

# IBM Research Report

## Crystallinity and Wet Etch Behavior of HfO<sub>2</sub> Films Grown by MOCVD

**Katherine L. Saenger, Cyril Cabral, Jr., Paul C. Jamison, Edward Preisler**

IBM Research Division  
Thomas J. Watson Research Center  
P.O. Box 218  
Yorktown Heights, NY 10598

**Andrew J. Kellock**  
IBM Research Division  
Almaden Research Center  
650 Harry Road  
San Jose, CA 95120-6099



Research Division

Almaden - Austin - Beijing - Haifa - India - T. J. Watson - Tokyo - Zurich

# Crystallinity and Wet Etch Behavior of HfO<sub>2</sub> Films Grown by MOCVD

Katherine L. Saenger<sup>1</sup>, Cyril Cabral, Jr.<sup>1</sup>, Paul C. Jamison<sup>1</sup>, Edward Preisler<sup>1</sup>, and Andrew J. Kellock<sup>2</sup>

<sup>1</sup>IBM Semiconductor R & D Center, IBM T.J. Watson Research Center, Yorktown Heights, NY;

<sup>2</sup>IBM Almaden Research Center, San Jose, CA.

## ABSTRACT

The crystallinity and wet etching behaviors of ultrathin (<10 nm) HfO<sub>2</sub> films grown by metal organic chemical vapor deposition (MOCVD) were examined as a function of deposition temperature, film thickness, and post-deposition annealing. Films 3 nm in thickness deposited at 400 or 500 °C were amorphous as-deposited and slowly etchable in aqueous HF; after annealing at 700 °C, the same films showed some nanocrystallinity and were impervious to HF. However, thicker films grown under the same conditions showed significant crystallinity and were impervious to HF even as-deposited. These observations, in combination with measurements on various samples etched back by an Ar<sup>+</sup> ion damage/wet etch process, suggest a film structure comprising an initially amorphous near-interface region capped with a HF-resistant crystalline upper layer. It was found that the initially amorphous near-interface region (the bottom 1-3 nm) of films grown at 500 °C can be induced to at least partially crystallize as the upper part of the film starts becoming crystalline as-deposited, but that this near-interface region remains at least partially amorphous after annealing at 700°C.

## INTRODUCTION

The expected limitations of SiO<sub>2</sub> gate dielectrics at equivalent oxide thicknesses (EOT) less than 1 nm have led to increased interest in high-k metal oxides such as HfO<sub>2</sub>. However, many structural characteristics of HfO<sub>2</sub> films remain poorly understood. For example, atomic layer deposited (ALD) HfO<sub>2</sub> films have been reported to have a crystallization temperature that increases as film thickness decreases [1], a percent crystallinity that depends on the deposition temperature [2], and a nanocrystalline or monoclinic structure depending on whether the HfO<sub>2</sub> is deposited on a chemical or thermal SiO<sub>2</sub> [3]. Film structure also affects HfO<sub>2</sub> etchability in dilute aqueous HF (dHF). While the exact reasons for this have not been completely determined, it is well established that annealed ALD HfO<sub>2</sub> films are impervious to dHF unless first subjected to some type of energetic ion bombardment [4].

In this paper we report on the crystallinity and wet etching behaviors of ultrathin (<10 nm) HfO<sub>2</sub> films grown by metal organic chemical vapor deposition (MOCVD) as a function of deposition temperature (T<sub>dep</sub>), film thickness, and post-deposition anneal (PDA) treatments. Much of the work we describe was motivated by a desire to understand an early observation: why is it that 3 nm HfO<sub>2</sub> films (deposited at 500 °C) etch in dHF while 5 nm HfO<sub>2</sub> films don't? What is the film structure and how does it vary through the thickness of the film? And how does the film structure change during growth (if at all) and with post-deposition annealing?

