

Spectroscopic characterisation of chemically modified porous silicon

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ABSTRACT

The discovery of room temperature photoluminescence in porous silicon has opened up a range of applications for this material in new areas such as optical, photodetector, photovoltaic, micromachine and sensors. For this reason there have been significant efforts in recent years directed at modification of silicon surfaces via formation of Si-C and Si-O-E (E = H, C, N) bonds on the silicon surfaces. However, research on bonding of metallorganic fragments to the silicon surface is scant. The main objectives of our work are to develop and investigate new ways of specific chemical bonding of selected metallorganic compounds to the Si surface and to prepare new types of silicon-based materials. New metallorganic composites have been developed on macro- and micro- porous silicon surfaces. The silicon surfaces have been effectively modified using inorganic and organometallic chemistry approaches. The work includes: (i) preparation and investigation of Cl-, HO-, and Cp- modified porous Si-surfaces; (ii) preparation and characterisation of iron oxide layers on porous silicon; (iii) characterisation of metallorganic layers on porous silicon by FTIR, EDX and Scanning Electronic Microscopy (SEM). There are strong possibilities that those composite materials will have a wide range of applications in nano-technology and optoelectronics.

Keywords: Porous Silicon, nanocomposites, IR spectroscopy

1. INTRODUCTION

Functionalisation of silicon surface by organic and organometallic reagents has been an active area of research due to its application in microelectronics^{1, 2}. A number of papers on the surface modification of silicon, including porous silicon have been published recently¹⁻⁶. The discovery of visible photoluminescence in porous silicon first by Pickering et al.⁷ and more recently by Canham⁸ opened up novel application for this material in new areas such as optical, photo detector, photovoltaic, micromachine, and sensor technologies. This discovery added more interest in the modification of silicon surfaces via formation of Si-C and Si-O-E (E = H, C, N) bonds on silicon surfaces^{3,4,9-15}. The most common way for chemical bonding of organic reagents to Si surface is the hydrosilylation of silicon-hydride terminated surfaces^{9,10}. There are also a few publications on reactions of metallorganic and amino reagents with Cl-terminated surfaces¹¹ and cycloaddition reactions on clean Si (100)¹². Most of this work is related to the attachment of organic groups to the Si surface using standard organic chemistry approaches. Research into bonding metallorganic fragments to the silicon surface is scant. Meanwhile, many metallorganic systems have been envisaged to be potential components and their incorporation onto a silicon surface might lead to very interesting and useful materials with potential application for spin-polarised electronics, innovative data memory devices, non-linear optics, sensors and molecular electronics components¹⁶. In this paper we report the preparation and characterisation by FTIR spectroscopy of Cl-, HO-, and cyclopentadienyl- (Cp)modified porous silicon -surfaces as well as iron oxide layers on porous silicon (PS).

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2. EXPERIMENTAL

2.1. Silicon sample preparations

All experiments were carried out using the Schlenk techniques under argon atmosphere.

The macroporous silicon used in this study has a system of regular cylindrical pores of micrometer diameter and high aspect ratio¹⁷. The starting material was single-crystal (100)-oriented Czochralski-grown n-type silicon with resistivity $\rho = 15 \Omega\cdot\text{cm}$. A standard photolithographic process was employed to form pits spaced 12 μm apart on the polished surface of the silicon wafer. Deep pores were etched electrochemically in a 2.5% aqueous-ethanol solution of HF for 300 to 450 min under backside illumination¹⁷ at a voltage of 5V and a constant current density of $j=3 \text{ mA}/\text{cm}^2$. The pore depth was 200-250 μm and pore diameter $d=3-4.5 \mu\text{m}$, which corresponds to the porosity of our triangular lattice 5.7-12.8%. The meso-porous silicon was prepared using a standard procedure of anodic etching of p-type Si(100) 4 inch wafer (resistivity 1-10 $\Omega\cdot\text{cm}$) with 1:1 48% HF(aqueous)/EtOH in a teflon cell.

Porous silicon wafers were first etched by a HF: NH_4F (4:1) mixture for 10 minutes followed by rinsing with de-ionised water (Millipore, 18.2 $\text{M}\Omega\cdot\text{cm}$) taking less than one minute. These etching conditions produce a mono-hydride porous silicon surface². The samples were then dried under argon gas.

