

Selective Etching of Native Oxide Using Vapor HF Processing

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We studied the vapor phase HF selective etching of native oxide in the presence of thermal and deposited oxides. The azeotropic HF/H₂O was diluted with vapor phase H₂O, azeotropic HCl/H₂O, or IPA. It was demonstrated that etch rates and time required to initiate etching was dependent on the reactant chemistry. Good etch selectivity for native oxide in the presence of thermal oxide was possible with the addition of the HCl, while IPA was required when TEOS was present.

1. Introduction

The selective etching of native oxide is required for many applications involving the manufacture of VLSI devices. HF Vapor (HFV) processing has the potential for increased selectivity since the etching reaction is normally preceded by the condensation of reactants on the wafer surface. Under a given set of processing conditions, this condensation step leads to a unique delay time for different types of oxides where no etching takes place. Recent work has shown that the vapor phase etch selectivity is strongly dependent on wafer temperature [1, 2], vapor pressure [3], and moisture content [4]. In this work, we present etch selectivity dependence on the chemistry of the reactants during HFV processing. Shown in Fig. 1 are several applications for HFV processing: 1) pre-gate oxidation [5], 2) pre-silicide deposition [6], and 4) pre-nitride deposition [7, 8]. In most applications, the native oxide must be selectively removed from a Si single crystal or poly surface in the presence of thermal or CVD oxides. This requires good control over the oxide etching process. While there are several alternatives for native oxide removal, each method has its potential problems as shown in Table I. Aqueous HF processing can have poor etch selectivity and cause particle deposition. Rapid thermal cleaning at high temperature in a hydrogen environment may cause surface pitting and undercutting of oxide sidewall structures. Surface damage and contamination are known to be related to plasma cleaning. Finally, vapor phase cleaning can cause residues if the by-products of the etch are not volatile. Also, selectivity control can be difficult. A comparison of particles and residual oxide thickness is listed in Table II for wet HF and HFV processes [9]. Both HF techniques left $< 0.4 \text{ \AA}$ of residual oxide, while the vapor process resulted in over an order of magnitude less particles. These particles

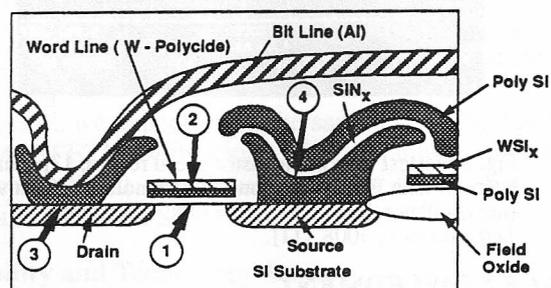


Fig. 1. Applications for HF vapor processing include :
1) Pre-gate Oxidation, 2) Pre-Silicide CVD, 3) Pre-Poly CVD, and 4) Pre-Nitride CVD.

can be removed by a Meagsonic clean but the native oxide is then regrown. A limitation of the vapor process is the inability to remove a thick thermal oxide. In this case, by-product residues are observed as "particles".

2. Experiment

Native oxide, thermal oxide, and annealed deposited oxide films were processed on a single wafer-low pressure HF vapor etcher [10]. In this system, azeotropic HF/H₂O, azeotropic HCl/H₂O, H₂O, and high purity IPA was transported to the wafer surface using N₂ carrier gas. The wafer was held in a SiC chamber at ambient temperature with pressures in the range between 50 and 350 Torr. Oxide thicknesses were measured using film thickness reflectometry and ellipsometry. Oxide etch rates and "delay times" (the time required to initiate the etch reaction) were then determined. SIMS epi-encapsulation experiments were used to measure the surface contamination levels and compare the vapor clean to a conventional HF strip.

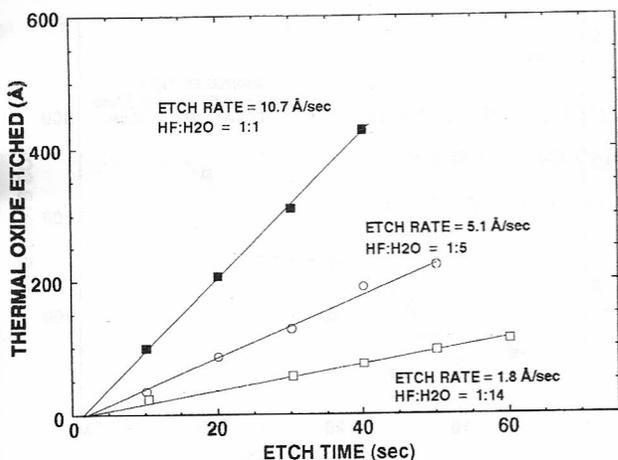


Fig. 2. Lowering The HF:H₂O carrier gas flow ratio reduces the thermal oxide etch rate but it has little affect on the delay time at low HF concentrations.

