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INFLUENCE OF HF ETCHING TIME AND CONCENTRATION ON SI WAFER IN THE MIXTURE SOLUTION OF $HF/HNO_3/CH_3COOH$

CHAN KOK SHENG*[1,2], RAZITA AARIF[3], ENGKU ABD GHAPUR ENGKU ALI[1, 2] AND MOHD FAIZ HASSAN[1, 2]

[1]*Advanced Nano Materials (ANoMa) Research Group, Faculty of Science and Marine Environment,* [2]*School of Fundamental Science,* [3]*Faculty of Ocean Engineering Technology and Informatics, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia.*

**Corresponding author: chankoksheng@umt.edu.my*

Abstract: Production of new semiconductor silicon (Si) wafer at the desired thickness for thinner microelectronic packaging not only requires high cost and energy but also causes the environmental pollution problem. However, this issue can be simply solved by using the one-step chemical etching to produce the Si chip at the desired thickness for suitable packaging. In this study, the effect of etching time on Si wafer in the $HF/HNO_3/CH_3COOH$ mixture solution has been carried out by varying the HF etchant concentration using the isotropic wet chemical etching method. The etching time studied is from 5 minutes to 30 minutes and the HF etchant concentration is in the range of (20-24) wt%. From the results, the variation of weight loss and depth etched is monotonically increased at prolonged etching duration. The etch rate was then determined from the variation of weight loss and depth etched against time. The results show that the etch rate of Si wafers decreases with time and increases at higher HF concentration. The surface of the Si wafer becomes smoothly polished after the etching as observed under the optical microscope. The X-ray diffractogram indicates that the crystalline peak intensity of the etched Si is higher than the pure one and the peaks related to Si shifts slightly to lower 2θ as the HF concentration increases. The present finding indicates that the desired thickness of chemically etched Si wafer can be potentially fitted in a thinner packaging for microelectronic devices fabrication, and hence reduces the energy and cost wasting for future sustainability.

Keywords: Energy saving, wet etching, HF, Si wafer, etch rate.

Introduction

Thin wafers have become a basic need for a wide variety of new microelectronic products, such as power and optoelectronic devices. Production of new semiconductor silicon (Si) wafer at desired thickness for thinner microelectronic packaging is usually costly that requires high energy consumption and also causes the environmental pollution problem. However, this issue can be simply solved by using the chemical etching method to produce the silicon chip at the desired thickness for suitable packaging. Mechanical grinding and plasma dry etch are the most common technique for wafer thinning due to its high thinning rate. However, the residual defect on the wafer surface that leads to wafer breakage with a rough surface still is produced by mechanical grinding. Thus, the chemical etching process is considered as an alternative method to produce a reliable thin wafer with a smooth surface of desired thickness. The most commonly used chemicals for isotropic wet etching on the silicon wafer are the combination of nitric acid (HNO_3) and hydrofluoric acid (HF) with the addition of acetic acid (CH_3COOH) as buffer for wet bench application (Shimura *et al.,* 1989; Kikuyama *et al.,* 1994; Prosenjit, 1997; Kooij *et al.,* 1999; Sheng *et al.,* 2008; Steinert *et al.,* 2008; Dwight *et al.,* 2011; Eyad *et al.,* 2017; Narasimha *et al.,* 2017; Nurhaziqah *et al.,* 2018).

In this study, the chemical etching effect on the silicon wafer was carried out by using different HF and HNO_3 etchant mixture concentrations with the addition of acetic acid. The concentrations of etchant mixture were (20% HF / 65% HNO_3, 22% HF / 65% HNO_3, 24% HF / 65% HNO_3) with ratio of 1:1. The

concentration of HF studied is in the range of (20-24) wt% that has never been reported before. The total thickness reduction and weight loss, etch rate, surface morphology and crystal structure of the silicon wafer were determined by using the analytical semi-micro balance, digital micrometre, optical microscope and X-Ray diffractometer (XRD), respectively. The main objective of this study was to investigate the time etching effect of HF concentration on the total thickness dissipation and weight loss, the etch rate and also to investigate the surface morphology and the crystallinity of the etched silicon wafer.

Materials and Methods

Before the etching process, some chemicals were used for solvent cleaning treatment on the silicon wafer. The purpose was to remove the oil and organic residue on its surfaces. The wafers were cleaned through the solvent cleaning method by using acetone and ethanol. For acetone, it still leaves its residue, therefore the ethanol was further used to clean off the acetone residue. In the cleaning process, the acetone was warmed up by hot plate stirrer at a temperature not exceeding 55 °C. The wafer samples were then placed into the acetone bath for 10 minutes. The samples were removed from the acetone and placed into the ethanol solution for 5 minutes, and then the samples were rinsed in distilled water and further dried by air.

