FORMATION OF SURFACE FEATURES IN BORON-DOPED SILICON (100) IN THE PRESENCE OF PROPAN-2-OL

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Sajeevi Sankalpani Withanage
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FORMATION OF SURFACE FEATURES IN BORON-DOPED SILICON (100) IN THE PRESENCE OF PROPAN-2-OL

Sajeevi Sankalpani Withanage

Thesis

Approved:  
Advisor  
Dr. Sergei F. Lyuksyutov

Accepted:  
Dean of the College  
Dr. Chand Midha

Committee Chair  
Dr. Sasa V. Dordevic

Interim Dean of the Graduate School  
Dr. Rex D. Ramsier

Faculty Reader  
Dr. Robert R. Mallik

Date  
Dr. David N. Steer
ABSTRACT

Silicon is the most commonly used material for semiconductor device fabrication. Atomic force microscope/microscopy (AFM)-based nanolithography is a technique used in nanofabrication. Techniques discussed in relation to this work include local anodic oxidation (LAO), Atomic Force Microscopy assisted Electrostatic Nanolithography (AFMEN), which have been studied for years and proven to be very flexible fabrication tools. In this study, we report the possibility of patterning nanostructures on silicon without external bias. Samples we have used in the study were HF passivated boron doped Si (100) wafers treated with propan-2-ol. Amplitude Modulated AFMEN (without bias voltage) has been selected for patterning the nanostructures in silicon. The tip was isolated from the carrier to prevent grounding and stray currents. Using the C++ codes, we were able to create raised nanostructures on the surface with the height ranging 2-25 nm under ambient conditions. Mechanism and theory of the formation of features is still under investigation. Furthermore, we present three hypotheses to explain feature formation: 1) effects due to boron defects on the surface, 2) electrification of the surface due to friction (triboelectrification), and 3) electrochemical nanocell formation modified in the presence of propan-2-ol.
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CHAPTER I

INTRODUCTION

Silicon is an element used for years in semiconductor electronics. The development of silicon based semiconductor devices created the need for new solutions to manufacture, research, and develop micro/nano electronics. Silicon in crystalline form has a diamond cubic structure from which unique electronic properties emerge along different crystallographic planes.

Atomic Force Microscopy (AFM) is a scanning probe technique which uses the forces between an AFM tip and substrate for imaging. Due to its interaction with the substrate in a nanosize region (defined by the tip size) in a small period of time, an AFM can be used with nanolithographic techniques including local anodic oxidation (LAO), thermo-chemical nanolithography, ‘dip-pen’ nanolithography, and Atomic Force Microscopy assisted Electrostatic Nanolithography (AFMEN). In LAO, voltage applied between the AFM tip and substrate ionize a water meniscus and locally oxidize the surface. AFMEN techniques use the local heating of the surface due to an electric field to create raised nanostructures on the surface. We modify these two techniques to create features in boron doped Si (100) substrates.
We etched and passivated Si samples with hydrofluoric acid (HF) to eliminate the natural oxide layer and protonate any dangling bonds. Propan-2-ol introduced to the surface and it was observed that the presence of propan-2-ol is critical for writing to be successful. C++ codes were used to create dots on the surface using tapping mode with no external bias applied between the tip and the Si surface. We were able to create raised features in the surface using this method and attempted to find the dependence of the height and area of the features with the exposure time.

We discuss bias-less formation of features using three hypotheses. First is the effect of boron induced protrusions in the surface for the feature formation. Different configurations of B atoms in the surface lead to change in surface structure and surface energy [27, 28]. The density of these protrusions in the region we tap the region may cause the creation of features and variable size of the features. Second hypothesis is the electrification due to tip-surface interactions. The tip can accumulate charges during its tapping near the surface which create an electric field locally due to charge separation. This electric field can create raised surface features similar to the other AFMEN techniques. The third hypothesis is an electrochemical nanocell with the presence of propan-2-ol. When the tip is near the surface, the passivated surface reacts with propan-2-ol leaving a hydroxyl substitution on the surface and \( \text{C}_3\text{H}_8 \) (g) evolving out of the meniscus.
CHAPTER II

BACKGROUND

2.1 Silicon

Silicon is the most commonly used material for semiconductor device fabrication. It is an inexpensive material due to being the third most abundant element in the Earth crust (after Carbon and Iron) and is easily purified. It exists in forms of crystalline, polycrystalline or amorphous forms. Silicon has a $3s^2 3p^2$ configuration in the outer shell hence can donate or accept 4 free electrons for the electronic properties. Silicon has a diamond cubic crystal structure with cube side (a) of 5.43Å [1]. Two atom basis consists of two identical atoms at (0,0,0) and (1/4,1/4,1/4)a, with packing fraction 0.34, as shown in Figure 2.1.

