Indentation modulus and hardness investigation of crystalline silicon surfaces treated by inductively coupled plasma reactive ion etching

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Abstract. In this paper we present an investigation of the influence of different roughness of etched silicon surfaces on the measured nanomechanical properties. For the etching, inductively coupled plasma (ICP) reactive ion etching (RIE) was performed on the surface of silicon samples with different crystal orientations (i.e., Si <100>, Si <110>, and Si <111>). Different roughness levels were obtained on each sample by changing the bias voltage through the high-frequency (HF) power. The surface roughness was measured using atomic force microscopy (AFM). The obtained surface roughness for the same etching conditions was different for different crystal orientations. The nanomechanical properties were measured using nanoindentation.

1. Introduction
Micromachining is a technology to fabricate microstructures such as Micro-Electro-Mechanical-Systems (MEMS), pillars and wires with dimensions down to the micro-meter size. Micromachining includes the technology that can remove and grow ultra-thin layers on substrates. In the process of micromachining, two or more different materials are joined together constructing the microstructure as desired [1]. Furthermore, silicon as an abundant material has been widely used to produce integrated circuits, sensors, and tips for atomic force microscopes (AFM). Moreover, micromachining is also well-established to develop microstructures. Most important processes used are diffusion, deposition and etching. On the one hand, the etching process in micromachining is the most important manufacturing technique to remove unwanted material. On the other hand, it can lead to problems due to residues or imperfections of the etching process for example when bonding two structures or when measuring the mechanical properties using nanoindentation [2].
In this study inductively coupled plasma reactive ion etching (ICP-RIE) was used to etch silicon substrates of different crystal orientations [3]. It is aimed to investigate the effect of the roughness generated on silicon by ICP-RIE on the measured mechanical properties (indentation hardness ($H_{IT}$) and modulus ($E_{IT}$)) measured using nanoindentation [4],[5]. The surface roughness surface of unetched and etched silicon samples is measured using AFM.

2. Silicon sample fabrication

2.1. Fabrication procedure

In this work, detailed investigations of silicon material with a focus on the impact of surface roughness on nanoindentation measurement results were carried out. Initially, 4-inch silicon wafers (Siegert Wafer GmbH, Germany) were diced into smaller 15 mm × 15 mm pieces (Figure 1(a)). This step was followed by cleaning the samples in a RCA (Radio Corporation of America)-type solution (i.e., $H_2O_2:H_2SO_4 = 1:1$) [6] inside a quartz beaker and boiled on a hot plate at a temperature of 90 °C to remove any organic residues and residual particles, e.g. from the dicing step. This decontamination process created a thin oxide layer on the silicon surface (figure 1(b)), which is later removed using buffered hydrofluoric acid (HF, 6-7 %) prior to the processing (figure 1(c)). Subsequently, the unmasked silicon surface was treated by an ICP-RIE process at a cryogenic temperature (Sentech Instrument GmbH, Germany) (figure 1(d)). Finally, the same procedure (i.e., treatment in a RCA-type solution and oxide removal by HF) was performed on the etched silicon surface (figure 1(e)). Then the surface roughness and the mechanical properties were determined using AFM and instrumented indentation testing (IIT), respectively (figure 1(d)).

![Figure 1](image.png)

**Figure 1.** Schematic of sample-fabrication procedure for roughness investigation on an etched silicon surface: (a) Initial surface state after dicing a 4-inch Si wafer into smaller pieces of 15 mm × 15 mm substrate, (b) cleaning procedure using a RCA-type solution followed (c) by removal of native oxide using buffered hydrofluoric acid (HF, 6-7 %). (d) Subsequently, the Si surface was etched by cryogenic ICP-RIE and (e) etch residues were removed. (f) Measurement of surface roughness and mechanical properties was performed by AFM and nanoindentation, respectively.

2.2. ICP-RIE parameters

To describe the relationship between surface roughness and nanomechanical properties, different etch parameters were investigated on cleaned silicon samples of different crystal orientations (i.e., Si "100", Si "110", and Si "111"). As a starting point, a "standard" recipe with an etch temperature of -95 °C, an ICP power of 150 W, a high-frequency power of 10 W (bias = -31 V), a gas flux of 60 sccm and 7 sccm for each SF$_6$ and O$_2$, respectively, and a chamber pressure of 1.0 Pa was used within 30 minutes of etching. In this case, the change of surface roughness was realized by changing the energy of the incident ion during the etching process.
(i.e., HF power). As shown in Table 1, higher bias was obtained by applying higher HF power. In total, three etch recipes were used during the etch experiments, denoted by A, B and C. Furthermore, it has to be noted that each recipe was performed at the same time on the three different silicon crystal orientations.

