

Selective Removal of High- k Gate Dielectrics

D. SHAMIRYAN, M. BAKLANOV, M. CLAES,
W. BOULLART, AND V. PARASCHIV

IMEC, Leuven, Belgium

Continuous downscaling of integrated circuits brought an end to the era of SiO₂. In gate dielectrics, it is being replaced by materials with high dielectric constant, so-called high- k dielectrics. One of the challenges in the integration of the high- k material is removal of those materials selectively over the substrate. This work is one of the first attempts to review current state of the art of the high- k removal. Two main approaches are discussed: dry (plasma) removal and wet removal. First, the fundamentals and limitations of both approaches are presented, then an overview of the existing experimental data is given. It is concluded that the best results could be obtained by combining the dry and wet approaches.

Keywords High- k dielectrics; High- k etching; Plasma etching; Wet etching

Introduction

The excellent dielectric properties of SiO₂ have aided the evolution of microelectronics for several decades. Thermally grown SiO₂ has a low number of defects, high resistivity, large band gap, and excellent dielectric strength and provides a stable interface with Si.

However, continuous downscaling of the semiconductor devices constantly brings new challenges to semiconductor device manufacturing. The dimensions of the semiconductor devices follow a trend known as Moore's law that states that the number of transistors that can be inexpensively placed on an integrated circuit increases exponentially, doubling approximately every two years (Moore, 1965). As the dimensions are scaled down, conventional materials cannot comply anymore with the stringent requirements of scaled devices, and new materials must be investigated and integrated into the existing processing technology.

Scaling of the gate dielectric thickness became one of the main issues recently. Silicon dioxide has reached its limits for thinning down. Thin (<1.2 nm) SiO₂ suffers from increased gate leakage, reduced reliability, and increased dopant diffusion. It was shown that scaling SiO₂ thickness below 1.0–1.2 nm does not result in increase of transistor drive current (Timp et al., 1997).

In order to alleviate further downscaling of semiconductor devices, SiO₂ is currently being replaced with materials of high dielectric constant, so-called high- k dielectrics (Wilk et al., 2001). High- k dielectrics are mostly metal oxides with k value

Address correspondence to D. Shamiryan, IMEC, Kapeldreef 75, Leuven 3001, Belgium.
E-mail: shamir@imec.be

ranging from 10 to 80. So-called “equivalent oxide thickness” (EOT) is used in order to benchmark different high- k values with SiO_2 :

$$t_{EOT} = t_{diel} \left(\frac{k_{\text{SiO}_2}}{k_{diel}} \right)$$

where t is the thickness and k_{SiO_2} is equal to 3.9. A detailed review of high- k material engineering, physical, and electrical characterization is given in a book edited by Baklanov et al. (2007).

After gate patterning, the remaining high- k layer must be completely removed from the substrate. The complete removal of the high- k layer is dictated by the necessity for good electrical contact to source and drain areas. The remaining high- k could prevent silicidation of those areas. Another concern is that high- k could interfere with ion implantation (Bersuker et al., 2004). Therefore, the high- k layer should be removed after gate patterning, preferably by plasma etching as a last step of the gate etch process.

Recently, a number of papers dedicated to high- k removal have been published. Even though full understanding of the high- k etch mechanisms has not been yet achieved and the reported results are sometimes contradictory, we would like to make a first attempt to summarize the collected data and draw some preliminary conclusions without aiming at being complete and comprehensive. In this work, we review existing data on high- k removal approaches (wet, dry, and their combinations).

Types of High- k Dielectrics

High- k dielectrics are mostly metal oxides that have k value ranging from 9 to 80. The k values of binary metal oxides are summarized in Table I.

Every high- k material has some advantages and disadvantages. For example, Al_2O_3 is a well-studied stable material that is used in many applications, but its k value of 9 is rather low. Another example, TiO_2 , has an attractive k value of 80–110, but due to the presence of several stable oxidation states of Ti^{3+} and Ti^{4+}

Table I. Dielectric constant of various high- k materials

Material	Dielectric constant k
SiO_2	3.9
Si_3N_4	7
Al_2O_3	9
Gd_2O_3	10
Sc_2O_3	13
Y_2O_3	15
Dy_2O_3	16
HfO_2	25
ZrO_2	25
Ta_2O_5	26
La_2O_3	30
TiO_2	80

it has reduced oxide states. This reduced oxide has many oxygen vacancies, which are detrimental for device performance (Wilk et al., 2001). One of the most promising candidates currently is HfO_2 , which is rather stable in contact with Si and SiO_2 . The main disadvantage of HfO_2 is its rather low crystallization temperature (around 500°C) (Gusev et al., 2003). Crystallization is undesirable from the device performance point of view and also poses problems for the wet removal of this dielectric, as will be shown below.

