HF CONCENTRATION CONTROL IN IC MANUFACTURING

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ABSTRACT

The etching of SiO_2 layers from silicon surfaces is one of the most critical steps in wet processing technology. Although numerous studies have been performed to analyze the mechanisms and kinetics of these processes, little attention has been given to monitoring and controlling the chemical concentrations in the process baths. Chemical concentration control is becoming crucial to wafer processing in order to obtain consistency and more cost-effective IC manufacturing. This paper demonstrates the use of conductivity sensors to monitor and control the concentration of HF etching solutions. Effects of etch byproducts on the conductivity measurements have been investigated. Once the etch byproducts are characterized and accounted for, results showed that a much more stable etch process can be obtained and the bath life can be extended even in the presence of etch by products.

INTRODUCTION

Life of etching baths can be extended for longer periods of time if an accurate and continuous control of chemical concentrations is provided [1]. Compared to standard analytical techniques for chemical concentration e.g. NIR, UV spectroscopy [1], conductivity cells provide fast, very cost-effective, and real-time control of HF concentration. If the temperature is held constant, and the conductivity of the HF solution is maintained, the etch rate of SiO_2 can be accurately controlled as well [1].

Electrodeless conductivity sensors were used to accurately monitor and control the concentration of HF acid during the etching of thermal oxide from silicon surfaces [1]. However, the etch by-products can affect the linear conductivity-concentration relationship. This effect is magnified when etching thick oxide layers in dilute HF baths. A correction must be developed to correlate the amount of SiO_2 etched with the change in conductivity [2]. Results showed that these techniques are suitable for monitoring and controlling the etch rate in IC manufacturing environment.

EXPERIMENTAL

The experiment was performed on Akrion's Fully Automated GAMA wafer processing station in the Class 1 Application Laboratory at Akrion. Fifty 200-mm wafers with sufficient amounts of thermal oxide on both sides were prepared for the test. A standard HF process tank was used. The etching process was conducted at 21°C in an initially mixed 100:1 (H_2O:HF) HF bath. The conductivity sensor for monitoring the HF bath was calibrated and the reading for the aforementioned HF concentration typically

ranged from 6600 to 6800 µS/cm at 21°C. In addition, the bath's conductivity and temperature were recorded by a PC with automated data acquisition software.

For the test of etching process characterization, a lot of 50 oxide wafers were immersed in the HF bath for 3 hours, without deionized water or HF injection, followed by rinse and dry. The characteristic curve of conductivity versus etch time under the specific system setting was developed and used as a key parameter for the control scheme.

For the test of new algorithm evaluation, a batch of 50 oxide wafers was processed in the HF bath followed by rinse and dry. This process sequence was repeated, without chemical changeout, for 23 test runs. The chemical process time of each run was 25 minutes, which was estimated to have etched the oxide of 560 Å in thickness in a fresh HF bath. The actual etch rate for each run, however, was obtained using an ellipsometer to measure the oxide thickness change of the test wafers. The control system was activated to let the system spike whenever needed.

RESULTS AND DISCUSSION

Results showed that the etch by-products have an effect on the linear dependence of conductivity and HF concentration. Since HF is consumed in the reaction, one would expect that the conductivity should drop as wafers are introduced into the bath. However, it was observed that conductivity increased with the amount of SiO_2 etched in the bath while the oxide etch rate drops as shown in figure 1. This observation was again confirmed by immersing 50 oxide wafers (8") in the 0.5% HF bath for an extended time and monitoring the change in conductivity as illustrated in Fig. 2. The amount of SiO_2 can be calculated and the relationship of conductivity versus the amount of dissolved SiO_2 can be simulated as shown in Fig. 3.

Process Characterization

From Fig. 2 and 3, it is obvious that the bath's conductivity increased with process time regardless of the consumption of HF by oxide etching. The mass of dissolved SiO_2 from both sides of the wafers can be calculated as follows:

$$\text{Mass} = (\pi/4) \times D^2 \times (t \times 2) \times \rho \times N, \text{ where } t = ER \times \text{time} \tag{1}$$

where D is the diameter of the wafer; t is the removed oxide thickness on one side of the wafer (which can be obtained by multiplying average etch rate (ER) with the time), ρ is the density of the thermal oxide, and N is the number of wafers being processed. With the equation, process time can be converted to the dissolved SiO_2 mass, and the relationship of conductivity versus SiO_2 mass can then be plotted (Fig. 3). Using linear regression analysis, the slope of fitted data for the conductivity increment was estimated as 97.5 µS/cm·g, and it would serve as a key parameter specifying the process characteristics under the present sensor setting and test conditions.

