Preparation of Aryldiazonium Salt Monolayers on Si(100) Surface by Chemomechanical Method

Li-qiu Shi∗, Lin Zhanga, Feng Yu, Yong-da Yanb, Taosunb, Shen Dongb

a. College of Mechanical Engineering, Jiamusi University, Jiamusi 154007, China
b. Center for Precision Engineering, Harbin Institute of Technology, Harbin 150001, China

(Dated: Received on May 30, 2011; Accepted on August 1, 2011)

Functionalizing and patterning of the silicon surface can be realized simultaneously by the chemomechanical method. The oxide-coated crystalline silicon (100) surface is scratched with a diamond tool in the presence of aryldiazonium salt (C₆H₅N₂BF₄). Scratching activates the silicon surface by removing the passivation oxide layer to expose fresh Si atoms. The surface morphologies before and after chemomechanical reaction are characterized with atomic force microscopy. Time-of-flight secondary ion mass spectroscopy confirms the presence of C₆H₅ and provides evidence for the formation of self-assembled monolayer (SAM) on silicon surface via Si−C covalent bonds by scratching the silicon in the presence of C₆H₅N₂BF₄. C₆H₅ groups further bond with surface Si atoms via Si−C covalent bonds as confirmed from infrared spectroscopy results. We propose that chemomechanical reaction, which occurred during scratching the silicon surface, produce C₆H₅ groups from aryldiazonium salt. The relevant adhesion of SAM is measured. It is found that SAM can reduce the adhesion of silicon. The monolayer can be used as anti-adhesion monolayer for micro/nanoelectromechanical systems components under different environments and operating conditions.

Key words: Chemomechanical, Silicon, Monolayer, Aryldiazonium salt

I. INTRODUCTION

Traditionally, fabrications of silicon-based devices require complex processes. An alternative approach by the combination of convenient mechanical fabrication and chemical treatment is of great importance. During last few years, chemomechanical modification of silicon has emerged as a simple and convenient approach for simultaneously functionalizing and patterning silicon surfaces [1−6]. Generally, the steps of chemomechanical surface functionalization with a diamond tool are: (i) An oxide terminated silicon substrate is prepared. (ii) The surface is scribed with the system in the presence of a reactive compound. (iii) The unreacted compound is removed. We hypothesize that the mechanism of formation of the new monolayer on silicon is closely related to the reaction of aryldiazonium salts with highly active surface species, bare silicon.

When an oxide-coated silicon surface is scribed, Si−Si or Si−O bonds are mechanically broken, producing a chemically active surface that reacts with a variety of molecules, covalently binding them directly to a crystalline silicon substrate [7]. This procedure takes place in an open laboratory with compounds that have not been degassed to otherwise specially treated. Scratched silicon is already known to react with 1-alkenes [8], 1-alkynes [9], aldehydes [10], epoxides [11], and acid chlorides [12].

The chemomechanical method was used to modify the silicon surface to form self-assembled monolayers in the presence of aryldiazonium salt (C₆H₅N₂BF₄). The aryldiazonium salt solution, because of the rich and versatile chemistry of activated aryl groups, can modify silicon surface and produce functional self-assembled monolayer (SAM) to connect Si atoms with other molecules [13−15]. The functionalizing and patterning silicon surface can be realized simultaneously. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS), Fourier transform infra-red spectroscopy (FTIR), and atomic force microscopy (AFM) were used to characterize the samples. Adhesive force of oxide-coated Si(100) surface and phenyl-terminated monolayer was measured using AFM.

II. EXPERIMENTS

A. Sample preparation and handling

All sample preparations were carried out in the air at room temperature with compounds that had not been degassed. Si(100) wafers (p-boron, 460±15 μm, test grade) were used and bought from Shenzhen. All chemicals were analytical grade and used as received. Super pure water was obtained by Milli-Q water sys-
SiC bond between the carbonyl and the silicon surface. This would be indicated by arrows.}

B. Scratching Si surface

Mechanical scratching was performed in a fluid cell, which includes the reactant solution (70% C₆H₂N₂BF₄ solution). The diamond tool was brought into contact with the surface at a set of normal forces and moved over a region large enough (about 4 mm²) to easily accommodate TOF-SIMS and FTIR measurements. Then, the chips were rinsed with ethanol and water thoroughly, and then dried with N₂.

