A Study on the Damage Layer Removal of Single-Crystal Silicon Wafer After Atmospheric-Pressure Plasma Etching

Weijia Guo
Department of Mechanical Engineering,
National University of Singapore,
EA-02-17, 9 Engineering Drive 1,
Singapore 117575
e-mail: e0204981@u.nus.edu

Senthil Kumar Anantharajan[1]
Mem. ASME
Department of Mechanical Engineering,
National University of Singapore,
EA-05-25, 9 Engineering Drive 1,
Singapore 117575
e-mail: asenthil@nus.edu.sg

Xinquan Zhang
Machining Technology Group,
Singapore Institute of Manufacturing Technology,
73 Nanyang Drive,
Singapore 637662
e-mail: zhangxq@simtech.a-star.edu.sg

Hui Deng
Department of Mechanical and Energy Engineering,
Southern University of Science and Technology,
No. 1088 Xueyuan Road,
Shenzhen, Guangdong 518055, China
e-mail: dengh@sustc.edu.cn

In this study, atmospheric-pressure (AP) plasma generated using He/O_2/CF_4 mixture as feed gas was used to etch the single-crystal silicon (100) wafer and the characteristics of the etched surface were investigated. The wafer morphology and surface elemental composition were analyzed using scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. The XPS results reveal that the fluorine element will be deposited on the wafer surface during the etching process when oxygen was not introduced as the feed gas. By detecting the energy and intensity of emitted particles, optical emission spectroscopy (OES) is used to identify the radicals in plasma. The fluorocarbon radicals generated during CF_4 plasma ionization can form carbon fluoride polymer, which is considered as one factor to suppress the etching process. The roughness was measured to be changed with the increase in the etching time. The surface appears to be rougher at first when the plasma etching occurred on the subsurface damaged (SSD) layer, and the subsurface cracks would show on the surface after a short-time etching. After the damaged layer was fully removed, etching resulted in the formation of square-opening etching pits. During extended etching, the individual etching pits grew up and coalesced with one another; this coalescence provided an improved surface roughness. This study explains the AP plasma etching mechanism, and the formation of anisotropic surface etching pits at a microscale level for promoting the micromachining process. [DOI: 10.1115/1.4046377]

1 Introduction

As a primary semiconducting material, silicon wafer has been increasingly popular, due to its relatively low cost and ease of fabrication of micro-electronic components and devices. Because of its well-documented mechanical and electrical properties, silicon is considered as an ideal material for experimental study [1,2]. Nowadays, as electronic applications shrink in size, thin silicon wafer is more and more crucial for advanced semiconductor technology. Stricter and higher standard are being imposed on wafer thinning technology [3]. Back grinding is still the most common wafer thinning technique and it can thin down wafers from 725 μm to less than 100 μm [4]. Although it has a high thinning speed, subsurface damage (SSD) induced by back grinding is unavoidable, including microcrack, residual stress, and dislocations [4,5]. These damages are responsible for the degraded mechanical properties of the produced wafers including low fracture strength of ultrathin silicon wafer causing handling problems and various challenges in dicing and packaging assembly [3,6]. This makes it necessary to develop damage-free postgrinding processes to realize damage layer removal and stress relief. Chemical mechanical polishing (CMP), wet chemical etching, plasma etching, and dry polishing were considered as a postgrinding process to reduce the microcracks and surface roughness of the processed wafer [7–9].

Chemical mechanical polishing is a standard process for final surface finish of silicon wafers. It can be used to produce smooth silicon surface with low total thickness variation values. To get higher material removal rate, higher thrust force is required, which may induce wafer cracks and further penetration of subsurface damage [3,7]. The polishing slurry may cause environmental pollution problems and hence it is becoming a less attractive option. Wet chemical etching is another common method for the removal of surface damages, crystal defects, and microcracks and prevents further propagating crystalline defects [3,10]. However, the large amount of chemical and its disposal costs are extremely high. Hence, dry polishing processes are being developed which uses special polishing wheel for dry polishing of silicon wafers to relieve stress on silicon and it does not use any chemicals, slurry, or water [11]. Similar to CMP, high removal rate is only obtained when higher polishing force is exerted, which will induce further SSD propagation [7].

