel. The mesitylene served as a high boiling point solvent. A maximum power setting of 450 W was used to ramp the temperature of the reaction mixture to 180 °C within ten minutes, where this temperature was held for an additional fifty minutes (Fig. 2a). The temperature of the reaction mixture was continuously monitored during the reaction run through the use of an integrated infrared sensor. After cooling the reaction to room temperature, the PSi samples were removed from the reaction mixture and washed with THF, DCM, ethanol, and pentane. Samples were quickly transferred to a

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