C. Instrumentation

The monolayers were characterized by AFM, IR, and TOF-SIMS. AFM images scan were carried out using Dimension 3100 (Digital Instruments) in contact mode with the same “V”-shape tip (Si₃N₄ cantilever, with the length of 200 µm and the elastic constant of 0.12 N/m). All imaging tests were carried out in air at the temperature of 300 K with the relative humidity of 60%. Scan rate is 1.5 Hz. Scan size is 3 µm. IR of the monolayer was recorded on AVATAR 360 FT-IR spectrophotometer. The infrared light was incident on one of the 45° bevels of the ATR crystal. Spectra of the monolayer were recorded with s- and p-polarized light. The spectra were averaged over 60 scans. TOF-SIMS (TFS-2000 TOF SIMS) was performed with a monoisotopic 25 kV ⁶⁹Ga⁺ primary ion source in “bunched mode” to achieve a mass resolution of about 10⁴ (m/Δm). The primary ion (target) current was typically 3 pA, with a pulse width of 20 ns before bunching, and the raster area of the beam was 300 µm × 300 µm.

III. RESULTS AND DISCUSSION

A. Surface morphology

Figure 1 shows the surface morphology of the sample fabricated in air and in aryldiazonium salt. As shown in Fig.1(a), the 3D mapping displays the groove structures indicated by arrows on the surface. However, groove structures disappear and there are groups and lattice structures on the silicon surface scribed in aryldiazonium salt as shown in Fig.1(b). This could be regarded as a proof that the scratch endows silicon atom with energy and the silicon connects with the aryldiazonium salt. Some relatively flat areas are occasionally observed from Fig.1(b): the roughness of the areas is as low as 2.5 nm for a 3 µm × 3 µm region with 19.16 nm height range. Topography and roughness difference in scribed area in air and in aryldiazonium aqueous solution (forming self assembled molecules) can be found by AFM. However, it could not deduce that assembled molecules are connected to silicon surface with covalent bonds rather than physical adsorbed to it. Therefore, the spectral analysis is used to explain that organic molecules assemble on the scribed silicon surface with covalent bond.

B. TOF-SIMS of monolayers on silicon surface

TOF-SIMS provides chemical information about surfaces in the form of characteristic atomic and molecular fragments. In this work, by TOF-SIMS, we demonstrate the existence of the C–C bond between the carbon substrate and the aryl group resulting from the electrochemical grafting of different diazonium salts on glassy carbon. In the static mode, this technique is powerful in the characterization of the chemical structure of self-assembled monolayer [16–18]. The TOF-SIMS results can also shed some light on the structure of the organic layer. TOF-SIMS spectra of silicon scratched under the aryldiazonium salt solution contained numerous hydrocarbon fragments, as well as fragments containing carbon, hydrogen, and silicon. To observe the consequence of the grafting, we have focused on the low mass domain (m/z<150).

Figure 2 shows the intensity of a hydrocarbon fragment (CH, C₅H₄, C₆H₅) in the positive ion TOF-SIMS spectra as a function of the number of carbon atoms in the adsorbate. The peaks at m/z≈64 and 77 can be interpreted, respectively, as C₅H₅ and its parent at m/z≈13. The peaks at m/z=105 and 77 can be interpreted, respectively, as SiC₅H₅ and its parent at m/z=28. The peak at m/z=41 could be due to SiC₆H₅ to SiCH₃.

TOF-SIMS also provided evidence for the formation of monolayer on scribed silicon surface via Si–C covalent bonds by scratching the silicon in the presence of C₆H₅N₂BF₄. First, the C₆H₅ witnesses the presence of
phenyl groups on the surface. Secondly, it may be concluded that the phenyl group is bonded to the substrate through C−Si bonds \((m/z=41\) and 105\) as evidenced by the presence of such fragments \((^{28}\text{SiCH} \text{ and } ^{28}\text{SiC}_6\text{H}_5)\) from the surface. This provides clear-cut proof that the organic layers are covalently grafted to the surface, and it also supports the grafting mechanism involving aryl radicals Ref.[7]. In general, the observed fragment ions and their interpretation are similar to those of an analysis of diazonium grafted 4-nitrophenyl films [19].

