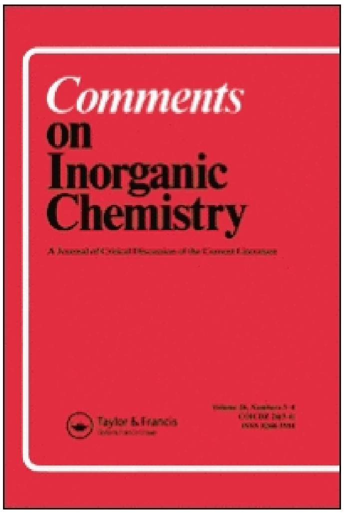

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Chemical Modification of Crystalline Porous Silicon Surfaces

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Chemical Modification of Crystalline Porous Silicon Surfaces

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A large number of mild chemical reactions have recently been developed to modify porous silicon surfaces for optical or sensor applications. The modification reactions generally fall into two classes: those which link a reagent to the Si surface through Si-O linkages, and those which use Si-C linkages. Examples of these reactions and the relative advantages of each approach are presented.

Keywords: *porous silicon, electrochemistry, surface chemical modification, silicon-oxygen bond, silicon-carbon bond*

1. INTRODUCTION

Visible room-temperature photoluminescence from porous silicon layers fabricated on the surface of single-crystal silicon wafers was first reported by Canham in 1990[1] and the phenomenon was subsequently confirmed by other research groups.[2,3] The light-emitting properties

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that Canham reported for porous Si were intriguing. Since the emission energy was well above the bandgap of bulk silicon, the energy (or color) can be tuned throughout the visible spectrum by changing the preparation conditions, and the quantum efficiency was comparable to that of direct bandgap compound semiconductors.[4]

Porous Si is comprised of a high surface area network of silicon nanocrystallites. It is synthesized by electrochemical corrosion of single-crystal silicon substrates in fluoride-containing solutions. Under the appropriate conditions, a matrix of photoluminescent silicon nanocrystallites results.[5] The most commonly used hypothesis to explain light emission in the visible range from porous Si is the confinement of charge carriers in quantum-sized nanocrystallites generated during the electrochemical etch.[1,4,6–9] The current density, hydrofluoric acid concentration, presence or absence of illumination during etching and, in particular, the doping type and resistivity of the silicon all influence the morphology of the porous layer.[1,10,11] For example, lightly doped p-type material tends to produce a sponge-like pore morphology, whereas n-type material and heavily doped p-type silicon tend to give rise to dendritic or columnar features. Porosities typically range from 50% to greater than 90%, with light emission generally occurring efficiently for the higher porosity material. The surface of porous Si obtained by electrochemical oxidation is terminated with hydrogen atoms.

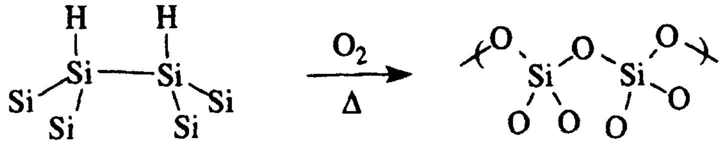
Since porous Si has a high surface-to-volume ratio, chemical species on the porous Si surface can influence the photophysical and chemical properties of this material dramatically. Much effort has recently been expended investigating fundamental photo- and electrochemical processes in order to probe the effects of these surface species on the electronic structure and optical properties of nanocrystalline Si. The hydrogen-terminated material oxidizes slowly in air, often resulting in loss of photo- or electroluminescent properties.[12–15] Many studies have been directed at understanding the chemical properties of H-terminated silicon surfaces in order to protect porous Si from loss of its luminescent properties. In addition, interest in porous Si for its potential application as chemical or biological sensors has led to considerable development of the surface chemistry.[16–19] Of particular interest have been reactions which impart functionality, such as molecular recognition, to the material.