The materials used in this study were HF, HNO_3, acetic acid and the silicon wafer. Different etchant concentrations of HNO_3 and HF with a ratio of 1:1 were prepared with the addition of CH_3COOH, in which the concentrations of HNO_3 was fixed at 65 wt% and the HF concentrations used were 20 wt%, 40 wt% and 65 wt% as tabulated in Table 1. Firstly, the Si wafer was dipped into the etchant mixture with the time interval of five minutes up to 30 minutes dependent on the etchant concentration. The wafer was then washed with distilled water and dried by air before characterizations. Analytical semi-micro balance (model GH-202 series) was used to measure the total weight loss while the digital micrometre (model DTG03L) was used to determine the total thickness reduction of the silicon wafer. Optical microscope (model TM-1000 Hitachi) and XRD (model MiniFlex II) were used respectively to study the surface morphology and crystallinity of the silicon wafer before and after the etching. The variation of total thickness reduction and weight loss was calculated based on the equations below:

$$XL = X_f - X_i \quad (1)$$

$$WL = W_f - W_i \quad (2)$$

where the X_f, X_i, W_f, W_i denote the initial and final thickness, initial and final weight, respectively, while XL and WL indicate the thickness and weight loss, respectively. The etch rate was then determined by the variation of total thickness reduction and weight loss against time using the following equations:

$$\text{Etch rate for thickness reduction} = \frac{XL}{t} = \frac{X_f - X_i}{t} \quad (3)$$

$$\text{Etch rate for weight loss} = \frac{WL}{t} = \frac{W_f - W}{t} \quad (4)$$

Table 1: Etchant concentrations of HF, HNO_3 and CH_3COOH

Samples	Etchant concentrations (wt%)		
	Hydrofluoric acid (HF)	**Nitric acid (HNO_3)**	**Acetic acid (CH_3COOH)**
C1	20	65	20
C2	22	65	20
C3	24	65	20

Results and Discussion

Three different etchant concentrations of HF had been employed in this study, which was 20 %, 22 % and 24 % while the etchant concentration of remained the same at 65 %. Both etchants were mixed to a ratio of 1:1 with the addition of acetic acid (20 %) for the purpose to study the HF etching effect on a silicon wafer as listed in Table 1. The silicon wafers were etched up to 30 minutes with a time interval of five minutes. Figure 1 and 2 show the variation of total thickness reduction and weight loss of the present samples, respectively. The highest variation of total thickness reduction of the silicon wafer was 330 μm for 24 % HF etchant concentration, following by 22 % HF and 20 % HF etchant concentrations with the total thickness reduction of 300 μm and 250 μm, respectively. For the variation of total weight loss, 24 % HF etchant concentration also gives the highest value, which is 307.1 mg, comparing to 22 % HF and 20 % HF etchant concentrations, which are 274.3 mg and 257.1 mg, respectively. Consequently, it could be noted that the variation of total thickness reduction and weight loss of silicon wafer for 24 % HF was the highest among the etchant concentrations. This result shows that the thinning effect could effectively occur on the Si, which is essential to be used in the micro-electronics devices packaging. Moreover, the thickness reduction and weight loss increase rapidly during the initial stage for the first 10 minutes, after that, it rises slowly as time progresses. This means that the thickness dissipation could be accurately controlled by selecting the appropriate etching time for desired wafer thickness production. HF is a weak acid, especially when presents alone in very small concentrations, it does not completely dissociate into H^+ and F^- ion in water (Kikyuama *et al*., 1991). However, the etching process would be active when both acids of HF and HNO_3 are mixed, depending on the etchant concentration used and the initial thickness of silicon wafer to be etched. This characteristic is attributed to the oxidation of permanent existing Si–H bonds at the silicon surface by the reactive NO^+ species. N_2O_3 serves as a reservoir for the generation of NO^+ leading to complete coverage of the silicon surface with reactive species at high intermediate concentrations (Marco *et al*., 2006).