Plasma etching is a noncontact damage-free etching technique which avoids mechanical stress to the wafer surface and maintains its original physical and mechanical properties [12]. In addition, this dry etching method is both cost-effective and environmentally friendly, without using slurry. Another advantage is that plasma dry etching process has a high etching rate due to the presence of highly reactive radicals in plasma [13]. Furthermore, for chemical plasma etching, although the ion energy is relatively low, the pressure required for generating plasma system can be in atmosphere, which avoids the expensive vacuum chamber and reduces the limitation of the sample size by the vacuum system. Atmospheric-pressure (AP) plasma for silicon wafer thinning yields surfaces with less or no subsurface damage as compared to that of CMP or other mechanical polishing methods.

Therefore, in this study, the focus is on the use of AP plasma and its effect on the surface of the single-crystal silicon wafer. The surface is characterized using field emission scanning electron microscope (FESEM), atomic force microscope (AFM), and X-ray photoelectron spectroscopy (XPS). The chemical composition and reactions are determined using the optical emission spectroscopy (OES). AP plasma etching mechanism and the formation of anisotropic surface etching pits at microscale would be investigated, to promote the application for AP plasma etching to micromachining process.

---

[1] Corresponding author.

Contributed by the Manufacturing Engineering Division of ASME for publication in the JOURNAL OF MICRO- AND NANO-MANUFACTURING. Manuscript received October 21, 2019; final manuscript received February 3, 2020; published online March 27, 2020. Assoc. Editor: Lawrence Kulinsky.

2 Experimental Setup and Trials

2.1 Silicon Wafer Used in This Study. Lapped silicon (100) wafers (SUNSON Electronic Technology Co. Ltd., Shenzhen, China) with 1–30 Ω cm resistivity and thickness of 400 μm were used in this study. The silicon wafer was sliced from the ingot using resin bonded diamond wire, without further fine finishing process. The initial surface roughness of the Si wafer is measured to be around the R_a value of 362 nm. A SSD layer exists and one SSD model for silicon wafers induced by wire sawing was proposed in Ref. [5], as shown in Fig. 1. As indicated in this figure, a damage layer of 1 to 100 μm exists in the silicon wafer, Since SSD layer can deteriorate the mechanical property, optical property, and electronic property, it is necessary to eliminate it and improve the quality of the silicon wafer [5].

2.2 Experimental Setup. The developed experimental setup is shown in Fig. 2. It consists of a RF plasma generator and an amplifier unit (function generator and matcher controller), MFC (mass flow controller and display), chiller unit, gas cylinder unit, and optical three-axis platform. The silicon wafer sample was placed on the movable stage. Before plasma treatment, samples were cleaned with acetone and alcohol by ultrasonic cleaner, then rinsed with de-ionized water, and finally dried by compressed nitrogen. Plasma will be generated to process silicon wafers.

2.3 Atmospheric-Pressure Plasma Etching Conditions. The experimental parameters used in AP plasma etching with or without the addition of O_2 are shown in Table 1. The distance between the silicon wafer and plasma nozzle is kept at 5 mm.

2.4 Measurements Methods. To understand the mechanism of the AP plasma etching of silicon wafer, the emission spectra of plasma was measured by a fiber optic spectrometer (Avantes, AvaSpec-3648-2, EINST Technology Pte Ltd., Singapore). Different durations of etching was performed on the silicon wafer surfaces under AP plasma of certain gas ratio between He/CF_4 and O2 (Air liquide, Singapore) . Before and after plasma etching, FESEM (Zeiss Ultra-Plus) was used to characterize the surface morphology change and XPS was used to analyze the surface components. AFM images were observed to confirm the surface topography change. The surface roughness of the processed surfaces was measured using by Infinite Focus 3D measurement system (Bruker Alicona).

