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Wetting properties of silicon films from alkyl-passivated particles produced by mechanochemical synthesis

Steffen Hallmann [a], Mark J. Fink [b], Brian S. Mitchell [a,*]

[a] *Department of Chemical and Biomolecular Engineering, Tulane University, 300 Lindy Boggs, New Orleans, LA 70118, USA*
[b] *Department of Chemistry, Tulane University, 2015 Percival Stern Hall, 6283 St. Charles Ave., New Orleans, LA 70118, USA*

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ABSTRACT

A facile and efficient method using high energy ball milling (HEBM) to produce surfaces with a static and advancing contact angle in the superhydrophobic regime consisting of alkyl-passivated crystalline silicon particles is described. Deposition of the functionalized silicon material forms stable films on a variety of surfaces due to strong hydrophobic interactions between the individual particles. The process offers the ability to control the particle size from a micro-scale to a nano-scale region and thus to tune the surface roughness. Because of changing surface morphology and the decreasing surface roughness of the films due to the increasing milling times the static and dynamic contact angles follow a polynomial function with a maximum dynamic advancing contact angle of 171°. This trend is correlated to the commonly used Wenzel and Cassie-Baxter models.

1. Introduction

The large-scale production of crystalline superhydrophobic silicon films is still a technical challenge, since the majority of approaches is based on lithographic techniques followed by a chemical treatment [1,2]. Silicon self-cleaning surfaces might have applicability not only in photovoltaics, but also in a wide variety of other applications, such as anti-fogging and anti-oxidation coatings [3]. A solid substrate is termed superhydrophobic when the contact angle (CA) of water is greater than 150° and the contact angle hysteresis is below 5°. Superhydrophobic surfaces from nature, including the Lotus leaf [4], the Namib Desert Beetle [5], the Gecko [6], and the Water Strider [7,8] show a combination of micro- and nanometer scale structures, which are vital for the superhydrophobic properties [9]. These structural features are applied to artificial surfaces mainly via two approaches: establishing a combination of micro- and nanostructures on hydrophobic substrates, or chemically altering a micro- and nanoscale structured surface with materials of low surface energy [10]. Various fabrication methods have been proposed based on these approaches, including lithographic patterning [1,11–13], vapor deposition [14,15], utilization of templates [16], chemical deposition [17–19] self-assembled monolayers [20], layer-by-layer (LBL) [21,22], sol–gel methods with phase separation [23,24], plasma etching [25,26], and bottom-up approaches [27]. Previously we reported that high energy ball milling (HEBM) is an alternative route to the production of functionalized silicon nanoparticles [28]. This top-down method can be tuned to form alkyl-passivated silicon particles with a size distribution from tens of microns to single nanometers in diameter. In this communication, we report the formation and characterization of these particles to form stable films that may be further developed for superhydrophobic applications.

The HEBM process is fast and produces large quantities of material. The milling of silicon wafers in a reactive organic medium leads to a simultaneous production of crystalline silicon particles and the chemical passivation of the particle surface by alkyl groups covalently linked through strong Si—C bonds. Fig. 1 illustrates the reaction, later confirmed by NMR studies.

HEBM causes the silicon wafer to fracture and thus exposes reactive silicon radicals and silicon–silicon double bonds to the surrounding reactive milling medium. These groups react with the carbon–carbon double bond of an arbitrary alkene to give the Si—C bond. The process has also been demonstrated to form silicon nanoparticles functionalized with alkynes, alkenes, alcohols and carboxylic acids [29].

The advantages of this process include the rapid production of large quantities of functionalized silicon particles in a one step process, the possibility to be scaled up, a tuneable particle-size distribution, and control over the polarity and hydrophobicity of the covalently bound surface molecules. The resulting films are stabilized by hydrophobic interactions between the alkyl chains on the surface of the particles [30–32] and thus exceed the stability of a loose particle film. Due to the inter-particle attraction we were able to coat different substrates with various surface structures.

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* Corresponding author: Fax: +1 504 865 6744.
E-mail addresses: fink@tulane.edu (M.J. Fink), brian@tulane.edu (B.S. Mitchell).

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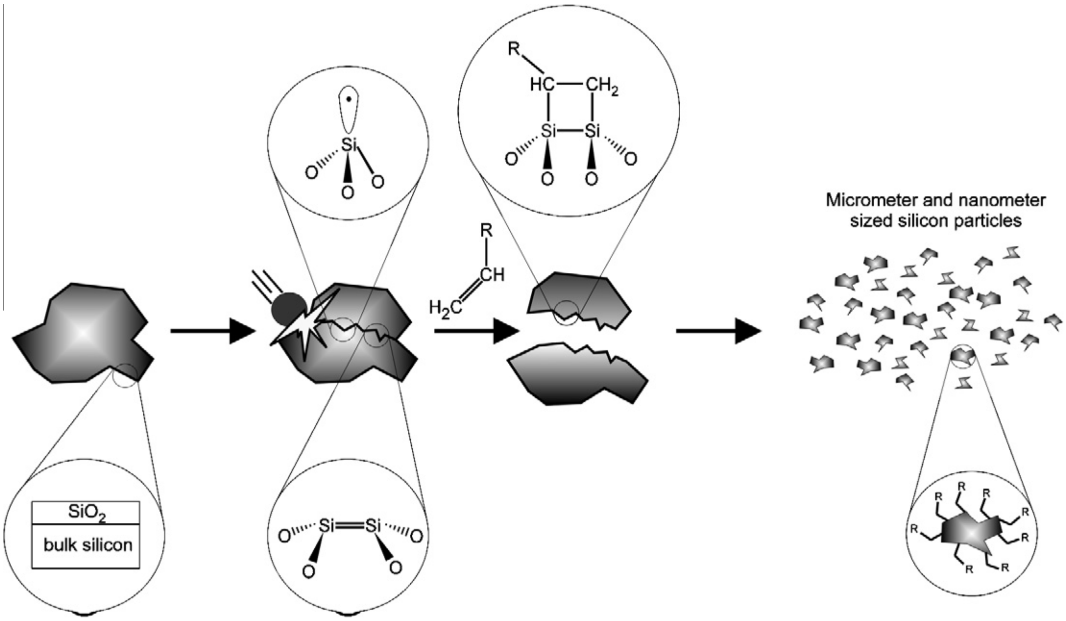