To generate -OH functionalities on the silicon surface we followed a procedure as reported earlier¹⁵ with slight modifications. The silicon samples were cleaned for 1 h in a $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (7:3 v/v) mixture at $\sim 80^\circ\text{C}$ and then cooled to room temperature. The cleaned substrates were rinsed with de-ionised water then treated further with a $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_3$ (5:1:1 v/v/v) mixture and dried under vacuum.

2.2. Chemical binding of cyclopentadienyl functionality

A solution of cyclopentadienylsodium (CpNa) in THF was prepared according to published procedure¹⁸. Two different procedures for the chemical binding of Cp to the silicon surface have been used in this work.

2.2.1 Bonding of Cp via a spacer.

Hydroxylated porous silicon substrates were immersed in a 1:50 (v/v) solution of (3-chloropropyl)triethoxysilane (1 ml) and triethylamine (0.5 ml) in n-hexane (50 ml). The samples were then treated in ultrasonic bath for 20 minutes. Washings were done with dry hexane and diethyl ether and then dried with argon gas. The samples were then treated with CpNa in THF, sonicated for 30 minutes and kept over night. The solution of CpNa in THF was decanted, silicon samples were washed 3 times with dry THF and dried in vacuum for 12 hours at the room temperature.

2.2.2 Direct bonding of Cp

The H-terminated porous silicon wafers were irradiated under UV light in presence of Cl_2 gas. The resulting Cl-capped porous silicon was treated with metallated Cp, placed in an ultrasonic bath for 30 minutes and kept over night.

2.3. Preparation of $\text{Fe}(\text{OBU}^t)_2(\text{THF})_2$ precursor

NaOBU^t (0.68 g, 7.08 mmol) was added to FeBr_2 (0.76 g, 3.54 mmol) in THF (100 ml) at ca. 0 $^\circ\text{C}$. The mixture was stirred for 24 h at the ambient temperature, filtered and the filtrate then was used in further experiments on functionalisation of Si surfaces.

2.4. Preparation of iron siloxane and iron oxide on silicon layers

The $\text{Fe}(\text{OBU}^t)_2(\text{THF})_2$ precursor solution in THF was added to the -OH functionalised macroporous silicon samples and the mixture was sonicated for one hour. Silicon surface was washed 3 times with dry and 2 times with wet diethyl ether and then dried under vacuum. Silicon samples were heated up to 100 $^\circ\text{C}$ under vacuum for 12 hours using oil bath.

2.5. FTIR spectroscopy

Fourier transform infrared (FTIR) measurements were performed in transmission mode using a Digilab FTS-6000 spectrometer. The sample was placed either in the main chamber of spectrometer, using a Perkin-Elmer micro-sampling attachment, or on the positional stage of a UMA 500 IR microscope. For measurements in the main chamber a wide band MCT detector in the wavenumber range of 450-6000 cm^{-1} with a resolution of 2 cm^{-1} and 8 cm^{-1} was used. A narrow band MCT detector with a spectral range of 4500-750 cm^{-1} was used in a UMA 500 IR microscope. A total of 128 scans were summed to increase the signal-to-noise ratio in both cases.

2.5. Photoluminescence spectroscopy

Room temperature photoluminescence (PL) spectra were measured with a Renishaw 1000 micro-Raman system. The excitation wavelength was 514.5 nm from an Ar^+ ion laser (Laser Physics Reliant 150 Select Multi-Line) with a typical

laser power of $\sim 20 \text{ W cm}^2$ in order to avoid excessive heating. The 100x magnifying objective of the Leica microscope focused the beam into a spot of about $1 \mu\text{m}$ in diameter. Typically PL spectra were measured from a few different spots on the external surface of as received micro-porous silicon sample and on the same sample after the chemical bonding.

