

Etching of zirconium oxide, hafnium oxide, and hafnium silicates in dilute hydrofluoric acid solutions

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Oxides and silicates of zirconium and hafnium are actively being considered and tested to replace SiO_2 as the gate material. Though these materials have the high-dielectric constant ($k \sim 20\text{--}25$) needed to provide a larger equivalent oxide thickness, they are very refractory and difficult to etch by wet and dry methods. In this paper, work done on wet etching of ZrO_2 , HfO_2 , and HfSi_xO_y in dilute hydrofluoric acid (HF) solutions is presented and discussed. Experiments were done on various high- k films deposited by metalorganic chemical vapor deposition. It was found that the as-deposited high- k films can be dissolved with a good selectivity over SiO_2 in dilute HF solutions, but heat-treated high- k films are difficult to etch with good selectivity over SiO_2 under the same conditions.

I. INTRODUCTION

The primary means by which the semiconductor industry has achieved unprecedented gains in productivity and performance is by device scaling. However, continued downscaling of feature sizes is putting great demands on some existing materials such as SiO_2 and has spurred interest in the introduction of new materials. In no area is this issue more clear or urgent than in the fabrication of metal oxide semiconductor devices. Here, the challenge is to reduce the gate oxide (currently SiO_2) thickness to less than 1.5 nm without suffering from high leakage current.¹ The use of a material with a dielectric constant (k) higher than conventional SiO_2 as a gate oxide would allow thicker films to be used in the fabrication of devices.² For example, an 8.6-nm layer of ZrO_2 of dielectric constant $k \sim 23$ is equivalent to a 1.5-nm layer of SiO_2 of dielectric constant $k \sim 4$.

Many high- k materials have been investigated for gate dielectric application. High- k materials that are thermally stable in contact with Si are the most attractive. Oxides and silicates of rare earth metals Zr and Hf, such as HfO_2 , ZrO_2 , and Hf silicates, fall in this category. Both HfO_2 and ZrO_2 have similar material characteristics; have moderate dielectric constants of approximately 20–25, as well as low lattice mismatch and good thermal expansion matching with silicon.^{3–7} One of the drawbacks with HfO_2 and ZrO_2 and their silicates is that they are difficult to etch due to their refractory nature.

For the deposition of ZrO_2 and HfO_2 films, both physical vapor deposition (sputtering) and chemical vapor

deposition (CVD) [metalorganic chemical vapor deposition (MOCVD) and ALCVD] techniques are used. Due to the fact that sputtering results in unwanted interfacial states, CVD techniques are more commonly used. In the MOCVD technique, organic precursors such as zirconium/hafnium trifluoroacetylacetone and zirconium/hafnium *t*-butoxide are used. The films deposited by ALCVD technique generally use inorganic precursors such as chloride and nitrate salts of Zr and Hf. The films deposited by ALCVD technique are denser than those deposited by MOCVD technique.⁸

One of the key processing steps in the fabrication of gates is the selective removal of the gate oxide from unwanted areas. Both dry- and wet-etching methods have been attempted for this purpose. Since dry etching methods appear to damage the underlying silicon, wet etching has recently received much attention.⁹

Wet etching of HfO_2 , ZrO_2 , and their silicates has been attempted in many chemicals such as hydrofluoric acid (HF), HCl, $\text{HCl-H}_2\text{O}_2$, H_3PO_4 , H_2SO_4 , and so forth. Of the chemicals investigated, HF appears to be the promising candidate. It has been found¹⁰ possible to etch sputter-deposited ZrO_2 films at a rate of 7 Å/min and 6 Å/min in 200:1 HF and 100:1 HF solutions, respectively, at 21 °C. ALCVD ZrO_2 films are amenable to etching in 10:1 HF solutions at a rate of 16.7 Å/min in a spin process tool.¹¹ As-deposited HfO_2 films having an etch rate of 80 Å/min in 10:1 HF solution become nearly unetchable¹² when subjected to annealing at 700 °C. It has also been reported that as-deposited HfSi_xO_y films are harder to etch in dilute HF solutions containing 1% HF, whereas the same films etch at a much faster rate in 49% HF solutions.¹³ Selective etching of heat-treated HfSi_xO_y films was carried out in dilute fluoride-based solutions at

80 °C. Etch selectivity of 20:1 over TEOS was obtained for hafnium silicate film containing 40% SiO₂. Decrease in etch rate of silicate films with increasing SiO₂ content was also observed.¹⁴

