Development of Superhydrophobic Surfaces via Isotropic Etching and Plasma Sputter Deposition

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The partial masking followed by the chemical etching is a well-developed method in the fabrication of microelectromechanical systems (MEMS). When there is an anisotropic chemical etching demand, the aqueous solution tends to have extremely oxidizing compounds especially hydrogen fluoride (HF). Consequently, the traditional masking methods such as photolithography which is based on the photosensitive polymers may fail to protect the substrate as polymers also become removed by such a harsh etching solution. In the current study, a two-step deposition and chemical etching method is developed to form micron-sized arrays of silicon micropillars. A set of <100> silicon wafers undergoes a physical vapor deposition (PVD) of a silicon carbide (SiC) thin film. Prior to the deposition, an extremely fine mesh made of woven thin stainless steel wires is used to partially cover Si substrates. As a result, an array of micron-sized patches of SiC is deposited underneath each opening of the mesh while the rest of the substrate remains uncoated. In the next phase, the substrate is immersed in a highly corrosive solution (a mixture of hydrofluoric acid, nitric acid, and acetic acid). After giving some minutes of chemical etching, the uncoated parts of the substrate suffer from the etching process while those micron-sized patches formed previously to protect the substrate against the severe corrosive solution. Consequently, the bare silicon exposed to the solution is corroded and leaves a micron-sized pillar beneath the protective SiC coat. The etched substrates are used latterly to receive a thin film of the hydrophobic material such as polytetrafluoroethylene (PTFE). The AFM analysis shows the topography of the surface and the morphology of the etched surface is studied by using the scanning electron microscopy (SEM). The results demonstrate extremely high wetting contact angle of the mentioned surface. It is proved that there is an optimum corrosion time which leads to the highest contact angle.

Keywords: Isotropic etching; Silicon texturing; plasma sputter deposition; Superhydrophobic surface; microelectromechanical systems.

1. Introduction

There are various applications for surface-textured ceramics; a ceramic crucible with a porous surface is more resistant to alloy corrosion [1], photocatalytic surfacing surfaces with slight porosity demonstrate better performance [2], and some MEMS components such as microchanneling and drilling [3]. Various models have been proposed to explain the electrochemical treatment of silicon wafers either with bias voltage or simple chemical reaction [4]. The use of an acidic solution containing hydrofluoric acid (HF) is common in classic electrochemical cells dealing with silicon [5]. Silicon has oxidizable characteristics that may have a problem for electrochemists who are working with Si electrode but an advantage to fabricate porous Silicon. Silicon has a −0.8V potential relative to standard hydrogen electrode in pH=0. In contact with organic solutions such as water, silicon forms a silica layer that also has protective aspects against corrosion [6]. Initial silicon is normally a single crystal with well-defined crystallographic orientation. The most common case is the standard <100> silicon wafer [7]. In order to have a successful Si electrochemical etching, the removal of the silica layer is mandatory. A highly concentrated HF solution (up to 90 wt%) has a remarkable and unique property to dissolve glass during the following reaction [1][8].

\[
\text{SiO}_2 + 4\text{HF} = 2\text{H}_2\text{O} + \text{SiF}_4
\] (1)

Considering a corroded cavity on the surface, the whole chemical etching process may have two regimes; the first is called anisotropic [9] which belongs to the corrosion mechanisms at which the material removal rate is not equal in all directions due to preferential crystal orientations. These preferential directions vary from an etchant solution to another. For the alkaline solution (KOH), the corrosion rate in (110) direction is several times higher than (111). If the Si substrate is a single crystal with <100> orientation, the final result will be deep pits with (111) side walls [10]. In the second etching regime which is called isotropic, corrosion rate has the same order of magnitude in all directions. This mechanism is dominant while using HF-based solution. In order to provoke anisotropic etching on Si wafers, the etchant solution is supposed to have HF accompanied with other oxidizing acids such as nitric acid (HNO3) or acetic acid (CH3COH) or a mixture of them. This class of solutions is abbreviated as HNA (hydrofluoric, nitric, acetic) [11]. The chemical reaction governing this type of etching is not fully studied. However, the principal

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reactions of the overall etching route are the following equations.

\[ 3\text{Si} \rightarrow 3\text{Si}^{4+} + 12e^- \quad (2) \]

\[ 4\text{NO}_3^- + 12e^- + 16\text{H}_3\text{O}^+ \rightarrow 4\text{NO} + 24\text{H}_2\text{O} \quad (3) \]

\[ 3\text{Si} + 4\text{NO}_3^- + 16\text{H}_3\text{O}^+ \rightarrow 3\text{Si}^{4+} + 4\text{NO} + 24\text{H}_2\text{O} \quad (4) \]