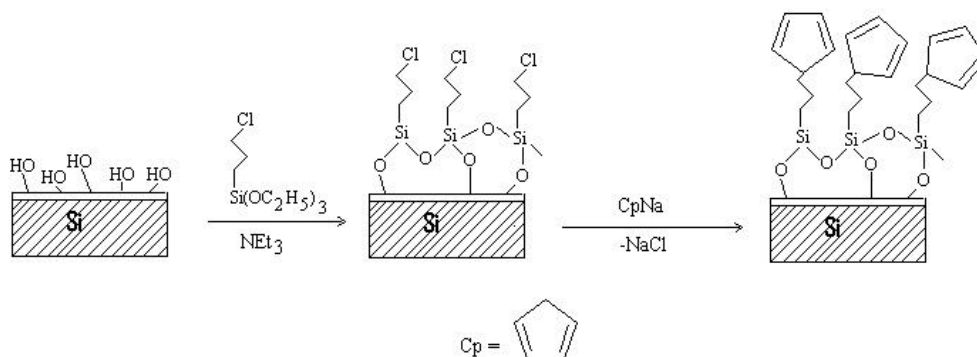
2.6. Conductivity measurements

The electrical conductivity was done by a four-point probe method. The technique involves passing a fixed known current between the outer probes and measuring the corresponding voltage drop across the inner probes. Geometric factors such as the probe spacing and sample thickness must be taken into consideration in order to get a reasonable estimate of resistivity. For a particular set-up, Resistivity, $\rho = 4.532 (V/I) x$, where x is the wafer thickness, V is the voltage in mV and I is the current in mA. The constant 4.532 is a correction factor to allow for the fact that current does not flow in a straight line between the outer probes but rather in an arc-like path.

3. RESULTS AND DISCUSSION

3.1. Preparation and characterisation of Cp- modified porous Si-surfaces

Although there are publications on ring compounds like cyclohexene and cyclohexadiene on silicon surfaces^{19,20}, we can see that a very little work has been carried out on the binding of five membered ring to silicon surface²¹. In this part of our work we report a chemical binding of cyclopentadienyl (Cp) ligand (five membered ring) to porous silicon surfaces. The cyclopentadienyl groups have been attached to the silicon surface either *via* organic (3-halogenopropyl) siloxy spacer or directly *via* C-Si/surface bond. The sample with (3-chloropropyl) siloxy spacer was prepared according to Scheme 1. A clean hydroxylated silicon surface was first treated with (3-chloropropyl) triethoxysilane to introduce the chloroalkyl functionality¹⁵. The process was monitored by FTIR spectroscopy (Figure 1), which clearly showed the presence of Si-O-Si and Si-O-C in the range $1000\text{-}1100 \text{ cm}^{-1}$, CH_2 vibrations at 2934 and 2852 cm^{-1} and $\text{CH}_2\text{-Cl}$ vibrations at 1228 and 1280 cm^{-1} .



Scheme 1 Bonding of cyclopentadienyl groups to the silicon surface through a (3-chloropropyl) siloxy spacer

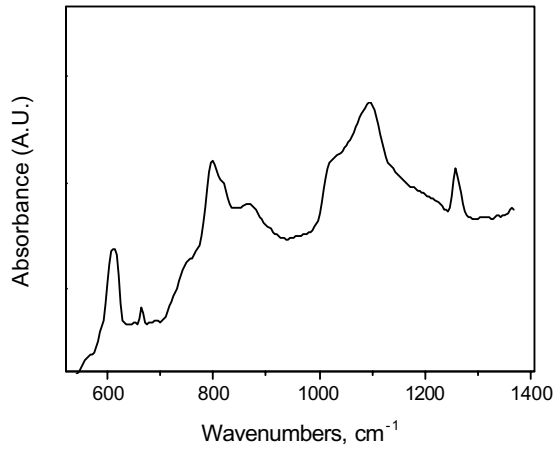


Figure 1. FTIR spectra of the $(OC_2H_5)_3Si(CH_2)_3Cl$ spacer on porous Si surface.

The chloro-alkyl functionalised surfaces were then treated with a solution of cyclopentadienylsodium (CpNa) in THF at the ambient temperature. The samples were washed with dry THF and then dried in vacuum. The FTIR spectra (Table 1) of the samples contain CH_2 , SiC, Si-O-Si and Si-O-C bands of the spacers and characteristic cyclopentadienyl bands at 2964 and 798cm^{-1} .

