Communication

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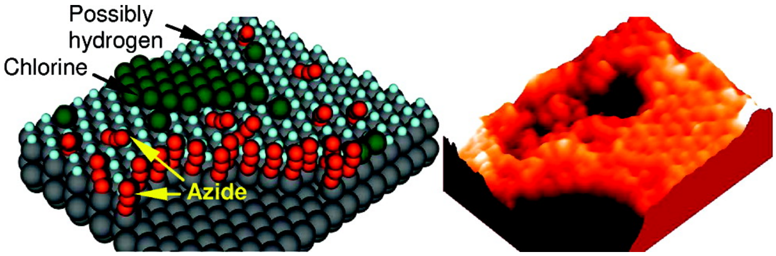

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Azidation of Silicon(111) Surfaces

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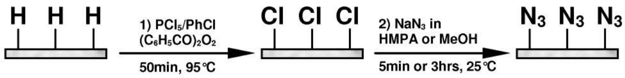
The passivation of nonoxidized silicon surfaces has emerged as a potential method for protecting the silicon surface from oxidation,[1−3] improving the electronic properties of ultrathin silicon films,[4,5] and adding new chemical function to those surfaces.[6−13] The Si(111) surface has provided the template for much of this chemistry. While the atop sites on the unreconstructed Si(111) surface may be fully passivated with H, Cl, or Br atoms, those surfaces are unstable to oxidation.[14] 100% passivation of the atop sites with methyl[15] or acetyl[16] groups has also been achieved. Those surfaces (H_3C-/Si(111) and HC≡C-/Si(111)) are stable against oxidation, which is reflective of both the high coverage and stability of the Si−C bond. In this communication, we report on a two-step chlorination/azidation process (Scheme 1) for the chemical passivation of Si(111) surfaces with azide groups and on the detailed chemical and structural characterization of those surfaces.

The substrates utilized were (111)-oriented, Sb-doped, n-type Si wafers with a low miscut angle of ±0.5° and a resistivity of 0.005−0.02 ohm·cm. Please see the Supporting Information (SI) for the detailed wafer cleaning and sample preparation. The chemical nature and stability of the resulting azide-modified Si(111) surfaces were then characterized by X-ray photoelectron spectroscopy (XPS), multiple internal reflection infrared (IR) spectroscopy, and scanning tunneling microscopy (STM) and spectroscopy (STS).

XPS data were collected to follow the steps of Scheme 1 (Figure 1A) and showed the partial disappearance of Cl (80−90%) and appearance of nitrogen peaks corresponding to the presence of azides. Peaks from oxygen and carbon are possibly adventitiously adsorbed surface species.[15] Partial methoxylation of the surface[17] may also contribute to this. The inset of Figure 1A shows two peaks at 400 and 404 eV with an intensity ratio of 2:1, similar to what is seen for azide groups on gold[18] and graphitic[19] surfaces. No sodium signal was observed from the azide-modified surfaces. The corresponding IR spectra (referenced to SiO_2-/Si(111)) are shown in Figure 1B. The observation of C−H vibrations in all spectra is due to either adventitiously adsorbed carbon or partial surface methoxylation. The disappearance of the Si−H stretch mode (2082 cm^{-1}) upon chlorination was expected.[20] The most striking feature is the appearance of a unique azide symmetric stretching mode at 2168 cm^{-1}, which is blue-shifted by ca. 122 and 63 cm^{-1} with respect to either azides in solution (see SI) or organic azides[18,21] with nitrogen bonded to a carbon atom, respectively. These large frequency shifts suggested the formation of a covalent Si−N bond. The azide symmetric stretch at ~2170 cm^{-1} observed for silyl azide (SiH_3N_3)[22,23] supports this assignment.

By taking the ratio of the normalized, integrated band intensities of N1s and Si2p peaks, the coverage of azide on Si(111) was obtained (calculated[24] assuming that 100% coverage means every atop silicon site is capped by an azide group) and plotted as a function of reaction time in Figure 2A (circles). For HMPA solvent, the azide coverage reaches ~55%, with a fast, pseudo-first-order rate constant of 0.037 s^{-1}. This may be due to the extremely strong solvation ability of cations by HMPA. The corresponding reaction in MeOH was much slower, taking 2−3 h to reach a lower level of azide coverage (~25%).

Scheme 1



Scheme 1

We also utilized XPS to monitor the stability of the N_3-/Si(111) surface in air (relative humidity: 60%). These data are plotted to show the time-dependent growth of equivalent surface monolayers of SiO_2[15] and are presented in Figure 2B. Raw data are in the SI. The N_3-/Si(111) surfaces are stable in air relative to chlorinated Si(111), but a full equivalent monolayer of SiO_2 does grow after a 2 week exposure to air. The rapid initial oxidation observed for Cl-/Si(111) was absent for N_3-/Si(111), possibly because the most reactive Cl-sites had been replaced with azide. The N_3-/Si(111)

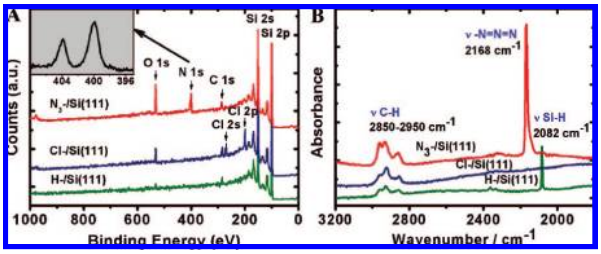


Figure 1. Spectroscopic characterization revealing the surface chemical changes that occur from H-/Si(111) to Cl-/Si(111) to N_3-/Si(111). (A) XPS survey scans. The inset is a high resolution view of the N (1S) region for N_3-/Si(111). (B) IR spectra (referenced to the SiO_2-/Si(111) surfaces) of the same surfaces. N_3-/Si(111) surfaces were prepared from the HMPA method. Similar results were also obtained from surfaces prepared from the methanol solution.

