Influence of eccentric nanoindentation on top surface of silicon micropillar arrays

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Abstract. In this paper we present an investigation of the influence of nanoindentation location on the top surface of silicon micro-pillar. This silicon micro-pillar array which will be employed as a micro force sensor array based on three-dimension silicon (3D Si) structures, is fabricated by near UV nanoimprint lithography (NIL) technique and etched by Cryogenic Inductively Coupled Plasma (ICP) sequentially. To determine its mechanical properties, those micropillars are measured by instrument indentation testing (IIT) to obtain its hardness and reduced modulus. For the measurement, a Berkovich diamond indenter is utilized to penetrate a single and also multiple point indentations on a micro-pillar surface. Afterwards, these results are compared to the indentation at the central point of the tested pillar and Si bulk as its reference to examine the influence of different probing locations on the measured reduced modulus and hardness.

1. Introduction

Semiconductor microstructures created in 3D such as micropillars, microwires, and microrods are widely employed in sensing of physical properties (e.g., humidity, mass, vibration, and force) due to their increased area surface-to-volume ratio [1]. These sensors are often fabricated by top-down and/or bottom-up approaches, and always yield different precision level of dimension [2]. It is therefore important to characterize the micromechanical properties of these sensors using standard methods. Using nanoindentation, for instance, mechanical properties like stiffness ($S$), hardness ($H$) and indentation modulus ($E_{IT}$) can most reliably be measured and evaluated. However, several error sources and uncertainties during nanoindentation measurements may be pronounced including pile-up, indentation size effect, drift, surface forces, and structural heterogeneities [3][4]. Moreover, micropillar nanoindentation revealed smaller indentation moduli compared to the bulk material. A procedure for correcting this effect was already developed and confirmed on crystalline silicon micropillars. It is the so-called material compressibility, which has been identified as an additional source of uncertainty [5].
The other problem which appears in the measurement is a drift of the equipment. It mainly causes a mishit of indentation point. In addition, center points of surface are eventually hard to find because the shape of the micropillar top face is not always perfectly circular. A lower value of the reduced modulus of the pillar was found when the point of indentation was not exact in the pillar centre [6]. Thereby, to investigate all these problems, the current study considers the eccentric indentation of a silicon micropillar as an important uncertainty contribution.

2. Silicon micropillar arrays fabrication

2.1. Fabrication procedure

To investigate the error source of eccentric nanoindentation, some samples of silicon micropillar were fabricated using three 4-inch single-crystal silicon wafers (Si <100> and Si <110>, Siegert Wafer GmbH, Germany and Si<111>, Wacker Siltronic AG, Germany). They were diced into square chips of 15 mm × 15 mm (Figure 1(a)) in size. Subsequently, a cleaning process using RCA and buffered HF solution was applied (Figure 1(b)) to clean the substrate from residuals and the thin natural oxide layer. After cleaning, the substrate was coated by spin-coating with UV-sensitive resist (mr-NIL210-200nm, Figure 1(c)). Prior to the nanoimprint resist deposition, a several-nanometer-thick adhesion film (mr-APS1) was attached. Afterward, the sample was located at the bottom of a home-made vacuum chamber which has a transparent lid to transmit the UV light into the chamber. Subsequently, a flexible and transparent PDMS (polydimethylsiloxane) stamp was mounted above the substrate Figure 1(d)). The air between PDMS stamp and substrate was evacuated after the lid has been put on the chamber to isolate the process from the ambient environment. The PDMS stamp that has protrusions on bottom-side surface was moved down slowly to the substrate. This embossing process was accompanied by UV illumination (wavelength ~368 nm) of the substrate through the lid for 5 minutes (Figure 1(e)). To ensure a homogeneous pressure between stamp and the substrate, nitrogen gas (N₂) was filled inside the chamber at ~3 bar. As a result, after the stamp was detached from the substrate, the resist on top of the sample was imprinted conformingly to the surface topography of the PDMS stamp.

