THE USE OF OZONATED HF SOLUTIONS FOR POLYSILICON STRIPPING

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ABSTRACT

Ozone-based HF chemistry is proposed to substitute the conventional HF/HNO_3 mixture for polysilicon stripping in wafer reclamation. The etching characteristics of ozonated HF solutions are investigated. Similar to its HF/HNO_3 counterpart, HF/O_3 was found to strip polysilicon films through a simultaneous oxidation-and-etching process. The strip rate was determined by the rate-limiting step in the competition between the oxidation and etching reactions; whichever slower would govern the overall kinetics. Because of the nonstop etching nature of the chemistry on both silicon and silicon oxides, the feasibility of the process application is evaluated, based on the etch selectivity between the polysilicon and the underlying thermal oxide.

INTRODUCTION

Mixtures of nitric acid (HNO_3) and hydrofluoric acid (HF) have been commonly used in the semiconductor industry to strip polysilicon films from process monitor wafers for wafer reclamation. In reclaiming factory, this chemistry is typically applied in concentrated forms, and thus the wafers are severely roughened and need to be polished afterwards. To reduce the turn-around time and costs, some IC manufacturers conduct in-house wafer reclaiming in which the polishing step is skipped. Due to the nonstop etching nature of HF/HNO_3 chemistry on silicon, the mixture in such application has to be diluted and the chemical ratio needs to be properly controlled to prevent the wafers from being damaged [1,2]. However, the exothermic reaction from HNO_3 mixing with water as well as the use of the dual acid chemistry increase the difficulty of maintaining the temperature and chemical ratio of the processing bath. In addition, a great deal of DI water is required after the process to rinse off the strong, viscous nitric acid. Also, the use of the hazardous HNO_3 always raises the concerns and costs in storage/handling, waste disposal, and personnel safety.

As has been well known as a strong oxidant [3], ozone may be an ideal alternative to substitute nitric acid for in-house poly stripping. Ozone can be constantly generated at a point-of-use basis and mixed with HF solutions in stable concentrations without causing temperature variation. Also, the single acid (HF) system can render electrodeless conductivity sensors applicable for fast, accurate, cost-effective monitoring and control of the concentration of HF acid during the stripping, accordingly extending the bath life [4]. Compared to HNO_3, additionally, ozone decades to oxygen quickly in atmosphere, significantly reducing the environmental concern. In this study, the etching characteristics and process effectiveness of ozonated HF solutions were evaluated to explore the feasibility of the proposed chemistry.

EXPERIMENTAL

The experiment was conducted on an AKrion's GAMA wet station in the Class 1 Applications Laboratory at AKrion LLC. Ozone was generated from oxygen gas using a commercial ozone generator and was introduced into hydrofluoric acid (HF) solutions through a liquid/gas mixer. The bath was recirculated at a fixed flow rate at 20°C during the stripping process. The concentrations of HF and dissolved ozone were varied from test to test for the characterization of poly etching.

150-mm silicon wafers coated with approximately 1000 Å (or 2000 Å) polysilicon films on 400 Å SiO_2 layers were used in this study. Recognizing the difficulty of producing uniform etching across a large surface area at high rates, smaller samples were used for the etch rate characterization test. A number of poly wafers were cut to ~ 25 mm × 50 mm coupons, and the sample was gripped by a piece of ¼" PFA tubing with a slotted end for immersion in the bath. On the other hand, full sheets of poly wafers were also tested to verify the actual stripping characteristics. Oxide etch rates were also characterized at different bath concentrations using thermal oxide wafers (> 1000 Å). The thickness of polysilicon films (or thermal oxide films) was measured with a Rudolph AutoEL II ellipsometer before and after each run of tests. Etch rates were then estimated based on the process time applied and the change of film thickness.

RESULTS AND DISCUSSION

Similar to how HF/HNO_3 chemistry has worked, ozonated HF solutions are anticipated to etch silicon based on the concept of a simultaneous process of oxidizing the Si with ozone and etching the SiO_2 with HF. According to the hypothesis, HF alone cannot strip the poly film but the oxide. Figure 1 shows a consistent result that the etch rate of polysilicon in HF was negligible regardless of the chemical concentration, while the thermal oxide etch rate was proportionally increased with the increase of HF concentration. Also note that whether the O_3 appears in the HF solutions did not influence the oxide etch rate; a linear regression analysis of the oxide etch data in Fig. 1 (with or without O_3) indicated a confidence level of 97.6%, suggesting that ozone was not involved in the oxide etching reaction.