2. SURFACE MODIFICATION THROUGH Si-O BONDS

Most efforts to functionalize porous Si have focused on formation of silicon oxide (SiO_2) species, either with thermal, chemical, or electrochemical reactions. Oxidation lowers the reactivity of the material and in some cases can improve the stability of properties such as photoluminescence. In addition, the chemistry of silicon oxide surfaces has been well developed for applications such as chromatography or catalysis, and so the conversion of the Si-H surface to an oxide surface provides a convenient entry into a wide range of existing functionalization methods.

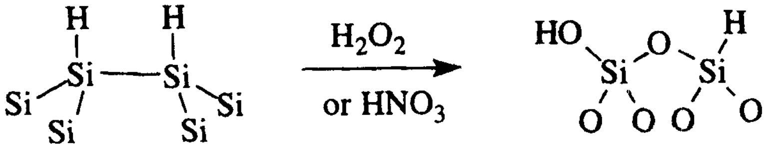
2.1. Thermal Oxidation

It has been found that very stable material can be generated by rapid thermal oxidation in an oxygen atmosphere at high temperatures (typically > 750°C).[20–22] The luminescent chromophore in porous Si is then isolated behind an electronically insulating thick silicon oxide layer. The oxidation process generates photoluminescent defect sites at the Si/SiO_2interface in many instances.[23,24] Although this approach has met with some success, oxidation of the interface is not desirable for electroluminescence applications. Electroluminescent device efficiency is generally hindered when the luminescent silicon nanocrystallites are covered with an insulating oxide layer.



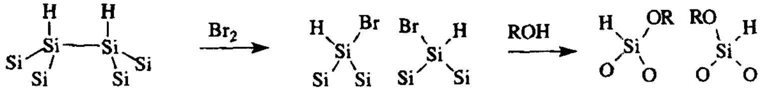
2.2. Hydrogen Peroxiden/Nitric Acid

Oxidation with organic or inorganic chemicals offers an alternative to thermal oxidation. These reactions are attractive because they can be performed at room temperature and in many cases lead to oxides with unique properties. The inorganic reagents hydrogen peroxide[25–27] and nitric acid[25] are commonly used to oxidize porous Si. These chemical oxidations provide good electronic surface passivation, they allow chemical functionalization, and they improve the stability of the material to environmental aging without burying the sample in a thick oxide layer. The photoluminescence spectrum obtained from oxidized samples is typically blue shifted from the original material and the intensity of photoluminescence is generally preserved or increased.



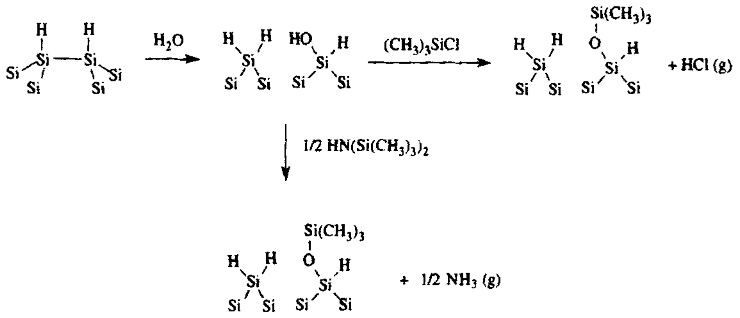
2.3. Halogen Vapor

Exposure of freshly etched (H-terminated) porous Si to vapors of halogens such as Cl_2, Br_2, or I_2 breaks the Si-Si surface bonds and creates a reactive Si-halide species.[17,28] The halide can be converted to a variety of silicon ether (Si-OR) surface species by subsequent exposure to alcohols or silanols.[29] Similarly, hydrolysis by water produces an Si-OH surface.