In the first part of this paper we show how the damage/wet etch technique demonstrated for ALD films with an O<sub>2</sub> reactive ion etch (RIE) damage step [4] also works for MOCVD films with an Ar RIE damage step. We then examine the relationship between film structure and dHF

etchability in 3 nm HfO<sub>2</sub> films as a function of annealing and show that the disappearance of etchability correlates with the appearance of a nanocrystalline phase. We next examine the relationship between film thickness and dHF etchability in as-deposited films and again find that the disappearance of etchability correlates with the onset of crystallinity. The remainder of the paper investigates film structure as a function of film thickness (as-deposited, or etched back to isolate the film's near interface region), T<sub>dep</sub>, and post-deposition annealing.

## EXPERIMENT

HfO<sub>2</sub> films were deposited by MOCVD on 100-oriented single crystal Si wafer substrates pretreated to form either a thin (0.5-1.0 nm) layer of chemical silicon dioxide or silicon oxynitride. Films were deposited to thicknesses of 3, 7, and 70 nm for T<sub>dep</sub> = 400 °C and to 3, 5, and 7 nm for T<sub>dep</sub> = 500 °C. PDA treatments were performed by rapid thermal annealing (RTA) in N<sub>2</sub> at temperatures ranging from 400 to 1000 °C, at times ranging from 30 s to 10 min. Film thicknesses (as-deposited and etched-back) were measured by ellipsometry (Rudolph FE-IIIId) and confirmed by Rutherford Backscattering Spectroscopy (RBS) with 2.3 MeV <sup>4</sup>He ions.

Etchability in dHF was primarily inferred from 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 dHF for both the etchability measurements and wet etch steps following RIE damage was typically used in a 10:1 dilution (i.e., about 5 wt% HF in H<sub>2</sub>O) at room temperature.

The Ar ion damage step for the damage/etch experiments was performed in a TCP etcher (LAM 9400), on either full 200-mm wafers or on sample pieces secured to 200-mm wafer substrates. Common to all treatments was the 5 mTorr pressure of Ar, 60 sccm flow, and 100 W top power; bottom powers ranged from 100 to 300 W (self-bias ~-60 to -160 Vdc) and times ranged from 10 to 30s. CF<sub>4</sub> sputter etching (for selected etch-back experiments) was performed on sample pieces in a 13.56 MHz parallel plate reactive ion etching system (Plasmalab μP-RIE 80) at 20 mTorr, 20 sccm flow, and ~-300 Vdc self-bias.

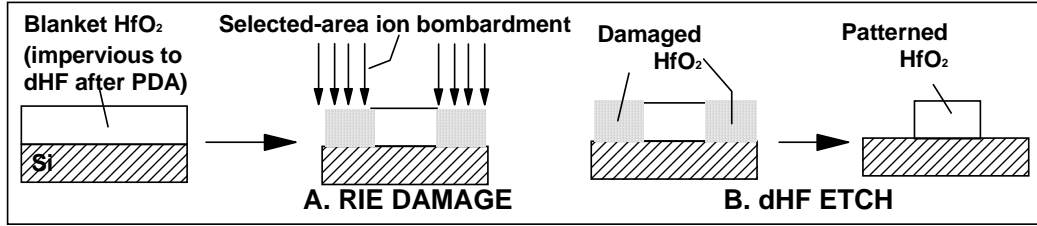
Bragg-Brentano  $\theta$ -2 $\theta$  x-ray diffraction (XRD) scans were performed with a Philips PW1729 x-ray diffractometer over the 2 $\theta$  range 20 to 55° using Cu Ka ( $\lambda$  = 0.15418 nm) typically at scan speeds 200 s/deg. Atomic force microscopy (AFM) was performed with a Digital Instruments NanoScope in the tapping mode configuration.