Table 1. Etching parameters using ICP-RIE.

| Sample (etched Si) | Orientation | Treatment (Recipe) | Temp. (°C) | ICP Power (ion density) (W) | HF Power (ion power) (W) | Bias (V) | Gas ratio SF6/O2 | Pressure (Pa) |
|-------------------|-------------|--------------------|------------|-----------------------------|--------------------------|----------|-----------------|--------------|
| S1                | Si <100>    | A                  | -95        | 150                         | 10                       | -31      | 89.6/10.4       | 1            |
| S2                | Si <110>    | A                  | -95        | 150                         | 10                       | -31      | 89.6/10.4       | 1            |
| S3                | Si <111>    | A                  | -95        | 150                         | 10                       | -31      | 89.6/10.4       | 1            |
| S4                | Si <100>    | B                  | -95        | 150                         | 30                       | -71      | 89.6/10.4       | 1            |
| S5                | Si <110>    | B                  | -95        | 150                         | 30                       | -71      | 89.6/10.4       | 1            |
| S6                | Si <111>    | B                  | -95        | 150                         | 30                       | -71      | 89.6/10.4       | 1            |
| S7                | Si <100>    | C                  | -95        | 150                         | 50                       | -100     | 89.6/10.4       | 1            |
| S8                | Si <110>    | C                  | -95        | 150                         | 50                       | -100     | 89.6/10.4       | 1            |
| S9                | Si <111>    | C                  | -95        | 150                         | 50                       | -100     | 89.6/10.4       | 1            |

3. Experiment

3.1. Roughness analysis

Figure 2 shows AFM topography images of the unetched (i.e., S1, SII and SIII) and etched silicon samples (i.e., S7 to S9). The surface roughness of all samples was measured within a 10 μm x 10 μm scan area using a Dimension Icon AFM in the tapping mode, equipped with an OTESPA cantilever.

Figure 2. AFM topography images (a) unetched Si <100> as the SI, (b) unetched Si <110> as the SII, (c) unetched Si <111> as the SIII, (d) etched Si <100> as the S7, (e) etched Si <110> as the S8 and (f) etched Si <111> as the S9 (red circle: contamination excluded from evaluation).
The obtained surface topographies for each sample were assessed using the SPIP 6.7.3 software (Image Metrology) (figure 2) to determine the values of mean roughness ($S_a$), root mean square roughness ($S_q$), and peak to peak roughness ($S_z$) [7]. Regions of interest (ROI) were used to define areas on the images to be analysed and to exclude contaminated areas. As a result, representative results of roughness were obtained by excluding areas covered by unwanted residual particles (figure 2(e)). The images were line-wise offset-corrected, then tilt-corrected using a polynomial of first degree and finally Gauss low-pass-filtered using a relative filter wavelength of 1/7 of the profile length. Outliers with a deviation from the mean value greater than two standard deviations were removed from the data set.

3.2. Instrumented indentation test

A Hysitron Triboindenter TI 950 equipped with a three-sided pyramidal Berkovich diamond indenter with a tip radius $R_{tip}$ of $(150 \pm 15)$ nm was used to measure the nanomechanical properties of each sample (i.e., $H_{IT}$ and $E_{IT}$). Prior to the measurements, the integrated optical microscope and the piezo-stage of the instrument were successfully calibrated using a “soft” material (i.e., an aluminum sample). Additionally, the instrument compliance was determined to be 2.76 nm/mN. The contact area of the indenter was measured within a contact depth $h_c$ ranging from 30 nm to 200 nm. The contact area function $A_c$ is determined to be $24.5 h_c^2 + 1253 h_c$ ($30 \text{ nm} < h_c < 200 \text{ nm}$). The indentation results were then analyzed using the Oliver and Pharr method [8].