Fundamentals of High- k Dielectric Removal

As was stated in the introduction, high- k dielectric has to be removed from the source and drain areas after gate processing. The removal process must comply with several requirements:

- Selectivity to the substrate: This is one of the most strict requirements—as the high- k is removed from the substrate, the substrate should not be damaged. The Si substrate damage, also known as Si recess, compromises the device performance. The damage could be a result of Si etching (physical removal of Si) or oxidation of Si if an oxidative plasma is used. An example of Si recess is shown in Figure 1.
- Selectivity to other materials in the gate stack: As high- k is removed, the gate should be obviously preserved. This means that the high- k removal step should not induce any distortion to the already patterned poly-Si and/or metal gate.
- Etch rate: This is usually not a concern as the thickness of high- k dielectric to be removed is limited to several nanometers (usually less than 5). As a result, even very low etch rate can be tolerated, especially if it allows high selectivity.

Dry and Wet Approaches

There are two main approaches to high- k removal: wet etch and dry (plasma) etch. Each approach has its own advantages and disadvantages.

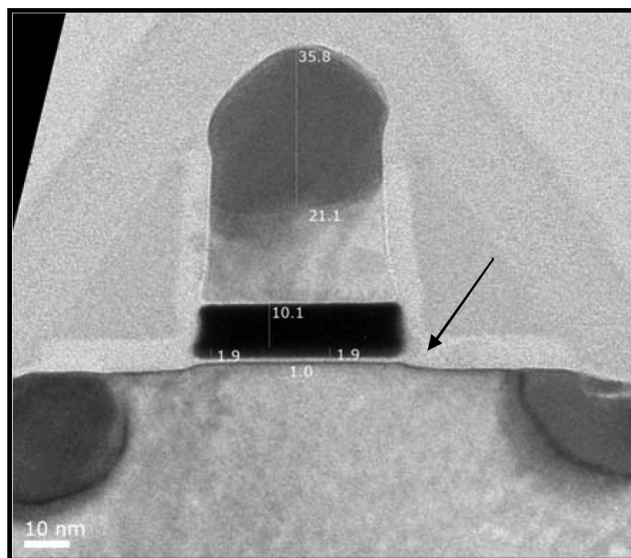


Figure 1. Transmission electron microscopy image of a metal gate (poly-Si/TaN/ HfO_2). The Si recess is indicated by an arrow.

Dry Etch

The main advantage of dry high- k removal is the possibility of achieving anisotropic etching with zero lateral etch rate. Another beneficial aspect of the dry etch is its cost effectiveness, as the high- k removal in that case is just one additional step in the gate etch process. There are, however, several inherent challenges of the dry etch. The main one is the requirement of sufficient volatility of the etch product since the plasma etch is based on removal of the etch product by evaporation/sublimation (eventually ion-assisted). As a criterion of sufficient volatility one can take equilibrium vapor pressure of the reaction product. In other words, the boiling temperature of the etch product at the typical etch pressures (from several mTorr to hundreds of mTorr) should be comparable with the substrate temperature (usually 20°–80°C). As will be shown below, number of recently evaluated potential high- k candidates have etch products that have too high boiling points to be removed dry. In some cases elevated substrate temperature could help, but it requires more complicated plasma etch hardware.

Wet Etch

The main advantage of wet etch is high selectivity over the substrate and other materials in the gate stack. Another advantage is that the range of the materials that can be etched wet is quite wide. The main disadvantage of wet etch is its isotropic nature: materials are etched laterally and vertically at the same rate. As a result, an undercut will be created under the gate. In the worst case, when too long wet over-etch is used, the smallest structures could be lifted off as all the high- k material is etched away beneath them. Another disadvantage of the wet etch is the fact that the etch rate depends on the crystallinity of the high- k dielectrics, and in the worst case a poly-crystalline high- k cannot be removed by wet chemistry, as will be shown below.

It is obvious that neither dry nor wet removal alone can work in all cases and very often a combination of dry and wet removal is used, as will be shown in the last section of this work.

Fundamentals of Dry Removal

In an ideal case approximation, dry etch processes are typical heterogeneous reactions where etch products are removed from the reaction zone. The reaction starts with adsorption of active species (radicals and excited molecules, A) formed in plasma. Then, chemical transformations occurring in the adsorption layer form adsorbed reaction products (C). This step might have a complicated mechanism including diffusion of adsorbed species and formation of number of intermediate states (B_i). The final step is desorption of the reaction products. These steps can be described by a system of simple reactions as shown below:



where (S) are surface active (adsorption) centers.

