

# IBM Research Report

## A Selective Etching Process for Chemically Inert High-k Metal Oxides

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# A Selective Etching Process for Chemically Inert High-k Metal Oxides

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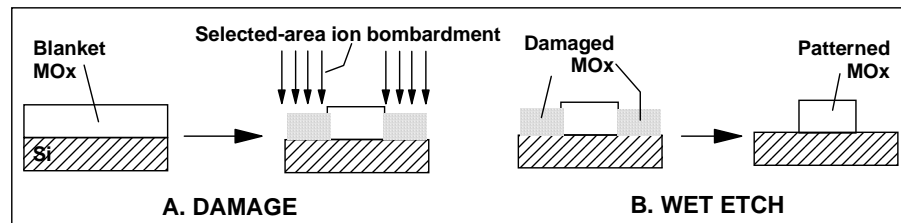
## ABSTRACT

Once annealed, high-k metal oxides such as  $\text{HfO}_2$  and  $\text{Al}_2\text{O}_3$  can be extremely difficult to etch by wet chemical methods. Here we describe how ion bombardment at relatively low energy (a few hundred eV) can be used to make exposed regions of annealed  $\text{HfO}_2$  films etchable in aqueous HF-based solutions.  $\text{HfO}_2$  layers, 2-5 nm in thickness, were deposited by atomic layer chemical vapor deposition (ALCVD) on Si substrates, annealed at 700 °C, and subjected to selected-area ion bombardment supplied by an oxygen plasma in a reactive ion etching tool. Etch times (as indicated by time to "dewet") were examined as a function of  $\text{HfO}_2$  thickness, the power and time of oxygen plasma treatments, post-oxygen-plasma anneals, and wet etch chemistry. Strategies for etching thicker films and additional data provided by electrochemical open circuit potential (OCP) measurements will also be discussed.

## INTRODUCTION

High-k metal oxides such as  $\text{HfO}_2$  and  $\text{Al}_2\text{O}_3$  are being investigated as gate dielectrics for advanced CMOS devices due to the expected limitations of  $\text{SiO}_2$  at equivalent oxide thicknesses (EOT) less than 1 nm. However, integration of these metal oxide films into devices requires the existence of selective and controllable patterning processes. Conventional wet etches typically have no effect on these films, which are extremely chemically inert once they have been annealed, and reactive ion etching (RIE) processes, while effective, typically lack the selectivity required to prevent damage to underlying layers (such as silicon).

The etch method described here is shown schematically in Fig. 1. It comprises two basic steps: a selectively applied ion (or other charged particle) bombardment process to "damage" the metal oxide (MOx) film followed by an aqueous HF-based wet etch to selectively remove the regions of the film that have been damaged. For this work, the ion bombardment is provided by a relatively mild oxygen plasma treatment whose effects are largely localized to the top ~3 nm of the bombarded surface, a thickness roughly comparable to the thickness of the film being etched.



**Fig. 1.** Schematic of etch process showing damage (A) and wet etch (B)

It has long been known that ion implantation (I/I) damage can increase the wet etch rate of  $\text{SiO}_2$  films [1, 2]. Recently this approach has been used to enable the etching of chemically inert  $\text{HfO}_2$  and  $\text{Al}_2\text{O}_3$  metal oxide films [3, 4]. However, the low energy, plasma-based ion

bombardment of the present work may often be preferred to the higher ion energies typically used for implantation if (i) the metal oxide films are thin (i.e., of a thickness comparable to the "damage depth") and/or (ii) the ion implantation would induce unacceptable substrate damage. It is even possible to etch thick films with this technique if one is willing to employ multiple damage/etch cycles to remove a succession thin damage layers one at a time.

Interestingly, the damage induced by ion bombardment can often be reversed by annealing, allowing "rework" if the damage was inadvertently applied to the wrong regions of the metal oxide film. Annealing may also be desirable after the damaged metal oxide regions have been wet etched if substrate damage needs to be repaired.

## EXPERIMENT

HfO<sub>2</sub> films were deposited on p-type 100-oriented single crystal Si wafer substrates treated in a "standard clean 1" solution of NH<sub>4</sub>OH and H<sub>2</sub>O<sub>2</sub> to produce a thin (0.5-1.0 nm) layer of chemical silicon dioxide. The HfO<sub>2</sub> was deposited by atomic layer chemical vapor deposition (ALCVD) in an ASM/Microchemistry Pulsar 2000 tool using alternating pulses of HfCl<sub>4</sub> and H<sub>2</sub>O at a pressure of 0.4 Torr and a substrate temperature of 300 °C. As-deposited film thicknesses (2-5 nm) were measured by ellispometry (Rudolph FE-IIIId). Unless noted otherwise, all films were given a post-deposition rapid thermal anneal (RTA) in N<sub>2</sub> at 700 °C for 30 s shortly after deposition. In a few selected cases, films were also annealed after the ion damage step.