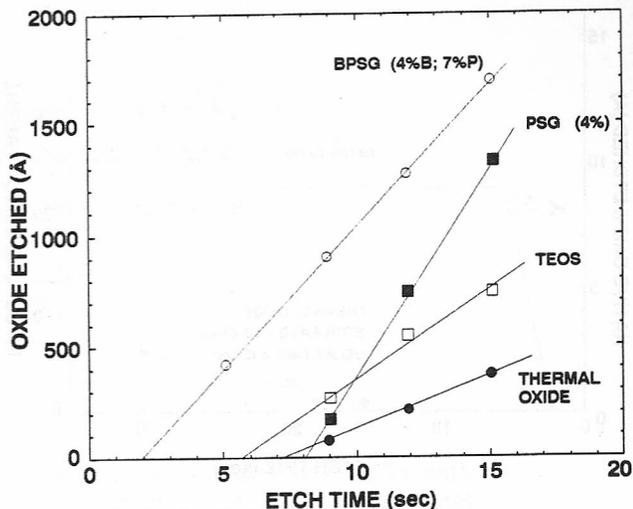


Fig. 3. Etch rates and delay times using azeotropic HF are strongly dependent on the oxide type.

Table I. Limitations of Cleaning Methods.

CLEANING METHOD	PROBLEMS
Aqueous HF	Particles, Selectivity Control
Rapid Thermal Clean	Surface Pitting, Oxide Undercutting
Plasma Cleaning	Surface Damage, Contamination
Vapor HF	Residues, Selectivity Control

Table II. Particle on 150 mm Wafers (>0.3 μm)

CLEAN CONDITION	OXIDE	ADDERs
Aqueous HF + SRD	< 4 Å	1184
Aqueous HF + Meg + SRD	9 Å	17
HFV	< 4 Å	12
HFV - 200 Å Oxide Strip	< 4 Å	2,348

3. Results and Discussion

The etch rate of thermal oxide depends on the ratio of N₂ carrier gas flowing to the azeotropic HF/H₂O and H₂O sources. As shown in Fig. 2, the etch rate corresponding to HF:H₂O carrier gas ratios of 1:1, 1:5, 1:14, result in etch rates of 10.7 Å/sec, 5.1 Å/sec, and 1.8 Å/sec, respectively. Under these low etch rate conditions, the etch rate decreases as the HF:H₂O carrier flow ratio is decreased, however, this dilution has little influence on the etch delay time. HFV etch characterization for a wide range of oxides, as shown in Fig 3, indicates that etch rates and delay times are strongly dependent on the oxide type. Under these less dilute processing conditions using only the azeotropic HF source, the etch rate of thermal oxide is 48 Å/sec and the delay time is 7.1 sec. Also shown on Fig. 3 are etch rate curves for BPSG, PSG and TEOS with delay times of 2.0, 8.1 sec, and 5.7 sec, respectively. This data shows that more hygroscopic films such as BPSG will condense the HF/H₂O layer that is required to initiate etching more rapidly than a thermal oxide. For certain applications, this ability to

Table III. Oxide Etch Characteristics.

FILM TYPE	HF/H ₂ O slm	Dilutant slm	RATE Å/sec	DELAY sec
Ther. Ox.	15	None	48	7.1
Ther. Ox.	7.5	7.5	10.7	2
Ther. Ox.	2.5	12.5	5.1	3
Ther. Ox.	1	14	1.8	3
Ther. Ox.	2.5	12.5-HCl	3.3	12
BPSG	15	0	129	2.0
PSG	15	0	189	8.1
TEOS	15	0	78	5.7
TEOS	2	1-H ₂ O	13	12
TEOS	2	1-IPA	0.4	40

etch a deposited oxide without affecting a thermal oxide is a great advantage [4]. Etch rate and delay times are summarized in Table III.

In contrast to the HF/H₂O etch in Fig. 2, diluting the HF source with an azeotropic HCl source increases the delay time substantially. Etching a thermal oxide with a HF:HCl carrier gas flow ratio of 1:5 gives an etch rate of 3.3 Å/sec and a delay time of 12 sec. This increase in thermal oxide delay time allows selective removal of native oxide in the presence of thermal oxide, as shown in Fig. 4. In this case, the delay time for the native oxide is less than 6 sec so the thermal oxide is not etched by the time the native oxide is completely removed. A similar improvement in etch selectivity is found when using azeotropic HF/H₂O diluted with IPA. As shown in Fig. 5a, the complete removal of a native oxide can result in an unacceptable over etch of CVD oxides when using HFV HF/H₂O. In this case, nearly 200 Å of TEOS is removed during the time required to ensure complete removal of the native oxide. A greatly improved selectivity is found for TEOS when the HF/H₂O mixture is diluted with vapor phase IPA. As seen in Fig. 5b, the addition of the IPA has increased the TEOS delay time from 12 sec using the HF/H₂O mixture, to over 40 sec with the IPA dilution. In contrast to the TEOS delay time, the delay time for the native oxide is essentially unchanged when IPA is used. Complete removal of the native oxide can