2.4. Trimethylchlorosilane/Hexamethyldisilazane

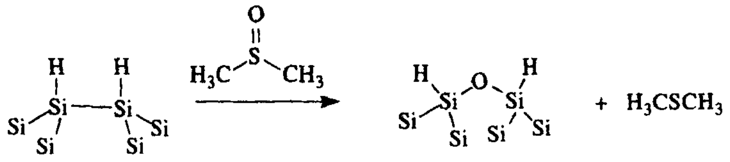
Trimethylsiloxy groups have been grafted to the surface of porous Si by exposing the material to vapors of trimethylchlorosilane[30] ($(CH_3)_3SiCl$) or hexamethyldisilazane[30,31] ($((CH_3)_3Si)_2NH$ (HMDS) in a wet atmosphere. Trimethylchlorosilane reacts with a surface hydroxyl group, forming a surface-bound trimethylsilicon group and HCl.[30] The hexamethyldisilazane reaction proceeds by interaction of the amine group of HMDS with adsorbed water on the surface of porous Si, which generates hydroxide that subsequently attacks and oxidizes the porous Si surface. The $Si(CH_3)_3$ group ends up attached to the silicon oxide layer.[30,31]



2.5. Dimethyl Sulfoxide

A stable oxide layer can also be generated on porous Si by exposure to liquid dimethyl sulfoxide (DMSO).[32] The DMSO reaction proceeds rapidly at room temperature, delivering an oxygen atom to the silicon surface and dimethylsulfide as a byproduct. The oxide layer is very defective, and porous Si samples oxidized in this manner show near complete loss of photoluminescence. The oxidation reaction is proposed to produce radical surface traps (dangling bonds) which reduce the intensity of the steady state photoluminescence spectrum by acting as non-radiative recombination centers.

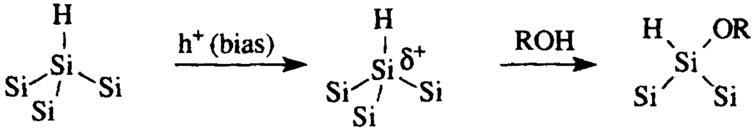
The rate of oxidation is reduced if the DMSO reaction is carried out in the presence of radical traps. In addition, photoluminescence intensity is preserved if the DMSO oxidation reaction is carried out in the presence of high concentrations of butylated hydroxytoluene (BHT). BHT acts as a radical trap by delivering a hydrogen atom. The added BHT is proposed to form a more electronically passive oxide layer by hydrogenating surface radicals generated during the DMSO oxidation reaction.



2.6. Electrochemical Oxidation

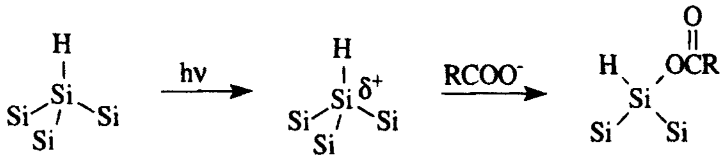
The surface of freshly prepared porous Si can be oxidized anodically in electrolytes that dont contain fluoride ion. Oxide coatings as thin as a monolayer in thickness can be formed in aqueous KNO_3 electrolytes (typically 0.1 M) at current densities of 0.1–100 mA/cm^2. The electrochemical oxides exhibit good electronic passivation of the surface.[2,33–35]

Chazalviel *et al.* have reported methoxy derivatization of the p-type porous Si surface by anodization of the porous layer in anhydrous methanol electrolyte (10 mA/cm^2, 20 sec).[36,37] The silicon is biased positive vs. a counter electrode, where the conduction and valence bands are bent such that electrons are driven into the bulk of the semiconductor, making the silicon surface more positive. Alcohols attack the electron deficient porous Si surface resulting in a surface-bound Si-OR species. These authors also reported that prolonged treatment of porous Si in alcohol results in dissolution of the porous layer, presumably by removal of Si atoms as $Si(OCH_3)_4$. The luminescence intensity is found to be preserved under these conditions.



