



Research paper

Synthesis of nanoscale silicon oxide oxidation state distributions: The transformation from hydrophilicity to hydrophobicity



William Laminack^a, James L. Gole^{a,b,*}, Mark G. White^{c,*}, Serdar Ozdemir^a, Andrew G. Ogden^b, Holly J. Martin^c, Zongtang Fang^d, Tsang-Hsiu Wang^d, David A. Dixon^{d,*}

^a School of Physics, Georgia Institute of Technology, 837 State Street, NW, Atlanta, GA 30332-0430, United States

^b School of Mechanical Engineering, Georgia Institute of Technology, 837 State Street, NW, Atlanta, GA 30332-0430, United States

^c Dave C. Swalm School of Chemical Engineering, James Worth Bagley College of Engineering, Box 9595, Mississippi State University, MS 39762, United States

^d Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487-0336, United States

ARTICLE INFO

Article history:

Received 1 April 2016

Revised 19 April 2016

In final form 21 April 2016

Available online 23 April 2016

Keywords:

Silicon oxide

Nanostructures

Hydrophobic

Hydrophilic

Oxidation state changes

X-ray photoelectron spectroscopy

Reflectance infrared spectroscopy

Thermogravimetric analysis

Scanning electron microscopy

ABSTRACT

Silicon oxide nanostructures which span the range from hydrophilic to hydrophobic have been synthesized. The surface chemistry of these silicon-based nanostructures was analyzed using a combination of X-ray photoelectron spectroscopy, reflectance infrared spectroscopy, scanning electron microscopy, and thermogravimetric analysis. The dominant oxidation state for the nanostructured oxides shifts from an average oxidation state of +III to a combination of +II and +III oxidation states. A correlation of the ability to adsorb water with variations in the surface Si:O ratios was observed showing a transition from hydrophilic to hydrophobic character.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Silica is widely used as a support surface so its surface chemistry is of great importance as it relates to the ability of the material to interact with both polar and semi-polar liquid systems [1]. As hydroxyl groups attach to the silicon atoms of the silica structure at the surface, the silica surface becomes hydrophilic and capable of hydrogen bonding to a number of molecules including water. In concert with the hydroxylation process, there can be a complementary change in the oxidation state of the silicon atom. Concomitantly, the ability of the silica surface to absorb water is intimately related to the nature of the surface silicon oxidation state [2].

Stable compounds of silicon might be expected to show oxidation states of 0, +II, and +IV associated with the equilibrium

solids of silicon and silicon oxide. Literature data for the Si 2p electron binding energy (eBE) from X-ray photoelectron spectroscopy (XPS) measurements of tetravalent silicon in an annealed quartz sample (eBE = 103.4 eV) and zero-valent silicon in an annealed metalloid (eBE = 99.3–99.9 eV) [3,4] sample have been reported as have XPS peaks at 100.5 and 103 eV [5] for a silicon oxide film prepared by evaporation under vacuum of a silicon monoxide powder. The observed XPS peaks were interpreted as intermediate oxidation states (+I and +III) of Si in a “non-equilibrium” surface oxide film. At the interface of Si and SiO₂, a thin layer of SiO_x has been reported [6] that has been modeled [7] as either (1) a heterogeneous distribution of separate domains with each domain having a phase with the following stoichiometry [Si₂O_n, n = 0, 1, 2, 3, 4], or (2) a single domain of stoichiometry SiO_x where five basic units are present in this film in a random fashion (Si–(Si_{4–n}O_n), n = 0–4). Solids sputtered from Si show oxidation states of silicon 0 to +IV depending upon preparation conditions. XPS [8] has been used to distinguish between these oxidation states, which appear to be separated by ~1.0 eV per formal oxidation state. Data obtained from the NIST XPS Database [9] indicate a range of eBE = 98.7–99.6 eV for Si(0), eBE = 101.7–102 eV for Si(II), eBE = 101.7–103.8

* Corresponding authors at: School of Physics, Georgia Institute of Technology, 837 State Street, NW, Atlanta, GA 30332-0430, United States (J.L. Gole). Dave C. Swalm School of Chemical Engineering, James Worth Bagley College of Engineering, Box 9595, Mississippi State University, MS 39762, United States (M.G. White). Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487-0336, United States (D.A. Dixon).

E-mail address: dadixon@au.edu (D.A. Dixon).

for Si(III), and eBE = 103.0–104.1 eV for Si(IV). In a recent analysis of the XPS spectrum of amorphous silicon monoxide [10], two bands were observed. The binding energies obtained by a deconvolution of these bands were 99.8(1) eV for Si(0), 100.6 eV for Si(I), 101.6 eV for Si(II), 102.7 eV for Si(III), and 103.8 eV for Si(IV). The suboxides (Si(n), n = I, II, III) are not considered discrete compounds but are a result of Si atoms in a matrix of 1, 2, and 3 O atoms and it is thought that these materials are only found in the transition region between Si and SiO₂ [11]. This hypothesis may require revision [1,12].

The current results demonstrate that, at the nanoscale, the mechanism associated with a change in silicon oxidation state, and the transformation from hydrophilicity to hydrophobicity can be correlated with an apparent change in the silicon to oxygen ratio. This change correlates directly with the conversion of silica nanospheres that subsequently agglomerate to form silicon-based nanowires. By increasing the silicon content of the nanostructured oxides that were synthesized, the system can transform from hydrophilic to hydrophobic. We combine the results of XPS, FTIR, SEM and TGA analysis, in concert with molecular electronic structure cluster calculations, to demonstrate the nature of water binding to the resultant silicon surface oxidation states, associated with the oxides and hydroxides, and the notably more hydrophilic character of silicon in its average +III and +IV oxidation states.