Figure 2.1 Silicon Crystal Structure
**Crystallographic planes of Si and Miller indices**

In crystallography, the Miller indices are three integers \((h, k, l)\) used to specify a family of different lattice planes. Different notions are used to designate crystal planes and directions. The \((hkl)\) are crystal planes, the \([hkl]\) are equivalent planes, the \([hkl]\) are crystal directions, and the \(<hkl>\) are equivalent directions [2]. Figure 2.2 shows the crystallographic planes of silicon.

![Crystallographic planes of Si](image)

Figure 2.2 View of Si unit cell in different directions; (a): view in \((100)\) direction; (b): view in \((110)\) direction; (c): view in \((111)\) direction

Because of these different surface structures, properties of the Si surfaces are different along different directions. Commercially available crystalline silicon wafers are cut along different crystallographic planes. The wafers used in this study were Si \((100)\). In these wafers, the \((100)\) surface is parallel to the top surface of the wafer and the primary flat of the wafer is parallel to \((110)\) plane [3], as shown in Figure 2.3.
Figure 2.3. Illustration of Primary and secondary flats of n-type and p-type silicon wafers for {111} and {100} surfaces.

Band structure of Silicon

Silicon has energy gap of 1.12 eV at room temperature (300K) and 1.17 eV at 0 K [2]. In semiconductors, the small number of electrons penetrate this energy gap determine all the electronic properties of the material.

The first Brillouin zone of silicon contains six symmetric points.

\[
\begin{align*}
\Gamma &= 2\pi/a \ (0,0,0), & X &= 2\pi/a \ (1,0,0), \\
L &= \pi/a \ (1,1,1), & W = 2\pi/a \ (1,1/2,0), \\
K &= 2\pi/a \ (3/4,3/4,0), & U = 2\pi/a \ (1,1/4,1/4)
\end{align*}
\] (2.1)
The line that joins Γ (center of the Brillouin zone) to X is denoted by Δ is in <100> direction. Λ joins Γ to L is along <111> direction and Σ joins Γ to K is along <110> direction [4].

![Diagram of first Brillouin zone of diamond structure](image)

**Figure 2.4** First Brillouin zone of diamond structure. X, L, Γ denotes some of the symmetric points and Λ, Δ are lines joining some of these points (symmetric directions) (Reprinted with permission from [4]).

The band structure of silicon is obtained by plotting energy in these symmetry lines with wave vector $k$. Figure 2.5 shows the band structure of silicon at 0 K using $k.p$ method [5].

For silicon, the minimum of the conduction band is in the <100> direction near the X point at $0.85\pi/a$ and the maximum of the valence band is at $k = 0$ (Γ point). Si is an indirect band gap material since the top of the valence band and the bottom of the conduction band are not at the same $k$-point [6].
Doping silicon with impurities (n-type doping with phosphorous or p-type doping with boron) narrow the band gap. Model developed by Slotboom et al. [7] widely used to describe band-gap narrowing of silicon.

\[
\Delta E_g = E_o \left( \ln \left( \frac{N}{N_o} \right) + \sqrt{\ln^2 \left( \frac{N}{N_o} \right) + C} \right)
\]

(2.2)

Where N is the impurity concentration and \( E_o, N_o, C \) are constants depend on the material. For silicon \( E_o=0.009\text{eV}, N_o=10^{17} \text{ cm}^{-3} \) and \( C=0.5 \).
Natural Oxidation of Silicon Surface

Silicon surface oxidize by the exposure to oxygen forming silicon dioxide (SiO₂).

This can be either a “dry oxidation” or a “wet oxidation”.

\[ \text{Si} + \text{O}_2 \rightarrow \text{SiO}_2; \text{ dry oxidation} \]  \hspace{1cm} (2.3)

\[ \text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2; \text{ wet oxidation} \]  \hspace{1cm} (2.4)

Surface oxidation of silicon has been studied for years because of its great importance in planar electronic device fabrication. Deal \textit{et al.} [8] have derived following equation for the oxide thickness as a function of time.

\[ \frac{x_0}{A/2} = \left(1 + \frac{t + \tau}{A^2/4B}\right)^{\frac{1}{2}} - 1 \]  \hspace{1cm} (2.5)

With \[ A = 2D_{eff}\left(\frac{1}{k} + \frac{1}{h}\right), \ B = 2D_{eff}C^*/N_1 \] and \( \tau = (x_i^2 + Ax_i)/B \)  \hspace{1cm} (2.6)

where \( x_0 \) is the oxide thickness, \( x_i \) is the thickness of initial oxide layer, \( t \) is time, \( D_{eff} \) is the effective diffusion coefficient, \( k, h \) are rate constants, \( C^* \) is the equilibrium concentration of the oxidant in the oxide, and \( N_1 \) is the number of oxidant molecules (gas phase) at the surface in a unit volume.

