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Effect of HNO_3 Concentration on Etch Rate and Structure of Si Wafer Etched in the Mixture of HF and HNO_3 Solutions

F. Nurhaziqah K[1], C. K. Sheng[2*], K. A. M. Amin[2], M. I. N. Isa[2], M. F. Hassan[2], E. A. G. E. Ali[2], K. H. Kamarudin[2] and R. Aarif[1]

[1] *Universiti Malaysia Terengganu, School of Ocean Engineering, 21030 Kuala Nerus, Terengganu, Malaysia.*

[2] *Advanced Nano Materials (ANoMa) Research Group, Universiti Malaysia Terengganu, School of Fundamental Science, 21030 Kuala Nerus, Terengganu, Malaysia.*

The new microelectronic products require the silicon (Si) wafer to be thinned to less than 150 μm in thickness. Residual defect on the wafer surface that leads to wafer breakage with a rough surface still be produced by mechanical grinding. Thus, chemical etching method is essentially applied to produce a reliable thin wafer with smooth surface of desired thickness. In this work, we studied the wet chemical etching effect of different HNO_3 concentrations on total thickness and weight loss, etch rate, morphological and structural properties of Si wafer in the mixtures of HNO_3 and HF. The results showed that the total thickness and weight loss increases with the increasing of HNO_3 concentration and etching time. Higher HNO_3 concentration causes higher etch rate, and the etch rate decreases at prolonged etching time. A smoother and clearer homogeneous Si surface image was observed by optical microscope as the etching time and HNO_3 concentration increase. XRD analysis shows that the intensity of etched Si wafer is higher than the pure one, which might indicate the smoother surface formation after etching. The findings of present study can be valuably referred to produce a reliable and desired Si thin wafer which is crucial in integrated circuit fabrication.

Keywords: etch rate, silicon, nitric acid, structure, microscope

I. INTRODUCTION

Thin wafers have become a basic need for a wide variety of new microelectronic products. These include power devices discrete semiconductors, optoelectronic components and integrated circuits for Radio Frequency Identification (RFID) systems. New concepts in microelectromechanical systems (MEMS) devices require wafer to be thinned to < 150 μm in thickness. Mechanical grinding is the most common technique for wafer thinning due to its high thinning rate. Commercially available grinding systems typically use a two-step process that starts with a coarse grinding at high rates (5μm / sec) and then a subsequent fine grinding process at a reduced rate (1μm / sec) to remove most of

*Corresponding author:chankoksheng@umt.edu.my

the damage layer that is created by the coarse grinding step. However, there still remains a defect band near the wafer surface. The thickness of this defect zone is dependent upon the grinding conditions. The residual defects can cause stress in the thinned wafer that leads to additional bow and can result wafer breakage. The most cost effective process is wet etching. Wafer that have been thinned using a final wet etch process on the backside will have less stress compared with mechanical grinding. Wafer breakage will be reduced and after dicing the chips, it will have fewer cracks and chip-outs [1]-[4]

The new microelectronic products require wafer to be thinned at the desired thickness. Residual defect on the wafer surface that leads to wafer breakage with a rough surface still produced by mechanical grinding. Etching process is applied in this study to produce a reliable thin wafer with smooth surface of desire thickness. Abdur-Rahman *et al.* (2017) has reported the influence of IPA concentration and the etching time on the pyramidal surface structures on etched mc-Si in alkaline solutions [5].Narasimha Rao *et al.* (2017) has studied the etching behaviour of Si in 20 wt% KOH with addition of hydroxylamine for the fabrication of bulk micromachined MEMS, in which the etch rate and undercutting are improved significantly [6]. High etch rate is very useful to achieve larger etch depth in less time in comparison to common etchant.

In the manufacturing company, high etch rate is demanded to increase the productivity that eventually reduces the cost of end product. In this study, we investigated the isotropic wet etching effect of HNO_3 concentration on total thickness and weight loss, etch rate, morphological and structural properties of Si wafer in the mixtures of HF and different HNO_3 concentrations. The total thickness and weight loss percentage were measured using gravimetric method, the morphological image was obtained by optical microscope and the crystalline structure was characterized by XRD