Table 1 Assignment of the IR bands for Cp-modified porous silicon.

Assignment	Cp/PS (bonded <i>via</i> spacer $(O(C_2H_5)_3Si(CH_2)_3Cl)$, [cm^{-1}]	Cp/PS (bonded directly to Si), [cm^{-1}]
$\nu(CH_2)$	2964, 2927, 2907, 2852	
$\nu(C=C)$	1449, 1670	1449, 1720
$\delta(CH_2)$	1200, 1264	1172, 1227
$\nu(C-C)$	1099	1105
$\delta(Si-O-Si) + \delta(Si-O-C)$	1000-1100	-
$\delta(CH)$	1021	1020
$\nu(SiC)$	798	803
$\pi(CH)$	816	815

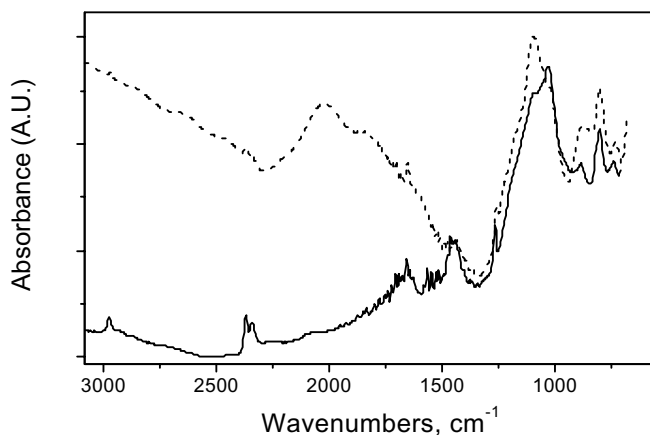
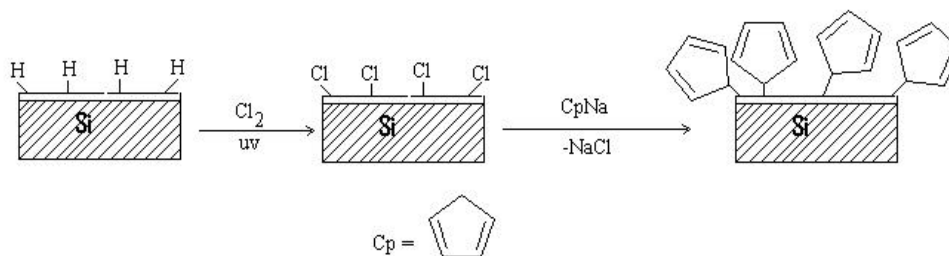


Figure 2. FTIR spectra of cyclopentadienyl bonded via spacer (solid line) and directly to the silicon surface (dotted line).

Direct bonding (without a spacer) of cyclopentadienyl groups to the silicon surface was performed according to Scheme 2. The chlorinated silicon surface was prepared by UV-initiated reaction of chlorine with the clean silicon-hydride terminated surface. The Cl-functionalised surface was then treated with solution of CpNa in THF at the ambient temperature. The FTIR spectrum (Table 1) of the sample contained characteristic cyclopentadienyl bands 815 cm^{-1} , SiC band at 803 cm^{-1} , which indicate the presence of cyclopentadienyl ring attached to the surface. It should be noted that SiC band at 803 cm^{-1} is much more intense when cyclopentadienyl is directly bound to Si surface. In addition noticeable feature appeared in the range $1440\text{--}1520\text{ cm}^{-1}$. We believe that this band belongs to C=C stretching vibration of cyclopentadienyl ligand, which is bonded to the Si surface.



Scheme 2. Direct bonding of cyclopentadienyl to silicon surface.

EDX of the both cyclopentadienyl functionalised silicon samples indicated the presence of NaCl, which was left after the reaction of CpNa with the Cl on the surface. SEM (Figure 3) image of the silicon surface have also shown that pores are filled with the spacer and NaCl.