Adsorption rate of the reactive species depends on the frequency of their collision with the surface being etched, condensation coefficient σ , and degree of

surface coverage θ :

$$R_a = \sigma \cdot \frac{P}{\sqrt{2\pi mkT}} (1 - \theta) \cdot \exp\left(-\frac{E_{ads}}{RT}\right) \quad (2)$$

The degree of surface coverage, θ , is defined as a ratio of the concentration of all adsorbed species (θ_{AS} , $\Sigma\theta_{BIS}$, θ_{CS}) to the total (initial) concentration of surface adsorption centers S_0 . Adsorption is a first-order reaction and usually is not the rate-limiting step.

More challenging stages are the chemical transformations of the adsorbed compounds and desorption of final reaction products. In the case of simple monomolecular transformation in the adsorbed layer, the reaction rate is proportional to the frequency of vibration ν of the adsorbed products and surface coverage θ_{AS} :

$$R_r = \nu \cdot \theta_{AS} \cdot \exp\left(-\frac{E_r}{RT}\right) \quad (3)$$

where E_r is the activation energy of the reaction. However, as mentioned above, mechanisms of surface reactions might be more complicated. In the case of the Langmuir-Hinshelwood mechanism, the reaction rate is proportional to the product of surface concentrations of adsorbed reactants $R_{LH} = k_{LH}\theta_{AS}\theta_{BS}$. The reaction rate constant k reflects characteristics of reactant surface diffusion (both pre-exponential factor and activation energy). Eley-Rideal reactions are defined by interaction of gas-phase reactants with molecules located in adsorbed layer ($R_{ER} = k_{ER}P \cdot \theta$). The kinetic characteristics are similar to processes having the adsorption as the rate-limiting step. A typical example is reaction of Si with fluorine atoms. The rate-limiting step in this case is reaction of F atoms from gas phase (plasma) with SiF_x complexes formed in the previous stage.

Upon reaction, the etch products must be desorbed from the surface, which can be challenging in the case of high- k etching. Materials with high dielectric constant have relatively large polarizability. It originates from the more polar nature of high- k compounds. This is the reason why they are mostly oxides of metallic elements from groups 3 and 2 of the periodic table. Therefore, they have a tendency to form ionic-like bonds with halogens, which normally are used in dry etch. Such compounds with ionic bonds tend to have low volatility and, therefore, the products desorption might be the rate-limiting step:

$$R_d = \nu \cdot \theta_{CS} \cdot \exp\left(-\frac{E_{des}}{RT}\right) \quad (4)$$

where ν is frequency of vibration of the adsorbed molecules perpendicular to the surface, θ is the degree of surface coverage by the reaction products, E_{des} is activation energy of desorption, which is normally close to the sublimation enthalpy (ΔH_{subl}) of the reaction products.

In the presence of ion bombardment, the rate of desorption depends on equilibrium vapor pressure of the reaction products and the yield of ion-induced sputtering. To control the anisotropy and selectivity to the bottom layers, it is important to be able to control the ratio of spontaneous and ion assisted etching.

In order for etch to proceed the etch products should be (i) desorbed from the surface (which is a kinetic temperature-driven process described by Equation (4))

and (ii) prevented by redeposition on the surface from the gas phase by working at low pressure (lower than the saturated vapor pressure of a particular etch product at the substrate temperature). The maximum rate of spontaneous evaporation (without ion sputtering) is described by the Hertz-Knudsen equation:

$$J_v = \sigma \frac{P_0 - P}{(2\pi mkT)^{1/2}} \quad (5)$$

where P_0 is the equilibrium vapor pressure at the given temperature and P is pressure in the etch chamber. The volatility of the etch product can be estimated based on the saturated vapor pressure at the etch temperatures. The exact values of the saturated vapor pressure can be obtained from the JANAF tables (1985). If the etch product is not listed in the JANAF tables, its volatility can be estimated based on its boiling point. The boiling points for most of the materials are documented for atmospheric pressure (760 Torr), while the plasma etch is usually performed at pressures ranging from 2 mTorr to several hundreds of mTorr. In order to estimate the saturated vapor pressure of an etch product one can use the Clausius-Clapeyron equation:

$$\ln\left(\frac{P_{atm}}{P_{etch}}\right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_{etch}} - \frac{1}{T_{atm}}\right) \quad (6)$$