Semiaqueous formulations containing an organic solvent, HF (25 wt%), and small amounts of water have been used to etch as-deposited and heat-treated MOCVD HfO₂ films.⁹ Measured etch rates vary from 2.1 Å/min to 14.3 Å/min for as-deposited films and from 1.7 Å/min to 10 Å/min for heat-treated films. Because HF also etches silicon dioxide, it is often difficult to achieve selectivity between HfO₂ and SiO₂. The best etch rate selectivity (etch rate of HfO₂/etch rate of SiO₂) that was obtained was in the neighborhood of 0.3. Ion-implantation has been used to enhance the wet chemical etching of HfO₂ films in heated H₃PO₄ and H₂SO₄ solution. An implant dose of 10¹⁵ atoms/cm² increased the etch rate of HfO₂ in phosphoric acid at 155 °C from 0.45 Å/min to 1.5 Å/min.¹⁵ It has also been reported that low energy ion bombardment improves the etching of annealed HfO₂ films in aqueous HF solutions.¹²

The main drawback with using concentrated HF solutions for the dissolution of zirconium and hafnium oxides is that selectivity with respect to SiO₂ is compromised at these concentrations. The semiconductor industry is willing to accept etch rates as low as 1 Å/min provided the etch process is highly selective to the high-*k* over SiO₂. The objective of this work was to investigate the dissolution of ZrO₂, HfO₂ and Hf-silicate films in *very dilute* HF solutions that could provide etch rates of at least 1 Å/min as well as good selectivity (selectivity ratio of at least 2:1) with respect to SiO₂.

II. EXPERIMENTAL

A. Theoretical work

Pourbaix, solubility, and speciation diagrams were constructed using the commercially available STABCAL software.¹⁶ STABCAL performs stability calculations for an aqueous system under equilibrium conditions. Input to the software included the free energy of formation of various Zr and Hf compounds and concentration of fluoride.

To understand the etching behavior of ZrO₂ and HfO₂ in aqueous hydrofluoric acid solution, Pourbaix diagrams were constructed for Zr-F-H₂O and Hf-F-H₂O systems. The percentage of zirconium and hafnium present in dissolved form when 1 L of fluoride containing aqueous solution is equilibrated with 1.31E-03 gm ZrO₂ (or 1.41E-03 gm HfO₂) was determined. Complete solubility of Zr and Hf would yield a solution concentration of 1.096E-05 M and 6.72E-06 M, respectively. The concentration of dissolved Zr (or Hf) in solution was calculated as a function of pH.

Speciation diagrams for zirconium and hafnium in aqueous solutions were also constructed for the same total amount of Zr and Hf as those used for solubility calculations. Speciation diagrams were constructed for two cases, that is, considering only aqueous species and considering both aqueous and solid species.

B. Experimental work

Dissolution experiments were done using electronic (ppb) grade HF (49%). High-*k* films deposited by MOCVD technique using alkoxide-based precursors were kindly supplied by International Sematech. The deposition temperature, initial thickness, and refractive index of these films are tabulated in Table I. All the high-*k* films were determined amorphous by electron diffraction. Films, unless stated otherwise, were not subjected to postdeposition annealing. Heat-treated ZrO₂ films were prepared by processing as-deposited films through a poly furnace at 550 °C for 2 h under vacuum with nitrogen.

Dissolution of ZrO₂, HfO₂, HfSi_xO_y, and TEOS (silica films made from tetraethyl ortho silicate) in HF was studied in PFA (perfluoroalkoxy) beakers. Samples of size 2 cm × 2 cm were suspended into 250 mL of solution maintained at ambient conditions. At the end of the dissolution experiments, samples were removed, rinsed with DI, dried with N₂, and characterized for thickness with a Gaertner Ellispometer (Model L116C) using a He/Ne laser of wavelength 632 nm at an incident angle of 70°. Thickness measurement was done at five different locations on each sample prior to and after the dissolution experiments.

III. RESULTS AND DISCUSSION

A. Pourbaix diagrams

The influence of fluoride ions on the stability of ZrO₂ and HfO₂ in aqueous solution was analyzed through the construction of Pourbaix (potential-pH) diagrams for the Zr-F-H₂O and Hf-F-H₂O systems. As mentioned in Sec. II(A), the construction of these diagrams was carried out using the STABCAL software that is commercially

TABLE I. Refractive index, initial thickness, and deposition temperature of various high-*k* films used in this work.

	Refractive index (n)	Thickness (Å)	Deposition temperature (°C)
ZrO ₂	2.13	760 ± 40	485
HfO ₂	1.9	460 ± 15	485
HfSiO _x (30%) ^a	2.08	198 ± 20	525
HfSiO _x (60%) ^a	1.61	262 ± 20	525
HfSiO _x (80%) ^a	1.725	217 ± 10	650
TEOS	1.46	3000 ± 100	400

^a mol% of SiO₂.