## RESULTS AND DISCUSSION

### New results on HfO<sub>2</sub> damage/wet etch process

Here we show that the damage/wet etch technique demonstrated for ALD films with an O<sub>2</sub> RIE damage step [4] also works for MOCVD films with an Ar RIE damage step. Fig. 1 shows a schematic of the damage/wet etch process of Ref. 4, and Table I summarizes the RBS results for the atoms/cm<sup>2</sup> of Hf and Ar in a 3 nm MOCVD HfO<sub>2</sub> film at various stages in the process. This particular film was deposited on a chemical SiO<sub>2</sub> at 500 °C and given a post-deposition anneal (PDA) at 700 °C for 30 s to make it impervious to dHF; the conditions for the Ar RIE damage step were 300 W bottom power for 10s. The data indicate that there is some Hf loss and Ar incorporation after the RIE step, that the Ar disappears after a post-RIE anneal, and that the

final wet etch step (20 s 100:1 dHF + 30 s 10:1 dHF) removes all the Hf as well as the implanted Ar.



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

**Table I.** RBS results for Hf and Ar remaining after various stages of the Ar RIE damage/wet etch process. The HfO<sub>2</sub> thickness assumes bulk density and stoichiometric oxygen content.

Stage in etching process	Hf (#/cm <sup>2</sup> )	Ar (#/cm <sup>2</sup> )	Ar at% in HfO <sub>2</sub>	HfO <sub>2</sub> (Å)
After PDA	8.5E+15	0	0	30.9
After PDA + RIE	6.5E+15	1.1E+15	5.6	23.7
After RIE + dHF	0	0	0	0
After RIE + 2nd PDA	6.5E+15	0	0	23.8

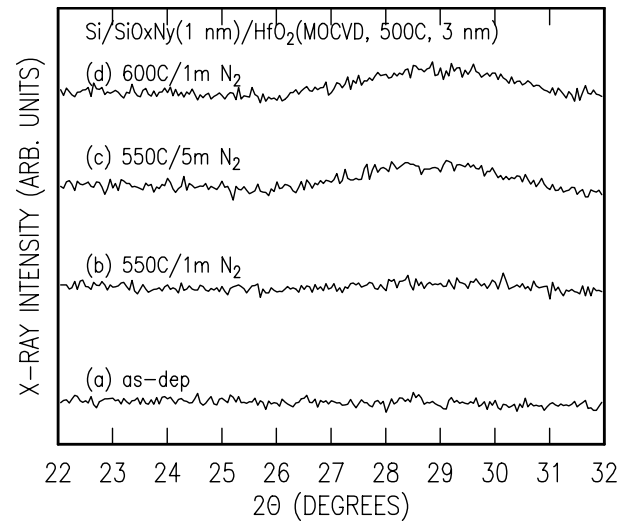
### **Crystallinity and etchability of MOCVD HfO<sub>2</sub> films vs. annealing and thickness**

We now examine the relationship between film structure (crystallinity) and dHF etchability of 3 nm HfO<sub>2</sub> films (deposited on a silicon oxynitride) as a function of annealing treatment. Fig. 2 shows XRD spectra for four annealing conditions: no anneal (a), 550 °C/1 min N<sub>2</sub> (b), 550 °C/5 min N<sub>2</sub> (c), and 600 °C/1 min N<sub>2</sub> (d). Films (a) and (b) dewet in 10:1 dHF after 25 and 35 s respectively; films (c) and (d) did not dewet after over 600 s. It is clear that the disappearance of etchability correlates with the appearance of a nanocrystalline phase.

We next examine the relationship between film thickness and etchability in as-deposited films on chemical SiO<sub>2</sub>. Table II lists the dewet times and XRD intensity in the 2θ ~ 28-30° region. Again it is clear that the disappearance of etchability correlates with the onset of crystallinity.