where T_{atm} and T_{etch} are the boiling points at atmospheric and etch pressure, respectively, P_{atm} and P_{etch} are atmospheric and etch pressures, respectively, ΔH_{vap} is enthalpy of vaporization, and R is the universal gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$). This equation is valid only in the conditions when ΔH_{vap} doesn't depend on temperature. However, this approximation is acceptable for our rough estimation. It should be also noted that this equation is valid if the T_{etch} is above the melting point of the etch product. If etching occurs below the melting point then Equation (6) should be used to calculate vapor pressure at the melting point and enthalpy of sublimation should be used instead of enthalpy of evaporation to calculate the vapor pressure at the etch temperature:

$$\ln\left(\frac{P_{melt}}{P_{etch}}\right) = \frac{\Delta H_{sub}}{R} \left(\frac{1}{T_{etch}} - \frac{1}{T_{melt}}\right) \quad (7)$$

When the enthalpies of vaporization and sublimation are known (*CRC Handbook of Chemistry and Physics*, 2004–2005), one can easily find the vapor pressure at the desired temperature using Equations (6) and/or (7).

However, the enthalpies are not always known. In that case they can be estimated based on the boiling point of a material. According to Trouton's rule (Trouton, 1884), enthalpy of evaporation of a material is proportional to its boiling point. This fact could be explained by considering change of entropy for conversion from a liquid to a gas similar for different materials. Similarly, if we presume that change of entropy for conversion from a solid to gas (sublimation) is the same for different materials, then the enthalpy of sublimation should be proportional to the boiling point. Indeed, by plotting known enthalpies of evaporation and sublimation versus boiling points (the data are taken from the *CRC Handbook of Chemistry and Physics*, 2004–2005) one can see linear dependencies, as shown in Figure 2.

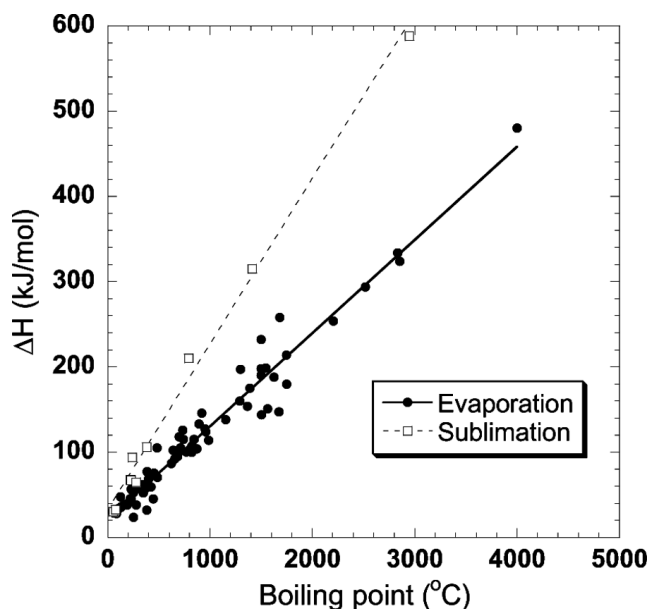


Figure 2. Enthalpy of evaporation (solid circles) and sublimation (empty squares) vs. boiling point at atmospheric pressure along with linear fit.

These linear dependencies correspond to the empirical equations

$$\Delta H_{\text{vap}} = 20.90 + 0.109 \cdot T_{\text{atm}} \quad (8)$$

$$\Delta H_{\text{sub}} = 32.28 + 0.194 \cdot T_{\text{atm}} \quad (9)$$

where the enthalpies are expressed in kJ/mol and boiling temperature in °C. Comparison between saturated pressure for TaCl_5 from the JANAF tables, calculated using known enthalpies of vaporization and sublimation and the estimations from the boiling point, is shown in Figure 3.

Based on those approximations we can estimate saturated vapor pressure of an etch product as function of boiling temperature at atmospheric pressure. The limit of volatility of an etch product could be roughly put at 0.1 mTorr (Shul and Pearton, 2000), however, for high- k etch lower etch rates can be tolerated as the amount of material to be removed is usually less than 5 nm. We can put the volatility limit at roughly 0.001 mTorr. The saturated vapor pressure at a wafer temperature of 60°C as a function of boiling temperature at atmospheric pressure is plotted in Figure 4, along with the volatility limit.