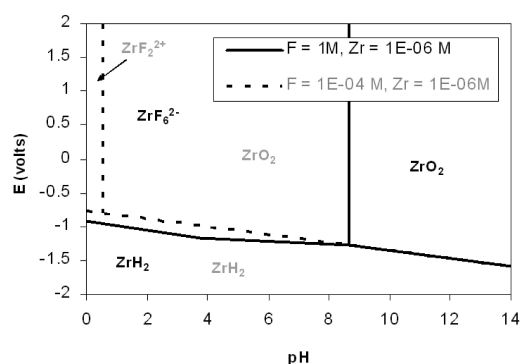


FIG. 1. Pourbaix diagram for Zr-F-H₂O system (dotted line/light gray font: low F).

available. Figure 1 presents Pourbaix diagrams for Zr-F-H₂O system for a dissolved zirconium concentration of 10^{-6} M (~100 ppb) at two different fluoride concentrations of 10^{-4} and 1 M. In acidic solutions containing 1 M fluoride characterized by a redox potential more positive than -1 volt, ZrO₂(s) is only stable at pH values greater than 8. Zirconium oxide should dissolve as an aqueous fluoride complex (ZrF₆²⁻) in the solution if the pH is reduced to below 8, at the same solution potential. At a pH of 3 and solution potential of approximately 400 mV used in the etching experiments, the dissolution of ZrO₂ to ZrF₆²⁻ is thermodynamically favorable. Noting that the light gray font in the figures depicts lower fluoride concentration, the pH range of solubility may be seen to decrease as the fluoride concentration is lowered to 10^{-4} M. At the lower fluoride concentration, the pH has to be lowered to below 1 to dissolve zirconia in the form of cationic ZrF₂²⁺.

To study the effect of fluoride on the stability of HfO₂ in aqueous solution, Pourbaix diagrams (Fig. 2) were constructed for two different cases: 1 M fluoride and 10^{-6} M hafnium, and 0.001 M fluoride and 10^{-6} M hafnium. HfO₂ can be converted to solid HfF₄ using high-concentration fluoride solutions at acidic pH values characterized by a solution potential more positive than -1.5 volt. For example, at a fluoride concentration of

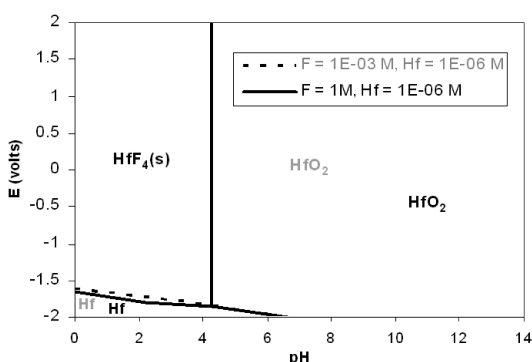


FIG. 2. Pourbaix diagram for Hf-F-H₂O system (dotted line/light gray: low F). (Note: 1 M of F⁻ = 1.7%.)

1 M, HfF₄(s) is likely to form at pH values below 4 when the dissolved Hf concentration in solution is 10^{-6} M (or 200 ppb). If the fluoride concentration is lowered to 10^{-3} M in solution, the stability of HfO₂ increases, and no complexation by fluoride is predicted. (Note: 1 ppb Hf = 5.602×10^{-9} M)

Hafnium silicate films, HfSi_xO_y, appear to be the leading candidates for high-*k* applications. Unfortunately, no thermodynamic data is available for these silicates, and hence construction of Pourbaix diagrams for hafnium silicate-water system was not possible.

B. Solubility diagrams

The solubility diagram for zirconium and hafnium oxides is shown in Fig. 3. In 0.001 M fluoride solutions, almost all Zr (10^{-5} M) can be dissolved at pH below 5. The solubility of Hf oxide in the same solution is calculated to be rather low, approximately 10^{-8} M. Even though Hf forms a number of aqueous fluoride complexes, it also forms an insoluble HfF₄, which reduces its solubility. Increasing the fluoride concentration to 0.1 M does not result in any significant change in solubility of ZrO₂ and HfO₂.

C. Speciation diagrams

Speciation calculations were done for Zr-F-H₂O and Hf-F-H₂O systems, and these are shown in Figs. 4(a) and 4(b). In these calculations, the fluoride concentration was fixed at 0.001 M. If only aqueous Zr species are considered, then it can be seen from Fig. 4(a) that above pH of 6, only neutral hydroxide species Zr(OH)₄ is thermodynamically stable. If the pH is lowered below 6, cationic and anionic Zr fluoride complexes become more dominant. For example, at pH 4, about 90% of Zr would exist in form of ZrF₆²⁻ species. If both aqueous and solid species are considered, soluble fluoride species are predicted to form only below pH 4 [Fig. 4(b)].