After the surface oxidation by nitric acid, Si substrate becomes susceptible and reacts with HF or F\(^+\) forming Si-F bond and finally will result a compound like SiF\(_4\), which gradually moves away from solution/solid interface. The H\(_2\)NO\(_3\)/HF fraction plays a significant role in smoothness of the corroded surfaces. High H\(_2\)NO\(_3\)/HF fraction are favorable in cases which an extremely smooth finished surface is required. In fact, the final surface tends to be smoother while the corrosion rate is controlled by diffusion. The related reactions tend to release products in gas form and the accumulation of bubbles is predictable. The trapped gas pockets can partially interrupt advance of the etching process. Consequently, it is suggested to provide a reaction cell containing sufficient stirring apparatus [12, 13].

In physical vapor deposition (PVD), the atoms or the molecules are transferred to the gas phase without any chemical reaction. It usually involves low pressure and not necessarily high temperature. Consequently, a wide range of coatings consisting of elements, alloys, ceramic compounds, as well as polymeric materials is practical thanks to PVD methods [14]. In magnetron sputter deposition, which is a well-developed PVD technique, the driving force to take compounds from so-called target to gas phase is ion sputtering. A commercialized radio frequency sputtering system is capable of producing SiC thin film from an initial pure SiC target [15]. As the sputtering procedure takes place in low temperatures, sputtered SiC coatings are usually demonstrated amorphous structures. However, a post-deposition thermal treatment may give sufficient activation energy to amorphous silicon carbide to become crystallized [16]. A SiC thin film can act as an excellent inhibitor to protect metals and alloys against corrosive chemical agents. Some studies involving classic polarization curve tests revealed that a SiC coated magnesium sample has a corrosion resistance up to ten times more than a bare one [17].

Silicon and its derived micron-sized mechanical and electrical structures are building blocks of the modern microelectromechanical Systems (MEMS). Thanks to its favorable mechanical and electrical properties, the silicon has a wide range of applications such as pressure sensors, thermodynamics, and optics. Nowadays, there are silicon-based sensors to measure any conceivable physical quantity. In order to have desired microstructure, it is necessary to remove some parts of the silicon wafer while keeping another parts. The concept of selectivity comes from the ability of the whole etching processes to distinguish these parts [18].

In the current study, a novel method to fabricate micro–textured silicon wafers is developed. The method is capable of producing a variety of shapes and patterns depending on the mask design. The texture tailored surface can be either a building block of a major MEMS system or be used as a roughened substrate for a superhydrophobic coating. The latter is carried out depositing a thin film of PTFE.

2. Materials and Methods

It is possible to deposit a thin film of silicon carbide via magnetron plasma sputtering (MPS). As an applicable rout to deposit ceramic refractory thin films on the intended substrate, MPS technique is performed using LEYBOLD Z550 radio frequency magnetron plasma sputtering equipment. Standard silicon wafers in \(<100>\) crystal growth direction are used as the substrate. 1×1 cm\(^2\) Si plates are cut, mounted, and fixed on substrate holders of the sputtering machine. The distance between substrates and sputtering canon are kept to be 30 cm. A12 cm in diameter SiC target obtained from Kurt J. Lesker Co., containing 0.5 wt. % impurity is mounted in Radio Frequency Magnetron Plasma Sputtering (RFMPS) canon (Fig. 1). In order to have desired masking performance, a fine mesh (Fig. 2) with aperture size in 100±10 µm dimensions is installed and fixed upon substrates. The intention of sputtering in this phase is to form a thin SiC protector film upon Si substrates (Fig. 3).

As the whole plasma sputtering process involves electron exchange, it is possible for the target to become positively charged. Consequently, the ions tend to deviate from target, due...
to the repulsive Coulombic force between two positively charged subjects. As a result, less ions are able to reach the target. This phenomenon is very common in targets made of electrically insulating materials such as ceramics in case of this study silicon carbide. In order to solve this problem, instead of using a DC electric field, alternative fields are used. The frequency is not so high (40 kHz) and falls in the radio frequency (RF) range. The alternative change in electric field direction removes built-up electrons which cannot leave the target due to the insulating characteristics. Therefore, RF source is selected to perform the plasma sputtering. The power is maintained to be 300 W. The bios voltage is measured to be 500 V. Argon as plasma gas is injected to the reaction chamber with flow rate equivalent to 60 SCFM and the chamber pressure is kept to be 10−2 mbar. After a sputtering run for 1 hour, the radio frequency source is turned off. In order to protect as-deposited thin film, the vacuum pump maintains to keep the pressure less than 10−6 mbar for two hours until the substrates cool down gradually.