The graph should be read as follows. If an etch product has the melting point below etch temperature (i.e., it stays in the liquid phase between the boiling point and the etching temperature, e.g., TiBr_4), then the top “evaporation” curve gives the saturated pressure. If the melting point is above the sublimation point at atmospheric pressure (i.e., the etch product stays in a solid phase, e.g., HfCl_4), then the bottom “sublimation” curves gives the saturated pressure. If the melting point is somewhere between the boiling point and the etch temperature, then the pressure curve has inflection at the melting point (in Figure 4 examples of 200°C and 300°C are given). From this simple approximation one can see that if etching occurs at 60°C, the etch product should have the boiling point not higher than 400°–500°C

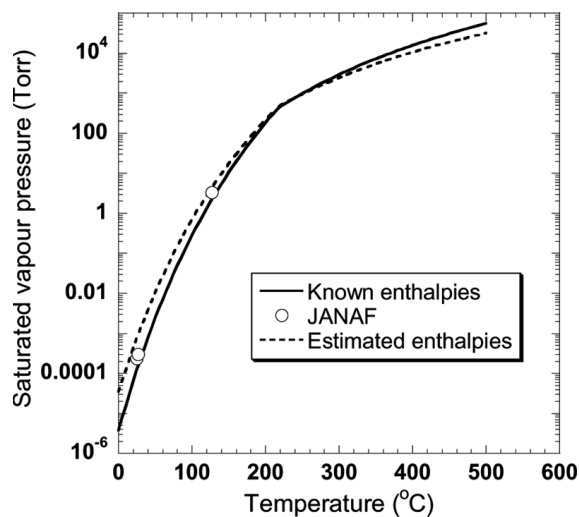


Figure 3. Saturated vapor pressure of TaCl_5 as function of temperature from JANAF tables (1985), (circles); calculated using Clausius-Clapeyron Equations (6) and (7) with known enthalpies of vaporization and sublimation (*CRC Handbook of Chemistry and Physics*, 2004–2005; JANAF, 1985) (solid curve), and with the enthalpies estimated from Equations (8) and (9) (dashed curve).

(depending on the melting point). Similar curves for different etch temperatures could be easily calculated using Equations (6)–(9).

The melting points and boiling points (if known) of most stable halides of the elements used in high- k materials are listed in Table X in the appendix. One can see that the halides can be divided into two groups based on the volatility of their halides. The first groups consist of refractory metals (Zr, Ta, Ti, Hf), the second one of rare earth metals (Y, La, Dy, Gd, Sc). The halides of the first group are

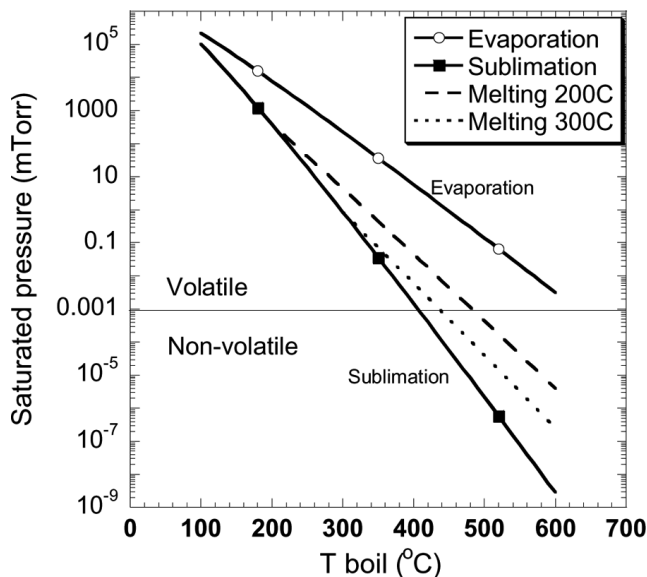


Figure 4. Saturated vapor pressure at 60°C as function of boiling temperature at atmospheric pressure.

relatively volatile (with boiling point of the most volatile chlorides below 350°C at atmospheric pressure), while the second group does not produce any volatile compounds (the boiling points are not available, but high melting points indicate low volatility of those compounds).

The above calculations allow first assessment of the possibility of plasma etch of a certain material. For example, if the wafer temperature is 60°C and the pressure in the etch chamber is 5 mTorr, then it is possible to etch materials that form product with boiling temperature at atmospheric pressure less than about 400°C. If a high-temperature reactor is used, e.g., 350°C, then the maximum boiling temperature of the reaction product at atmospheric pressure could be as high as 950°C. If applied to hafnium etch products, the calculations show that HfF_4 is not volatile at typical close-to-room temperature etch reactors, while HfCl_4 should be volatile enough. The halides of the rare earth metals would require very high temperatures in order to be volatile.