It is showed that for relatively larger times \( (t \gg A^2/4B \text{ and } t \gg \tau) \),

\[ x_0^2 \approx Bt \]  \hspace{1cm} (2.7)

and for relatively smaller oxidation times \( (t \ll A^2/4B) \),
\[ x_0 \equiv \frac{A}{B}(t + \tau) \]  

So for the silicon wafers used in this study since they exposed to air for longer period of time, the oxide thickness is proportional to \( \sqrt{t} \) 

The oxide layer can be removed by etching in hydrofluoric acid (HF). This involves the following chemical reaction [20]

\[
\text{SiO}_2 + 6\text{HF} \rightarrow 2\text{H}^+ + \text{SiF}_6^{2-} + 2\text{H}_2\text{O} 
\]

2.2 Atomic Force Microscopy (AFM)

The Atomic Force Microscope is one of the scanning probe microscopes with the ability to generate high resolution three dimensional images with nanometer scale resolution. It was first reported by Binnig et al. [9] following the invention of Scanning Tunneling Microscope in early 1980’s. AFM uses an atomically sharp tip mounted on a cantilever spring. The force between the tip and the sample distinguishes the operation of the AFM.

The piezo-electric scanners move the sample with respect to the tip and the feedback mechanism allows the piezo-scanners to maintain the tip at either constant height or constant force mode above the sample surface. A laser beam is reflected by the cantilever and captured at a photodetector which converts the signal to an image at the display system.
Figure 2.6 Schematic representation of AFM operation.

Figure 2.7 Force-Distance curve for AFM. Different AFM modes are illustrated according to the distance between the tip and the sample surface.
The Van der Waals force is the major contributor in the cantilever deflection when AFM tip is engaged with the surface. The force distance curve in Figure 2.7 above explains the three basic modes of operation of AFM depending on the distance of the tip from the sample, contact mode, non-contact mode, and tapping mode.

In contact mode, the tip scans the sample in close contact with the surface. The force which causes the cantilever deflection is repulsive. Cantilevers with low spring constant are used in order to prevent the damage to the surface though it is still a possibility. Except the Van der Waals repulsive force, the capillary force due to the thin water meniscus on the sample surface which is highly attractive and the cantilever exerted force is also present during the contact mode. Considering the water meniscus to be homogeneous, the capillary force is almost constant, but the force exerted by the cantilever is changing. These two forces are balanced by the repulsive Van der Waals force. The total force on the surface is ranging between $10^{-8}$, $10^{-6}$ N [10]. This mode is used for fast scanning and surface friction measurements.

The vibration of the cantilever is used in non-contact mode. High resonant frequency tips are used in this mode; the spring constant of the cantilever is large, and the cantilever is shorter than in contact mode. The total force exerted by the AFM tip ($10^{-12}$ N) is much lower than that in contact mode, and hence is mostly used to study soft or elastic samples. The AFM tip vibrates at near-resonant frequency with certain amplitude. It detects the change in the resonant frequency, due to changes in attractive
forces, as the distance to the sample surface changes. The images of non-contact mode are highly sensitive to the water condensation the sample surface.

The tapping mode is similar to the non-contact mode. The tip is brought closer to the sample so at the lowest point of the vibration tip barely tap the sample. It also called the Amplitude Modulated (AM) mode will describe briefly below.

2.3 AFM Lithography

Different lithographic techniques assisting AFM are in use for surface modifications of polymers, metals and semiconductors. Local oxidation nanolithography also called nano-oxidation, local anodic oxidation (LAO) or anodization, Atomic Force Microscopy assisted Electrostatic Nanolithography (AFMEN), Local chemical nanolithography, and Dip-pen nanolithography are the widely used techniques.

the substrate for its deposition [23, 24]. This process uses the tip of cantilever as a pen for drawing patterns. Through the meniscus created between the tip and substrate, ink Dip pen nanolithography is a process in which a molecular ink is being delivered on molecules transport to the substrate and self-assemble. It is the first commercial scanning probe lithography.

Thermo-chemical nanolithography is the flexible chemical nano-patterning process. It uses hot tip to make chemical changes on the surface for nano-patterns. Moving a heated cantilever from position to position by varying heat at different locations, a fine nano structure can be built up [25, 26].
Local Anodic Oxidation (LAO)

In LAO, the tip is brought near the surface and meniscus forms between tip and sample due to the surface tension of water. When a voltage applied between tip and the sample electrons move from tip to meniscus ionize water forming OH\(^-\) and H\(^+\) ions [12].

For silicon, following reaction occur at the sample surface [11].

\[
\text{Si} + 2\text{h}^+ + 2(\text{OH}^-) \rightarrow \text{Si(OH)}_2 \rightarrow \text{SiO}_2 + 2\text{H}^+ + 2\text{e}^- \quad (2.10)
\]

where h\(^+\) in the equation denotes a hole in bulk silicon.

At the tip the following reactions occur:

\[
2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2 \quad (2.11)
\]

Photoemission spectroscopy on silicon proved the structures formed were silicon oxide [11].