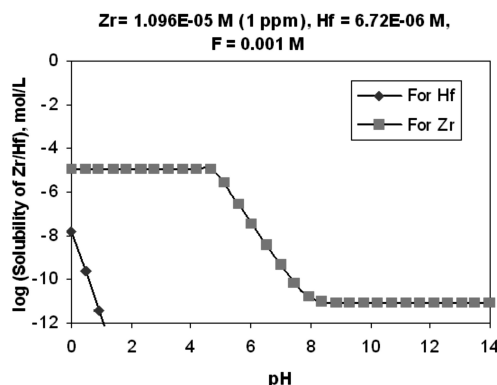


FIG. 3. Estimated solubility of ZrO₂ and HfO₂ in 0.001 M fluoride solution. (Note: 10^{-5} M of Zr and 10^{-6} M of Hf in solution indicate 100% solubility; 1 M of F⁻ = 1.7%.)

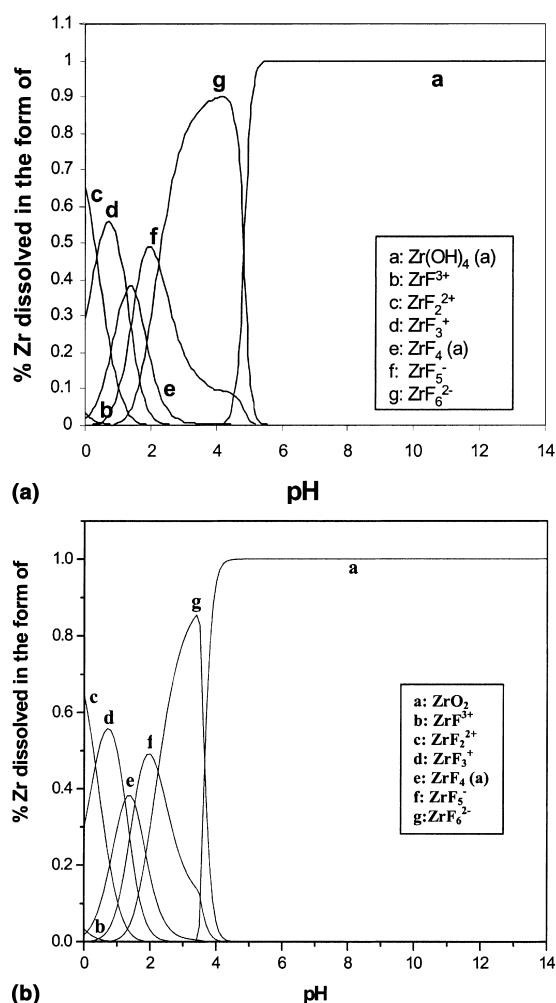


FIG. 4. (a) Speciation diagram for Zr-F-H₂O system considering only aqueous species. (b) Speciation diagram for Zr-F-H₂O system considering both aqueous and solid species.

The calculations were repeated by increasing the fluoride concentration from 0.001 M to 0.1 M. If only aqueous Zr species are considered, then below pH of 8, both cationic and anionic Zr fluoride complexes become dominant. If both aqueous and solid species are considered, soluble fluoride species are predicted to form below pH 7.

In the case of Hf, considering only aqueous Hf species in the calculations, it can be seen from Fig. 5(a) the anionic hydroxide $\text{Hf}(\text{OH})_5^-$ is the dominant species above pH 9. At pH values below 9, both cationic hydroxide species and fluoride species dominate. If both aqueous and solid species are considered in the calculations, solid HfO_2 becomes the dominant species in the entire pH range.

The same calculations were repeated by increasing the fluoride concentration from 0.001 M to 0.1 M. As shown in Fig. 5(b), in solutions containing 0.1 M fluoride, if the pH is maintained below 3, then a neutral solid species