Presence of ion irradiation increases the process window: for instance, materials that have a boiling temperature of about 100°C at 5 mTorr, can still be etched at 20°–60°C with yield typical for ion-assisted chemical etching. Materials with boiling temperature higher than 100°C show the etch rate equal to pure physical sputtering.

It should be noted that assessment of the boiling temperature will not provide exact information on etch rate or selectivity, as the latter depends on many other parameters. This assessment shows only a possibility of etch product evaporation: if the boiling temperature is too high, the plasma etch will be almost impossible.

In the presence of ion bombardment the etching is believed to follow the law proposed by Steinbrüchel (1989):

$$Y(E) \approx A \cdot (E^{1/2} - E_{th}^{1/2}) \quad (10)$$

where Y is the sputtering yield of the reaction products, E is the ion energy, E_{th} is the threshold energy for sputtering, and A is a constant depending on the particular projectile-target combination. Steinbrüchel showed that this equation is valid not only for pure physical sputtering, but also for ion-assisted etching of Si with F^+ , Cl^+ , and $\text{Ar}^+ + \text{Cl}_2$. As will be shown below, many authors observed similar dependence on ion energy for high- k etch.

The key factor is the threshold energy. If the ions' energy exceeds the threshold energy and the reaction products are efficiently removed from the reaction zone, the rate of sputtering can significantly exceed the values predicted by Equation (5). However, the sputtering threshold also depends on sublimation energy and, according to Stuart and Wehner (Stuart and Wehner, 1962; Mantenieks, 1997), $E_{th} \approx 4E_{\text{subl}}$. Therefore, estimations with Equation (6) are always useful when new materials are introduced and needed to be plasma etched.

If the etch reaction rate is determined by chemical transformation in adsorbed states, it is important to analyze probability of certain chemical transformations. They can be based on comparison of bond strengths of initial molecules and reaction products and also in analysis of enthalpy of formation of reaction products. Such data for presently popular high- k materials are tabulated in Table VIII and Table IX in the appendix.

From the above consideration one can see that the dry etching of most of the high- k materials is a considerable challenge. Formation of fluorides is usually favorable, but their volatility is very low. Chlorides are relatively volatile, but their

formation is not energetically favorable. A possible means to etch high- k is finding a way to form chlorides in plasma, like in the case of SiO_2 etching by fluorine where highly volatile SiF_4 is formed in the presence of carbon and ion bombardment.

Fundamentals of Wet Removal

Low volatility of the reaction products of high- k materials with halogens necessitates application of intensive ion radiation. It generates problems related to the etch selectivity, which is especially important for precise removal of remaining residues at the end of the dry etch processes. In this case application of wet etching is extremely important. The wet etching is a pure chemical process that provides a high degree of chemical selectivity if an appropriate chemistry is chosen. On the other hand, one can significantly change the energetic balance of the etch reactions.

Generally, wet etching can be considered as introduction of an additional step when the gas-phase reaction product is dissolved in a liquid. The dissolution in most of cases is thermodynamically favorable, and, therefore, the final energetic balance can be written as $\Delta E = E_{\text{des}} - E_{\text{diss}}$ (Figure 5). Therefore, the dissolution of the reaction products makes the reaction more energetically favorable and the final ΔE values depend on solvent (E_{diss}).

The wet processes have additional advantage related to significant reduction of activation energy in comparison with desorption into the gas phase. Mechanism of the reduction can be understood by using ideas of transition state theory (TST). Transition state theory is a theory of the rates of elementary reactions that assumes a special type of equilibrium (quasi-equilibrium) between reactants and activated complexes. In desorption, the activated complex has a molecular structure similar to that of the final reaction product. Therefore, the activated complex can also be solvated with energetic characteristics similar to those of the final reaction product. This leads to reduction of the energy of activated complexes for a value proportional to the energy of dissolution of the reaction products. In Figure 5, solvent 2 provides

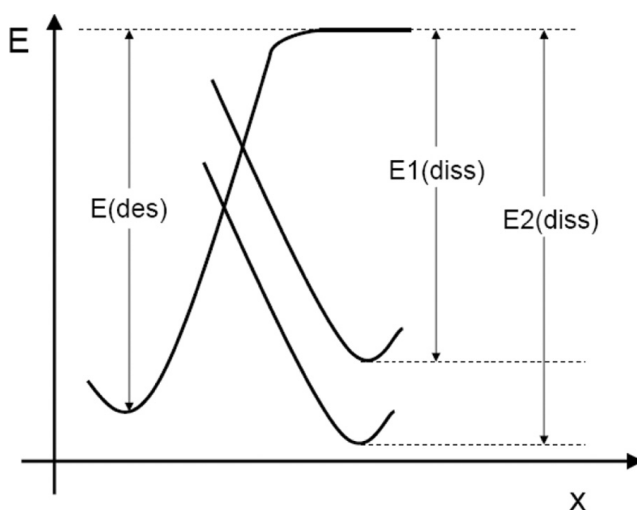


Figure 5. Change of energy of the reaction products during desorption into vacuum and dissolution in liquids. The dissolution of the reaction product is more energetically favorable in solvent 2.

higher dissolution energy than solvent 1. Therefore, the choice of appropriate solvents that provide high degree of dissolution of the reaction product can significantly increase the etch efficiency without losing the etch selectivity.