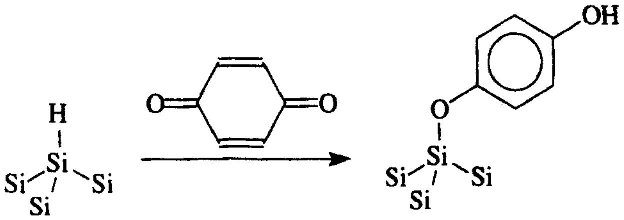
2.7. Photoelectrochemical Oxidation

The electronic structure of a semiconductor provides a source of electrons or holes that can be used to induce a reaction, and photoelectrochemical reactions have been developed to modify the silicon surface this way. For example, the surface of n-type porous Si has been derivatized photoelectrochemically in a formic acid/sodium formate electrolyte.[38] The functionalization is accomplished when n-type silicon is illuminated under reverse-bias conditions. Photoelectrons are driven into the bulk of the semiconductor, charging the silicon surface slightly positive and allowing nucleophilic attack by the formate electrolyte. A variety of carboxylic acids and alcohols can be induced to attack the surface in a similar fashion, resulting in a surface bound Si-ester species.[38–40] Photoluminescence is typically reduced after such treatments.



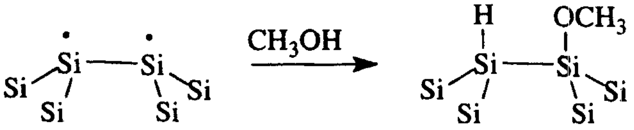
2.8. Abstraction of Surface Hydrides

The native hydrides on the porous Si surface can be used to reduce chemical oxidants such as benzoquinone. It has been demonstrated that porous Si reacts with 1,4-benzoquinone to give a surface-bound Si-p-hydroxyphenoxy group.[41] The resulting material is about 86% less photoluminescent than the freshly etched porous Si surface, presumably because the organic group acts as an efficient non-radiative surface trap. Photoluminescence from the modified material is more efficiently quenched by water vapor than from the freshly etched material, and less efficiently quenched by benzene vapor than the freshly prepared material due to the altered hydrophilic character of the surface.



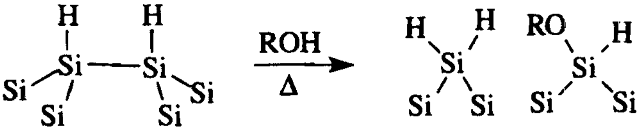
2.9. Dissociative Adsorption of Alcohol

The reaction of unpassivated porous Si with methanol was investigated by Yates and co-workers.[42,43] Surface hydrogen from electrochemically prepared porous Si was completely removed by flash annealing, in vacuum, to 750 K. The sample was then exposed to 9 Torr of methanol at 300 K. The authors showed that the adsorption of CH_3OH proceeded by cleavage of the O-H bond to form Si-OCH_3 and Si-H on the surface of porous Si.



2.10. Thermal Modification with Alcohols

Laibinis and co-workers have derivatized the surface of porous Si by reaction with liquid alcohols to form a covalently attached layer.[44] Unlike the gas-phase work described in Section 2.9, the modification does not use a preliminary thermal hydrogen desorption step. The porous Si samples are derivatized in neat alcohol (ethanol, 10-undecanol, and many other substituted alcohols) or in anhydrous dioxane solutions (0.1 M) at temperatures between 20 and 90°C. Under an atmosphere of N_2, the reactions take 0.5 to 24 h depending on the specific conditions. The authors suggest that the reaction between alcohols and the porous Si surface occurs with cleavage of Si-Si bonds, providing sites for attack of ROH to give Si-OR and Si-H species.[44] Similarly, Hory *et al* have studied the effect of exposure of porous Si to boiling methanol for 15 min.[35] The authors reported that the treatment results in a certain loss of hydrogen and formation of Si-OCH_3 groups on the surface, accompanied by extensive oxidation. The extra oxidation is attributed to residual water present in the solvent.