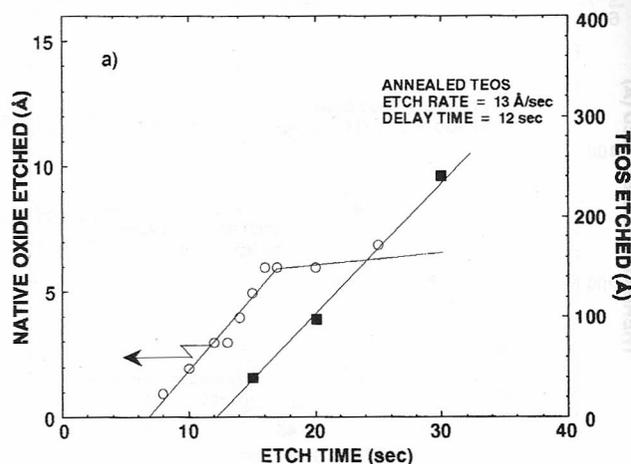
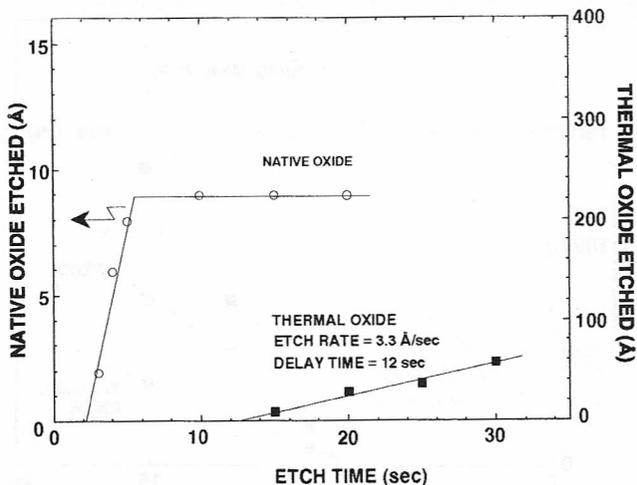


Fig. 4. Diluting the azeotropic HF/H₂O with azeotropic HF/HCl increases the delay time and allows selective removal of native oxide in the presence of thermal oxide.

Table IV. Wafer Surface Contamination (at/cm²).

Cleaning Condition	Oxygen	Fluorine	Carbon
HF Vapor	2.0 e 13	< 1.7 e 9	1.2 e 13
HF Vapor + IPA Dry	5.0 e 13	< 1.7 e 9	4.0 e 13
HF + IPA Vapor	1.8 e 12	< 1.7 e 9	6.0 e 12

take place with little or no etching of the TEOS.

Considerations other than etch selectivity are important when determining the most appropriate vapor etch chemistry. While vapor phase HF/H₂O/HCl has been found to give equivalent electrical results compared to aqueous cleaning for a pre-gate oxide clean [5], this vapor mixture is not suitable for a pre-epi clean. However, a dilution of the vapor process with IPA has produced high quality epi. Listed in Table IV are results of a SIMS epi-encapsulation analysis which indicates that HF/IPA vapor cleaned wafers show less carbon and oxygen than wafers cleaned with vapor phase HF only. The low fluorine levels are due to the desorption of fluorine below the temperature of epi deposition.

4. Conclusion

Our investigations conclude that a HF vapor process can be used to selectively remove native oxide in the presence of thermal oxide or TEOS. In the case of the thermal oxide, the azeotropic HF/H₂O mixture is diluted with an azeotropic mixture of HCl/H₂O. This mixture would provide an effective means of removing a native oxide prior to a gate oxidation. Selective removal of native oxide in the presence of TEOS is made possible by diluting the azeotropic HF/H₂O with IPA. Pre-cleans for poly emitters and silicon nitride could benefit from this improved selectivity.

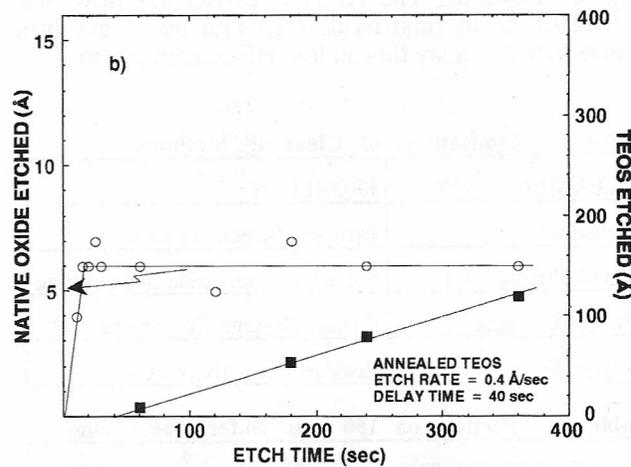


Fig. 5. A comparison of vapor phase a) HF/H₂O and HF/H₂O/IPA shows that etch selectivity of native oxide vs. TEOS is improved when IPA is added.

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