In the measurements, load-controlled (LC) indentations were carried out using forces between 1 mN and 10 mN, while depth-controlled (DC) indentations were performed using depths between 40 nm and 200 nm. In the latter case, the maximum force was 11.2 mN. For both cases, 5-2-5 LD or DC mode was used, which means 5 s of loading time, 2 s of holding period, and 5 s of unloading time. The indentation modulus ($E_{IT}$) of the sample can be calculated from the measured reduced modulus ($E_r$) given by

$$\frac{1}{E_r} = \frac{(1 - v_S^2)}{E_T} + \frac{(1 - v_T^2)}{E_T}$$

(1)

For the Berkovich diamond indenter, a Young’s modulus $E_T = 1140 \text{ GPa}$ and a Poisson ratio of $\nu_T = 0.07$ are used. The Poisson ratio of silicon was taken from [9] to be $\nu_S = 0.278$. Meanwhile, $H_{IT}$ can be calculated using

$$H_{IT} = \frac{P_{max}}{A_c}$$

(2)

where $P_{max}$ and $A_c$ are the maximum applied load and the contact area under the load, respectively. Three unetched crystalline silicon samples (i.e., SI to SIII) are measured using the DC mode with indentation depths ranging from 68 nm to 194 nm, while the etched silicon samples (i.e., SI to S9) were measured using the LC mode with maximum indentation loads ranging from 5 mN to 9 mN. Typical load-displacement curves obtained on unetched Si <100> SI are shown in Figure 3(a). At the maximum indentation depth (i.e., 194 nm) a phase transformation occurs during loading [10]. This leads to an abnormal unloading curve as can be seen in figure 3(a). For comparison the indentation curves of the etched Si <100> S1 are shown in figure 3(b). Clear result differences between unetched (i.e., SI) and etched Si <100> (i.e., S1) samples are obvious as the etched Si <100> (i.e., S1) shows very disperse indentation curves.
Figure 3. Nanoindentation load-displacement curves for (a) an unetched sample Si <100> (i.e., S1) using the DC mode and (b) an etched sample Si <100> (i.e., S1) using the LC mode.

4. Result and Discussion

$H_{fr}$ and $E_{IT}$ calculated from measured reduced moduli ($E_r$) are given in Table 2. Different ion power parameters of the ICP-RIE etching treatment (recipes A to C) were used to produce different surface roughness. However, surfaces treated by recipes A and B do not show considerably different results with regard to their $Sa$ values. The samples, which had been processed using recipe C, exhibit at least a factor of two higher roughness values. Thus, the recipe B is not optimum to etch the surface deeper than recipe A. In addition, it can be concluded that different crystal orientations influence the etching process. Correspondingly, Si <100> (i.e., S1, S4, S7) had shown higher $Sa$ values compared to Si <110> (i.e., S2, S5, S8) and Si <111> (i.e., S3, S6, S9) (i.e., $Sa$(Si<100>) > $Sa$(Si<110>) > $Sa$(Si<111>). Furthermore, the relationship between the $Sa$ values and the obtained $E_{IT}$ and $H_{IT}$ values was investigated. Figure 4(a) and (b) depict these dependencies. The plotted indentation modulus and hardness values of the etched sample (etched indentation modulus ($E_e$) and hardness ($H_e$)) were plotted normalized to their unetched silicon values (unetched indentation modulus ($E_u$) and hardness ($H_u$)). Plotted are the indentation moduli ratios ($E_e/E_u$) and the hardness ratios ($H_e/H_u$) depending on surface roughness. As $Sa$ increases, $E_e/E_u$ and $H_e/H_u$ of the samples (S1 to S9) decrease. Here, the lowest $E_e/E_u$ and $H_e/H_u$ of all etched samples was obtained for recipe C and the SI Si <100> sample. For the maximum obtained roughness ($Sa = 55$ nm) the deviation of the measured indentation modulus amounts to more than 30 % and the deviation of the indentation hardness amounts to more than 50 % (sample S7). For the smallest roughness investigated ($Sa = 5$ nm) the deviation of the indentation modulus amounts to only 7 % (S6 Si <111> and S3 Si <111>).

Table 2. Roughness, indentation modulus and hardness of unetched and etched silicon samples.