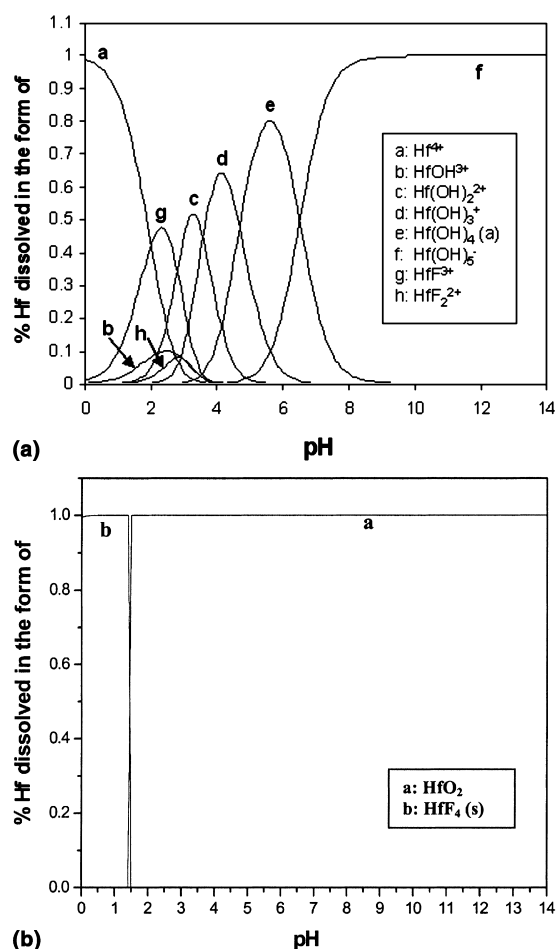


FIG. 5. (a) Speciation diagram for Hf-F-H₂O system considering only aqueous species. (b) Speciation diagram for Hf-F-H₂O system considering both aqueous and solid species.

HfF_4 can form, which can decrease the solubility of HfO_2 in fluoride solutions.

D. Etching results

1. MOCVD ZrO_2 and HfO_2

The first series of experiments were done to characterize the kinetics of dissolution of ZrO_2 and HfO_2 . Four different time intervals, that is, 10 min, 20 min, 30 min, and 60 min, and three different concentrations of HF, namely, 0.001%, 0.005%, and 0.01%, were chosen. The results are as shown in Figs. 6 and 7, respectively.

It can be seen that both ZrO_2 and HfO_2 dissolve at a constant rate at all concentrations of HF investigated. The higher the HF concentration, higher is the dissolution rate. This can be attributed to decrease in pH (from 3.6 for 0.001% HF solutions to approximately 3 for 0.01% HF solution) as well as increase in fluoride concentration. At a HF concentration of 0.01%, ZrO_2 and HfO_2 dissolve at a rate of 7.7 Å/min and 2.4 Å/min, respectively.

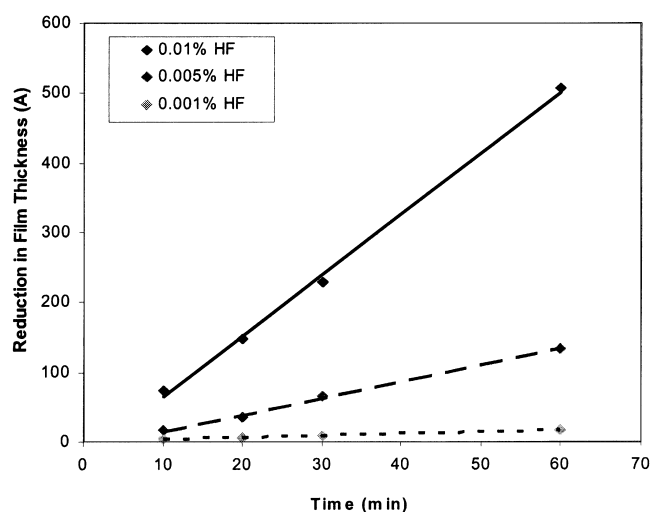


FIG. 6. Kinetics of dissolution of as-deposited MOCVD zirconium dioxide in HF solutions of different concentration.

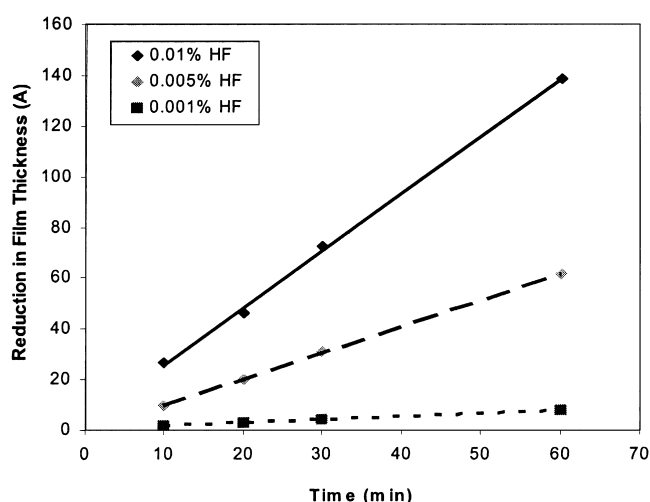


FIG. 7. Kinetics of dissolution of as-deposited MOCVD hafnium dioxide in HF solutions.