### **Crystallinity/structure vs. thickness and annealing**

Figs. 3 and 4 show XRD spectra for HfO<sub>2</sub> films deposited on chemical oxide as a function of thickness and PDA conditions for T<sub>dep</sub> = 400 °C (Fig. 3) and T<sub>dep</sub> = 500 °C (Fig. 4). Four



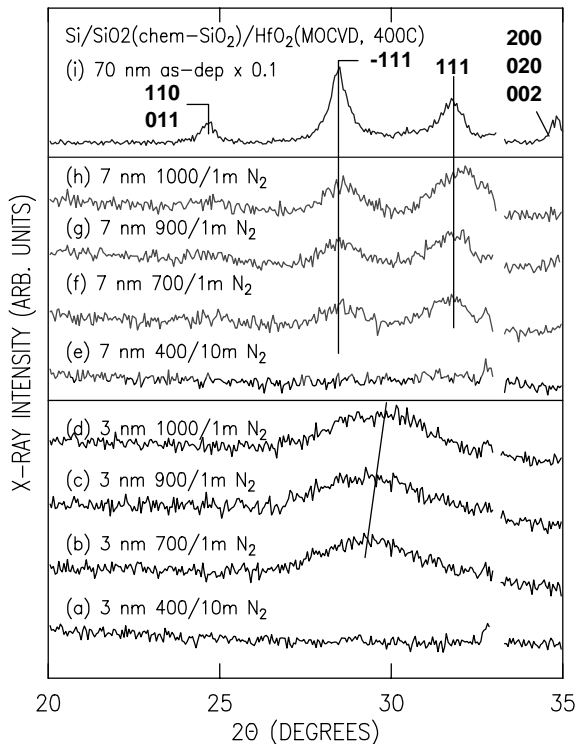
**Fig. 2.** XRD spectra of 3 nm HfO<sub>2</sub> deposited on SiO<sub>x</sub>N<sub>y</sub> at 500 °C, as a function of annealing.

characteristic spectra are seen corresponding to the following phases: amorphous (no peaks, e.g., Figs. 3a and 4a); nanocrystalline (a broad, weak peak at  $2\theta \sim 28-30^\circ$ , e.g., Fig. 3b); a single monoclinic peak (-111 at  $2\theta \sim 28.4^\circ$ ) with or without the nanocrystalline phase (e.g., Figs. 4e and h); and a random monoclinic phase (e.g., Fig. 4i).

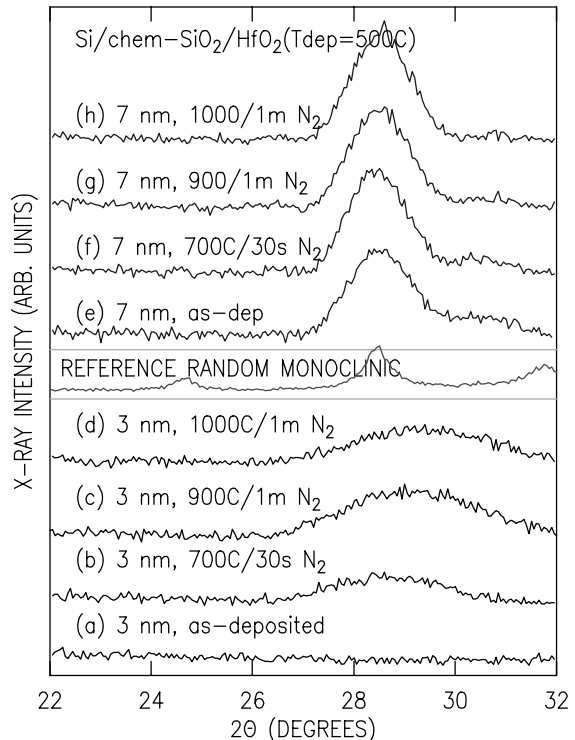
Several features of the data, summarized in Table III, are worth noting. The 3 nm films never show a clear monoclinic phase, even after at 1000 °C annealing. The nanocrystalline phase peak in the 3 nm films shifts to higher angles as annealing temperature increases, possibly indicative of film densification. The structure of the annealed 7 nm films is strongly affected by Tdep: the Tdep = 500 °C films never show more than one monoclinic peak (-111) whereas the 400 °C films show several. And finally, the nanocrystalline phase seen in the as-deposited 7 nm Tdep = 500 °C films gradually disappears as the PDA temperature increases from 700 to 1000 °C.