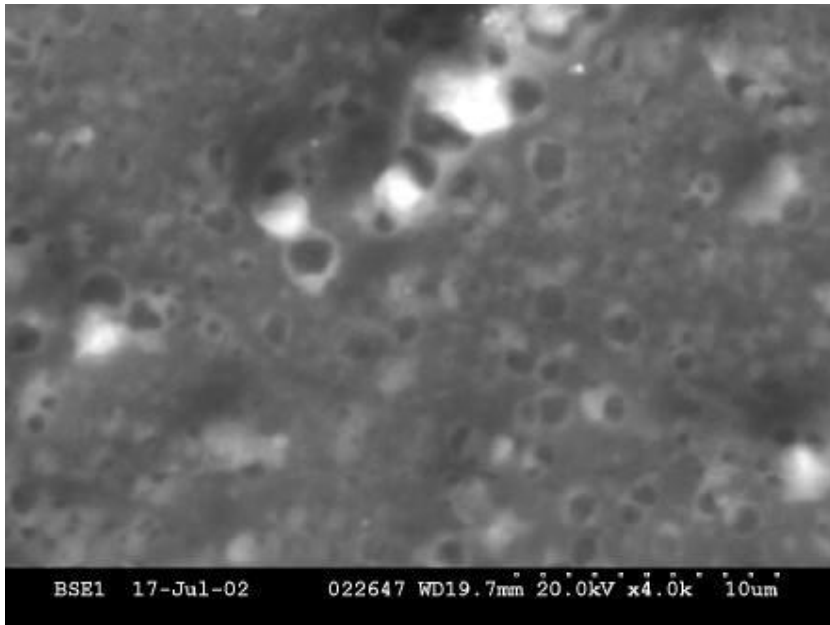
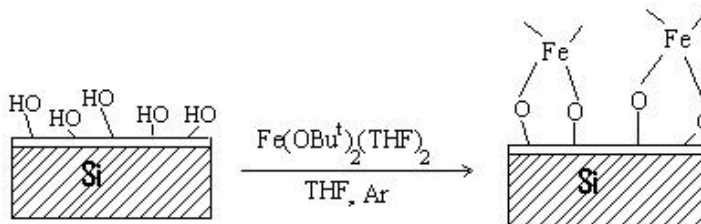


Figure 3. SEM image of cyclopentadienyl functionalised silicon surface.

The preliminary measurements of PL spectra at room temperature show for micro-porous silicon (after oxidation and oxide removal in HF solution) the presence of band at ~ 720 nm, which was substantially reduced in intensity after bonding to porous silicon surface both spacers, and all functional groups (iron oxide and cyclopentadienyl). Conductivity measurement by 4 point probe method did not show any substantial changes within the error of the experiment.

3.2. Preparation and characterisation of iron oxide layers on porous Si-surfaces

In this part of our work we performed bonding of the iron oxide moieties to the meso-porous silicon surface through the Fe-O-Si linkage. The preparation of iron oxide layers on silicon surface was performed according to Scheme 3. A clean hydroxylated silicon surface was treated with $\text{Fe}(\text{O}i\text{Bu})_2(\text{THF})_2$ precursor solution in THF. After the ultrasonic treatment silicon surface was washed with diethyl ether and dried under vacuum. Then silicon samples were heated up to 100°C under vacuum for 12 hours. The prepared layers have been studied by FTIR and micro-Raman spectroscopy. The IR spectrum (Figure 3) have shown a shoulder at 1036 cm^{-1} , which was assigned to Fe-O-Si stretching vibrations²². There are also a broad band at 1097 cm^{-1} attributed to Si-O linkage²³. A band at 1625 cm^{-1} is the characteristic for bending mode of Fe-OH groups. There are also typical for Fe_2O_3 intense absorptions at 600 cm^{-1} (not shown here).



Scheme 3. Preparation of iron oxide layers on silicon surface.