The ion damage step of our etch process was performed in a parallel plate reactive ion etching system (Plasmalab  $\mu$ P-RIE 80). The 24-cm-diam powered electrode was water-cooled and driven by a 13.56 MHz 300 W power supply. Sample pieces were placed on a 20-cm-diam Si wafer in contact with a graphite susceptor plate on the powered electrode. O<sub>2</sub> was selected as the working gas (dominant ion O<sub>2</sub><sup>+</sup>) because it was readily available and not expected to chemically etch HfO<sub>2</sub>. All plasma treatments used an O<sub>2</sub> pressure of 20 mTorr and a flow of 20 sccm. Typical treatment time and power was 150 W (self-bias voltage of -280 Vdc) for 1 min, though powers and times were examined over the range 0.2 to 5 min and 50 to 300 W.

Some plasma treatments were also done with a CF<sub>4</sub> working gas (also at 20 mTorr and 20 sccm flow) until it was realized that the CF<sub>4</sub> plasma was directly etching the HfO<sub>2</sub>. The etch rate (ER) at 150 W was found to be about 2.2 nm/min. While this rate is slow compared to the ER of Si substrate under the same conditions (about 27 nm/min) it is much faster than the ER of HfO<sub>2</sub> in O<sub>2</sub> (about 0.8 and 1.1 nm/min for 150 and 300 W, respectively). Ar and Ar/O<sub>2</sub> working gases are expected to work similarly to pure O<sub>2</sub>, and might be preferable if a photoresist is used as a mask (instead of the small Si pieces used for these feasibility experiments).

The wet etch step of our etch process was typically performed in 10:1 dilute HF (about 5 wt% HF in H<sub>2</sub>O) at room temperature. However, a few experiments were also done in a commercial 50:1 buffered oxide etch (BOE) (about 39 w% NH<sub>4</sub>F and 1.0 wt% HF in H<sub>2</sub>O) to verify that this step could be done in a solution more compatible with photoresist masks.

HfO<sub>2</sub> ERs were primarily determined by dewet times, i.e., the time required to turn the sample surface from hydrophilic (sheeting, indicative of an oxide layer) to hydrophobic (dry and

water-repelling, indicative of a H-terminated Si surface). The dewet time was usually extremely clear. ERs, where listed, were taken to be equal to the HfO<sub>2</sub> film thickness divided by the dewet time. Electrochemical open circuit potential (OCP) measurements [5, 6] were also performed on selected samples to provide a more quantitative indication of etch behavior.

Rutherford Backscattering Spectroscopy (RBS) with 2.3 MeV <sup>4</sup>He ions was used for quantitative measurements of Hf areal density (atoms/cm<sup>2</sup>). This allowed (i) confirmation of film thicknesses provided by ellipsometry, (ii) estimation of HfO<sub>2</sub> sputter etch rates during plasma treatments, and (iii) verification (on selected samples) that no Hf remained after dewetting.

## RESULTS AND DISCUSSION

We begin with dewet data selected to demonstrate the dramatic effect of a preferred O<sub>2</sub> plasma treatment on the etchability of HfO<sub>2</sub> films. This is followed by additional data from experiments directed towards understanding the range and mechanisms of ion damage enough to allow optimization of the ion energy and dose for films of different thicknesses. We conclude with some OCP data for a more quantitative indication of etch behavior.

### Effect of annealing and O<sub>2</sub> plasma treatment on HfO<sub>2</sub> wet etch rates

Table I shows the effect of a post-deposition anneal on the HfO<sub>2</sub> ERs. ERs of the as-deposited films are about 8 nm/min in 10:1 HF; after annealing (700 °C/30 s N<sub>2</sub>) the films become nearly unetchable, with no dewetting seen even after 10 min in 10:1 HF (corresponding to an upper bound ER of 0.3 nm/min).

**Table I.** Dewet times and ERs in 10:1 HF for HfO<sub>2</sub> films with and without a post-deposition anneal in N<sub>2</sub> at 700°C for 30 s.

HfO <sub>2</sub> thickness/treatment		Dewet time	Etch Rate (nm/min)
Thickness	Anneal		
4.6 nm	No	33 s	8.4
2.9 nm	Yes	>600 s*	< 0.3

\*Did not dewet

**Table II.** Dewet times of 2.9 nm-thick annealed HfO<sub>2</sub> films as a function of etchant and O<sub>2</sub> treatment.