3 Results, Analysis, and Discussion

3.1 Characterization of Atmospheric-Pressure Plasma. The emission spectra of the He/CF_4/O_2 mixture plasma are shown in Fig. 3. From the spectrum, some typical spectral lines were presented, such as: CF_n at 220–340 nm, F atom at 600–750 nm, O atom at 777 nm and 845 nm, and He at 587 nm and 706 nm [14–16]. The emission intensity of different radicals detected from the generated plasma itself and the plasma optical emission spectrum in etching process were found to have a large difference. As shown in the solid line in Fig. 3, strong peaks corresponding to CF_n radicals can be observed, while in the dashed line, only limited emission of CF_n is detected. In addition, a minor decrement in the intensity of O atoms can be observed when Si etching is in process. The emission intensity of F atom at certain wavelength was also decreased.

Based on the OES spectrum, a large amount of CF_n radicals, F and O atoms are consumed by the chemical reactions on the silicon surface during plasma etching. Oxidation reactions first occurred on the silicon surface from previous study [17], then CF_n radicals will be involved into the etching reactions, during which silicon oxide will be converted to volatile species, F atom will also react with silicon oxide and form back to oxygen. This is the

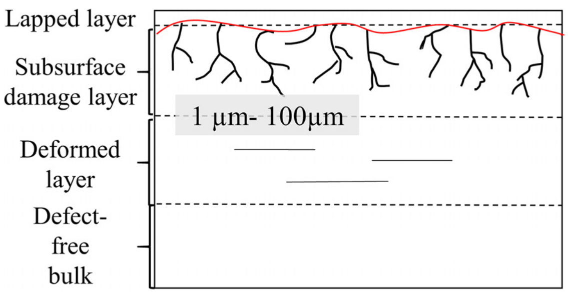

Fig. 1 Schematic of subsurface damage for lapped silicon wafer

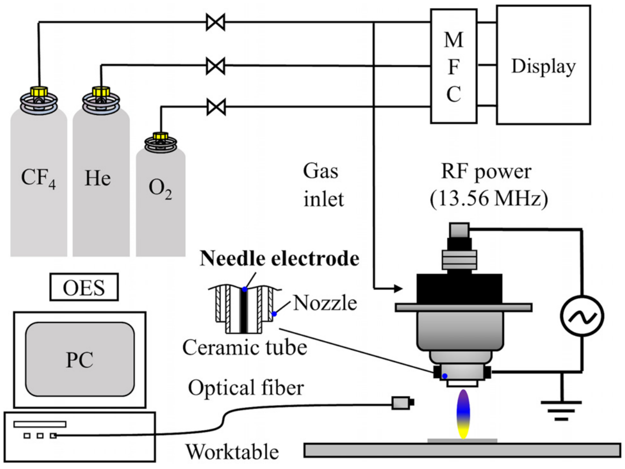

Fig. 2 Experiment setup of atmospheric-pressure plasma etching

Table 1 Experimental conditions

Parameters	Values
RF power	40 W
Gas	He:5 slm CF_4:30 sccm (O_2:25 sccm)
Gap	5 mm
Etching duration	5/15/30/45/60 min

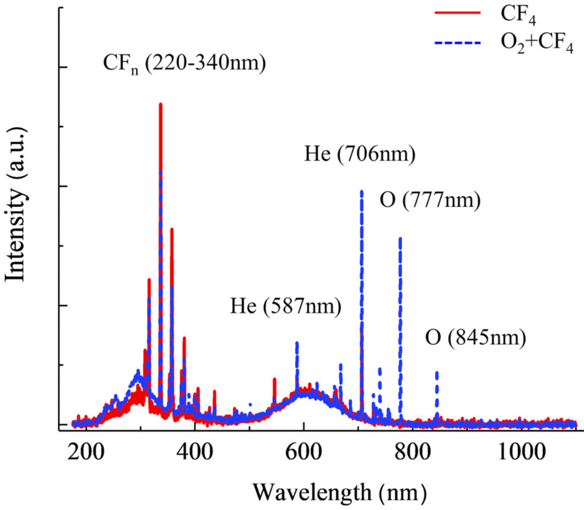

Fig. 3 Emission spectrum of plasma at He: 5 slm, CF_4: 30 sccm, O_2: 25 sccm (dashed line: spectrum when Si etching is in process; solid line: spectrum of generated plasma; corresponding wavelengths are identified in nm)

reason why O atom only shows a minor decrease in the OES spectrum [18].

