



Functionalization of undoped and p-doped Si (100) using atomic force microscope tips in the presence of propan-2-ol, butan-2-ol and toluene



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ABSTRACT

A technique, based on amplitude modulation of Atomic Force Microscope (AFM) tips, in the absence of an applied bias voltage, is reported in this study. Under ambient humidity conditions, ultra-sharp *n*-doped silicon tips (spike radius ~ 1 nm) oscillating at 160–250 kHz generate raised nanostructures ~ 50 –200 nm wide and ~ 2 nm high on undoped or *p*-doped Si (100) surfaces pretreated with certain neat organic solvents. The solvents in the present work are propan-2-ol, butan-2-ol, or toluene. AFM is used to characterize the nanostructures which are found to be stable for at least 96 h. It is suggested that mechanical stress associated with the oscillatory Hookean energy (~ 5 –15 eV) of the tip promotes cleavage of residual solvent bonds on the surface. This bond cleavage, and the presence of surface defects, which may be critical in the formation of surface-solvent bonds (specifically Si–O–C or Si–C) to create the observed nanostructures, is discussed. The process described here to create raised nanostructures is distinctly different from all other reported techniques to date.

1. Introduction

Most of the mask-less scanning probe lithography (SPL) techniques capable of modifying surfaces (including Si, polymers, graphene, and assembled monolayers) below the visible light diffraction limit with a lateral resolution of less than 50 nm, are based on the robust manipulation of sharp tip asperities in the proximity (~ 1 nm or less) of those surfaces. Several comprehensive reviews describe the variety of SPL lithographic methodologies utilizing mechanical manipulation, chemical reactions, electrical, and also thermally induced tip-surface interactions [1–3]. Different physicochemical processes may occur on Si (*p*-, *n*-doped, or undoped) in the presence of sharp (1–50 nm) asperities robustly manipulated close to the surface (within several nanometers). These processes may be physical, electrochemical, or free energy driven.

Biasing a metallic tip under ambient conditions gives rise to local anodic oxidation where the dielectric breakdown of water allows for the transport of hydroxyl radicals to oxidize a small region beneath the tip [4,5]. This approach can be further extended to systems where the atmosphere is an organic gas [6]. By applying a tip-surface bias the functionalization of Si has been shown to occur predominantly through the creation of Si–C bonds [7].

A bias-less lithography technique on surfaces in AFM liquid cells containing some organic solvents has been reported [8] whereby the AFM tip scratches the surface allowing for the functionalization of

surface sub-layers with a liquid solvent through a process known as nanografting [9]. In that work, the liquid in the cell was carefully chosen so that freshly exposed scratched areas favor a functionalized surface over a relaxed, non-functionalized one. Nanografting further developed into a related lithographic method named nanoshaving [10] whereby the surface is first masked with a film which is subsequently removed via tip-manipulation in an AFM liquid cell. The exposed area is then functionalized and the remaining mask can be removed with subsequent surface treatments.

The AFMEN technique using electrically biased AFM tips (either in contact- or tapping mode) has been shown to effectively reshape surfaces and form nanostructures in polystyrene, poly-methyl-methacrylate, self-assembled organomercaptan molecules ($\text{CH}_3\text{-(CH}_2\text{)}_{18}\text{-SH}$), styrene butadiene, and amorphous CdS under levels of ambient humidity (10–60%) [11–14].

In the present work we report and discuss the fabrication of nanostructures on Si (100) by manipulation of an AFM tip in the proximity of the surface in the absence of an electrical bias. The work focuses solely on the influence of the mechanical stress imparted by the oscillatory energy of an ultra-sharp AFM tip on *p*-doped and undoped Si (100) surfaces after being treated by either one of three chosen solvents. The solvents, and their relative polarities with respect to water (which has a reference polarity value of 1) are: propan-2-ol (0.546), butan-2-ol (0.506) and toluene (0.099). At the same time we draw a distinction between well-established techniques such as local

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anodic oxidation of silicon [4,5], chemo-mechanical [9,15], and thermal and thermo-mechanical [16,17] processes.

2. Materials and methods

2.1. Sample preparation

Sample preparation and measurements were performed in a class-1000 clean room. Intrinsic and boronated (p-doped) Si (100) was initially cleaved from larger wafers using a diamond tipped scribe. The boron dopant concentration was 10^{15} cm^{-3} . Surface oxidation was removed by dipping the samples in a 25% aqueous HF acid solution for 10 s followed by a 10 s rinse in DI water. This procedure was repeated until the samples were visibly hydrophobic. Samples were then dipped into one of the three solvents (all spectroscopic grade with purity of at least 99.7%) for 10 s followed by another 10 s rinse in DI water.