Etchant	No O <sub>2</sub>	150 W/1 min O <sub>2</sub>
HF 10:1	> 10 min*	4 s
BOE 50:1	> 21 min*	20-25 s

t\* Did not dewet

Table II compares the dewet times of 2.9 nm-thick annealed HfO<sub>2</sub> films with and without a mild (150 W/1 min) O<sub>2</sub> plasma treatment. The O<sub>2</sub> treatment has a dramatic effect: the treated films become etchable in either 10:1 HF or 50:1 BOE, with dewet times for 10:1 HF decreased by over 2 orders of magnitude.

### Range and mechanisms of O<sub>2</sub> plasma damage

What film thicknesses are amenable to this damage/etch technique? And what doses and ion energies are optimum? To answer these questions we need to know something about the

range and mechanisms of ion damage. Table III shows how dewet times in 10:1 HF vary with HfO<sub>2</sub> film thickness for a given plasma exposure. The data indicate that the damage provided by a 1 min treatment at 150 W is extremely localized, enough to damage the full thickness of a 2.9 nm HfO<sub>2</sub> film, but not enough damage the entire thickness of a 4.6 nm HfO<sub>2</sub> film. Not surprisingly, RBS on the 4.6 nm HfO<sub>2</sub> film after a single damage/etch cycle (150 W for 1 min, followed by 10 s) found that 54% of the initial Hf remained. However, in a demonstration that thicker films can be etched with multiple damage/etch cycles, the film dewetted in 4 s after a second damage step, with RBS showing no residual Hf.

The localized nature of the plasma damage noted above is also suggested by additional data that an 8.7 nm overlayer of SiO<sub>2</sub> shielded a 2.1 nm HfO<sub>2</sub> film from 150 W/5 min plasma exposure sufficiently to prevent subsequent dewetting in HF.

**Table III.** Summary of dewet times in 10:1 HF for 3 thicknesses of HfO<sub>2</sub>, as a function of time and power of O<sub>2</sub> plasma exposure.

Conditions of O <sub>2</sub> plasma treatment			Dewet times (s) in 10:1 HF for various HfO <sub>2</sub> thicknesses		
Power (W)	Self-bias voltage (Vdc)	Time (min)	2.1 nm	2.9 nm	4.6 nm
0	0	-	No dewet (>1200)	No dewet (>600)	No dewet (>600)
25	80	1.0	No dewet (>300)	No dewet (>300)	-
50	140	1.0	25-35	No dewet (>300)	-
100	227	1.0	4	35-50	-
150	280	0.2	4	No dewet (>300)	-
150	280	0.5	4	20-35**a	-
150	280	1.0	4*	4*	No dewet (>690)
150	280	2.0	-	-	300-510**b
150	280	5.0	-	-	4
300	390	1.0	-	4	45-255

\* RBS showed no residual Hf; \*\* RBS showed residual Hf: 0.8% of initial (a), 18% of initial (b).

RBS also showed that substrate dewetting may not always be a completely reliable indicator of HfO<sub>2</sub> removal when dewetting is slow. Dewetting samples appeared to fall into two categories, those that dewetted almost immediately (and had been given "strong" damage treatments), and those that took a long time to dewet (and had been given "weak" damage treatments). Samples in the fast dewet category showed no residual Hf, whereas samples in the slow dewet category showed significant amounts of Hf (1-18% of initial). While the presence of Hf in the slow dewet samples indicates that sample dewetting may not always be a reliable indicator of complete HfO<sub>2</sub> removal, it appears that the dewet test is accurate when sample dewetting is fast.

The short (4 s) dewet time for the 4.6 nm film with 150 W/5 min O<sub>2</sub> plasma treatment was initially somewhat surprising, since we had expected the depth of the damage region to be

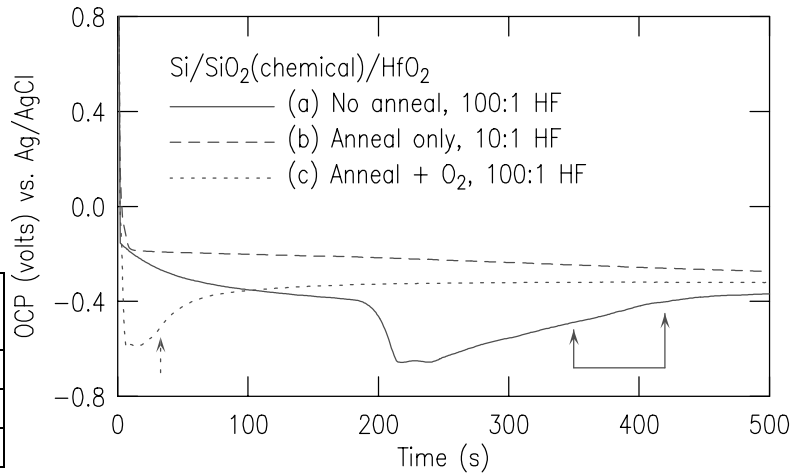
relatively independent of dose, and no sign of dewetting was seen after an O<sub>2</sub> plasma treatment at 150 W for 1 min. However, these results are easily explained by the fact that the plasma damage has a sputter etch component. RBS measurements on 4.6 nm HfO<sub>2</sub> films after 2 min of plasma exposure indicated sputter etch rates of 0.8 nm/min at 150 W and 1.1 nm/min 300W.