3.2 Silicon Surface Chemical Composition.

X-ray photoelectron spectroscopy technique was performed to analyze the chemical composition of the silicon surface before and after plasma treatment. The wide-scan XPS spectra of the original silicon surface are presented in Fig. 4. It is revealed that only Si, C, and O exist on the surface. From the XPS investigation results, there are four components on the surface, including Si 2p, Si 2 s, O 1 s, and C 1 s. C 1 s is due to organic contamination on the as-received surface. Therefore, the silicon sample surface is composed of Si, SiO_2 (native oxide) and organic carbon polymer contamination.

Figure 5 showed the XPS wide-scan results of the plasma treated silicon wafers under different conditions. After plasma treatment for 60 min, the surface without introducing oxygen into the feed gas shows an F 1 s peak in its wide-scan spectra, as shown in Fig. 5 (round dot line). The intensity of F 1 s peak shows an obvious decrease to the same amount as the as-received silicon wafer, after the etching of same duration, as shown in Fig. 5 (dashed line).

When oxygen is not introduced, carbon fluoride polymerization can occur on the surface, which may suppress the etching process. With the addition of oxygen, the concentration of F element on the surface is reduced to an ignorable value. Oxygen would react with carbon fluorides and form volatile CO/CO_2 to promote the etching process. Based on these results, $He/CF_4/O_2$ (5 slm/30 sccm/25 sccm) mixture was fed as reactive gas to study the surface morphology change and surface roughness trend after etching at different durations.

3.3 Surface Morphology and Surface Roughness.

The SEM image of the AP plasma processed samples is shown in Fig. 6. The results illustrate that obvious morphology changes happened on the silicon surface after different etching durations.

The as-received surface is shown as in Fig. 6(*a*). Although the surface is rough, no surface crack can be observed. The surface is chemically modified by previous machining process. After short duration of plasma etching (5 min), the lapped-induced chemically modified surface layer is removed, and subsurface cracks and hidden defects are opened and appear on the resulted surface [19], as shown in Fig. 6(*b*). When the subsurface damage layer is completely removed, an interesting phenomenon can be perceived. A series of individual square-opening pits can be observed in Figs. 6(*c*) and 6(*d*), which lead to a rougher surface, as shown in Fig. 7. The surface quality dramatically deteriorates with the appearance of hidden cracks and formation of small square-opening etching pits. The Ra roughness drops from the original roughness (338 nm) to a peak point after 30 min etching. As the processing progresses, the square-opening etching pits will grow up. With extended etching duration, the pits with larger size will coalesce with each other and the surface morphology has the trend to be flattened; this corresponds well to the surface roughness change as shown in Fig. 7, and the expansion and coalescence of the etching pits decrease the surface roughness and give a better surface quality.

This surface texture and topography feature of the etching surface were achieved by using the AFM as shown in Fig. 8. The cross section profile of the AFM result measured along the red line is also given later. It helps understand the real shape of the etching pits and confirm the anisotropic etching property during the plasma etching process. This feature is defined by the chemical reaction mechanism. The geometry of the etching pits is obtained through different etch rates that the plasma may exhibit against different crystalline planes [19]. The atoms lying on {111} planes appear more densely packed than those on {100} plane. A larger bond density leads to larger activation energy to separate the bonds from the surface. Therefore, the etching rate is slower on {111} surface, compared with that on {100} etch plane. The square-opening etching pits is therefore considered to be defined by four convergent {111} planes which interact with the {100} surface of the wafer [20], as shown in Fig. 9. The crystalline characteristic of Si wafer affects the performance of surface etching and its further application to micromachining process [21]. Wet chemical etching process is anisotropic [22], and based on the AP plasma experiments, it can be concluded that the etching process is also dependent on the crystalline orientation. KOH etching is an anisotropic process and widely used for the fabrication of microstructures on silicon wafers [23]. In order to use the KOH chemical etching, the wafer must be masked and immersed in the solution, whereas the AP process does not require mask and it is a dry etching process. Therefore, the precision control of the features can be done easily with AP plasma to avoid under-cutting.