3. SURFACE MODIFICATION THROUGH Si-C BONDS

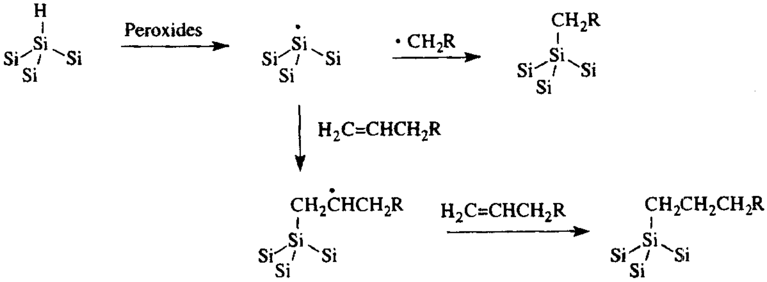
The Si-O bond in alkoxide or ester linkages is readily hydrolyzed, limiting the stability and applicability of these surface species for sensor applications. It is highly desirable to prepare modified porous Si surfaces that are chemically stable. The use of Si-C bonds is one such approach that has been shown to provide stable surface species. The reason for this greater stability arises from kinetic rather than thermodynamic considerations. The highly electronegative oxygen atom polarizes silicon atoms involved in Si-O linkages, making them susceptible to attack by nucleophiles. In contrast, Si-C is not as highly polarized and so is less susceptible to nucleophilic substitution. For example, tetramethoxysilane (TMOS) hydrolyzes rapidly in air to form SiO_2, while tetramethylsilane (TMS) is so stable that it is commonly used as an internal standard for NMR spectroscopy.

3.1. Radical Reactions

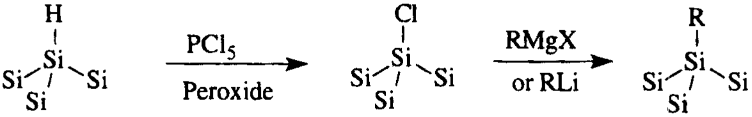
Linford and Chidsey have shown that single-crystal hydrogen-terminated silicon (H-Si(111) and H-Si(100)) surfaces can be derivatized with densely packed alkyl monolayers by photolysis of diacyl peroxides ($(CH_3(CH_2)_nC(O)O)_2$, n = 16 and 10) at 90–100 °C.[45,46] It is proposed that the alkyl radical, generated by thermal decomposition of the diacyl peroxide, abstracts a hydrogen atom from the silicon surface. The resulting silicon dangling bond either couples with another radical or stimulates the decomposition of another diacyl peroxide molecule. In the presence of an olefin, a surface-bonded secondary carbon radical can be formed, which then abstracts another hydrogen from an allylic position of an unreacted olefin to make the corresponding alkane on the silicon.

3.2. Halogenation/Alkylation

Lewis and co-workers have functionalized silicon with an alkyl layer in a two-step reaction.[47] In the first step, an HF-etched, H-terminated single-crystal silicon substrate is chlorinated with PCl_5 in a chlorobenzene solution containing benzoyl peroxide as the radical initiator. In the second step, the resulting Si-Cl surface is treated with an alkyl Grignard (RMgX, X = Br, Cl) or alkyl lithium (RLi) reagent to generate the sur-

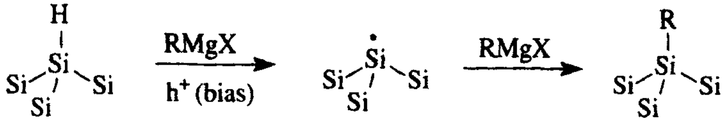


face-bound alkyl species. The authors report that these alkylated overlayers on the silicon surface impede the rate of surface oxidation of the silicon, and longer alkyl chains impart even more oxidation resistance.