However, one additional challenge is obvious from the presented figure. Reduction of activation energy increases possibility of redeposition of the reaction products back onto the substrate. Therefore, usage of fresh etch solutions (not saturated by the reaction products) is important.

Dry Removal

In this section we will review literature data on plasma etching of different high- k dielectrics using different plasmas. Since there are a lot of similarities between different high- k dielectrics, we decided to organize the data by the plasma used for etch.

Fluorine-Based Plasma

Historically, the first data on high- k materials etch properties were collected for fluorine-based chemistries. At that time high- k materials were used just as a stopping layer for SiO₂ etch, e.g., for fabrication of phase-shifting masks. One of the first reports on HfO₂ etching was published by Shih et al. (1993). Etch rate of HfO₂ using CHF₃ gas in a reactive ion etch (RIE) reactor at pressure of 50–100 mTorr and power of 100 W was 16 times lower than that of SiO₂. Similar results on etching HfO₂ and Sc₂O₃ with CHF₃/O₂ (95.6/4.4) plasma were reported later by Britten et al. (1996). The etch rate ratio of SiO₂/HfO₂/Sc₂O₃ was found to be 100/10/1 in RIE reactor at 40 mTorr and 150 W rf power. When HfO₂ was used as a stopping layer for SiO₂ grating etch, a lot of deposition was observed on the sidewall of the etched structures. The deposition was attributed to redeposition of sputtered HfO₂ and possible low volatile fluorinated etch products. No redeposition was observed when Sc₂O₃ was used as a stopping layer.

One of the first studies focused on etching of the high- k dielectrics, not just stopping on them, was performed by Norasetthekul, Park, and coworkers. They studied dry etching of TiO₂ (Norasetthekul et al., 2001), HfO₂ (Norasetthekul et al., 2002), and Sc₂O₃ (Park et al., 2001) using SF₆/Ar, Cl₂/Ar, and CH₄/H₂/Ar plasmas in an inductively coupled plasma (ICP) reactor. It was found that in SF₆/Ar Ar the TiO₂ etch rate is the highest, while the etch rate of Sc₂O₃ is the lowest, as could be expected from the volatility of the possible etch products (see Table X in the appendix). The etch rate versus ICP power for different high- k dielectrics is summarized in Figure 6.

CF₄ chemistry for HfO₂ etch was compared with Cl₂/HBr by Maeda et al. (2004). It was found that there is no large difference in etch rates (around 2 nm/min), but reasonable selectivity over Si and SiO₂ could be achieved only using Cl₂/HBr. Similar results were reported by Chen et al. (2004a), who found that the etch rate of HfO₂ is higher in HBr plasma than in CF₄ plasma, which can be attributed to higher volatility of hafnium tetrabromide. The threshold energies of the Steinbrüchel theory (Equation (10)) for etching of HfO₂ in Ar and Ar/CHF₃ were determined by Wang et al. (2006). They used a reactive ion beam to etch the high- k dielectric and found that the threshold energies for Ar and CHF₃/Ar are 108 eV and 78.9 eV, respectively. As well as Britten et al. (1996), the authors observed significant sidewall redeposition attributed to low volatility of the etch products. It should be noted that

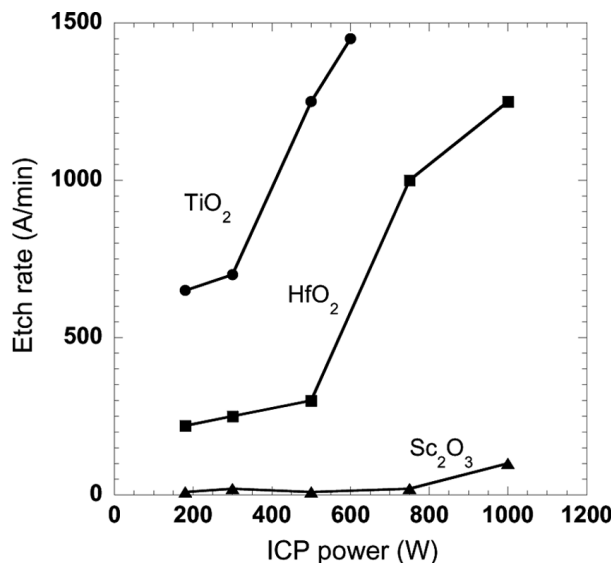


Figure 6. Etch rate of high-*k* dielectrics in SF₆/Ar plasma versus ICP power at 5 mTorr and 250 W bias power (Norasetthekul et al., 2001, 2002; Park et al., 2001).