4 Conclusions

In this paper, the surface morphology and elemental composition of silicon surface before and after AP plasma etching were

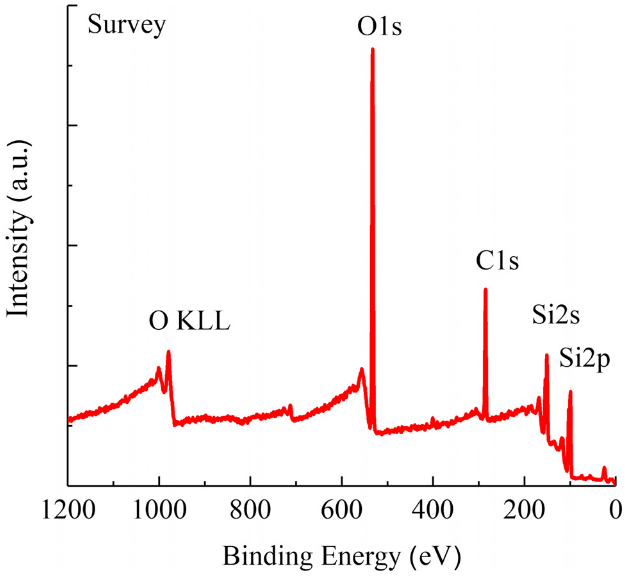

Fig. 4 XPS wide-scan of the as-received Si surface

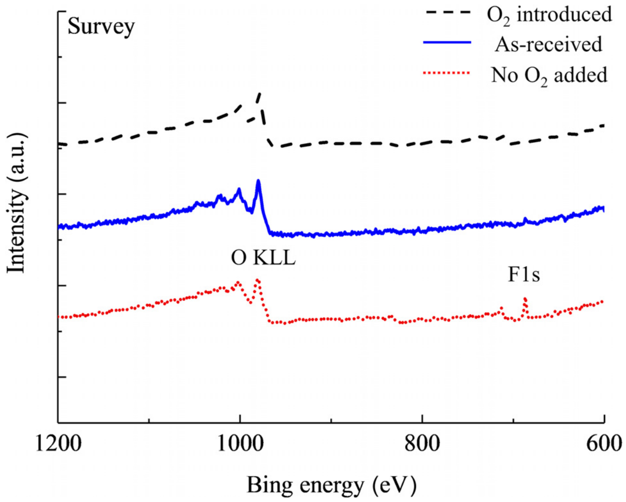

Fig. 5 Wide-scan of the plasma treated sample under different conditions (dashed line: 60 min $He/CF_4/O_2$—5 slm /30 sccm/25 sccm, solid line: as-received surface, and round dot line: 60 min He/CF_4—5 slm/30 sccm, no O_2 included)