**Table II.** Etchability vs. HfO<sub>2</sub> film thickness for as-deposited MOCVD films on chemical SiO<sub>2</sub>.

Tdep, °C	Film thickness (nm)	Dewet time (s) in 10:1 dHF	XRD peak intensity at 28-29° (cps)
400	3	15-18	0
400	7	33-36	0
400	70	Not etchable	370
500	3	31	0
500	5	Not etchable	28
500	7	Not etchable	67



**Fig. 3.** XRD spectra of Tdep = 400 °C films as a function of thickness and annealing conditions.



**Fig. 4.** XRD spectra of Tdep = 500 °C films as a function of thickness and annealing conditions.

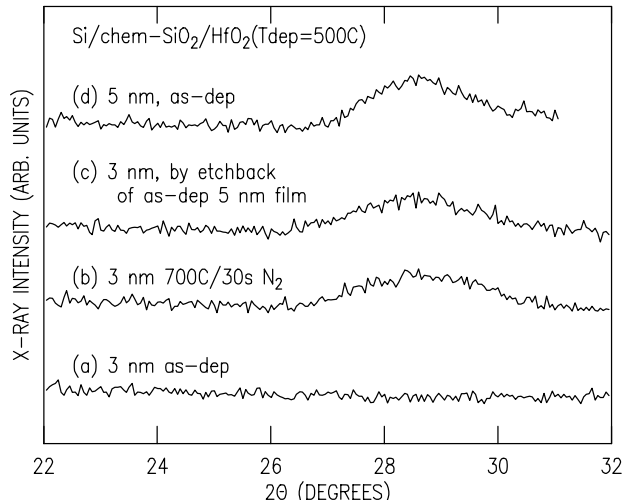
**Table III.** Summary of XRD results for HfO<sub>2</sub> films as a function of Tdep, film thickness and PDA treatment.

Tdep, °C	Film thick, nm	As-deposited	After 700 °C PDA	After 1000 °C PDA
400	3	Amorphous	Nanocrystalline	Nanocrystalline
400	7	Amorphous	Mono-random	Mono-random
400	70	Mono-random	Mono-random	Mono-random
500	3	Amorphous	Nanocrystalline	Nanocrystalline
500	5	Mono (-111) + Nano	Mono (-111) + Nano	Mono (-111) + Nano
500	7	Mono (-111) + Nano	Mono (-111) + Nano	Mono (-111)

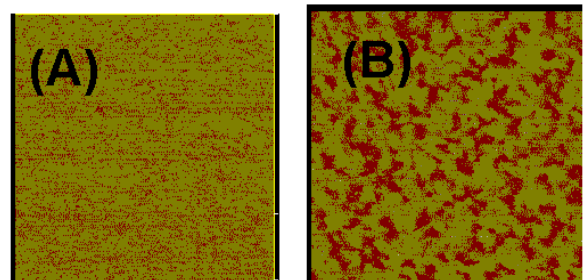
### Etch-back results and models

To gain a better understanding of film structure, selected films were examined after etch-back to the near interface region (bottom 1-3 nm). In a first experiment, an as-deposited 5 nm HfO<sub>2</sub> film (Tdep = 500°C) was etched back to 3 nm by Ar RIE (300 W bottom power for 10s)/wet etch (30 s 10:1 dHF) and found to have the same nanocrystalline structure seen in 3 nm films only after annealing (Fig. 5). AFM showed the etched-back film to be smooth, implying that the etch-back process ended on a relatively homogeneous crystalline layer and that the already-deposited near-interface region of the film at least partially crystallized while the upper part of the film was growing.

In contrast, 3 nm films (also with Tdep = 500 °C) annealed at 700 °C and then etched back to 1 nm by Ar RIE (100 W bottom power for 30 s)/wet etch (120 s 10:1 dHF) were very rough. Fig. 6 shows AFM data before and after the etch-back process, and Fig. 7 show a schematic of the film structure at various stages of the etching process. These results suggest that



**Fig. 5.** XRD spectra for directly grown and etched-back HfO<sub>2</sub> films 3 nm in thickness (Tdep = 500 °C). The as-deposited 5 nm and annealed 3 nm films are included for reference.