C. FTIR of monolayers on scribed silicon surface

FTIR spectroscopy has been successfully used to study monolayer [20]. Figure 3 shows FTIR spectra for original silicon and scribed silicon surfaces in the presence of C\(_6\)H\(_5\)N\(_2\)BF\(_4\), with an untreated silicon surface as a reference. In the original silicon FTIR spectra, oxidation is indicated by the observation of the \(\nu(\text{Si−O})\), centred around about 1090 cm\(^{-1}\). The peak at about 1624 cm\(^{-1}\) in Fig.3(b) displays the desired phenyl reactive functional group. The C−H stretching vibrations are near 2922 cm\(^{-1}\). Furthermore, the peak at about 1452 cm\(^{-1}\) shows the Si−C bond in the stretching region. There is an unexpected \(\nu(\text{Si−O})\) peak at 1092 cm\(^{-1}\) in Fig.3(b). The possible source of oxidation arises from incomplete scribing or uneven SAMs. The results from the infrared spectroscopy measurements on the SAMs of the aryldiazonium salt are a good conformation of the measurement by TOF-SIMS and indicate the presence of monolayer and the SAMs bonded to scribed silicon surface through Si−C bonds.

D. Mechanism of monolayer formation

A two-steps mechanism can be proposed to explain the formation of monolayers on scribed silicon in the presence of aryldiazonium salt [21]. As shown in Fig.4, in the first step, the one-electron reduction of the arenediazonium salt forms an arene radical. In the second step, the arene radical bonds covalently via C−Si bond to reactive exposed Si atoms to form SAMs as confirmed by our TOF-SIMS and IR results.

E. Adhesion of monolayers on scribed silicon surface

Adhesive force of oxide-coated Si(100) surface and phenyl-terminated monolayer on Si(100) surface measurements are performed in the “force calibration mode” and in ambient environment (22 °C, 40% RH) unless specified. Figure 5 shows the force distance curve. The horizontal axis gives the distance which the piezo travels while the vertical axis gives the deflection of the cantilever. By knowing the maximum deflection of the cantilever and its spring constant, it is possible to calculate the adhesive force. For example, the adhesive force of Si(100) as shown in Fig.5(a), which equals to 225 nN, and SAM is 97 nN. It shows that the presence of monolayer greatly reduces the adhesive force of Si(100).

The contact angles of water against Si(100) and SAM are also measured. The results indicate that the contact angles \(\theta\) can be ranked, \(\theta_{\text{Si}}(9^\circ)<\theta_{\text{SAM}}(40^\circ)\). It shows that SAM has larger contact angles, or in other words lower surface energy than Si(100), which means that it exhibits less hydrophilic.

IV. CONCLUSION

Phenyl monolayers are formed when the oxide-coated Si(100) surface is chemomechanically scratched with
a diamond tool in the presence of aryldiazonium (C₆H₅N₂BF₄). Scratching activates the silicon surface by removing the passivation oxide layer to expose fresh Si atoms. Exposed Si atoms covalently bond with deduced phenyl (C₆H₅) molecules to form SAMs as confirmed with AFM, TOF-SIMS, and IR studies. The method will have important implications for building nano- or micro-scale functional structures. The relevant adhesion of SAM is discussed. It is found that SAM can reduce the adhesion of silicon. The monolayer can be used as anti-adhesion monolayer for micro/nanoelectromechanical systems components under different environments and operating conditions.

V. ACKNOWLEDGMENTS

We thank Prof. Yang Gan of Harbin Institute of Technology, and Prof. Fu-long Yuan of Heilongjiang University for the help in the experiments. This work was supported by the Center for Precision Engineering of Harbin Institute of Technology, the Youth the Colleges and Universities in Heilongjiang Province in 2010 (No.1155G54), the Training Fund Project of Jiamusi University (No.RC2009-037), and the National Natural Science Foundation of China (No.51105174).


FIG. 5 Force distance curve for an AFM tip brought in contact with (a) Si(100) and (b) SAM. Spring constant is 0.4 N/m, cantilever deflection is 4div×140.6 nm/div.