Figure 2.8 Schematic and Process for Local Anodic Oxidation on Si Surface.
Tip induced oxidation of silicon using scanning tunneling microscope (STM) was first reported by Degata et al. in 1990 [33]. Avouris et al. [13] attempted to find the mechanism of this oxidation process, rate of the reaction and electric field dependence of the oxide growth rate. They also tried to identify the factors affecting the oxide thickness and lateral extent. It was found that lower humidity leads to more fine structures. The oxide growth rate evaluated as a function of electric field strength (Figure 2.9 (a)) found the high initial rates decrease faster with decreasing field strengths showing an electric field threshold $\sim 10^7$ V/cm. It also depends on the amplitude of the applied voltage. Figure 2.9 (b) led them to the conclusion that the oxide growth rate is proportional to $\exp(-X/L_c)$ where $X$ is the oxide thickness and $L_c$ is the characteristic decay length, which is proportional to the electric field.
Figure 2.9 (a): oxide growth rate as a function of electric field strength for three different tip bias voltages; (b): oxide growth rate as a function of oxide height for the three voltages (Reprinted with permission from [13]).

Anomalous electric currents up to 500 μA observed during LAO on n-type silicon by Lyuksyutov et al. [22]. They monitored the current between the tip and the negative bias for bias voltages (negative) ranging 0-50V. It was observed that a small ionic current (1-100 pA) varied nearly exponentially with the bias voltage. This was claimed to be the current associated with the transport of OH$^-$ ions. This current changed its behavior between the bias voltage -20 and -30 V. It saturated around 0.1 nA, then jumped to very
high currents 100 - 500 μA (-17 to -48 V bias voltages). This current observed to be Ohmic confirming it is an electronic current related to the electrical breakdown where the conduction by electrons dominated the ion flow. They also studied the oxide formation on the silicon surface below and above the breakdown. Figure 2.10 shows these experimental results.

Figure 2.10 AFM images for surface oxidation of n-type silicon (a): below the breakdown, (b): breakdown, (c): above the breakdown (Reprinted with permission from [22]).
The oxidation below the breakdown is due to the OH\textsuperscript{-} current from the dissociation of H\textsubscript{2}O as shown in Figure 2.8, additional rings we seen around the original feature at the breakdown. These rings correspond to the areas of high hole density on the Si surface due to the OH\textsuperscript{-} ions near the surface formed by the ionization of water at the breakdown [22].

All three modes of AFM can be used for LAO, but contact mode is widely used. Since the contact forces can damage the tip, Tello et al. [14] suggested using noncontact mode and studied the height and width dependence on the voltage pulse duration. They observed smaller oxide widths and taller features compared with the contact mode. This was explained successfully by the following relationship for the oxide growth rate.

\[
\frac{dh}{dt} \propto \exp\left(\frac{-W_{\text{eff}}}{k_B T}\right) F(h) \tag{2.12}
\]

\(F(h)\) relates to the thickness. \(W_{\text{eff}}\) is the energy barrier and is found to be smaller for the noncontact mode than for contact mode.

Legrand et al. [15] used a pulsed voltage method instead of a continuous bias in noncontact mode. They were able to oxidize silicon surface with an average of 2\text{V} which would not oxidize Si when applies in continuous way. Two new experimental parameters (instead of tip velocity and amplitude of the applied voltage) affecting oxidation kinetics were observed: the pulse duration and the phase of the pulse duration with respect to the cantilever oscillation. It was observed the oxide height is
proportional to the pulse duration while the height and width of the oxide growth vary sinusoidally with phase.

Local oxidation with tapping mode AFM was studied by Murano et al. [16] introduced a new parameter: the tip-sample separation which provided a way to modify the electric field between the tip and the sample. Advantages over the contact and noncontact modes were a reduction of damage to the sample surface while scanning and better characterization of oxide growth. Tapping mode AFM is a powerful technique for local oxidation nanolithography.

**Atomic Force Microscopy assisted Electrostatic Nanolithography (AFMEN)**

AFMEN uses the localized joule heating of the sample when an electric field is applied between the AFM tip and the sample to form nanostructures. The electrostatic attraction of the melted polymer toward the tip under the high non-uniform electric field ($10^8 – 10^9$ V/m) was able to form features in various polymer films.