Recognizing the trend of conductivity increment with the accumulation of dissolved SiO_2, a new control scheme was developed for the controlling software to prevent the system from being misled by the sensor to do unnecessary spikes. This can be expressed as follows:

Conductivity $_{(n+1)}$ = Conductivity $_{(n)}$ + (K × Mass$_{(n)}$ of dissolved SiO$_2$)   (2)

where K is the slope of the conductivity/mass characterization curve, and n is an integer representing the nth etching step since the HF bath is mixed. Given an estimated amount of oxide thickness to be removed, the conductivity setpoint would be renewed, according to equations 1 and 2, after each single etching process is completed. As such, the conductivity increment resulting from the effect of the dissolved oxide would be offset by the algorithm.

Evaluation of the Modified Control Scheme

      Based on the findings shown in Fig. 3, the K value for the formula of the new algorithm was determined as 100, and was incorporated into the control scheme for the evaluation tests. The recorded conductivity readings, including those in the overnight process-free period, are presented in Fig. 4 showing the track of conductivity variation in detail.

      In general, the new algorithm did govern the system to respond more properly than the old algorithm. For example, there would be no HF spike after Run #8 if the conductivity setpoint had not been reset with the incremental change by the new algorithm, and the etch rate thus would not have returned to the target value from 520 Å/25min at Run #6. The dramatic decrease of the etch rate starting from Run #5 to run #8 was due to disabling the process for a period of 5 minutes. With the exception of Runs #5 to #8, the bath conductivity for most of other runs actually increased faster than the predicted increment. This observation suggested that the conductivity/mass slope obtained from the 3-hour characterization test was unable to loyally reflect the dynamic nature of the process and oxide-induced conductivity change in a prolonged period. A more adequate slope parameter for better applications, therefore, needs to be identified. Analysis based on the experimental data obtained may provide a reasonable approach for the estimation. By neglecting the etch-rate trough (Runs #5 to #9), a line can be drawn across the actual conductivity data points in Fig. 4 from Run #1 to #13, reflecting a constant conductivity increment as 80 μS/cm per run. The corresponding etch rates for these processes (i.e. Runs #1 to #4 and #10 to #13) are relatively stable, with a value of about 560 Å/25min. Similarly, a line can also be drawn across the conductivity points from Runs #17 to #23 which show fairly constant etch rates of 530 Å/25min. The conductivity increment for these runs is 65 μS/cm per run. To have the new algorithm work properly, the setpoint increment should be consistent with the conductivity increment to offset the oxide effect. The setpoint change between two consecutive runs is thus identified ranging from 65 to 80 μS/cm per run for the specific experimental setting. We combine Eqs. 1 and 2 and convert them to a different form;

   Δ (Setpoint) = K × Mass = K × (B × t)   (3)

where B is a material constant including wafer diameter, density, lot size, etc. In the algorithm evaluation test, Δ (Setpoint) was 48 μS/cm per run with K = 100 μS/cm·g and t = 560 Å. Since B is fixed, a new slope parameter based on the data analysis aforementioned can be obtained; i.e. K = 166 μS/cm·g for Runs #1 to #13, or K = 143

μS/cm·g for Runs #17 to #23. An average K value of 155 μS/cm·g, therefore, may be used for the next experimental verification.

With a suitable K value incorporated into the algorithm, the adjustment of process parameters of the HF tank such as spike interval and duration and upper/lower conductivity control bands would then become significant in maintaining a stable HF concentration for oxide etching. During the course of the present experiment, the DI water replenishment was most frequently observed. The loss of bath liquid is mainly due to liquid evaporation and dragging by the product/carrier. The former is a time-dependent process at a constant bath temperature, while the latter would be determined by the throughput for a fixed carrier and lot size (surface area). The evaporation rate of the bath was estimated to be about 130 ml/hr. while the liquid carried away by the product/carrier was estimated as 70 ml per lot. These values plus the HF spike rate of about 7 ml/sec, whenever required, would provide a baseline for the determination of some process-specific settings.

Recognizing the trend of conductivity increment with the accumulation of dissolved SiO_2, a new algorithm was developed to prevent the system from injecting unnecessary HF or water. Given an estimated amount of oxide thickness to be removed, the conductivity setpoint would be renewed after each single etching process is completed. As such, the algorithm would offset the conductivity increment resulting from the effect of the dissolved oxide, and the control system would meet the process requirements. The modification enabled the system to respond more accurately compared to the situation where the effect of etch by-products was neglected. As shown in figures 5 and 6, the etch rate stayed within limits for almost 7 days.

Analysis

The total molar conductivity of a solution is based on each ion's individual conductivity contribution for infinitely dilute solutions. When solutions become more concentrated, ion-ion interactions increase. These interactions, as well as the presence of other species (primarily HF_2^-, H^+, and F^-), lead to an observed (measured) conductivity value of approximately 6200 μS/cm for 1:100 HF:H_2O mix. Nevertheless, it is plainly shown that the conductivity of a freshly mixed solution is primarily based on the concentration of H^+, or in this case the 0.6 moles present in a solution of 50 liters.