An attempt was made to determine the order of dissolution reaction for ZrO_2 and HfO_2 with respect to HF concentration. Log-log plots of rate of change of thickness of films versus concentration of HF are shown in Fig. 8. From the plots, the reaction order (with respect to free HF concentration) was calculated to be 1.1 and 1, respectively, for the dissolution of ZrO_2 and HfO_2 . The rate equations for the dissolution, in terms of film thickness X , can be represented as follows:

$$\frac{dX}{dt} = -11357[\text{HF}]^{1.1} \quad \text{\AA}/\text{min M}^{1.1} \quad \text{for } \text{ZrO}_2$$

$$\frac{dX}{dt} = -1495[\text{HF}]^1 \quad \text{\AA}/\text{min M}^1 \quad \text{for } \text{HfO}_2$$

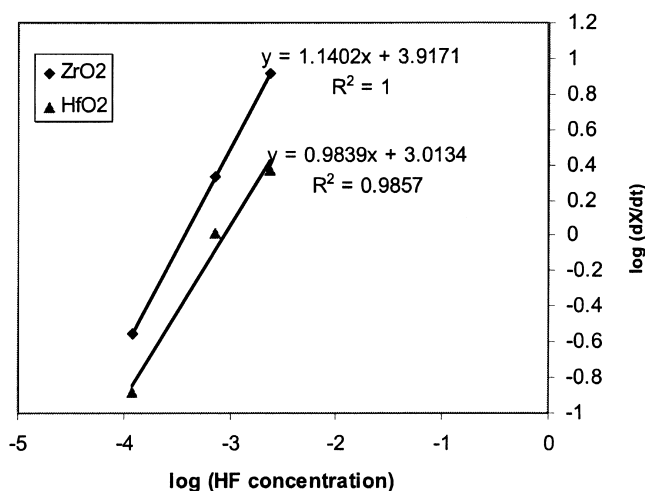


FIG. 8. Removal rate of ZrO_2 and HfO_2 films as a function of (free) HF concentration (in mol/L).

2. Hafnium silicates

The dissolution of MOCVD Hf-silicates was investigated in 0.01% HF solution, and the results obtained are displayed in Fig. 9. For comparison purposes, the results for HfO_2 and TEOS (SiO_2) are also displayed in this figure.

It may be seen that the dissolution of all the films is very linear with respect to time. As the amount of SiO_2 increases in the silicate films, the dissolution rate in HF decreases significantly. The etch rates are 1.7 $\text{\AA}/\text{min}$, 1.5 $\text{\AA}/\text{min}$, and 0.5 $\text{\AA}/\text{min}$ for HfO_2 films containing 30%, 60%, and 80% silica, respectively. The etch rate of TEOS ($\sim 0.1 \text{\AA}/\text{min}$) is lower than that of HfO_2 and hafnium silicates. It is apparent that the dissolution rates follow the order $\text{ZrO}_2 > \text{HfO}_2 > \text{HfSiOx (30\%)} > \text{HfSiOx (60\%)} > \text{HfSiOx (80\%)} > \text{TEOS}$. Etching selectivity values, calculated as the etch rate of high- k film divided by the etch rate of TEOS, are listed in Table II. It is clear

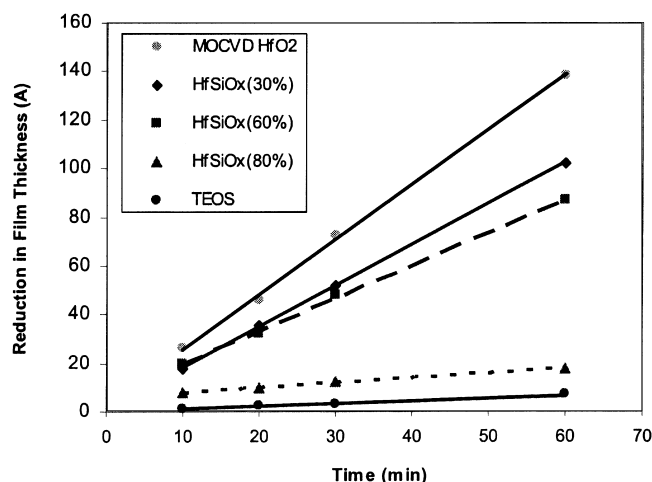


FIG. 9. Dissolution of hafnium silicates (containing different mole percent SiO_2) in 0.01% HF solutions.

TABLE II. Selective etching of MOCVD high-*k* films in different HF solutions.