By ozonating the HF solution, ploy etching seemed to become noticeable. Figure 2 shows that, at a HF concentration of 0.25%, 15 ppm of dissolved O_3 resulted in a poly etch rate of about 57 Å/min. Further increasing the ozone concentration in the HF, however, did not enhance the poly stripping in this situation (Fig. 2). The observations indicate that there must have existed a threshold value of ozone concentration for poly etching in the 0.25% HF solution. Beyond that value, the etching kinetics would be limited by the specific HF concentration.

On the other hand, with an O3 level of 55 ppm, the etching kinetics of poly films was dependent on the HF concentration ranging from 0.05 to 0.5%, as shown in Figure 3. The large data scattering, essentially resulting from non-uniform etching at high rates, started to appear at 0.5% HF and increased the difficulty and inaccuracy of film thickness measurement by the ellipsometer. Therefore, no small-coupon experiments were performed beyond 0.5% HF. Instead, full poly wafers were used to provide a qualitative

approach for the etching characteristics. Figure 4 shows the total amount of time required to strip the 1000 Å poly layer from the 150-mm wafer as a function of HF concentration. These results were then converted to etch rates and illustrated in Figure 5, with the data of small-coupon experiments (Fig. 3) included as reference. Since the full wafer etching data reflected the minimum rate on the wafer in a non-uniform etching situation, they may also be viewed as the lower-bound etch rates for the particular conditions (i.e. wafer size, tank configuration, fluid dynamics, chemical concentrations, etc.). From Figure 5, it is clear that the full-wafer poly etching reached to a plateau as the HF concentration increased. This suggested that there was also a rate-limiting step governed by the dissolved O_3 concentration (i.e. 55 ppm in this case) as long as the HF concentration reached a threshold value, similar to the phenomenon shown in Fig. 2.

As previously mentioned, poly stripping in HF/O_3 solutions is a simultaneous process of poly oxidation and poly-oxide etching. The experimental results (Figs. 2 and 5) have shown that this is a competition process between the oxidation reaction and the etching reaction. Whichever is slower would be the rate-limiting step and determines the overall poly etching kinetics. In this context, a solution with "high" O_3 level relative to HF concentration would always maintain a finite oxide layer on the silicon surface, while the solution with "low" O_3 level relative to HF concentration would produce bare Si surface. This inference has been proved by examining the surface hydrophobicity of poly samples after dipping into various solutions (corresponding to the conditions in Figs 2 and 5). The experimental observations are outlined in Table 1.

Table 1: The surface state of a poly sample after dipping into various solutions

O_3 level in 0.25% HF	Surface State	HF conc. with 55ppm O_3	Surface State
0 ppm (low O_3 vs HF)	hydrophobic	0.05 % (high O_3 vs HF)	hydrophilic
15 ppm (high O_3 vs HF)	hydrophilic	0.1 % (high O_3 vs HF)	hydrophilic
25 ppm (high O_3 vs HF)	hydrophilic	0.25 % (high O_3 vs HF)	hydrophilic
38 ppm (high O_3 vs HF)	hydrophilic	0.38 % (high O_3 vs HF)	hydrophilic
55 ppm (high O_3 vs HF)	hydrophilic	0.5 % (high O_3 vs HF)	hydrophilic
--	--	1 % (high O_3 vs HF)	hydrophilic
--	--	2 % (low O_3 vs HF)	hydrophobic
--	--	3.33 % (low O_3 vs HF)	hydrophobic

From a technological viewpoint, one of the most important factors determining the feasibility of HF/O_3 application in poly stripping is the etching selectivity between the poly film and the oxide film by the chemistry. Since there is an oxide layer underneath the polysilicon film and since the poly stripping is most likely a non-uniform process, the slowest etching spot on the wafer surface has to be completed before the oxide at the quickest etching spot is fully removed, in order to avoid the onset of attack on the silicon substrate. According to the etch rate results obtained from the experiments (Table 2), the HF/O_3 chemistry apparently shows the greatest poly/oxide selectivity (~8) in the HF(0.5%)/O3(55 ppm) mixing condition (at 20ºC). In the worst-case scenario (i.e. the etching of poly and underlying oxide starts concurrently), the attack of silicon substrate would not occur unless the poly to be stripped is more than eight-time thicker than the thermal oxide. In the case of this study, the poly film (1000 or 2000 Å) is only 2.5 to 5 time thick compared to the underlying oxide (400 Å), the stripping should be completed in 6 to 12 minutes (based on the lower-bound etch rate of 167 Å/min in the

HF(0.5%)/O3(55 ppm) solution) and the remaining oxide can be stripped in another dedicated HF tank in which the etching will stop at the oxide/silicon interface. Increasing the HF concentration greater than 0.5%, although enhancing the stripping efficiency, does not favor the etching performance since the selectivity decreases (Table 2 and Figure 6).