At this point, the amount of chemical byproduct formed in an HF etching reaction needs to be determined. Using the chemical reaction equation below:
$$6HF + SiO_2 >>>>>> H_2SiF_6 + 2\ H_2O \tag{4}$$

To etch 560 Å from two sides of 50 (200 mm) wafers, the total amount in grams of SiO_2 removed will equal to 0.399 grams (density = 2.27 g/cm^3) of SiO_2 or 0.00664 moles.

Since HF is being consumed, or 0.00664 moles x 6 = 0.04 moles for each run of 50 wafers, the concentration of H^+ and F^- will also be smaller. However, this amount when compared to initial amount of HF (11.45 moles) can be significant after processing many wafers in the HF bath. The slope (or correction factor) from figures 2 and 3 was obtained assuming a constant etch rate during the 3 hour test period (equivalent to 7 manufacturing

runs i.e. 180 min / 25.667 min. per run = 7 runs). However, that is not true since the HF is being consumed. It is estimated that about 2.45% of the HF were consumed during the immersion test as can be seen from figures 2 and 3. A quick estimate of the ratio between the etch byproduct and the total concentration of the conductive species $[H^+]$ (from both HF and H_2SiF_6) can be summarized in the following example (0.5% HF in 50 liter bath):

Run #	HF, moles	HF, moles/l	H_2SiF_6, moles	$[H^+]$, moles/l
0	11.45	0.229	0.0	0.01284
7 (no spike)	11.17	0.223	0.04648	0.01364
7 (HF spike)	11.45	0.229	0.04648	0.01376

It can be easily seen from the table above that the contribution of H_2SiF_6 to the conductivity as represented by $[H^+]$ for these 7 runs is (0.01364-0.01284)/0.01284 = 0.062 or 6.2%. This increase in the conductivity of the byproduct (H_2SiF_6) must be accounted for i.e. this increase should be eliminated in order for the conductivity to remain as a true indication of the HF concentration. In addition, the decrease in HF concentration during these runs must be also compensated for in order to maintain a constant etch rate. Thus, an additional correction factor was used on top of that obtained from figure 2 and 3 to compensate for the consumed HF and offset the increase in conductivity due to the etch byproducts. Clearly, a correction to the conductivity measurement is deemed necessary. These estimates are in good agreement with manufacturing data. As shown in figures 5 and 6, the etch rate is within the manufacturing acceptable range once the proper correction is made.