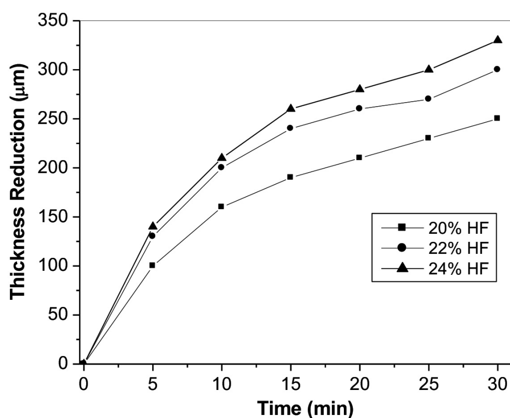

Figure 1: Variation of total thickness reduction versus etching time

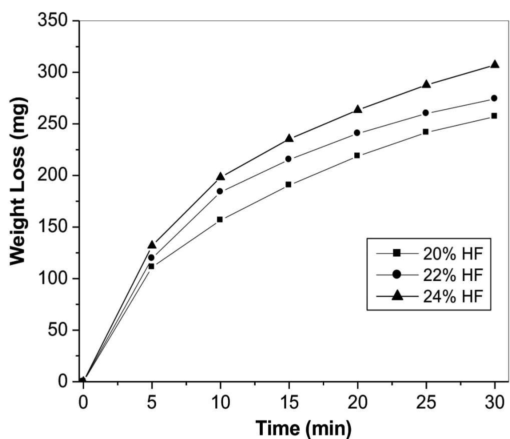

Figure 2: Variation of total weight loss versus etching time

Furthermore, the etch rate for total thickness reduction and weight loss of the present samples is depicted in Figure 3 and 4, respectively. Based on the plot shown in the figures, the etch rate of silicon wafer increases as the HF etchant concentration increases. The range of thickness reduction etches rate of silicon wafer for half an hour is from 0.139 μm/s to 0.467 μm/s. The highest etch rate of thickness reduction is determined to be 0.467 μm/s at 24 % HF etchant concentration when compared to the 22 % and 20 % HF etchants with etch rate of 0.433 μm/s and 0.334 μm/s, respectively. On the other hand, the

etch rate of weight loss at 24 % HF also gives the highest value, which is 0.4396 mg/s as compared to the others, 0.3986 mg/s and 0.3703 mg/s for 22 % and 20 % HF etchants, respectively. Thus, it is worth to point out that the 24 % HF gives the highest etch rate of thickness reduction and weight loss of silicon wafer as compared to 22 % and 20 % HF concentrations. Variation in etchant concentration gives the difference in the etch rate of a silicon wafer. On the other hand, the etch rate of thickness reduction and weight loss for all silicon wafers increases for the first five minutes of etching and then decays gradually until the entire etching period. This indicates that the rate of reaction becomes slower and it is controllable and applicable for wafer thinning process.

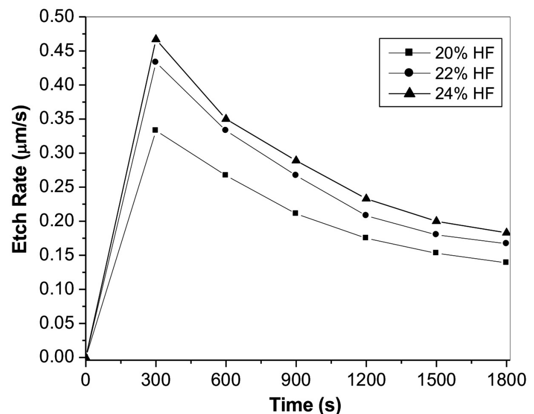

Figure 3: Etch rate of thickness reduction versus etching time

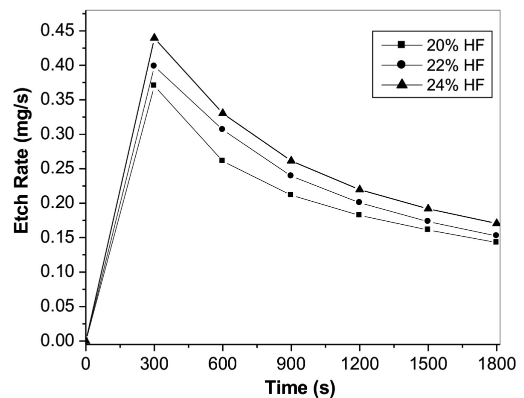

Figure 4. Etch rate of weight loss versus etching time

Addition with acetic acid would substantially help to increase the wettability of the hydrophobic silicon surface and hence improve and homogenize the etch rate, as reported in the literature (Shobha & Min, 2011). To control the variation in etch rate as the wafers are processed, there are several alternatives, by either increasing the etching duration or either spiking the chemical mixture with the active ingredient HF or to continuously remove and replenish the chemical solution or some combinations of these. The spiking with HF can be combined by adding enough chemical mixture to make up for the amount lost during the change over to the rinse cycle. Although both techniques will maintain a more stable etch rate, increasing etch time would decrease the wafer throughput and require periodic shutdown for chemical disposal and refill resulting in lower system utilization (Milind *et al*., 2000; Shobha & Min, 2011).