Table 2: Etch rates and selectivity of polysilicon and thermal oxide in HF with 55 ppm O_3 at 20°C

HF (%)	Etch Rate (Å/min)			Poly/TOX Selectivity
	TOX	Small Poly	Poly Wafer	
0.05	--	3.8	--	--
0.1	2.2	12.5	--	5.7
0.25	8.5	60	34	7.1 (4)
0.38	15.4	119	--	7.7
0.5	20.6	325	167	15.8 (8.1)
0.7	34.6	--	--	--
1	43.4	--	200	(4.6)
2	*88*	--	235	(2.7)
3.33	*146.5*	--	250	(1.7)

1. The etch rates of TOX in *Italic* are the extrapolated values from Figure 1.
2. The selectivity values in parenthesis are based on the lower-bound poly strip rates.

CONCLUSION

The etching behavior of ozone-based HF chemistry on polysilicon has been characterized at various O_3 levels and HF concentrations. Test results showed that the process was a competition between the poly oxidation by O_3 and poly-oxide etching by HF. At a fixed temperature, the slower rate in either of the two reactions determines the overall etching kinetics. Based on the experimental data, the process seems feasible when proper HF and O_3 concentrations are met; 1000 Å (or 2000 Å) poly films can be stripped in reasonable periods without fully etching the underlying thermal oxide and causing damages on the silicon substrate. The process can be implemented on existing AKrion's tools without major modifications. Given the benefits of easier bath's monitoring/control, safer to use, and more environmental friendly processes, the proposed chemistry appears to be promising to replace the conventional application of concentrated HF/HNO_3 mixtures for wafer reclaiming.

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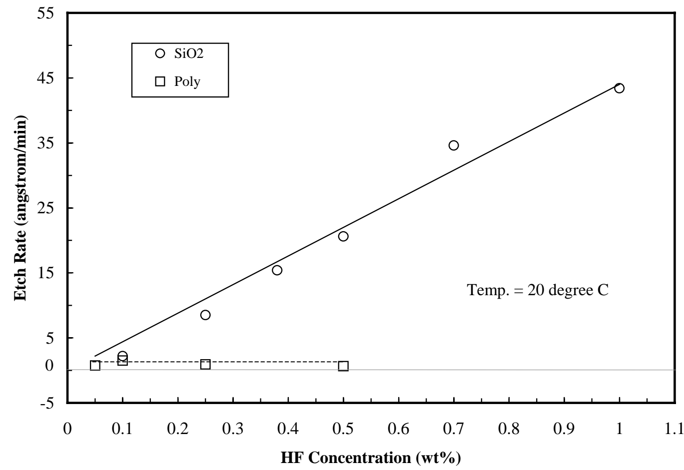