There are various possible implementations of AFMEN including contact AFMEN, z-lift AFMEN and AM-AFMEN

**Contact AFMEN**

Contact AFMEN is the first developed AFMEN technique [17]. In this method, two dielectric layers (air and polymer) placed between the AFM tip and a conducting Au/Pd substrate. Tip surface separation kept 1-5 nm and 0-50 V bias voltages were applied. These conditions led to large electric field under the tip ($10^8 – 10^{10}$ V/m).
Dielectric breakdown occurred under this large electric field, hence current flow from tip to conducting substrate. The polymer is then brought above the glass temperature and can flow. The pressure \( p(z) \) applied on this melted dielectric liquid by the electric field attracts it towards the tip to form a raised feature. This electrostatic pressure is given by

\[
p(z) = -\varepsilon_0 \frac{(\varepsilon - 1)(\varepsilon + 2)}{6} E(z)^2
\]  \hspace{1cm} (2.13)

Where \( \varepsilon_0 \) is the dielectric constant in air, \( \varepsilon \) is the dielectric constant in the polymer film and \( E \) is the strength of the electric field. \( z \) is the cylindrical coordinate defined in Figure 2.11.
Figure 2.12 Local Joule heating of the dielectric film due to current flow. The arrows are the electric field lines and red lines are isotherms. $T_g$ is the glass transition temperature, $T>T_g$ the film is highly unstable with regards to small perturbations (Reprinted with permission from [17]).

**AM Mode**

Amplitude Modulated AFM is one of the three basic modes used in AFM techniques which also called tapping mode. This mode is a key advance in AFM since it can be used to analyze soft samples with high resolution. In AM mode the cantilever taps across the sample surface under ambient air conditions. This tapping is done by oscillating the cantilever at its resonant frequency when the tip is not in contact with the surface. The amplitude decreases or increases depending on the bumps or
depression present on the sample surface. The study of this change in the amplitude helps in the identification of surface features.

Figure 2.13 AM (Tapping) mode AFM, tip oscillates few to few hundreds of nanometers above the sample.

Compared with the contact mode, AM mode is more flexible in motion of the tip, interaction between the sample and the tip and controlling the configuration of tip-sample junction [18] which earns a huge advantage for AFM based nanolithography.

Amplitude Modulated AFM based Electrostatic Nanolithography (AM-AFMEN)

Compared to the other AFMEN techniques, AM-AFMEN attracts more interest due to having more control. This technique was first used in nanopatterning of polymers [18]. Figure 2.14 shows a schematic representation of AM-AFMEN process.
The tip oscillates at 200 – 400 kHz above the film. Figure 2.15 (a) shows the relationship between the amplitude and distance for different bias voltages. Curve 1 corresponds to no bias voltage, curves 2 and 3 corresponds to negative bias voltages. Curve 1 steep decrease to zero (contact with surface) reasoning the driving force of the piezoscanner overcome by the Coulombic and Van Der Waals interactions. Application of a negative bias voltage allows maintaining a nonzero distance between the tip and the sample (curves 2, 3). Figure 2.1b (b) shows the variation of oscillating amplitude with the bias voltage.
Figure 2.15 (a): Oscillating amplitude – tip distance dependence. Curve 1 is without a bias voltage, curve 2 (-9V) and curve 3 (-18V) for negative bias voltages for 35 nm polystyrene on Au-Pd substrate, (b): Oscillation amplitude – bias voltage dependence for the same sample at two different tip-film distances. Curve 1 for 30 nm and curve 2 for 50 nm (Reprinted with permission from [18]).
The microsecond contact between the tip and the sample (since the frequency of oscillations between 200 – 400 kHz) in each tap is a discrete event. The change of oscillating frequency allows for controlling heat generation hence the size of the nanofeatures. This method successfully patterned 10 – 50 nm size dots in 20 – 50 nm thick samples of polymethylmethacrylate (PMMA) and polystyrene (PS) [18].

The z-lift AM-AFREN for CdS was reported by Dolog et al. [19] using Digital Instruments nanolithography package combined with a C++ code. Four basic steps were followed during the procedure. The tip was brought towards the sample until the vibration amplitude (0.5-3V) becomes three times larger (reference point) as the first step. Then the tip was raised to 10-50 nm while oscillating. A bias voltage of -10 to -40 V applied and slowly retracted to 150 - 400 nm and brought back to the reference point. Finally the lateral displacement of the tip changed to 300 - 500 nm and brought back to the reference point. They created 150 nm wide, 40 nm high nanostructures on amorphous CdS with this technique. These nanostructures were consistent with time; no structural changes were seen after 7 days.

AM-AFREN is a method that can use to form nanoscale features (using mass transport) in thin planar films without direct contact and external heating with relatively higher processing speed and high resolution [18].
CHAPTER III

EXPERIMENTAL METHODS, DATA AND RESULTS

All experiments were performed in a class 100 clean room with a Veeco Metrology Digital Instruments Dimensions 3100 AFM. The AFM was mounted on an acoustic/vibration isolation system which enhances the quality of imaging by minimizing the effects of external vibrations. It can also be used to air seal the microscope for high sensitivity measurements. The controller station consists of a Nanoscope IV interface engaged to a PC with Windows NT operating system with display and control monitors (Figure 3.1). It also is connected to a lock-in-amplifier, and oscilloscope for external bias nanolithography and monitoring the feedback signal from the tip.