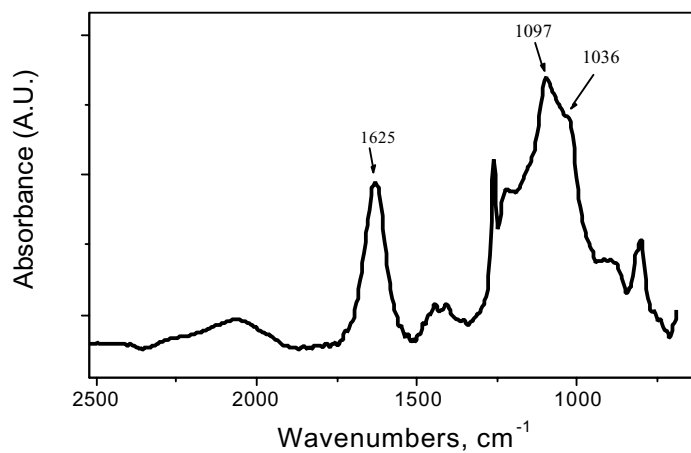


Figure 4. FTIR spectrum of iron oxide on porous silicon layers.

The presence of iron in the sample have also been confirmed by the EDX, which clearly showed Fe peak. A SEM image of the iron oxide – porous silicon composite (Figure 5) have shown that pores are filled with micro- and nanoparticle of iron oxide.

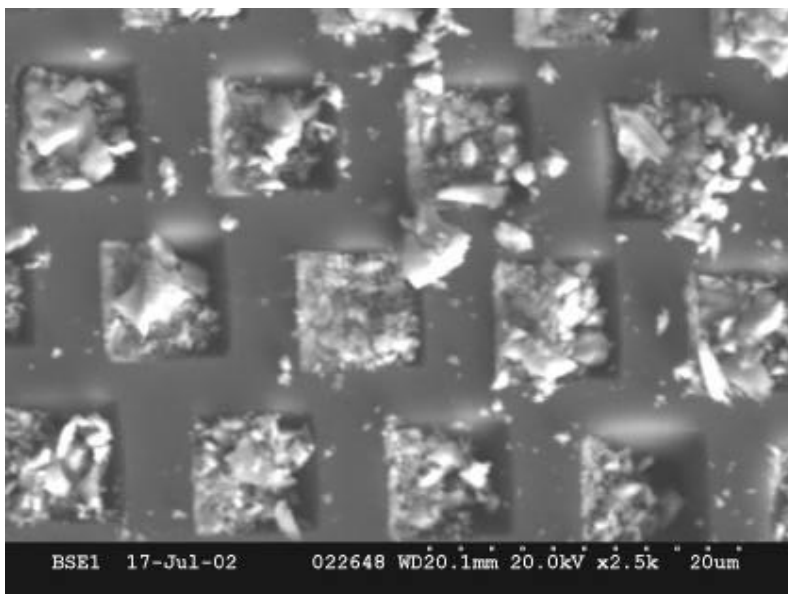


Figure 5. SEM image of iron oxide particles on porous silicon.

4. CONCLUSIONS

Thus we have shown that porous silicon surfaces can be effectively functionalised with cyclopentadienyl and iron oxide groups using organometallic approaches. The functionalised silicon surfaces are conveniently characterized by FTIR, EDX and SEM. Further research on sensor properties of the samples are currently in progress.