Figure 1: Etch rates of poly and SiO_2 versus HF concentration

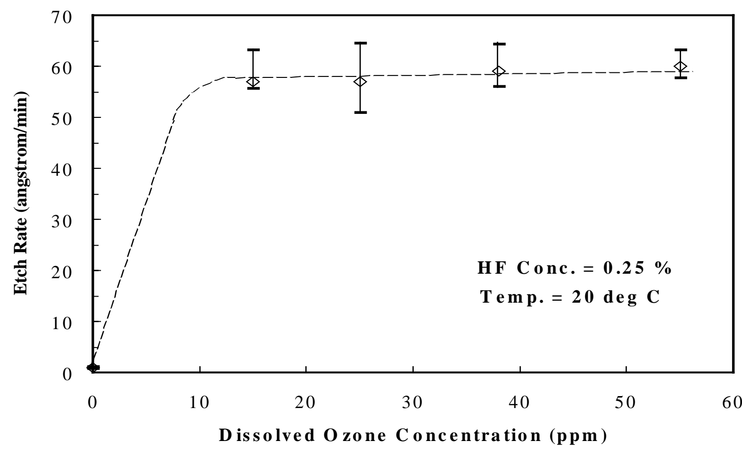

Figure 2: Etch rates of poly in 0.25% HF with various O_3 levels

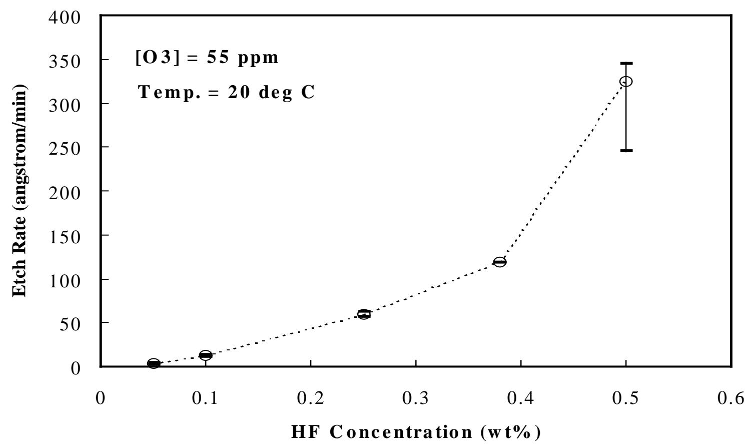

Figure 3: Etch rates of poly (small samples) in HF with 55 ppm O_3

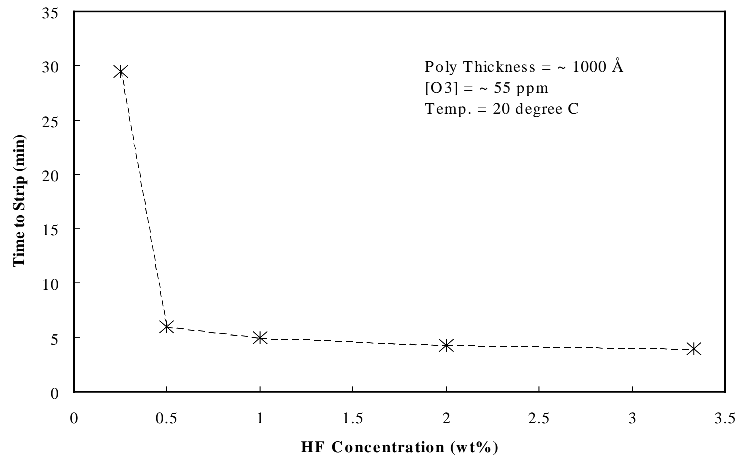

Figure 4: Etch time required for stripping entire poly wafers in HF/O_3

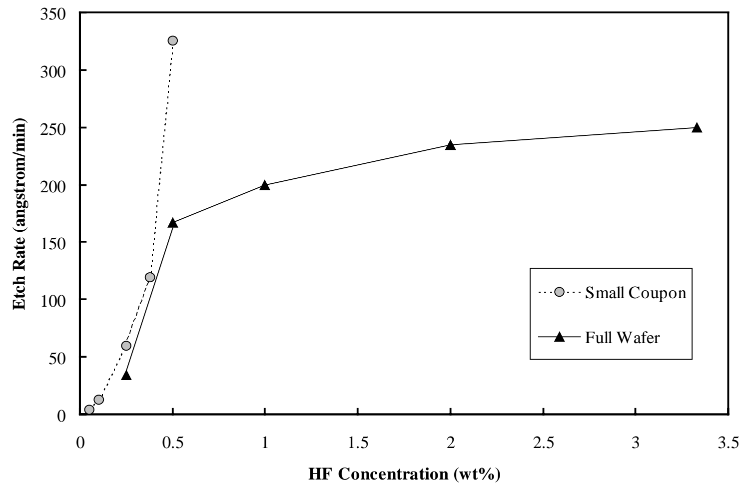

Figure 5: Etch rates of poly on full wafers in HF with 55 ppm O_3

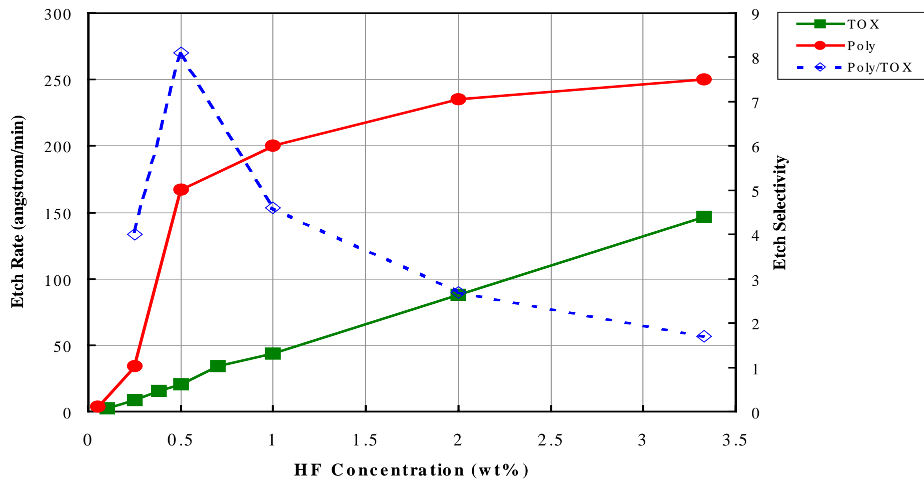

Figure 6: Etch rates and selectivity for poly and thermal oxide in HF with 55 ppm O_3

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