Two HNA solutions are prepared with mixtures of hydrofluoric acid, nitric acid and acetic acid (Table 1). Nitric and hydrofluoric acid perform the whole oxidation and SiO2 removal chain of reactions while acetic acid has only diluting role. Solution A is less corrosive due to less volume fraction of principal acids and solution B can be considered extremely aggressive. After being selectively masked, Si samples are immersed in two different HNA solutions. In order to avoid inhomogeneous etching caused by reaction product gas bubbles, a mechanical agitation is required. After giving 1 to 5 minutes, literally, nothing happened for Si wafer in solution A. This observation might be attributed to the fact that solution A will take more time to start to chemically attack the specimens. In contrast with solution A, an exothermic chemical reaction started as soon as having physical contact between solution B and Si substrates followed by a huge release of reaction gases.

Since every chemical corrosion has time-dependent characteristics, the current wet etching procedure is done by giving variable reaction times ranging from 1 up to 4 min. After removing from chemical solutions, the samples are rinsed with distilled water. In order to completely remove the residues of the chemical attack, an ultrasound bath using acetone as liquid is performed. Finally, samples are air dried. The JEOL–6460LV Scanning Electron Microscope (SEM) is used to take images of the attacked Si wafers during chemical etching.

After the selective etching process, all the samples are coated using a plasma sputter deposition reactor and a pure PTFE target. The plasma power is kept to be 100 W and duration of 30 min. The target–substrate distance is maintained to be 30 cm. Argon is selected to be the plasma gas.

### Table 1. Chemical composition of HNA etchant solutions.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Concentration (wt. %)</th>
<th>Solution A (vol. %)</th>
<th>Solution B (vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>40</td>
<td>8.33</td>
<td>25</td>
</tr>
<tr>
<td>HNO₃</td>
<td>69</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>99</td>
<td>66.6</td>
<td>25</td>
</tr>
</tbody>
</table>

3. Results and Discussions

By immersing the samples, those parts of the Si wafer which are covered by fine mesh during the previous sputtering phase and did not receive protective SiC film became exposed to the harsh chemical agent and the pitting corrosion process takes place (Fig. 4). The initially formed crater begins to grow during the corrosion process until the protected part of the substrate becomes gradually isolated by four unifying craters (Fig. 5).

As can be seen in Fig. 5d, etching duration higher than 3 minutes results in an array of separated micron-sized picks (Fig. 6). Regardless of receiving protected SiC corrosion resistant layer, formation and growth of corrosion pit consume silicon underneath SiC and protective layer peels off and detaches from the substrate.
Figure 6. SEM micrograph with 45˚ tilted angle taken from the Si substrate after 4 minutes of chemical etching in solution B.

Figure 7. SEM micrograph of SiC deposited Si wafer after one minute chemical reaction with solution B.

Figure 8. AFM topography of deposited PTFE film.

Figure 9. CCD camera photograph of water droplet on PTFE coated silicon wafer which is selectively etched for 4 minutes.

In other words, there must be given intense attention to the etching duration. Insufficient etching time causes only small corrosion pits and long etching duration can simply eliminate all the protective layer and makes masking concept completely useless.

All selectively etched samples are PTFE coated via plasma sputter deposition. A smooth standard silicon wafer has also received the PTFE thin film for atomic force microscopy analysis (Fig. 8). For a textured Si that is immersed for two minutes (Fig. 5c) a contact angle of 130±5˚ is reported. An extremely high water contact angle is observed in the textured Si which is experienced etching durations higher than 3 min and its contact angle reaches to approximately 170±5˚, which is cumbersome to measure (Fig. 9). This behavior is attributed to the artificial roughness on substrates which leads to the Cassie state [19].

4. Conclusions

A state-of-the-art masking and texturing method is developed applicable to almost any area of technology that demands micron-sized smooth-contoured geometries. Besides the formation of uniform etched cavities, the method is capable of fabricating none-flat surfaces. Additionally, the method is economical as it is free of optical lithography step. The SiC deposition step forms a mask resistant to corrosion and makes available the use of extremely corrosive solutions and longtime etching procedures which may be a good choice when the objective is to gain the surface textures which their fabrication is a suitable choice for especial aqueous solutions and/or prolonged etching duration. After the wet etching, the Si samples possess a precise finished surface in micron size. Some abundant applications of this category of microfabrication are MEMS and microchannels. The artificially textured Si substrate demonstrates a remarkable effect on water contact angle. Extremely high wetting angles are reported after coating the substrate with PTFE.

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References