Relative humidity in the laboratory was approximately 50% and the temperature was held at 17 °C. Calibration of the AFM was performed using a periodic grating. Frequency of the cantilever was determined by program looking for the resonance amplitude from the Nanoscope auto tune program. This was performed to get the ideal conditions for tapping mode.
The tapping mode AFM tips used were MikroMasch Hi’Res –C14/Cr-Au chips. The tip was n-doped pyramidal silicon tip with a sharp diamond-like spike of radius 1nm and height 100-200nm attached to Au/Cr coated silicon cantilever of length 125(±5) μm, width 25(±3) μm, and thickness 2.1(±0.5) μm. The resonance frequency was given as 160(110-220) kHz and force constant 5.0(1.8-13) N/m. Tip was isolated from carrier using a piece of insulating material (Teflon tape) and breaking grounding contacts on the carrier. This prevented grounding and stray currents.

The samples surface was Boron doped p-type silicon (100) wafers from WACKER-CHEMTRONIC GMBH (Silitronic AG) with thickness 525±15 μm and a bulk Si resistivity of 0.01-0.02 Ω cm. The doped layer is approximately 10.8-13.8 μm thick with a resistivity of
8-12 Ω cm. The wafer was cut with a diamond tool to make ~1cm×1cm size samples. The samples were passivated with aqueous hydrofluoric acid (HF), rinsed, dipped into 2-propanol, and then rinsed again. The HF rinse was repeated until the surface was visibly hydrophobic (no water droplets on the surface). Both spectroscopic and electronic grades (99.5% and 99.8% pure) were tested. Tapping mode AFM imaging was performed to observe the cleanness of the surface (Figure 3.2).

![Tapping mode AFM image of Si surface after cleaning process with scanning speed 11.8 µm/s.](image)

A C++ program to construct a row of dots in tapping mode called “tap_fb_dots_row.cpp” was used for the experiments, but the no voltage applied to the tip. In the code the surface position is measured near the beginning of the row to estimate the amplitude set point necessary for desired tip-surface separation before performing the lithography. Following are the steps of this lithography process.
• Stop the scan and move the tip to the center of the row (x=0, y=0).

• Stop the feedback and lift the tip 50 nm above from the current position (z position)

• Approach surface to measure the change in amplitude.

• Approach surface in 0.5 nm steps with 0.05 μm/s speed, until the amplitude change meets the initial position. If this exceeds a critical value (this was set to 0.15 nm for all experiments) the code stops running by giving an error “Overestimation of tip-surface distance”. If it could not approach the initial position within these steps, it will exit with “Error in script”.

• Script run to find the amplitude set point (asp). if asp is smaller than initial asp (asp0) exit with “Warning”, if successful “D (t-s) is smaller than for imaging”.

• Enable the feedbacks to move the tip to the first dot position and execute the code to apply voltage to the specified position to draw the dots. This occurs in the following series of steps.

  Pause the lithography → disable the feedback → apply the “voltage pulse” with a specified voltage, and exposure time → enable the feedback → move tip to the next dot position.

• After executing the script for specified number of dots, enable the feedback and stop lithography.

• Unload the script from the nanoscope.
The geometrical configuration of the dots can be changed by the factors \( n_d \); the number of dots and \( d_x \); separation between dots in micrometers. Important lithographic settings were \( t_1 \); the exposure time for the first dot and \( v_1 \); voltage on first dot. We kept \( v_1 = 0 \) for all experiments i.e. no voltage applied between the tip and the sample. Measurements were taken by changing the exposure time (\( t_1 \)). Another important setting was ‘\( n_a \)’ to control the dot size, kept it constant at \( n_a = 12 \). The solution was rebuilt after every change for the parameters.

For imaging, scan size was set to 3µm with aspect ratio 2:1. The scan angle was kept to 0°. The scan rate set to 1.97Hz for slow scanning gave the tip velocity 11.8 µm/s. Data type was the height with the scale 10nm.

We started the experiments with \( t_1 = 10 \)s to draw 1-2 dots then decreased \( t_1 \) after every successful trial. To overcome the “Overestimation of tip-surface distance” error, the drive amplitude needed to be adjusted. For 10s exposure time it was found to be slightly larger than the drive amplitude given by the auto tune. Running the code after this adjustment showed “\( D (t-s) \) is smaller than for imaging” assuring all the initial conditions satisfied successfully and tip is ready to draw the dots.

For each run, the drive amplitude and the z-center position recorded. After the successful runs tip was moved to a new position using \( x \) and \( y \) offsets. We then followed the same steps with decreasing \( t_1 \) until the point that drawing the dots was impossible.
Figure 3.3 (a): Topography of a nanostructure formed on Si with 1s exposure time for
driver frequency 136.3 Hz and drive amplitude 109 mV. Data type Height with 10 nm
scale, (b): surface plot of the nanostructure (height of the structure is ~10nm).
The images were analyzed by section analysis to obtain the height as shown in Figure 3.4. Also, since the dots were ellipsoidal shaped, the semi-major and semi-minor diameters were measured in order to calculate the area of the nanostructures formed.