II. MATERIALS AND METHODS

The chemicals used are HNO_3 (Merck Co.), HF (Merck Co.), ethanol (Hamburg Co.), acetone (Hamburg Co.) and distilled water. All the apparatus were rinsed with distilled water before being dried to make sure that all apparatus used were free from any contaminants. Before the etching, the Si wafer underwent solvent cleaning process. The purpose was to remove oil and organic residues on its surface. The wafer was first cleaned using acetone and ethanol. For acetone, it leaves its own residue therefore the ethanol was used to clean off the acetone residue. The acetone was poured into glass beaker and warmed up on stirrer hot plate with temperature up to 55 °C. The wafer was then placed into the water bath contained ethanol for 10 minutes. The wafer was then removed from the bath and placed into the ethanol for 5 minutes. Then the

wafers were rinsed in distilled water and further dried in air

The chemical consists of different concentrations of etchant mixture which are constant concentration of HF with different concentrations of HNO_3. In this study, three different etchant concentrations were used to study the effect of chemical etching on Si wafer, in which 20 wt%, 23 wt% and 26 wt% HNO_3 etchant concentrations were mixed with 48 wt% HF etchant concentration for each Si wafer. Therefore, there are three different sets of etchant concentration mixture: HF 48 wt% / HNO3 20 wt%, HF 48 wt% / HNO_3 23 wt%, and HF 48 wt% / HNO_3 26 wt% with volume ratio of 1:1. Each of the Si wafers were etched for 70 minutes with time interval of 10 minutes. An analytical semi-micro balances model GH-202 was used to measure the total weight loss while the DTG03 digital micrometre was used to determine the variation of total thickness loss of Si. TM-1000 Hitachi optical microscope and X-Ray diffractometer (XRD) model Rigaku MiniFlex II were used to study the surface morphology and crystalline structure of Si before and after etching, respectively.

III. RESULTS AND DISCUSSIONS

Figure 1 and 2 show the total thickness and weight loss versus the etching time, respectively for the Si etched at three different HNO_3 concentrations of 20 wt%, 23 wt% and 26 wt% mixed with 48 wt% HF. Both figures show that the total thickness and weight loss of Si wafers etched by 23 wt% and 26 wt% HNO_3 etchant concentrations increase more rapidly as compared to the one etched by 20 wt% HNO_3 etchant concentration, which is the lowest among them. From the figure, the total thickness and weight loss increase with the increasing of etching time. The wafer thickness etched at 20 wt% HNO_3 concentration does not show any significant variation with etching time. However, the total thickness loss shows a significant increase with etching time at higher HNO_3 concentrations of 23 wt% and 26 wt%, in which the total thickness loss for 26 wt% HNO_3 is 43.06 %, which is the highest among them, and the 20 wt% and 23 wt% HNO_3 give the total thickness loss of 16.67 % and 39.40 %, respectively. The etching at 26 wt% HNO_3 etchant concentration has thinned the Si wafer into 440 μm with final weight of 0.3501 mg. Also, at 26 wt% HNO_3 concentration, the thickness loss variation curve becomes steeper as compare with the others, which indicates faster etching process occurred on the Si wafer that aggressively dissipated the sample thickness. On the other hand, the variation of total weight loss shows similar behavior, in which the highest total weight loss determined for Si wafer is 9.56 % for 26 wt % HNO_3, meanwhile for HNO_3 concentrations of 20 wt% and 23 wt% are 5.0163 % and 8.2144 % respectively.

HF is a weak acid, especially when presents in very small concentrations, it does not completely dissociate into H^+ and F^- ion in water [7]. How-

ever, the etching process would be active when both acids of HF and HNO_3 are mixed together, depending on the percentage of etchant concentration and the initial thickness of Si wafer to be etched. According to the Milind and Henry, they stated in their work that a mixture of HF and HNO_3 has density and viscosity closer to those of water [8]. Hence, the mass-transfer resistance or thickness of the effective transport-film for such a mixture can be quite low. Addition of thick viscous acid to the mixture which does not chemically participate in the etching reaction should not alter the chemical kinetics, but should increase the mass-transfer as a result of increase in viscosity [8]. The percentage of etchant concentration would be lower than the original concentration if the initial thickness was quite thin. It is because the Si wafer would be etched faster and vigorously which lead to the bigger variation if both original percentage concentrations was not used to mixed together.

In this study, since the initial thickness of Si wafer was only 660 μm. Thus, based on the present results, the percentage variation of total thickness and weight loss of Si wafer for 48 wt% HF/ 26 wt% HNO_3 gives the best Si thinned effect that is essential to be used in micro-electronics devices.