Solution	Etching time (min)	Material					
		MOCVD ZrO ₂		MOCVD HfO ₂		MOCVD HfSiOx (80%)	
		ER_{ZrO_2} (Å/min)	ER_{ZrO_2} ER_{TEOS}	ER_{HfO_2} (Å/min)	ER_{HfO_2} ER_{TEOS}	$ER_{HfSiOx (80\%)}$ (Å/min)	$ER_{HfSiOx (80\%)}$ ER_{TEOS}
0.01% HF	60	8.45	60	2.31	16.5	0.3	2
0.05% HF	20	37.4	10	19.4	5.4	6.3	1.7
0.1% HF	7.5	99.3	7.5	44	3.3	23.5	1.8
0.5% HF	1.5	449	5	178	2	141	1.5

MOCVD, metalorganic chemical vapor deposition; ER, etch rate.

that zirconium oxide, hafnium oxide, and hafnium silicate with low silica content can be selectively etched with respect to TEOS in this dilute HF solution. Even though the deposition temperatures of the different silicate films were slightly different, transmission electron microscopic characterization of the as-deposited films indicated that they were all amorphous. Hence, the decrease in etch rate with increase in SiO₂ content cannot be attributed to difference in crystallinity.

E. Selectivity

The selective dissolution of high-*k* films was further investigated in dilute HF solutions of different concentration, that is, 0.01%, 0.05%, 0.1%, and 0.5%. Table II lists the etch rate selectivity ratio, defined as etch rate of high-*k* film/etch rate of TEOS, in different HF solutions. Because the etch rate increased at higher HF concentrations, the selectivity ratio calculated for shorter etch times is listed for these higher concentrations. It is apparent from Table II that selective etching of ZrO₂ and HfO₂ films can be achieved in 0.05% and 0.01% HF solutions, even for longer etching times. In 0.5% HF solution, selective dissolution of ZrO₂ (selectivity ratio of 5) can be achieved, provided the etch time is kept short (<2 min). In case of HfSiOx (80%) films, good selectivity can be obtained only in 0.01% HF solution.

F. Heat-treated ZrO₂

During gate stack fabrication, gate oxide is exposed to temperatures varying from 400 °C to 900 °C used for dopant activation of polysilicon electrode. To form gate stack, the unwanted oxide needs to be etched away. Hence, it is important to study the wet-etching behavior of heat-treated high-*k* films. It has been reported in the literature that heat-treated high-*k* films are difficult to etch by wet techniques.⁶

Preliminary investigations on etching behavior of heat-treated MOCVD ZrO₂ films carried out at room temperature and at HF concentrations varying from 0.01 to 1% gave very low etch rates (<0.1 Å/min). Thus, subsequent investigations were carried out at 60 °C in two solutions containing 0.1% HF and 0.01% HF. The results

are tabulated in Table III along with the etch rates of TEOS films. At 60 °C, the etch rate of heat-treated ZrO₂ films in 0.1% HF is 3.3 Å/min, whereas in 0.01% HF solutions, the etch rate is only 0.3 Å/min.

It is apparent from Table III that a significant increase in etch rate of heat-treated ZrO₂ films may be obtained by increasing the temperature and HF concentration, but unfortunately TEOS films etch at much faster rate than heat-treated ZrO₂ films under similar conditions, resulting in poor selectivity between TEOS and heat-treated ZrO₂ films.

G. Mechanism of ZrO₂/HfO₂ dissolution in HF solutions

Based on the speciation plots and Pourbaix diagrams for the Zr–F–H₂O and Hf–F–H₂O systems, the dissolution of ZrO₂ and HfO₂ films in HF solutions is most likely to take place through the formation of fluoride complexes. Depending on the pH, the complexes could be cationic [ZrF₂²⁺, HfF₂²⁺] or anionic in nature [ZrF₆²⁻, HfF₆²⁻]. In case of HfO₂, the formation of HfF₄, a solid fluoride, is also possible. If this solid fluoride is to form on the HfO₂ film, the dissolution rate may be expected to decrease with time. Because no such decrease in dissolution rate is indicated in the experimental results, it is very plausible that the formation of insoluble HfF₄, if any, occurs in the bulk solution.

The measured selectivity in etch rates between ZrO₂ and SiO₂ and between HfO₂ and SiO₂ in very dilute HF solutions merits an explanation. The pH value and the

TABLE III. Effect of temperature on the etch rate of heat-treated ZrO₂ films and TEOS in HF solutions (etching time = 60 min).

Solution	Temperature (°C)	Heat-treated		$ER_{HT ZrO_2}$ ER_{TEOS}
		ZrO ₂ etch rate (Å/min)	TEOS etch rate (Å/min)	
0.1% HF	25	0.11	13.3	0.008
	60	3.3	25.9	0.13
0.01% HF	25	0.06	0.11	0.54
	60	0.3	0.41	0.7

ER, etch rate.

proportion of various fluoride species in 0.01, 0.05, 0.1, and 0.5% HF solutions are shown in Table IV. From the table it may be noted that in very dilute HF solutions (such as 0.01% HF), most of fluoride is in form of free HF and F^- , and in solutions containing higher fluoride concentration (such as 0.5% HF), free HF and H_2F_2 species dominate. Another interesting observation that can be made is that the concentration of HF_2^- species is very small in all fluoride solutions considered.