![Graph](image)

**Figure 3.4** Section analysis to measure the height of the dot: horizontal axis is the position in lateral direction and vertical axis is the height from the surface.

All collected data for height and area of the formed surface features were plotted as functions of exposure time to find the relationship. These are shown in Figure 3.5, and 3.6 below. Since the mechanism of this process is very complex and the less control in the variables affecting the surface feature formation (no voltage applied between the tip and the surface), it is hard to see a clear overarching trend.
Figure 3.5 Height variation of the surface features with exposure time. The time axis expressed in log scale for better visibility. No fitting was performed since no clear polynomial relationship between the variables observed.
Figure 3.6 Area of surface features for different exposure times. Area was calculated using the expression for the area of an ellipsoid. The time axis expressed in log scale.
CHAPTER IV

DISCUSSIONS

The mechanism and theory behind the formation of surface features on Boron doped Silicon under ambient conditions without bias is not completely formulated. Some important hypotheses which explain the possibility of this type of feature formation are discussed here.

4.1 Hypothesis I- Boron Defects

In order to explain our experimental observations, it is essential to understand the surface structure of the Boron-doped Si samples used in the experiments. The defects on the surface may affect the feature formation and the size of features. Liu et al. [27] studied the features on boron doped Si (100) surface in atomic resolution using scanning tunneling microscopy (STM) under vacuum. They imaged the topography of boron induced features on Si (100)2×1: H surface in two sample voltages: (a) -2V (empty state) and (b) +2V (filled state) and observed that the feature appear as a mound in (a) and hole in (b). Liu et al. [28] reported three major types of boron induced protrusions using STM topography in empty state (Figure 4.1)
From figure 4.1 it can be clearly seen that the protrusions make the neighboring atoms invisible giving four dimers for each protrusion. Deviation of dimers from their original position found to be large as 0.8 Å. They also attempted to calculate the surface energies for different B atom positions using a computer model. From the stains in the surface due to the B induced protrusions, it was seen that the adjacent atoms become adsorbed dimers and make a closed ring with neighboring atoms as shown in figure 4.2. Therefore four sites are available for B atoms, the adsorbed dimer positions \((A_1, A_2)\), surface \((B_1, B_2)\), subsurface \((C_1, C_2)\), and third layer \((D_1)\). Surface energies for various arrangements of Si and B atoms were calculated and found that the arrangement with one B atom at an adsorbed dimer position and two B atoms at the subsurface \((A_1, C_1, C_2)\) and Si atoms at the other positions make a symmetric ring with minimum surface energy of \(-4.35\) eV.
Figure 4.2 Possible positions of boron atoms. A1 and A2 are adsorbed dimers, B1 and B2 are surface atoms, C1 and C2 are subsurface atoms and D1 is a third layer atom. Surface energy varies with the position of B atoms in the ring.

It was seen that if B atoms do not attached to the surface, but second layer (subsurface) become purely B then the surface atoms lowered by 0.8 Å due to the short Si-B bonds. This concludes that the occupancy of B atoms at different sites tends to a surface changes. These changes might affect the nanolithography features, and also the chemistry at the surface during nanofeature construction may also affect.

Dopant density is also a very important parameter defining how he surface is constructed and the resistivity of the doped sample. Resistivity changes with the dopant density and resistivity is the quantity that specified for each samples. For an example the B doped Si substrates used in our experiments had the resistivity of $8 \text{ – } 12 \, \Omega \text{cm}$. Thurber et al. [29] discussed the dependence of resistivity on the dopant density. Figure 4.3 shows their experimental results using three different techniques, junction capacitance voltage, Hall effect, and nuclear track technique.
4.2 Hypothesis II – Electrification due to tip-surface interactions

Lyuksyutov *et al.* [32] reported formation of nanostructures in polymer films with no external bias using contact mode AFM. 10-30 nm wide lines with the height ranging 0.2-1 nm and nanoscale dots were created in thin polymer films about 30 nm thick. These nanostructures were formed as a result of the tip’s motion near the polymer film in short periods of time where the size of the features depends on the size of the water meniscus. This technique had several differences compared with AFMEN, the current measured in the film was much smaller proving that it is not associated with
the dielectric breakdown and no voltage applied. Figure 4.4 shows the nanostructures they formed in PMMA and PS.

Figure 4.4 Nanostructures formed in polymers with no external bias; (a): lines patterned in PMMA; (b): closeup image of one line; (c): dots patterned in PS (Reprinted with permission from [32]).

The authors explain this effect as a result of electrostatic friction at the nanoscale. During the motion of AFM tip, it collects charges from the surface which is well known as the electrification by contact or triboelectrification. In contact electrification, charges rearrange in the way that one surface gains electrons and the other surface gain positive charges due to holes. Electric field induced due to this charge separation which generates local heating in the polymer creates the nanostructures.