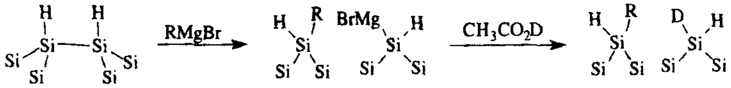
3.3. Electrochemical Methylation

The Grignard reaction described in the previous section apparently requires the surface activation step (pretreatment with PCl_5) in order to obtain reasonable coverages.[47] Activation of the silicon surface towards Grignard reagents can also be achieved electrochemically. Thus Chazalviel and co-workers have grafted methyl groups to porous Si surfaces by applying an electrochemical bias in electrolyte solutions containing Grignard or alkyllithium reagents.[37,48] The mechanism for alkyllithium and alkylgrignard reactions at porous Si surfaces is reported to involve hydride abstraction followed by alkylation at a Si surface atom. This chemistry is electrochemically assisted, and under the appropriate conditions nearly complete replacement of the surface hydrides can be achieved. The driving force for the reaction is the formation of a soluble metal hydride. It is noted that there is little or no change in the intensity of photoluminescence from porous Si after anodic functionalization with methyl groups, and the rate of air oxidation is clearly slower for the modified silicon samples.



3.4. Alkyl and Aromatic Grignard Reactions

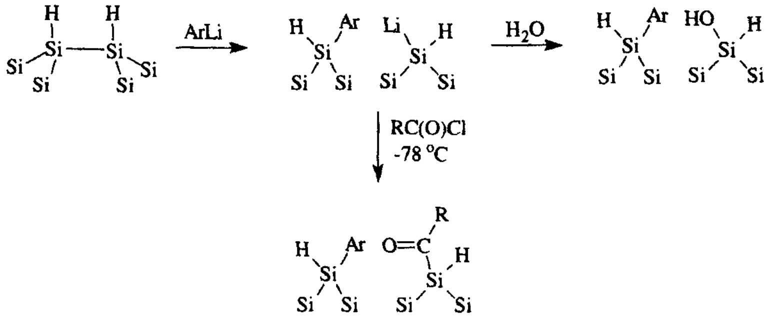
Laibinis and co-workers have reported the derivatization of porous Si surfaces by the Grignard reagents decylMgBr and 4-fluorophenylMgBr at room temperature without using an activating chlorination step or electrochemical assistance.[49] The product is a covalently Si-C bonded organic layer. If the Grignard reactions are quenched with HCl, CH_3CO_2D, or acetyl chloride before exposure to air, little formation of silicon oxide is observed. The authors have suggested that the Grignard reagent reacts with porous Si to produce silyl anions by cleavage of a Si-Si bond, forming Si-R and Si-MgBr species. Workup with the electrophilic reagent then replaces the MgBr species with the electrophile. It is also reported that photoluminescence properties of these modified porous Si samples are preserved and even enhanced upon functionalization.



3.5. Phenyllithium/Lithium Phenylacetylide

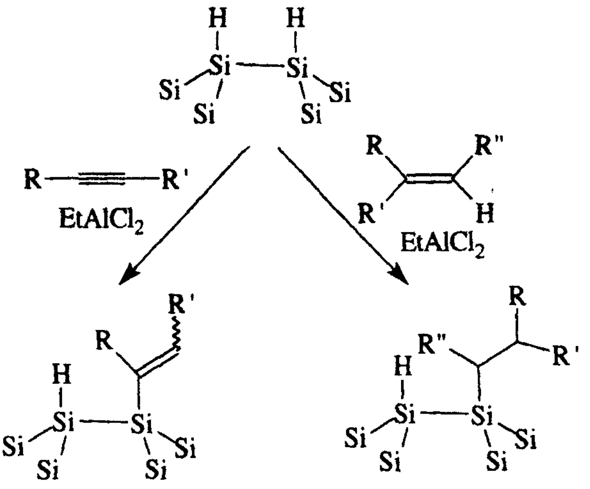
Exposure of porous Si to phenyllithium or lithium phenylacetylide results in grafting of the corresponding aryl to the silicon surface by formation of a Si-C bond.[50] Unlike the Si-O bonded compounds, the silicon bound aryls cannot be removed with an ethanolic HF rinse. This stability towards HF is a characteristic test for the Si-C linkage; if the functional group is bound to the surface via Si-O bonds it will be removed in an HF rinse. The alkylation reaction is thought to proceed by addition of the aryllithium reagent across a surface Si-Si bond, resulting in a Si-aryl and Si-Li species. The highly reactive Si-Li surface species is readily hydrolyzed by water, resulting in significant surface oxidation. Analogous to the MgBr intermediate of Section 3.4, the surface-bound Li provides a convenient means for subsequent addition of electrophiles (e.g., proton or acid chloride) to the porous Si surface with no or little surface silicon oxide formation. Note that the proposed Si-Si cleavage mechanism of aryllithium and Mg Grignard addition is distinct from the hydride abstraction mechanism proposed for the Grignard reactions described in Section 3.3. It is likely that both mechanisms are operative in these nucleophilic addition reactions.