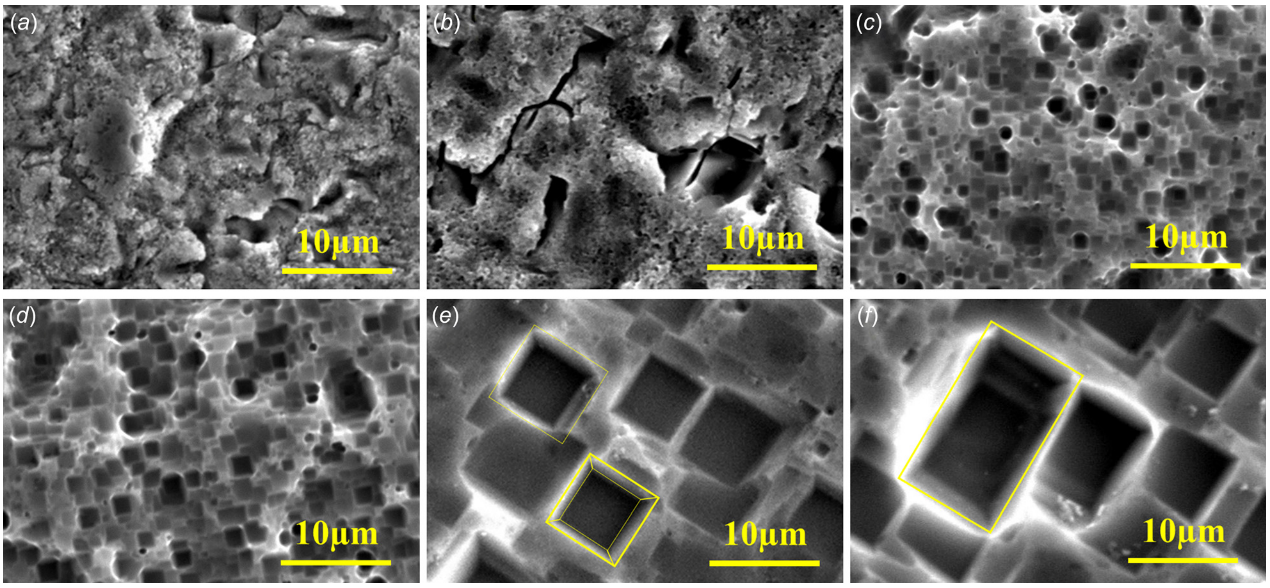

Fig. 6 **SEM images of AP plasma processed surface (He: 5 slm, CF_4: 30 sccm, and O_2: 25 sccm) with different processing time : (*a*) as-received surface, (*b*) 5 min, (*c*) 15 min, (*d*) 30 min, (*e*) 45 min, and (*f*) 60 min**

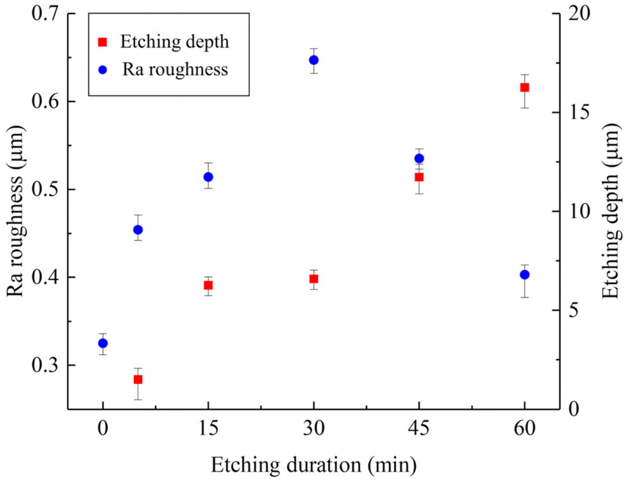

Fig. 7 **Ra roughness change with duration etching**

investigated. The radicals released from the generated plasma are also characterized. It is found that oxygen addition can promote the etching process. Initially, the chemically modified layer was removed and cracks appeared on the surface, which leads to the increase in surface roughness. As etching duration extended, individual square-opening pits forms through different etch rates of which the plasma may exhibit against different crystalline planes. After, the etching pits grow up to a certain level and coalesced with each other. The surface tends to be smoother with smaller surface roughness values. Therefore, for silicon wafers with thick damage layers, the AP plasma etching can be a promising method to provide a damage-free and smooth surface. At the same time, this work provides an explanation for AP plasma etching mechanism and the formation of anisotropic surface etching pits at microscale level, to promote the potential application of the AP plasma etching in micromachining process. It can be possible to be used for texturing silicon wafers for creating microfeatures using the AP plasma etching technique. Theoretical investigations are being made to validate the experimental findings.