We modify this effect to explain our experimental results. We have two deviations from above procedure: 1) we use tapping mode instead of contact mode and, 2) the surface is not a soft substrate (polymer). Addressing the first fact, in tapping mode the AFM tip vibrates very close to the surface and sometimes it slightly touch
(tap) the surface. Hence triboelectrification can occur in the tapping mode. The second fact makes the difference in the mechanism because the small electric field due to triboelectrification is not sufficient to heat up and melt the surface locally. We suggest the local oxidation works in our method since we perform the experiments in the ambient conditions. The presence of propan-2-ol provides more hydroxyl (OH⁻) groups to the system aiding the oxide formation. Since the B defects play a role in surface reconstruction and reactions, investigating pure Si and other surfaces need to confirm this hypothesis. Marchi et al. [31] showed experimentally the threshold voltage $V_t$ for oxide growth gives the minimum energy (due to the electric field) required to remove a hydrogen from the surface lies between -2V and -3V using Si (100) with different dopant types and densities.

4.3 Hypothesis III – Electrochemical Nanocell

In ambient conditions, the adsorbed water layer on the surface forms a water meniscus between AFM tip and the surface. This system can be considered as a nanoelectrochemical cell [30] since two electrodes (AFM tip and substrate) are separated by a small distance. Chemical reactions in this cell are following [30].

Reactions at the Si surface:

$Si + 2H_2O + 4h^+ \rightarrow SiO_2 + 4H^+$ \hspace{1cm} (4.1)

$2H_2O + 4h^+ \rightarrow O_2 \uparrow + 4H^+$ \hspace{1cm} (4.2)
Reaction at the tip:

\[ 4H_2O + 4e^- \rightarrow 2H_2 \uparrow + 4OH^- \]  \hspace{1cm} (4.3)

Reaction in water:

\[ 4H^+ + 4OH^- \rightarrow 2H_2O \]  \hspace{1cm} (4.5)

For our system, the mechanism we suggest is much similar to the nanocell, but in the presence of propan-2-ol. The steps of the proposed mechanism are described below.

**Adsorption:**

The polar end of propan-2-ol adsorbs to the surface. Whether a bond (hydrogen bond) forms or not at this point is up to investigation. Hence it is expressed as a wavy bond in Figure 4.5.

![Figure 4.5 Adsorption of propan-2-ol to the surface.](image)
The tip approaches and retracts:

As the tip approaches, a hydrogen atom on the surface is attracted and removed by the n-doped silicon. At the same time, the hydroxyl forms a dative bond with the surface. The transition state where the hydrogen from the surface is still “bonded” to the oxygen is presented in Figure 4.6. The reactions in this transition state can be more complex due to the presence of B atoms; the oxygen could also bond with a boron atom near the surface if the tip removed a hydrogen atom introduced in the passivation process.

![Figure 4.6 Bond formations at Si surface when tip approaches.](image)

The tip further retracts:

As the tip pulls away from the surface, hydroxonium transfers a hydrogen to the former propan-2-ol, creating propane leaving a hydroxyl group at the surface (Figure 4.7).
Figure 4.7 Final step of the reactions when tip moved away from the surface: $C_3H_8$ removed, leaving behind hydroxyl saturated surface.
CHAPTER V

SUMMARY

Surface oxidation and feature formation in silicon surfaces in external bias voltages has been studied for years. In this work bias-less formation of nanostructures on B-doped Si (100) surfaces has been demonstrated experimentally using AM-AFM lithography. H-passivated, propan-2-ol treated samples were used with isolated n-doped silicon tips. We highlight two novel facts in this procedure:

1. Bias-less (absence of external electric voltage) formation of features.
2. Presence of propan-2-ol is essential for features formation.

The spontaneous (seeded) growth of structures was observed after the AFM tip taps the surface with heights ranging 2-25 nm. The height and the area of the features depends on the tapping time where the shortest possible time to form a feature was less than 1 ms. Mechanism and theory of the formation of features is under investigation. Three possible scenarios to explain this effect have been discussed in this work:

I. Influence of defects in B-doped Si.
II. Triboelectrification during tip-surface interactions.
III. Formation of electrochemical cell in presence of propan-2-ol.
Boron induced protrusions change the surface structure and energy, hence affecting the mechanism of feature formation and size of the features. During tapping, the AFM tip accumulates charges and creates a small electric field which can oxidize the surface locally. In the third hypothesis, we attempt to modify the chemical reactions in the nanoelectrochemical cell in the presence of propan-2-ol.

We claim the features are silicon oxides as explained in the proposed mechanisms and further tests are needed to confirm. Other future work associated with this work involves developing complete mechanism for bias-less feature formation in the presence of propan-2-ol and formulating the height and area dependence to the tapping time. We also as a future work will attempt the method on graphene fluoride (GF) as well as other materials.
BIBLIOGRAPHY