2. Experimental and computational details

2.1. Synthesis

To prepare the silica nanostructures used in the present experiments, our tube furnace configuration [13–17] was used to heat a Si/SiO₂ mixture to a typical central region operating temperature well in excess of 1400 °C. With a 1:1 Si/SiO₂ ratio carefully mixed and placed in an alumina crucible in the central region, the starting material is vaporized as it is entrained in Ar. The present experiments were performed with a quartz tube of length 30 in. placed inside the inner alumina tube of the tube furnace to enhance reaction. The 50/50 Si/SiO₂ mixture is heated to temperatures ranging from 1400 to 1440 °C. The tube furnace pressure is set to 240 Torr and the flow rate of the Ar gas is 130 standard cubic centimetres per minute (sccm). The furnace is heated at a rate of 5 °C per minute and maintained at the desired temperature for 12 h. At 1400 °C, a white powder (Fig. 1(a)) of SiO₂ is synthesized as reported earlier [18]. The white powder consists of silica nanospheres. After processing at 1440 °C to obtain a higher silicon content, the samples collected from the tube furnace cold plate and inner wall of the quartz tube contain significantly more silicon and are olive-brown in color. As the temperature is raised from 1400 °C,

we generate “off white” samples and, at intermediate temperatures, it is possible to transform to samples which appear yellow in color. Alternatively, the Si/SiO₂ ratio can be increased as we attempt to enhance the formation of Si _{x} O ($x > 1$) based nanostructures extending to Si₂O.

2.2. X-ray photoelectron spectroscopy

A PHI 1600 XPS Surface Analysis System (Physical Electronics, Eden Prairie, MN) was used to obtain XPS data from an area approximately 800 μm in diameter. The instrument also uses a PHI 10-360 spherical capacitor energy analyzer and an Omni Focus II small-area lens to focus the incident electron beam. XPS data were obtained using an achromatic Mg K α X-ray source operating at 300 W and 15 kV. Survey spectra were gathered using an average of 10 scans with a pass energy of 26.95 eV running from 1100 eV to 0 eV. High-resolution spectra were gathered using an average of 15 scans with a pass energy of 23.5 eV and a step size of 0.2 eV. The incident sample angle was held constant at 45°. To determine charge effects, reference was made to the carbon 1s peak and to known Si(IV) reference compounds, with adventitious carbon assigned to eBE = 284.5 eV. Charge effects were assessed for the four samples, whose spectra were taken sequentially. For statistical analysis, measurements were taken on two samples per treatment and two spots per sample. The XPS data was collected and averaged using PHI Surface Analysis Software (Version 3.0, Physical Electronics, Eden Prairie, MN). The XPS data was then analyzed using the Spectral Data Processor, SDP, (Version 4.0, XPS International LLC, Mountain View, CA).

2.3. SEM analysis

The SEM analyses performed on the white powder samples shown in Fig. 1(a) as well as on the off-white to yellow powders generated in these experiments are virtually identical to SEM (LEO 1530) and TEM (Hitachi HT-2000) results reported previously [14,17]. The samples are found to consist of silicon oxide nanoparticles (nanospheres) which grow in size with increased temperature. Data for the olive brown samples (Fig. 1(b)) taken with an Hitachi 3500H is, however, distinct in that the nanostructure distributions appear to be converted to a dominance of Si _{x} O ($x \geq 1$) nanowires.

2.4. TGA

The samples (2–5 mg) were characterized for water absorption capacity in a thermal gravimetric apparatus (Cahn microbalance). The pretreatment included an initial heating cycle between room

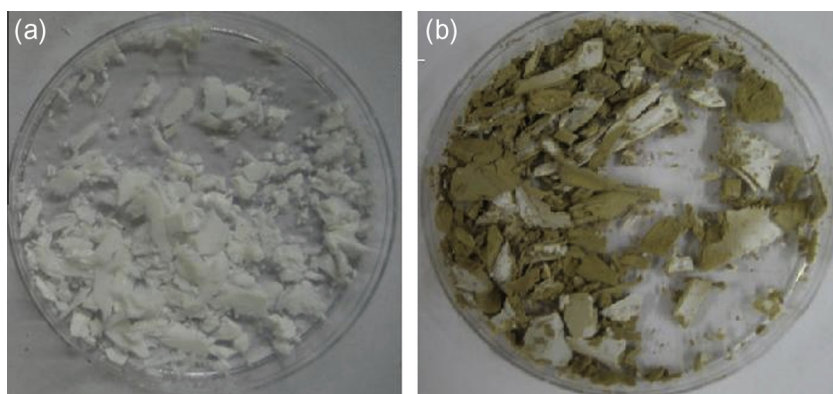


Fig. 1. Silicon/oxygen nanostructured powders synthesized at two distinct temperatures and experimental conditions (a) 1400 °C process. (b) 1440 °C process.

Download English Version:

<https://daneshyari.com/en/article/5378875>

Download Persian Version:

<https://daneshyari.com/article/5378875>

[Daneshyari.com](https://daneshyari.com)