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REFERENCES

1. H. N. Waltenburg, and J. T. Yates, Jr., "Surface Chemistry of Silicon," *Chem. Rev.* **95**, pp. 1589-1673, 1995.
2. M. R. Linford, P. Fenter, P. M. Eisenberg, and C. E. D. Chidsey, "Alkyl Monolayers on Silicon Prepared from 1-Alkenes and Hydrogen-Terminated Silicon," *J. Am. Chem. Soc.* **117**, pp. 3145-3155, 1995.
3. J. H. Song, and M. J. Sailor, "Functionalization of Nanocrystalline Porous Silicon Surfaces with Aryllithium Reagents: Formation of Silicon-Carbon Bonds by Cleavage of Silicon-Silicon Bonds," *J. Am. Chem. Soc.* **120**, pp. 2376-2381, 1998.
4. J. M. Buriak, and M. J. Allen, "Lewis Acid Mediated Functionalization of Porous Silicon with Substituted Alkenes and Alkynes," *J. Am. Chem. Soc.* **120**, pp. 1339-1340, 1998.
5. A.B. Sieval, R. L. H. Zuilhof, and E. J. R. Sudholter, "High-Quality Alkyl Monolayers on Silicon Surfaces," *Adv. Mater.* **12**, pp. 1457-1460, 2000.
6. J. E. Bateman, R. D. Eagling, D. R. Worrall, B. R. Horrocks, and A. Houlton, "Alkylation of Porous Silicon by Direct Reaction with Alkenes and Alkynes," *Angew. Chem. Int. Ed.* **37**, pp. 2683-2685, 1998.
7. D. D. Malinowska, M. S. Vassileva, Ts. Marinova, V. Krastev, M. Kamenova, and N. Tzenov, "Correlation between the photoluminescence and chemical bonding in porous silicon," *Thin Solid Films.* **255**, pp. 191-195, 1999.
8. L. T. Canham, "Silicon quantum wire with array fabrication by electrochemical and chemical dissolution of wafers," *Appl. Phys. Lett.* **57**, pp. 1046-1048, 1990.
9. J. M. Buriak, "Silicon-Carbon Bonds on Porous Silicon Surfaces," *Adv. Mater.* **11**, pp. 265-267, 1999.
10. J. M. Buriak, "Organometallic chemistry on silicon surfaces: formation of functional monolayers bound through Si-C bonds," *Chem. Commun.*, pp. 1051-1060, 1999.
11. W. F. Bergerson, J. A. Mulder, R. P. Hsung, and X. -Y. Zhu, "Assembly of Organic Molecules on Silicon Surfaces via the Si-N Linkage," *J. Am. Chem. Soc.* **121**, pp. 454-455, 1999.
12. R. Konecny, D. J. Doren, "Theoretical Prediction of a Facile Diels-Alder Reaction on the Si(100)-2x1 Surface," *J. Am. Chem. Soc.* **119**, pp. 11098-11099, 1997.
13. M. P. Stewart, and J. M. Buriak, "Photopatterned Hydrosilylation on Porous Silicon," *Angew. Chem. Int. Ed.* **37**, pp. 3257-3260, 1998.
14. N. Y. Kim, and P. E. Laibinis, "Derivatization of Porous Silicon by Grignard Reagents at Room Temperature," *J. Am. Chem. Soc.* **120**, pp. 4516-4517, 1998.
15. R. Cohen, N. Zenou, D. Cahen, and s. Yitzchaik, "Molecular electronic tuning of Si surfaces," *Chem. Phys. Lett.* **279**, pp. 270-274, 1997.
16. A. Nakamura, *Specially Promoted Research, Organometallic Conjugated System*, pp. 1995, 1997.
17. V. Lehmann, and H. Foll, "Formation mechanism and properties of electrochemically etched trenches in n-type silicon" *J. Electrochem. Soc.* **137**, pp. 653-659, 1990.
18. J. Kleinberg (ed.), *Inorganic Syntheses*, 7:101, McGraw-Hill Book Company, New York, 1963.
19. C. D. MacPherson, D. Q. Hu, M. Doan, and K. T. Leung, "Catalytic dehydrogenation and thermal chemistry of cyclohexene & 1-methyl-1,4-cyclohexadiene on Si(111) 7x7," *Surf. Sci.* **310**, pp. 231-242, 1994.
20. D. Q. Hu, C. D. MacPherson, and K. T. Leung, "Dehydrogenation of cyclohexene, 1,3-cyclohexadiene and 1,4-cyclohexadiene to Benzene on Si(111) 7x7," *Surf. Sci.* **273**, pp. 21-30, 1992.
21. B. Das, and K. L. Sebastian, "Molecular wheels on surfaces," *Chem. Phys. Lett.* **357**, pp. 25-31, 2002.
22. C. W. Jung, "Surface properties of superparamagnetic iron oxide MR contrast agents: ferumoxides, ferumoxtran, ferumoxsil," *Magnetic Resonance Imaging.* **13**, pp. 675-691, 1995.
23. J. E. Bateman, R. D. Eagling, B. R. Horrocks, A. Houlton, and D. R. Worrall, "Role for organic molecules in the oxidation of porous silicon," *Chem. Commun.* pp. 2275-2276, 1997.