It is also noted that functionalization with phenyllithium preserves some of the photoluminescence, while the lithium phenylacetylide reaction results in almost complete loss of photoluminescence from the Si nanocrystallites, presumably because the interaction of the phenylacetylide moiety with Si nanoparticle-based orbitals introduces states of the appropriate energy for nonradiative quenching to occur.



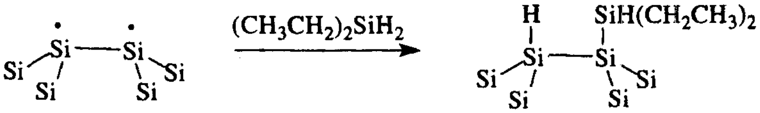
3.6. Lewis Acid Catalyzed Hydrosilylation

Buriak and Allen have reported that $EtAlCl_2$ mediated hydrosilylation of alkynes and alkenes yields vinyl and alkyl groups covalently bound to the porous Si surface.[51] Hydrosilylation of 3-butyn-1-ol, 5-cyano-1-pentyne and methyl 10-undecanoate was carried out, resulting in hydroxyl-, nitrile-, and methyl ester-terminated surfaces, respectively. Lewis acid-assisted addition of 1-Hexene and 2-methyl-2-butene require longer times due to the lower reactivity of alkenes relative to alkynes. It is also noted that the hydrophobic alkyl and alkenyl-terminated surfaces are remarkably stable in boiling water or in boiling aqueous KOH (KOH, pH = 10). Porous Si layers without such functionalization dissolve in seconds at pH 10. It should be noted that hydrosilylation reactions have also been achieved at single-crystal Si surfaces, although these reactions are mediated by a Pt hydrosilylation catalyst rather than a Lewis acid.[52]



3.7. Dissociative Adsorption of Diethylsilane

Dillon and co-workers have grafted ethyl groups to a porous Si surface by first vacuum-annealing (640–800 K) the material to remove surface hydrides and then exposing it to diethylsilane in ultra-high vacuum.[53] The FTIR spectra revealed that diethylsilane dissociatively adsorbs to the porous Si surface, forming Si-H and Si-CH_2CH_3. Although this reaction deposits a Si-C bound methyl species on the surface, the reaction that places it there involves Si-Si bond formation. Similar chemistry occurs with diethylgermane, in that case forming a Si-Ge bond at the surface. In the Ge chemistry, the alkyl group is found to migrate from Ge to Si surface atoms, so the net reaction results in formation of Si-C bonds.[54]



4. CONCLUSIONS

The suite of chemical reactions that have been developed to functionalize Si surfaces is still fairly small. This area is rapidly developing, driven by the needs of sensor and electronic device applications. The next few years should see increases in both the number of chemical reactions and in the types of applications for functional nanostructured Si surfaces.

Abbreviations: *porous Si (porous Si); hexamethyldisilazane (HMDS); dimethyl sulfoxide (DMSO); 2,6-di-tert-butyl-4-methylphenol (BHT).*

Acknowledgments

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