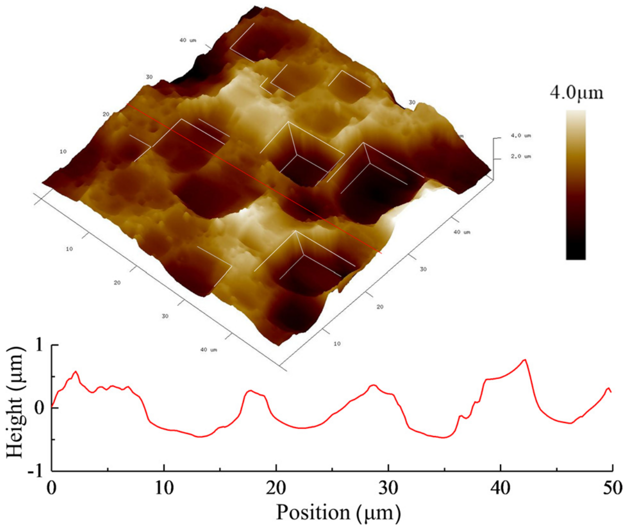

Fig. 8 **AFM images of AP plasma processed surface (He: 5 slm, CF_4: 30 sccm, and O_2: 25 sccm, 60 min)**

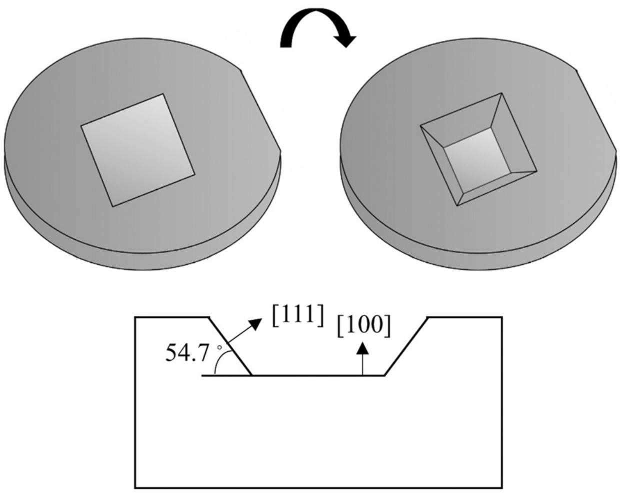

Fig. 9 **Schematic diagram of square-opening etching pits formation process**

Acknowledgment

This work is supported in part by NUS-SIMTech joint lab on large format machining.

Nomenclature

AFM = atomic force microscope
AP = atmospheric-pressure
FESEM = field emission scanning electron microscope
OES = optical emission spectroscopy
R_a = the surface roughness
XPS = X-ray photoelectron spectroscopy

References

[1] Maluf, N., 2002, “An Introduction to Microelectromechanical Systems Engineering,” Meas. Sci. Technol., **13**(2), p. 229.

[2] Ono, K., Nakazaki, N., Tsuda, H., Takao, Y., and Eriguchi, K., 2017, “Surface Morphology Evolution During Plasma Etching of Silicon: Roughening, Smoothing and Ripple Formation,” J. Phys. D, **50**(41), p. 414001.

[3] Marks, M. R., Hassan, Z., and Cheong, K. Y., 2015, “Ultrathin Wafer Pre-Assembly and Assembly Process Technologies: A Review,” Crit. Rev. Solid State, **40**(5), pp. 251–290.

[4] Pei, Z. J., Fisher, G. R., and Liu, J., 2008, “Grinding of Silicon Wafers: A Review From Historical Perspectives,” Int. J. Mach. Tool Manuf., **48**(12–13), pp. 1297–1307.

[5] Liu, T., Ge, P., Bi, W., and Gao, Y., 2017, “Subsurface Crack Damage in Silicon Wafers Induced by Resin Bonded Diamond Wire Sawing,” Mater. Sci. Semicond. Process., **57**, pp. 147–56.

[6] Azar, A. S., Holme, B., and Nielsen, Ø., 2016, “Effect of Sawing Induced Micro-Crack Orientations on Fracture Properties of Silicon Wafers,” Eng. Fract. Mech., **154**, pp. 262–271.

[7] Reiche, M., and Wagner, G., 2003, “Wafer Thinning Techniques for Ultra-Thin Wafers,” Adv. Packag., **12**(3), pp. 29–30.