| Sample    | Treatment (Recipe) | Orientation | $Sa$ (nm) | $Sq$ (nm) | $Sz$ (nm) | $E_{IT}$ (GPa) | $H_{IT}$ (GPa) |
|-----------|--------------------|-------------|-----------|-----------|-----------|----------------|----------------|
| (Unetched Si) S1 | -                  | Si<100>     | 0.1 ± 0.0 | 0.2 ± 0.1 | 10.9 ± 7.5 | 164.1 ± 1.9    | 10.2 ± 0.2     |
| (Unetched Si) SII| -                  | Si<110>     | 0.1 ± 0.0 | 0.2 ± 0.1 | 11.4 ± 9.7 | 169.2 ± 3.3    | 10.0 ± 0.2     |
| (Unetched Si) SIII| -                | Si<111>     | 0.3 ± 0.1 | 0.5 ± 0.3 | 16.5 ± 20.6 | 184.5 ± 2.7    | 10.3 ± 0.1     |
| (Etched Si) S1  | A                  | Si<100>     | 26.1 ± 3.3 | 32.3 ± 3.7 | 241.4 ± 15.7 | 128.1 ± 10.4   | 6.4 ± 1.1      |
| (Etched Si) S2  | A                  | Si<110>     | 12.8 ± 0.4 | 16.0 ± 0.4 | 126.1 ± 10.8 | 158.0 ± 11.7   | 10.1 ± 1.5     |
| (Etched Si) S3  | A                  | Si<111>     | 5.8 ± 0.2  | 6.9 ± 0.2  | 60.8 ± 7.0  | 168.8 ± 10.9   | 10.9 ± 1.0     |
| (Etched Si) S4  | B                  | Si<100>     | 24.2 ± 1.0 | 30.3 ± 1.2 | 228.4 ± 21.0 | 117.9 ± 14.6   | 5.6 ± 1.7      |
| (Etched Si) S5  | B                  | Si<110>     | 12.8 ± 0.6 | 19.3 ± 0.7 | 207.2 ± 8.9  | 154.7 ± 11.9   | 9.8 ± 1.6      |
| (Etched Si) S6  | B                  | Si<111>     | 5.1 ± 0.6  | 8.2 ± 0.7  | 91.3 ± 6.6  | 169.2 ± 9.0    | 11.3 ± 1.2     |
| (Etched Si) S7  | C                  | Si<100>     | 53.9 ± 2.9 | 64.3 ± 3.1 | 435.9 ± 49.0 | 111.7 ± 13.7   | 4.3 ± 1.1      |
| (Etched Si) S8  | C                  | Si<110>     | 44.0 ± 2.6 | 54.8 ± 2.5 | 391.9 ± 21.7 | 139.9 ± 32.9   | 7.9 ± 3.8      |
| (Etched Si) S9  | C                  | Si<111>     | 27.0 ± 0.5 | 31.9 ± 0.5 | 216.3 ± 6.3  | 153.9 ± 23.9   | 9.1 ± 2.9      |
Figure 4. Relationship between nanomechanical values and roughness ($S_a$) of etched silicon samples. Indentation moduli (a) and hardness (b) of etched samples are normalized to their unetched-samples values.

5. Conclusion
A quantitative study of the relationship between surface roughness and nanomechanical properties of different crystalline silicon materials was performed. Different surface roughness on three crystalline silicon samples was fabricated using ICP-RIE. The method used to obtain different roughness is to increase the HF power, i.e., the self-bias voltage. First finding of the presented study is that increasing surface roughness leads to strong error contributions to the measured nanomechanical properties. Deviations between measured indentation moduli up to 30 % and measured hardness values up to 50 % were observed for surface roughness values of $S_a = 54$ nm. Another finding was that the crystal orientation of the silicon sample has a strong influence on the obtained surface roughness due to ICP-RIE etching. The highest roughness was obtained for Si <100> and the lowest roughness for Si <111>. A possible explanation is the higher atomic area density of the Si <111> surface.

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References
[1] French P J, Sarro P M 2006 MEMS ed J G Korvink, Oliver P (Heidelberg: Springer) pp 805-845
[2] Marteau J, Mazeran P-E, Bouvier S, Bigerelle M 2012 Strain 48 pp 491-497
[3] Xia Y, et al 2014 Scanning 36 pp 134-149
[4] Sökmen Ü, et al 2009 J. Micromech. Microeng. 19 8pp
[5] Grau P, Ullner C, and Behncke H 1997 Materialprüfung 39 pp 362-367
[6] Joyce R, et al 2015 Mat. Sci. in Semiconduct. Proc. 31 pp 84–93
[7] Nemoto K, et al 2009 Meas. Sci. Technol. 20 084023 7pp
[8] Oliver W C and Pharr G M 1992 J. Mater. Res. 7 pp 1564-1583
[9] Hopcroft M A, Nix W D, and Kenny T W 2010 J. Microelectromech. Sys. 19 pp 229-238
[10] Chang L and Zhang L C 2009 Acta Materialia 57 pp 2148–2153