After nanoimprint lithography has been completely accomplished, residues of resist were removed by oxygen reactive ion etching (O₂-RIE) which is illustrated in Figure 1(f). This process was used to strip-off the excess residual resist layer and it stopped, when the silicon surface at the bottom of the embossed area was visible. This step was followed by anisotropic inductively coupled plasma (ICP-RIE) to remove silicon in the areas that were not covered by the resist Figure 1(g)). Here, the silicon substrate was physically bombarded chemically etched using sulphur hexafluoride (SF₆). This process generates silicon tetrafluoride (SiF₄) in the form of a colourless gas which was sucked out from the reactor. As a consequence, layer by layer of silicon were removed from its original substrate. Accordingly, this etching process had to be controlled to get the best vertical etching (anisotropic etching). There are some parameters that have to be taken into consideration. These parameters are (ICP and HF) power, ratio of (SF₆ : O₂) gas as well as pressure and temperature) in the chamber. The standard recipe that was used to fabricate these micropillar arrays can be seen in Table 1. Finally, after the pattern transfer was finished, the resist that still remained on top of the micropillars was cut-off (Figure 1(h)). The aspect ratio (AR) of the fabricated pillars can be calculated using the following formula:

\[ AR = \frac{H}{D}, \]

where \( H \) is the height and \( D \) is the diameter of a micropillar.
Figure 1. Schematic illustration of vertically aligned silicon-micropillar fabrication by near-UV NIL and cryogenic ICP-RIE for the investigation of eccentric nanoindentation: (a) Initial surface condition after dicing a 4-inch Si wafer into chips of 15 mm × 15 mm size, (b) cleaning process using an RCA-type and hydrofluoric acid solution (HF, 6-7 %), (c) spin coating of UV-sensitive resist, (d) pattern replication using a PDMS stamp, (e) exposure by UV radiation, (f) removal of a residual resist layer using O₂-RIE, (g) etching process by ICP-RIE, (h) resulting silicon micropillar array with desired height and diameter.

In the fabrication process, the micropillar height was set by an appropriate etching time, while its diameter was determined by the used stamp. Using standard recipes of O₂-RIE and ICP-RIE, three samples of silicon micropillars with different crystal orientations (i.e., Si <100>, Si <110> and Si <111>) were realized.

Table 1. RIE etching parameters

| Sample Name | Treatment (Recipe) | Temp. (°C) | ICP Power (ion density) (W) | HF Power (ion power) (W) | Bias voltage (V) | Gas flux SF₆/O₂ (sccm) | Chamber Pressure (Pa) | Etching Time (minutes) |
|-------------|---------------------|------------|-----------------------------|--------------------------|------------------|------------------------|-----------------------|-----------------------|
| S1, S2 and S3 | O₂ - RIE | 20 | 200 | 10 | -40 | -10 | 1 | 2.5 |
| S1, S2 and S3 | ICP - RIE | -95 | 200 | 10 | -33 | 60/7 | 1 | 30 |

2.2. Confocal Laser Scanning Microscope (CLSM)

To determine the accurate diameter and height of the micropillars, a CLSM (Olympus LEXT OLS 4000) is utilized with the silicon micropillar arrays. Table 2 shows the measurement result of height and diameter of the micropillars.

Table 2. Height and diameter micropillar measurement result using CLSM

| Sample Name | Crystal Orientation | Measurement Results |
|-------------|---------------------|---------------------|
|             |                     | Height (µm) | Diameter (µm) | Aspect Ratio |
| S1          | Si <100>            | 4.23 ± 0.01 | 1.84 ± 0.05 | ~2.29       |
| S2          | Si <110>            | 3.99 ± 0.05 | 1.58 ± 0.06 | ~2.52       |
| S3          | Si <111>            | 3.16 ± 0.01 | 1.26 ± 0.06 | ~2.51       |

SPIP™ 6.3 software (Image Metrology A/S, Denmark) is used to analyze the vertical and horizontal profiles from CLSM. Height measurement is evaluated by “histogram height evaluation”, while the diameter measurement is measured by the “particles and pore analysis” that both are provided as...
software modules. It can be seen that the etch rate of each silicon sample is different. Among the fabricated samples, S1 that has the crystal orientation \( <100> \) has the highest etch rate (\( \sim 134 \text{ nm/min} \)) which is followed by S2 (Si \( <110> \)) and S3 (Si \( <111> \)).