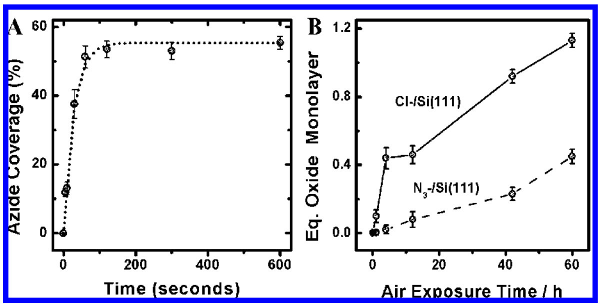


Figure 2. Kinetic plots. (A) Plot of surface coverage of azides versus time during the azidation process. The solid line is a first-order exponential fit of the data from which one can derive a pseudo-first-order rate constant of $k = 0.037$ s^{-1}. (B) Plot of equivalent monolayers of surface SiO_2 versus time for both N_3-/Si(111) and Cl-/Si(111).

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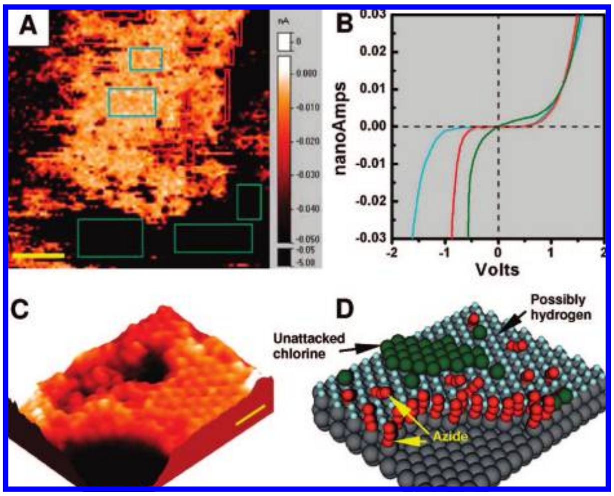

Figure 3. (A) CITS image of the azidated Si(111) surface (at −1.0 V, see SI for the topography, scale bar: 20 nm) together with (B) the averaged STS data (color-coded) from various regions of the surface. On this image, red boxes encircle step and etch pit edges, light blue boxes encircle terrace sites, and green boxes encircle regions of high surface conductivity. (C) Constant current STM image of the same Si(111) surface. $V_b = 1.85$ V, $I_t = 0.12$ nA, temperature = 77 K, scale bar: 1 nm. (D) Graphic illustrating the assigned chemical groups on the azidated Si(111) surface.

surface is unstable relative to the H_3C-/Si(111) and H_3C-CH_2-/Si(111) surfaces, both of which exhibit higher % coverages and long-term stability in air.[3b,c]

The morphologies of the azidated surfaces were studied by STM. Figure 3C displays a constant-current image from N_3-/Si(111) with low azide coverage (∼25%), where atoms (of unknown type) are resolved. In the large scan-area image (see SI for the STM topography image), both step edges and etch pits were observed, similar to that observed from Cl−Si,[25] indicating no significant morphology changes upon azidation. Current Imaging Tunneling Spectroscopy (CITS) data were collected (at −1.0 V and 77 K) in an effort to identify the surface species (Figure 3A), including step and etch pit edges (red), terrace sites (light blue), and regions of high conductivity (green). Three distinct regions (color coded on Figure 3A and B) were found in terms of yielding distinct $I-V$ tunneling curves, suggesting areas with different chemical origins. The terrace sites (light blue encircled regions) showed a band gap of ∼1.5 V, which is close to that (1.6 V) observed for H-/Si(111),[25] while step and etch pit edges (red) exhibit a gap value of ∼0.8 V. The high conductance regions (green) appear similar to that of Cl-/Si(111), namely, nonzero slope or nonzero density of states at zero bias.[25] We thus tentatively assign the red-encircled regions as azide-covered (see the drawing of Figure 3D). Upon higher coverage of azide (55%), the three distinct classes of $I-V$ traces are still observed but are more evenly distributed over the surface (see SI).

Methods to covalently attach the azide functionality to Si(111) have been developed and shown to yield different azidation kinetic rates, different final azide coverages, and different surface-area distributions, depending upon the azidation solvent. Similar to the previously reported HC≡C-/Si(111) surface, the N_3-/Si(111) surface should be useful for secondary functionalization through the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition ("click" chemistry).[26] Alternatively, reduction of the N_3-/Si(111) surface using the Staudinger reduction method[27] should produce an amine-terminated surface for the coupling of carboxylic acid molecules. Such chemistry is currently under investigation.

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Supporting Information Available: Experimental preparation, instrumentation, and analysis. IR spectroscopy of NaN_3 in MeOH. C, O elemental analysis. XPS data showing the azidation kinetics. XPS data comparing the air oxidation of Cl-/Si(111) and N_3-/Si(111). STM images from N_3-/Si(111) of low coverage (∼25%). Topography and CITS data from N_3-/Si(111) of high coverage (∼55%). This information is available free of charge via the Internet at http://pubs.acs.org/.

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