Another interesting finding is the apparent existence of a threshold dose for damage. The exposure time series for the 2.9 nm films at 150 W indicates that the film is impervious to aqueous HF after a 0.2 min dose, yet quickly and completely removed by aqueous HF after a 1 min dose. Borderline etching/dewetting was observed after a 0.5 min dose. While physical sputtering can contribute to the HfO<sub>2</sub> etching, the effects are small for these low doses (maximum of 0.8 nm removal, for the longest exposure time/dose).

Table IV shows that the damage induced by these O<sub>2</sub> plasma treatments can be at least partially repaired by annealing. However, complete repair of the damage (as measured by complete restoration of wet etch resistance) would require thermal treatments longer and/or hotter than 700 °C/1 min.

**Table IV.** Effect of post-plasma anneals on dewet times in 10:1 HF of 2.9 nm-thick HfO<sub>2</sub> films after a 150 W/1 min O<sub>2</sub> plasma treatment.

Post-plasma anneal	Dewet time in 10:1 HF
No anneal	4 s
400 °C/5 min N <sub>2</sub>	15-20 s
700 °C/1 min N <sub>2</sub>	240-690 s



**Fig. 2.** OCP data for three Si/SiO<sub>2</sub>(chemical)/HfO<sub>2</sub> samples.

Fig. 2 shows OCP data for three samples in dilute HF: "no anneal" Si/chemical SiO<sub>2</sub>/HfO<sub>2</sub> (4.6 nm), trace (a); and annealed (700°C/30 s N<sub>2</sub>) Si/chemical SiO<sub>2</sub>/HfO<sub>2</sub>(2.4 nm) with (c) or without (b) a 1 min O<sub>2</sub> RIE treatment at 150 W. HF concentrations of 100:1 and 10:1 were selected to give a convenient time scale for the measurement. Arrows indicate the time (or range of times) at which nominally identical samples showed dewetting in solutions of the same HF concentration. As expected, no dewetting was seen for the trace (b) sample even after 15 min in 10:1 HF.

While we cannot offer a definitive interpretation of each and every feature of these curves, some general statements can be made about the "no anneal" sample of trace (a) based on similarities to OCP data for Si cleaning and SiO<sub>2</sub> etching in HF solutions [6]. During the first phase of the etching, taking place over the time period 0 to 200 s, there is a gradual decrease in the OCP while the HfO<sub>2</sub> slowly etches. The HfO<sub>2</sub>/chemical oxide interface is reached at about 200 s. At this point the chemical oxide starts etching and the OCP abruptly drops, reaching a minimum at 220s when the last full monolayer of Si<sup>+4</sup> has been removed. The gradual rise in the

OCP trace after the minimum at 220 s corresponds to the removal of partially oxidized Si (i.e.,  $\text{Si}^{+1}$ ,  $\text{Si}^{+2}$ , and  $\text{Si}^{+3}$ ) and the gradual hydrogen passivation of the Si surface, which is complete when the OCP reaches a constant-potential plateau. A contact angle of  $\sim 20$  to  $30^\circ$  (the minimum required for Si dewetting) is predicted to occur at the approximate midpoint of this rising curve [6], in reasonable agreement with our independently measured range of dewet times (indicated by the arrows at 350 and 420 s).

The "anneal only" sample of trace (b) never progresses beyond the early  $\text{HfO}_2$  etching phase and never reaches a minimum, indicating an extremely slow etching that never reaches the Si surface. In contrast, the "anneal +  $\text{O}_2$ " sample of trace (c) is qualitatively similar to the "no anneal" sample of trace (a), except for the faster time scale, as indicated by the earlier OCP minimum and dewet arrow at 33 s.

## CONCLUSIONS

Chemically inert  $\text{HfO}_2$  films can be modified by low energy (a few hundred eV) ion bombardment to make them easily etchable in aqueous HF. This approach to patterning was demonstrated on ALCVD  $\text{HfO}_2$  films 2-5 nm in thickness, with ion bombardment provided by an oxygen plasma in a conventional reactive ion etching system. The observed sensitivity of  $\text{HfO}_2$  wet etch rates to film plasma treatment and annealing history additionally suggests that wet etch rates might provide a useful qualitative means for assessing unintentional damage done to metal oxide films during processing.

## ACKNOWLEDGEMENTS

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