**Fig. 6.** AFM images (1 μm<sup>2</sup> area) of annealed 3 nm films (Tdep = 500 °C) before (A) and after (B) thinning to 1 nm by an Ar RIE damage/wet etch process. The rms (peak-to-valley) roughness is 0.22 (0.62) nm for A and 0.47 (2.0) nm for B.

residual (dHF-etchable) amorphous regions remain in the near-interface region even after annealing.

The near-interface region of the  $T_{dep} = 400\text{ }^{\circ}\text{C}$  films does not appear to crystallize during growth. XRD of 70 nm films etched-back by  $\text{CF}_4$  RIE (Fig. 8) showed a clear monoclinic structure for films thinned to 14 nm thick films, but no peaks at all for films thinned to 7 nm.

## SUMMARY

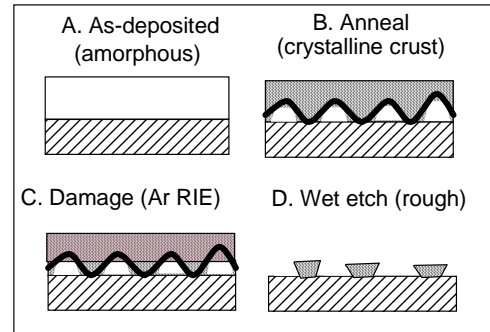
The crystallinity and wet etching behaviors of ultrathin (<10 nm)  $\text{HfO}_2$  films grown by metal organic chemical vapor deposition (MOCVD) were examined as a function of deposition temperature, film thickness, and post-deposition annealing. Film texture was found to have a strong dependence on  $T_{dep}$ : after annealing at  $1000\text{ }^{\circ}\text{C}$ , 7 nm films were random monoclinic for  $T_{dep} = 400\text{ }^{\circ}\text{C}$  and (-111)-textured monoclinic for  $T_{dep} = 500\text{ }^{\circ}\text{C}$ . For deposition at  $500\text{ }^{\circ}\text{C}$ , films thicker than a threshold thickness of  $\sim 5\text{ nm}$  have a "crystalline" top layer that is impervious to etching in dHF. Continued growth above this thickness can induce some crystallization in the bottom 3 nm of the already-grown film, though residual amorphous regions in this near interface region can remain even after annealing at  $700\text{ }^{\circ}\text{C}$ , based on the roughness of annealed 3 nm films etched back to 1 nm by a combination of Ar ion damage plus dHF wet etching.

## ACKNOWLEDGEMENTS

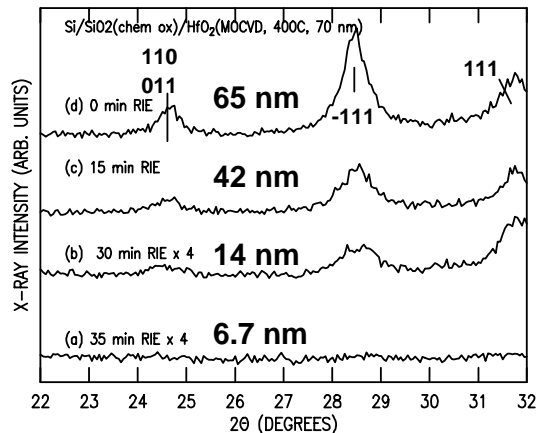
Keith R. Milkove and Edmund M. Sikorski are thanked for help with the Ar RIE.

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**Fig. 7.** Structure schematic of 3 nm  $T_{dep} = 500\text{ }^{\circ}\text{C}$  film during damage/wet etch.



**Fig. 8.** XRD spectra of as-deposited 70 nm films after thinning by  $\text{CF}_4$  RIE ( $T_{dep} = 400\text{ }^{\circ}\text{C}$ ).