Figure 3 and 4 display the etch rate of total thickness and weight loss versus etching time, respectively for the Si etched at three different HNO_3 concentrations of 20 wt%, 23 wt% and 26 wt%. The etch rate shows a decreasing trend

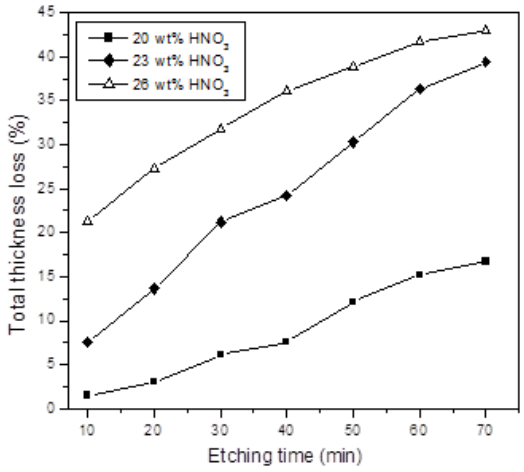

Figure 1. Total thickness loss versus etching time

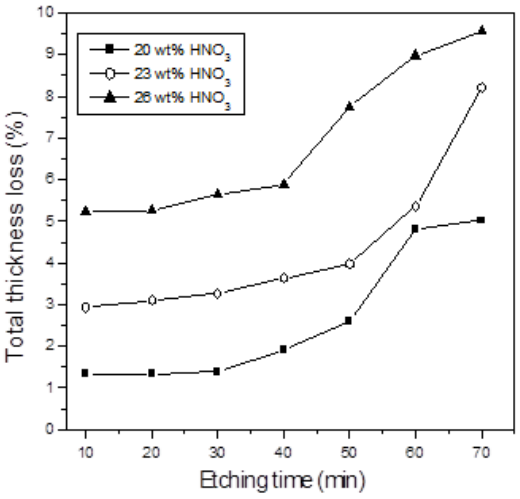

Figure 2. Total weight Loss versus etching time

as the etching time increases, which indicates a controllable silicon thinning process can be performed in order to obtain a desired silicon wafer thickness. Furthermore, it is worth to notice that the etch rate of silicon wafer increases when the HNO_3 etchant concentration is getting higher. This effect can be ascribed to the oxidation on Si surface by hole injection from HNO_3 increases at higher HNO_3 concentration, lead-

ing to faster dioxide dissolution by HF on Si [9]. The highest etch rate of thickness loss obtained for Si wafer is 0.0718 %/s for 26 wt% HNO_3 followed by 23 wt % and 20 wt % HNO_3 with maximum etch rate of 0.0657 %/s and 0.0278 %/s, respectively. This means an appropriate etching speed can be selected dependent on the fabrication condition. Similar effect can be observed for the etch rate determined from the total weight loss, at which the etch rate for 26 wt% HNO_3 is amongst the highest for these concentrations, followed by 23 wt % and 20 wt % HNO_3.

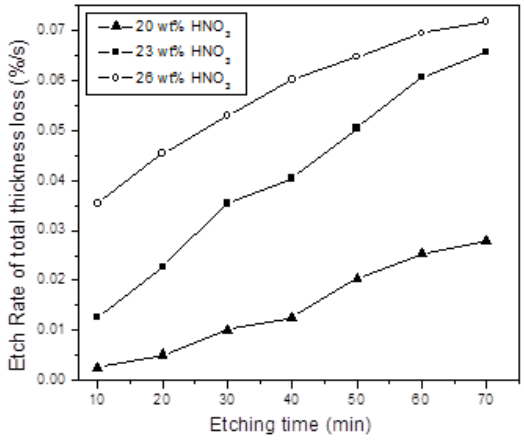

Figure 3. Etch rate of total thickness loss versus etching time

The surface image of the Si wafer before and after etching was monitored using optical microscope as presented in Figure 5, 6 and 7 with 100X magnification at different etching times of 10 minutes, 40 minutes and 70 minutes, respectively. From the figures, it can be clearly seen that there is a significant modification of Si wafer morphology, in which the Si wafer surface becomes smoother with clearer and brighter

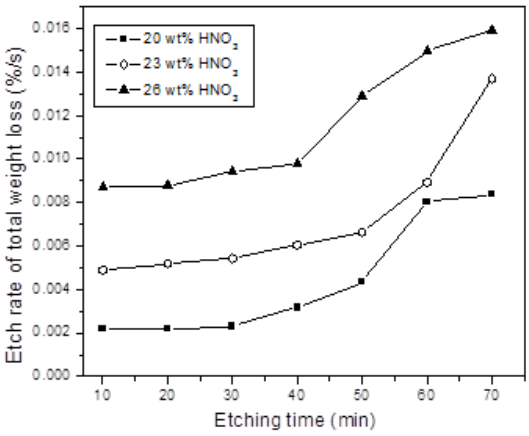

Figure 4. Etch rate of total weight loss versus etching time

homogeneous structure observed as the increase of etching time and also the HNO_3 concentration. This observed phenomena can be due to the more diffusion limited reaction occurred on the Si wafer with better polishing efficiency at higher etching time and HNO_3 concentration. In the industry, it has been observed that addition of a few viscous acids to the mixture of HF and HNO_3 decreases the roughness of Si wafer more efficiently for the same removal. Also, increasing the concentration of the thickener would increase the polishing efficiencies [8]. In this study, the polishing efficiency increases with increasing HNO_3 concentration and etching time, which leads to the formation of smooth and homogeneous surface. Thus, the HNO_3 concentration can be increased to improve the polishing efficiency. However, at higher HNO_3 concentrations, etching rates are uncontrollably high, and process control and runaway become a major concern in microelectronic fabrication.