The mixture concentration and the ratio of etchants also could affect the surface morphology. In this work, the surface morphology and crystalline structure were studied using the optical microscope and XRD, respectively. As from Figure 5 (a) - (c), it shows that the changes occurred on the silicon wafer after etching by using an optical microscope at a resolution of 100X. Based on the figures, it can be seen that a variety of silicon wafer surface morphology is produced at different HF concentrations. As compared to the one before etching, the etched silicon wafer surface is smoothened and becomes more homogeneous by demonstrating the presence of smaller grain size on it. This observation might indicate that the polishing efficiency increases with increasing HF concentration and etching time, leading to the formation of a smooth and homogeneous surface. This polishing effect can be explained by the oxidation on silicon surface by hole injection from HNO_3 increases at higher HF concentration, leading to a faster dioxide dissolution by HF on Si (Nurhaziqah *et al*., 2018; Chan & Dwight, 2018).

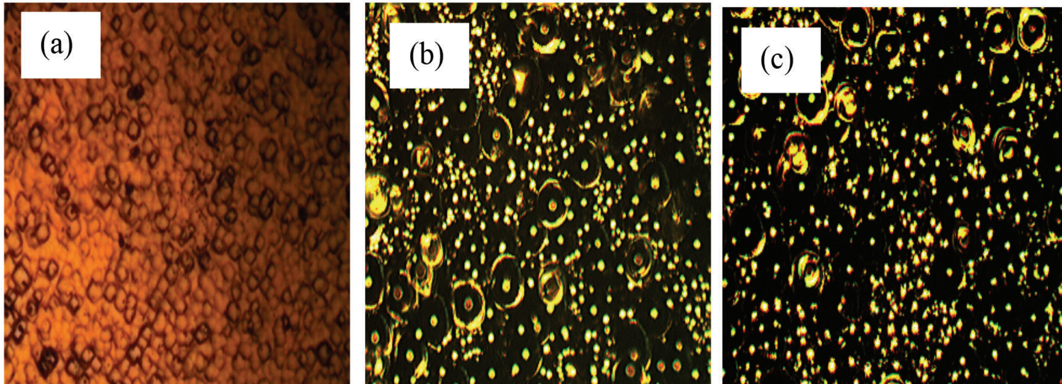

Figure 5: Surface morphology of Si (a) before and after etched with (b) 20 % HF and (c) 24 % HF

The crystalline structure of the present samples was determined by XRD for all the HF etchant concentrations used. Figure 6 shows the XRD results for the present samples. The range of the peak is observed between 69° to 70°. From the figure, two main peaks can be observed for pure Si and etched Si wafer, which may correspond to the reflectance from planes of bulk and polished Si surface. Particularly, the peak intensity of the etched silicon was found higher than the pure crystalline silicon, which might indicate a smoother surface formation with reduced lattice scattering for effective light-capturing at this typical concentration. Besides, some portions of silicon turn into the silicon dioxide after the etching process as indicated in the figure. Moreover, both peaks present in the diffractogram shift slightly to a lower value of 2θ with increasing HF concentration, implying higher inter planer spacing values of atomic layers in silicon, which is crucial in integrated circuits fabrication (Nurhaziqah *et al*., 2018).

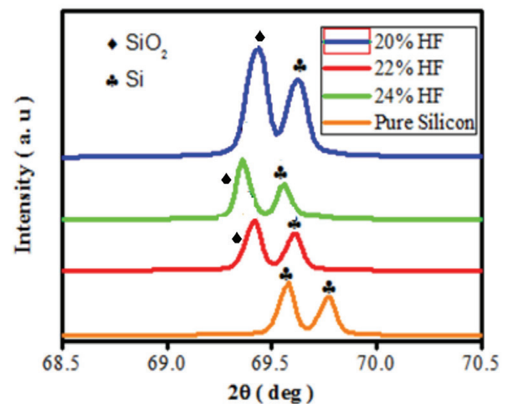

Figure 6: XRD pattern for different HF etchant concentrations

Conclusion

From this study, it can be concluded that the present etching gives a flexibly real-time controllable thinning effect on the silicon wafer to the desired thickness after being etched in the mixture solutions of $HF/HNO_3/CH_3COOH$. The etch rate of thickness reduction and weight loss increases with the increasing of etching time and HF concentration. After the etching, the surface structure of the silicon wafer is smooth polished and remained crystalline with silicon dioxide formation. The findings of the present study can be valuable referred to produce a reliable and desired Si thin wafer weight and thickness, which is crucial in integrated circuit fabrication.

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