[8] Mauer, L., Taddei, J., and Youssef, R., 2009, “The Role of Wet Etching in Silicon Wafer Thinning,” SSEC Technical Report.

[9] Siniaguine, O., 1998, “Atmospheric Downstream Plasma Etching of Si Wafers,” IEEE/CPMT International Manufacturing Technology Symposium, Austin, TX, Oct. 21, pp. 139–145.

[10] Hendrix, M., Drews, S., and Hurd, T., 2000, “Advantages of Wet Chemical Spin-Processing for Wafer Thinning and Packaging Applications,” IEEE/CPMT International Electronics Manufacturing Technology Symposium, Santa Clara, CA, Oct. 3, pp. 229–236.

[11] Disco Corporation, 2018, “Stress Relief (Dry polishing),” accessed Aug. 9, 2018, http://www.disco.co.jp/eg/solution/library/strelief.html

[12] Deng, H., Takiguchi, T., Ueda, M., Hattori, A. N., Zettsu, N., and Yamamura, K., 2011, “Damage-Free Dry Polishing of 4H-SiC Combined With Atmospheric-Pressure Water Vapor Plasma Oxidation,” Jpn. J. Appl. Phys., **50**(8S1), p. 08JG05.

[13] Deng, H., Ueda, M., and Yamamura, K., 2014, “Characterization of 4H-SiC (0001) Surface Processed by Plasma-Assisted Polishing,” Int. J. Adv. Manuf. Technol., **72**(1–4), pp. 1–7.

[14] Wang, R., Zhang, C., Liu, X., Xie, Q., Yan, P., and Shao, T., 2015, “Microsecond Pulse Driven Ar/CF_4 Plasma Jet for Polymethylmethacrylate Surface Modification at Atmospheric Pressure,” Appl. Surf. Sci., **328**, pp. 509–515.

[15] Kawata, H., Takao, Y., Murata, K., and Nagami, K., 1988, “Optical Emission Spectroscopy of CF_4+ O_2 Plasmas Using a New Technique,” Plasma Chem. Plasma Process, **8**(2), pp. 189–206.

[16] Park, J. S., Seo, D. S., Kim, H. W., and Hong, S. J., 2009, “Statistical Analysis of the Emission Intensity for Silicon-Dioxide Etching Using Optical Emission Spectroscopy Data,” J. Korean Phys. Soc., **55**(5), pp. 1873–1876.

[17] Anand, M., Cohen, R. E., and Baddour, R. F., 1981, “Surface Modification of Low Density Polyethylene in a Fluorine Gas Plasma,” Polymer, **22**(3), pp. 361–371.

[18] Beenakker, C. I. M., Van Dommelen, J. H. J., and Van De Poll, R. P. J., 1981, “Decomposition and Product Formation in CF_4-O_2 Plasma Etching Silicon in the Afterglow,” J. Appl. Phys., **52**(1), pp. 480–485.

[19] Frühauf, J., Gärtner, E., and Krönert, S., 2005, *Shape and Functional Elements of the Bulk Silicon Microtechnique*, Springer-Verlag, Berlin.

[20] Bassous, E., 1978, “Fabrication of Novel Three-Dimensional Microstructures by the Anisotropic Etching of (100) and (110) Silicon,” IEEE Trans. Electron Devices, **25**(10), pp. 1178–1185.

[21] Cheng, K., and Huo, D., 2013, *Micro-Cutting Fundamentals and Applications*, Wiley, New York.

[22] Shikida, M., Tokoro, K., Uchikawa, D., and Sato, K., 2000, “Surface Morphology of Anisotropically Etched Single-Crystal Silicon,” J. Micromech. Microeng., **10**(4), pp. 522–527.

[23] Debnath, K., Arimoto, H., Husain, M. K., Prasmusinto, A., Al-Attili, A., Petra, R., Chong, H. M., Reed, G. T., and Saito, S., 2016, “Low-Loss Silicon Waveguides and Grating Couplers Fabricated Using Anisotropic Wet Etching Technique,” Front. Mater., **3**, p. 10.