Knotter¹⁷ has reported that the first step in dissolution of SiO_2 in HF solutions is elimination of OH^- or H_2O from surface silanol group followed by reaction of nucleophiles (HF_2^- , H_2F_2). This is schematically shown in Fig. 10. Both the HF_2^- and H_2F_2 can assist in elimination of OH^- by coordinating FH part with HO part of the silanol group. This then brings the second F atom closer to Si atom. Monofluorides such as HF and F^- are not able to do this. Hence, in solutions containing a higher amount of HF_2^- or H_2F_2 , the etch rate of SiO_2 will be higher.

The above mechanism can be used in explaining the selectivity results. In dilute HF solutions, as mentioned above, only free HF and F^- are dominant species and hence the etch rate of SiO_2 is lower. In solutions of high fluoride concentration, along with free HF, H_2F_2 is present. This can help in elimination of OH^- from the surface silanol group and subsequently in etching of SiO_2 . Thus, the etch rate of SiO_2 is higher.

Like SiO_2 , the etch rate of ZrO_2 increases with increasing HF concentration. However, at low HF concentrations, the etch rate of ZrO_2 is much higher than that of SiO_2 . One plausible reason¹⁸ for this is the slightly weaker acidity of the $-OH$ sites on the surface of ZrO_2 as compared to those on SiO_2 . The pK_a of $Zr-OH$ sites is roughly 6.7, whereas that of $Si-OH$ sites is around 3.7. In very dilute HF solutions used in this study, pH values were close to 3, and hence the surface of ZrO_2 would have a higher proportion of $-OH$ sites than SiO_2 . Because, as discussed in the preceding paragraph, the interaction of $-OH$ sites with HF is critical for the initiation of the etching of oxides, ZrO_2 may be expected to etch faster than SiO_2 in dilute HF solutions.

TABLE IV. Proportion of various fluoride species in different HF solutions used for experiments.

Concentration of HF solution			Fraction of total fluoride present as			
(%)	(M)	pH	[HF] free	[F^-]	[HF_2^-]	[H_2F_2]
0.01%	5.87×10^{-3}	2.8	0.6916	0.284	0.0045	0.0076
0.05%	2.93×10^{-2}	2.4	0.7585	0.128	0.0112	0.0455
0.1%	5.87×10^{-2}	2.2	0.7218	0.0845	0.0142	0.0826
0.5%	2.94×10^{-1}	1.9	0.5161	0.0274	0.0164	0.2114

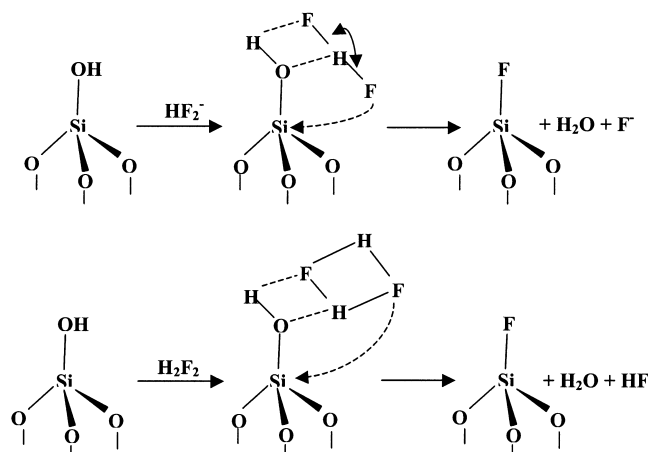
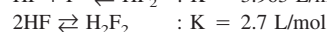
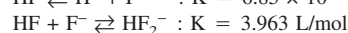
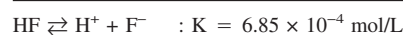


FIG. 10. Schematic showing reaction of HF_2^- and H_2F_2 assisted OH^- elimination for $-Si-OH$ group (after D.M. Knotter).

IV. CONCLUSIONS

It is possible to dissolve MOCVD ZrO_2 , HfO_2 , and HF-silicates in low concentrations of HF and at ambient conditions. An 0.005% HF solution can be used to get an etch rate of approximately 1 Å/min for both ZrO_2 and HfO_2 films. In 0.01% HF solutions, good etch selectivity can be obtained between high- k films and TEOS. In 0.5% HF solutions, good selectivity can be obtained provided very short etch times are used.

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