2.2. Patterning technique

A Digital Instruments/VEECO Dimensions 3100 Metrology atomic force microscope system and Nanoscope IIIa controller was used in this study. The patterning technique was conceptually developed from the AFMEN technique [18] previously used to generate nano-features on a variety of polymer films (10–500 nm thick). However, that AFMEN technique generated nano-features by mass transport of dielectric macromolecules in the presence of an applied electric field ($\sim 10^8$ – 10^9 V/m). In the present work, as mentioned above, *no external electric bias is applied at any time* between the tip and surface during the AFMEN process. The process was facilitated by mounting a Micromash Hi-Res C-14 n-doped silicon ultra-sharp tip (force constant ~ 5.0 N/m, spike radius ~ 1 nm) on a tip carrier isolated from the rest of electrical circuitry to avoid current leakage. The tip, oscillating at frequencies in the range 160–250 kHz, was then engaged by positioning it to within close proximity of either the p- or undoped Si (100) surface which had been treated previously with either propan-2-ol, butan-2-ol, or toluene as just described. An in-house written C++ code control protocol was used to manipulate the AFM tip, the details of which are as follows. First, the control protocol advances the tip towards the surface at a speed $0.05 \mu\text{m/s}$ to a distance where the vibration amplitude was suppressed by at least three orders of magnitude. In our setup the absolute tip-surface distance cannot be detected experimentally before the tip is engaged with the surface. However, as the tip engages, its oscillation amplitude is suppressed by the three orders of magnitude and at this point in the process the average tip-surface separation is ~ 1 nm. Second, features are created on the surface by the control protocol as shown schematically in Fig. 1(a–d).

3. Results and discussion

3.1. Formation of features

Fig. 2 displays sample nanostructures formed on silicon surfaces treated previously with either butan-2-ol, propan-2-ol, or toluene. It was possible to create nanostructures on all of the passivated undoped Si (100) surfaces pretreated with any of the three solvents, but on p-doped passivated surfaces nanostructures could only be formed when the surfaces had been pretreated with butan-2-ol or propan-2-ol. All nanostructures were patterned by exposing the surfaces for time periods of 1–10 s. The nanostructures were clearly observed four days after the patterning. The diameter, or largest dimension of all nanostructures presented in Fig. 2(a–e), is approximately $0.21 \mu\text{m}$. A bright circular dot appears within a larger patterned region. This region has no shape correlation with the circular dot location. In Fig. 2(f), of a passivated p-doped Si (100) surface exposed to toluene, no nanos-

tructure is observed indicating that toluene was ineffective for the patterning process. Taken in their entirety, the results displayed in Fig. 2 indicate that nanostructure formation depends on the choice of solvent and doping of the Si (100) surface: propan-2-ol and butan-2-ol is effective on both undoped and p-doped surfaces while toluene is only effective on undoped surfaces.

We also observed that for the p-doped Si treated with propan-2-ol (data not presented here) it was possible to form nanostructures when the tip was spatially confined even without executing the C++ patterning protocol code. This would suggest that the tip-surface separation itself may play a crucial role in shaping the geometry of the surface features. This was further evidenced by a series of nanostructures formed by changing the maximum approach distance during patterning with toluene on *undoped* Si. Increasing the tip-surface separation, during approach and subsequent patterning, was found to create more symmetrical nanostructures with smaller cross sectional areas. However, beyond a critical tip-surface separation it was no longer possible to form nanostructures. It is plausible that the change in the nanostructure geometry as the tip-surface separation is varied depends to some degree on the associated variation of the meniscus geometry and energetics.

3.2. Chemical processes on Si (100) surfaces involving solvents

We propose the chemical oxidation scheme of a Si surface treated with propan-2-ol presented in Fig. 3(b). Prior to the patterning protocol, initial passivation of the Si surface results in adsorbed protons at vacancy defect sites in the form of Si–H surface bonds. Passivation will also minimize any surface oxidation and contamination. The surface is subsequently rinsed with DI water which removes further contaminants and facilitates the formation of a physisorbed water layer. The polar nature of the adsorbed water layer allows for the oxygen species in the layer to align themselves on average closer to the surface. Next, a propan-2-ol rinse will again allow for a layer of alcohol to form above the water layer with the alcohol's hydroxyl groups oriented towards the water molecules due to hydrogen bonding. A further water rinse simply adds another layer of physisorbed water on top of the adsorbed alcohol. Water auto-ionizes into hydroxyl and hydronium ions under ambient conditions. Any water sandwiched between the propan-2-ol and hydrogenated (Si–H) surface may also auto-ionize, despite the fact that the liquid is confined, provided there is sufficient proton mobility; this is possible since protons are able to migrate between the adsorbed surface layers via a process similar to the Grothuss mechanism [19]. It should be noted that proton migration will be hindered by the presence of propan-2-ol since the two species may interact to form a dative bond producing isopropyl oxonium ions. The next step of the process is key, and occurs when the n-doped AFM tip is brought near the surface and spatially confined by the patterning protocol which causes the n-doping in the tip spike to generate a time-varying electric field. This gives rise to the proposed oxidation mechanism. Consider a propan-2-ol molecule in the water bilayer. As the tip approaches the surface, hydrogen atoms are more likely to attach to the lone pairs on the hydroxyl group on the propan-2-ol, forming an isopropyl oxonium ion as the hydroxyl group is converted to an oxonium group. As the tip retracts, Coulombic forces would then drive the partial rotation of the isopropyl oxonium ion such that one of the hydrogen atoms on the oxonium ion transfers to water molecules in the top layer of water. This in turn would allow the hydroxyl ions in the lower water layer to then oxidize the surface as there will be hydrogen bonding between the hydroxyls and surface Si–H groups. As the patterning protocol continues and the tip travels down a second time, the hydrated silicon surface loses more hydrogen atoms to form more isopropyl oxonium ions, subsequently oxidizing the surface through the remaining hydroxyl radicals. As the tip repeats this process, more and more of the area becomes oxidized by propan-2-ol acting as a proton-pump catalyst. This particular mechanism scheme requires the propan-

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