CONCLUSIONS

Results showed that controlled HF processes were significantly improved when compared to conventional processes without concentration control. The effect of etch by-products was correlated with the change in HF conductivity and has to be considered in the control scheme. When etching thick oxides in dilute HF solutions, the linear properties of bath conductivity versus HF concentration would be considerably affected by the accumulation of dissolved ionic products. The development of an empirical relationship between the bath conductivity and the amount of etched oxides was found necessary. Validation testing of the developed algorithm to retain stable etch rates in an extended HF bath life has been conducted on a production tool. The on-site experiment demonstrated the effectiveness of the new algorithm in achieving etch rates in a 585 Å ± 2.5% range over 7-day bath life. However, extending the bath life greater than 7 days is not recommended due to 1) the risk of building up high levels of contaminants in the bath, and 2) the possible breakdown of the linear assumption between the mass of etched oxides and bath conductivity.
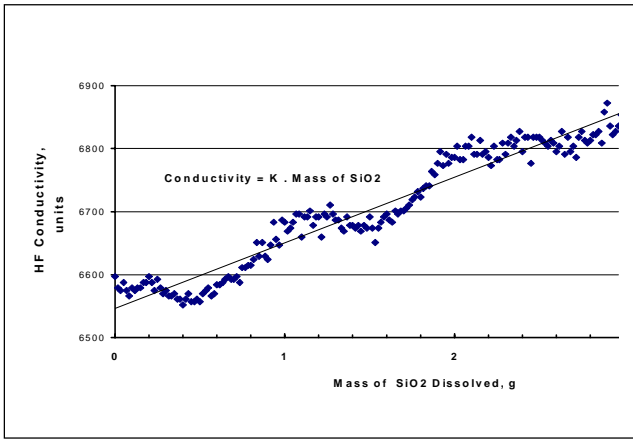
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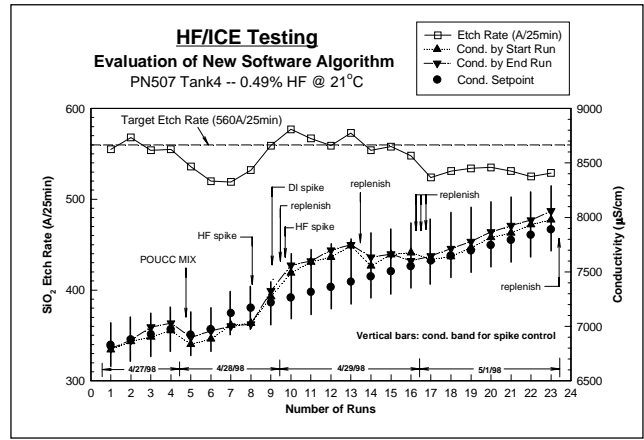2. G. Chen and I. Kashkoush, Akrion Technical Report, May (1998) (unpublished).
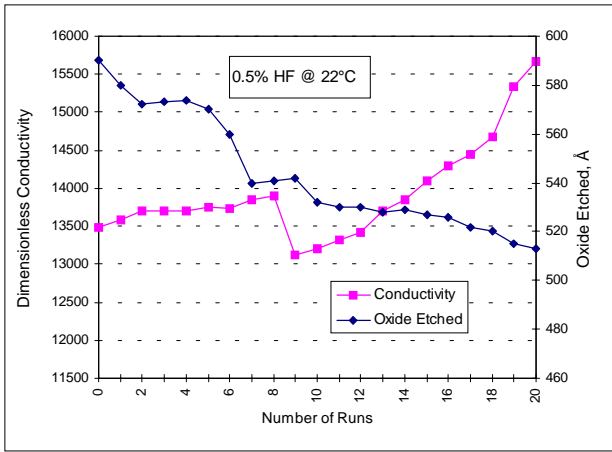
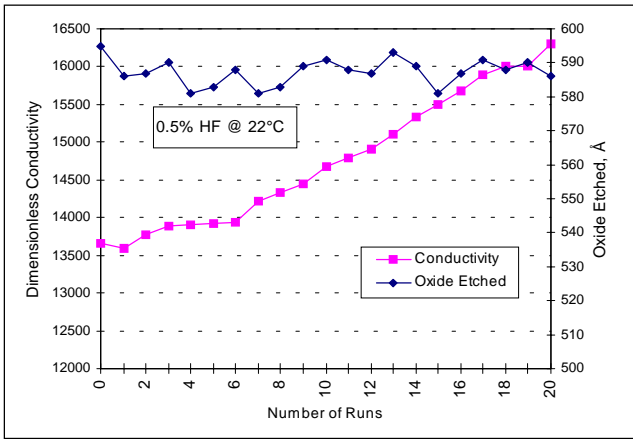**Figure 1: Effect of Dissolved SiO$_2$ on Etch Rate and Bath Conductivity**
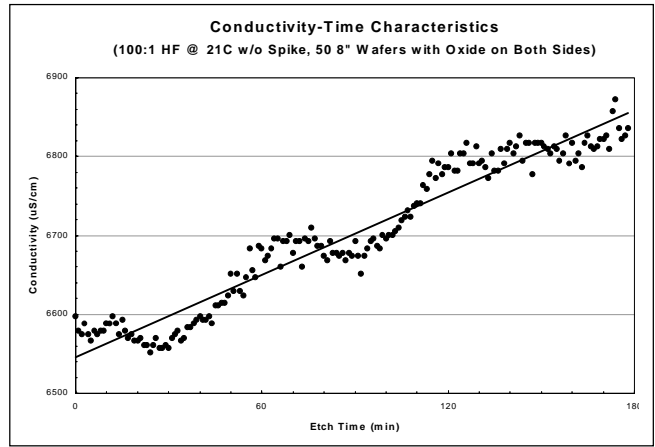
Figure 2: Characterization of Conductivity versus time in DHF processes.
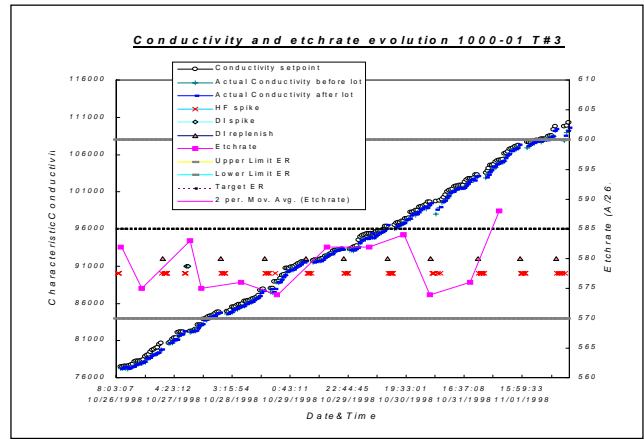

Figure 3: Characterization of Dissolved SiO$_2$ in DHF processes.

Figure 4: Etch Rate versus Time with Conductivity Corrected.

Figure 5: Stability of SiO$_2$ Etch Rate with Modified Algorithm.

Figure 6: Stability of SiO2 Etch Rate in DHF processes during IC Manufacturing.