3. Experiment

3.1. Bulk Silicon Samples

Firstly, the investigation begun by measuring the mechanical properties of bulk silicon. These bulk silicon samples were cut from the same silicon wafers, that were used to produce the silicon micropillar arrays. After the three silicon wafers are cut into chips of a size of \( 15 \times 15 \text{ mm}^2 \), those bulk samples were cleaned to remove the residues and unwanted organic layers. To measure the mechanical properties of bulk silicon, nanoindentation was applied. For the first test, each sample was being indented by a diamond Berkovich indenter in a series of indentations of \( 5 \times 5 \) arrays (i.e., S1 and S3) and \( 10 \times 10 \) arrays (i.e., S2). The applied force was varied from 100 \( \mu \text{N} \) to the 10 mN (the maximum realizable force for TI 950 Hysitron is at 10 mN). Each indentation process was performed in a three-step procedure, which were loading for 5 s, holding the maximum force for 2 s and unloading for 5 s (5-2-5 method). The data was carefully analyzed to get highly precise results. Therefore, some outliers which sometimes can be found in the measurement had to be excluded from the analysis. A number of things including a dirty sample or a pre-existing scratch or indent on the sample could cause these outliers [7]. Regarding to this problem, the used nanoindenter TI 950 has a feature which is called \textit{in-situ} SPM imaging to inspect the sample surface before and after indentation. Figure 2 represents the \textit{in-situ} SPM image of the samples (i.e., bulk Si \( <100> \), Si \( <110> \) and Si \( <111> \)) after the indentations were performed. The scan area of as \( 25 \times 25 \text{ µm}^2 \) was chosen to observe qualitatively all imprints of nanoindentation in the bulk silicon surface.

![Figure 2. In-situ Scanning Probe Microscopy (SPM) imaging of silicon bulk surfaces after nanoindentation is performed on (a) bulk Si \( <100> \), (b) bulk Si \( <110> \), and (c) bulk Si \( <111> \) sample.](image)

3.2. Micropillar Samples

To investigate the influence of eccentric nanoindentation, various indentations with depth control were equidistantly applied from the centre of the Si micropillars. Firstly, some micropillars were measured in the centre of the micropillar surface. Then, measurements were continued by eccentric nanoindentations for each micropillar. To mark the target indentation point, a green dot was used to mark the position of nanoindentation. In horizontal and vertical axes in the top view of a micropillar surface, the target points of indentation for S1 and S2 sample were radially made every 350 nm and 700 nm, respectively, from the centre, which can be seen in figures 3(a) and 3(b). While S1 and S2 samples have eight eccentric nanoindentation points, S3 sample had only 4 single eccentric nanoindentations (see figure 3(c)). It was because the surface area of S3 had a smaller area compared to S1 and S2 sample. In this measurement, all maximum indentation depth was set to 40 nm and 30 nm. Otherwise for 60 nm, only a single eccentric
nanoindentation was performed for all micropillars. To indent the micropillars in the centre, it was graphically determined by a reticle in the software.

Figure 3. Indentation locations was marked on (a) S1 sample, (b) S2 sample and (c) S3 sample.