Fig. 1. Schematic illustration of the mechanochemical synthesis of functionalized silicon particles. Open circles represent subsurface silicon atoms.

2. Material and methods

2.1. Materials

2.5 g of silicon wafer (as obtained from Silrac, undoped, mirror finish, orientation [1 1 1]) were milled under inert (nitrogen) atmosphere in a hardened tool stainless steel vial with three hardened tool stainless steel milling balls (12 mm diameter), equaling a 1:10 ratio of milling material to milling balls. The monocrystalline silicon wafers were milled in 25 ml octene (as obtained from Sigma Aldrich, 97% purity), representing the reactive milling medium, for various milling times, ranging from 1 min to 12 h. The milling product was concentrated by centrifugation for 30 min at 500 G in a Thermo IEC® Centra CL2 centrifuge and the resulting solid sediment phase was resuspended in 7.5 ml of the supernatant. The supernatant consists mainly of alkyl functionalized silicon nanoparticles with sizes smaller than 100 nm, whereas the sediment contains particles from a nanometer sized to a micrometer sized regime. The sediment suspension was stirred for 10 min before coating a desired surface (usually a 25 mm × 25 mm glass slide) through drop-wise deposition of 1 ml of the alkyl functionalized silicon particles in octene, which equals a mass of about 0.3 g of particles. A nanoparticle solution was produced from the remaining supernatant according to previous published protocols [28]. For characterization, films from the micrometer sized particles as well as the nanoparticle solutions were deposited on 25 mm × 25 mm glass slides as described above. The coated surface was dried for 10 min in air at room temperature and then exposed to a reduced atmospheric pressure for 10 min. Weight controls of samples dried for longer times under reduced atmospheric pressure and elevated temperature revealed that after this procedure the coating is completely dry and approximately 100 μm thick.

2.2. Characterization

Fourier Transformed Infrared (FT-IR) spectroscopy was performed using a Thermo Nicolet NEXUS 670 FT-IR. The same unit, with an attached NXR FT-Raman Module, was additionally used for Raman spectroscopy. FT-IR was achieved from deposit films of silicon particles obtained after various milling times on a KBr plate, and for the Raman spectroscopy, a mixture of alkyl-passivated silicon particles and KBr powder were analyzed in NMR tubes. Nuclear magnetic resonance spectroscopy was conducted in chloroform-d_1 soluble alkyl-passivated silicon particles using a Bruker 300 Avance instrument. The static and dynamic contact angles were measured with a Standard Goniometer (ramé-hart Model 250) with DROPimage Advanced v2.4 and a droplet volume of 7.5 μl. The used volume increase/decrease to measure the dynamic contact angles was 0.2 μl/s. The surface roughness was measured with an Alpha-Step® 500 Surface Profiler. For surface roughness measurements, the deposited films were coated with a thin layer of gold (ca. 1 nm–4 nm) by resistance evaporation in a Polaron SEM coating system (voltage 2.4 kV, current 20 mA for 90 s). The commonly used root mean square (RMS), was used to evaluate the surface roughness. X-ray diffraction studies were performed by the XDS 2000 from Scintag with a Si(Li), Peltier cooled detector and −43 kV, 38 mA X-ray radiation from a copper anode. Here, 0.07 g of the functionalized silicon particle material was deposited on a zero-background quartz-plate. For scanning electron microscopy (SEM) and energy disperse X-ray spectroscopy (EDS), the Hitachi S-3400 N scanning electron microscope with INCAx-sight from Oxford Instruments was utilized. BET measurements were carried out by using the ASAP 2010 from Micrometrics with nitrogen (Non-ideality factor 0.000066, Density conversion factor 0.0015468, Thermal transition hard sphere diameter 3.860 Å, Molecular cross-sectional area 0.162 nm^2.) Surface area was calculated using the standard BET equation.

3. Results and discussion

Stable hydrophobic coatings can be obtained via deposition of alkyl-passivated crystalline silicon particles on glass, polymer, ceramic and metal surfaces. These films bind strongly to the substrate but are damageable by scratching. Further film stability can be obtained by crosslinking alkyl-halogen functionalized particles, but that is the object of a different communication. The alkyl functionalized particles were produced by HEBM, with milling times ranging from 1 min to 12 h. During the milling of crystalline silicon, highly reactive silicon sites are exposed to the surrounding