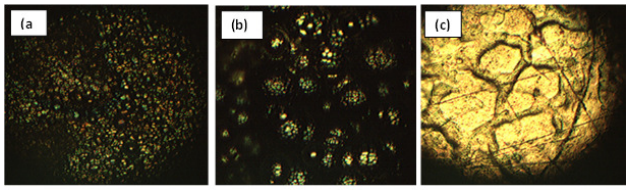

Figure 5. Surface morphology of silicon wafer etched at 20% HNO_3 with etching time: (a) 10 minutes, (b) 40 minutes and (c) 70 minutes.

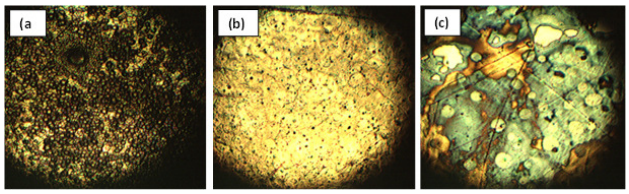

Figure 6. Surface morphology of silicon wafer etched at 23% HNO_3 with etching time: (a) 10 minutes, (b) 40 minutes and (c) 70 minutes.

Figure 8 depicts the typical XRD spectra of Si wafer etched with 23 wt% HNO_3 concentration at different etching times. From the figure, the intensity of etched Si wafer is higher than the pure one and increases with the increasing of etching time, which might also indicate the smoother surface formation due to removal of silicon dioxide after etching. From the figure, two main peaks can be observed for pure Si and also for etched Si wafer, which may correspond to the reflectance from planes of bulk and polished Si surface. Both peaks shift slightly to lower value of 2 with the increasing of HNO_3 concentration, indicating the higher values for inter planer spacing (d values) of atomic layers in Si. Similar effect is also observed for other HNO_3 concentrations at 20 wt% and 26 wt%, which is crucial

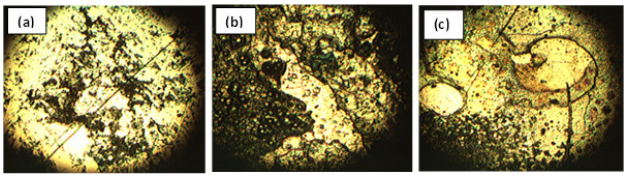

Figure 7. Surface morphology of silicon wafer etched at 26% HNO_3 with etching time: (a) 10 minutes, (b) 40 minutes and (c) 70 minutes.

in integrated circuit fabrication.

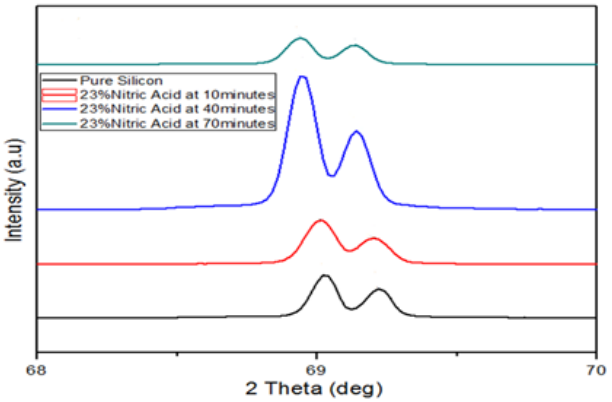

Figure 8. XRD spectra of silicon etched at 23 % HNO_3 concentration with different etching times.

IV. SUMMARY

In summary, the etch rate of thickness and weight loss of Si immersed in the mixture of HNO_3 and HF increase with the increasing of etching time and HNO_3 etchant concentration. A smooth and homogeneous Si structure was observed when etched at higher etching time and HNO_3 concentration due to polishing effect. XRD result indicates that the intensity of etched Si wafer is higher than the pure one and

increases with the increasing of etching time. Si wafer that etched with the mixtures of 26 wt% HNO_3 and 48 wt% HF gives the best etching rate when compared to the others. The present etching study indicates the etched Si can be potentially fitted into thinner packaged for microelectronics products fabrication.

V. ACKNOWLEDGMENT

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