4. Result and Discussion
Stiffness ($S$), indentation hardness ($H_{IT}$) and reduced moduli ($E_r$) are obtained from nanoindentation measurements, where the Oliver and Pharr method is used to analyze the unloading curve of each indentation [7]. In this case, $E_{IT}$ need to be calculated from the measured $E_r$ using:

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

According to the reference [8], Young’s modulus ($E_T$) of the diamond indenter is 1140 GPa while its Poisson ratio ($v_T$) is 0.07. Meanwhile, the Poisson’s ratio of silicon ($v_S$) that was used to fabricate the Si micropillar is 0.278. On the other hand, $H_{IT}$ can be obtained using

$$H_{IT} = \frac{P_{\text{max}}}{A_c}$$ \hspace{1cm} (3)

where $P_{\text{max}}$ and $A_c$ are the maximum applied load and the contact area, respectively. Figure 4(a) depicted that the bulk Si <100> has an $E_{IT}$ of $(164.1 \pm 1.9)$ GPa whereas its hardness ($H_{IT}$) amounts to $(10.2 \pm 0.2)$ GPa. For contact depths below 25 nm, $E_{IT}$ and $H_{IT}$ showed unreasonable values. One possible reason might be area function for shallow indentations is not valid.

On the other hand, $E_{IT}$ on the micropillar S1 shows smaller values compared to the bulk and following a parabolic dependence on the eccentricity, i.e., the distance of indentation from the center point (Figure 4(b)). After 320 nm from the center, the indentation result exhibited a deviation of 10 percent from the measured $E_{IT}$ at the center. However, $H_{IT}$ was almost unchanged and not influenced by the location on the micropillar surface.

Figure 4. HIT and EIT of (a) bulk Si <100> sample versus contact depth, and of (b) the S1 Si <100> micropillar sample versus radial distance from the centre (every multiple 100 nm).
To analyse the nanoindentation results, area of top surface of all pillars were divided into some radial areas. In this case, the area of radius I is the area which is started from the centre point to the radius of 100 nm while the area of radius II is started from the radius 100 nm to 200 nm and so on. Therefore, top surface of S1 sample was divided into six areas i.e., area of radius I (AoR I) to area of radius VI (AoR VI). For S2 and S3 samples, those areas which were smaller diameter from S1 have only five areas and four areas respectively. Each area is used to collect the indentation results that have been performed. Here, All $E_{IT}$ of the micropillars were already corrected by the compressibility effect for which the precise dimensions of the micropillars were needed. The complete measurement data can be seen in Table 3.

| Sample Name | Centre | Eccentric* (micropillar) |
|-------------|--------|-------------------------|
|             | $H_{IT}$ (GPa) | $E_{IT}$ (GPa) |
|             | AoR I   | AoR II | AoR III | AoR IV | AoR V | AoR VI |
| Bulk Si <100> | 10.2 ± 0.2 | 164.1 ± 1.9 | - | - | - | - |
| Bulk Si <110> | 10.0 ± 0.2 | 169.2 ± 3.3 | - | - | - | - |
| Bulk Si <111> | 10.3 ± 0.1 | 184.5 ± 2.7 | - | - | - | - |
| S1 Si <100>  | 15.1 ± 0.2 | 149.3 ± 0.1 | 141.2 ± 0.8 | 133.7 ± 6.4 | 119.3 ± 7.3 | 114.2 ± 6.8 | 86.9 ± 3.1 |
| S2 Si <110>  | 13.0 ± 1.3 | 146.9 ± 7.4 | 135.6 ± 9.0 | 111.3 ± 16.0 | 114.3 ± 6.9 | 101.2 ± 9.8 | - |
| S3 Si <111>  | 12.9 ± 0.9 | 173.3 ± 5.7 | 150.0 ± 9.5 | 137.8 ± 12.6 | 111.8 ± 8.4 | - | - |

5. Conclusion
The eccentric nanoindentations of fabricated micropillar have been demonstrated. It shows that the 10 percent deviation of $E_{IT}$ occurs after 320 nm, 275 nm and 250 nm from the center of micropillar S1, S2 and S3 respectively. It can be concluded that after 40 % of the radius of the pillar from the center, $E_{IT}$ obtained by nanoindentation result will not be valid for accurate measurement. In this case only $E_{IT}$ is influenced by the indentation location while $H_{IT}$ was almost constant. It is following a parabolic dependence on the eccentricity. Some factors which related to the smaller $E_{IT}$ versus the radial displacement are the elastic bending and/or buckling effect during the experiment.

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