etching threshold energies for Si and SiO₂ in F-containing plasmas were found to be in the range of 2–4 eV (Gray et al., 1993). One can see that much a higher threshold energy for HfO₂ than for Si makes selective removal of the high-*k*-using fluorine plasma extremely difficult.

In addition to the etch rates, etch products and surface composition of HfO₂ etched in fluorocarbon plasmas have been reported. The surface chemical composition is reported by Chen et al. (2004b) (for CF₄ etching) and Takahashi et al. (2005) (for C₄F₈/Ar etching). In both articles a significant amount of fluorine was found on the HfO₂ surface after exposure to fluorocarbon plasma. In the case of C₄F₈ etching, more fluorine and carbon was found by X-ray photoelectron microscopy (XPS) on the HfO₂ surface than on the SiO₂ surface, but less than on the Si surface, which was attributed to polymer formation. The polymer formation provided some selectivity over the Si substrate. Chen et al. (2004b) analyzed the surface of HfO₂, HfAlO, HfON, and HfSiO dielectrics after CF₄ plasma exposure by XPS and time of flight secondary ion mass spectrometry (TOFSIMS). They concluded that the surface of the studied high-*k* dielectrics is covered with nonvolatile hafnium (and aluminum, if present) fluorides, as summarized in Table II.

Table II. Results of surface analysis of Hf-based high-*k* dielectrics exposed to CF₄ plasma (Chen et al., 2004b)

Sample	Atomic % of F detected by XPS	Particles from surface detected by TOFSIMS	Etch products on the surface
HfO ₂	32.1	HF ⁺ , HFO ⁺ , HfF ⁺ ,	HfF _x (x = 1,2)
HfAlO	31.7	HF ₂ ⁺ , HfFOH ⁺ ,	HfF _x O _y ,
HfON	37.8	HfO ₂ H ₃ ⁺ , HFOH ⁺ , HfO ₂ H ⁺ ,	AlF _x (x = 1,2)
HfSiO	20.9	AlF ⁺ , AlF ₂ ⁺	

Volatile etch products were analyzed by Takahashi and Ono (2006) using a quadrupole mass spectrometer (QMS). In the case of HfO_2 etching by CF_4 , HfF_4 was concluded to be the main etch product. When $\text{C}_4\text{F}_8/\text{Ar}/\text{H}_2$ plasma was used, HFCH_x^+ ($x=0-4$) and HfH_xF^+ ($x=0-2$) were detected, and it was concluded that the Hf hydrocarbide-like metal-organic compounds are the volatile products in $\text{C}_4\text{F}_8/\text{Ar}/\text{H}_2$ plasma.

Summarizing the data obtained on high- k etching in fluorine-based plasma we can say that except for titanium and tantalum fluorides, the etch product are almost nonvolatile at close-to-room temperatures. Fluorides are formed but stay on the surface or redeposit on the sidewalls. Selectivity to the substrate is poor, as Si can be easily etched by fluorine-based plasma. In some cases the selectivity can be achieved using highly polymerizing gases (like C_4F_8) that result in more pronounced polymer deposition on Si than the dielectric. It can be concluded that the fluorine-based chemistries are not the preferred option for high- k etch. Even if the low volatility could be overcome by etching at elevated temperatures, the selectivity over the Si substrate will always be a concern.

Chlorine-Based Plasma

Chlorine-based plasma seems to be more attractive for high- k etching as volatilities of metal chlorides are higher than that of fluorides (see Table X in the appendix). However, the probability of the reaction is lower since metal-oxygen bond is stronger than metal-chlorine (see Table VIII in the appendix) and enthalpy of formation of oxides is larger than that of chlorides (see Table IX in the appendix). It has been known since the days of aluminum metallization that it is difficult to etch Al covered by native aluminum oxide (Al_2O_3) using only Cl_2 plasma. Some delay time is always observed before starting the Al etch, attributed to etching through the native oxide (Bruce and Malafsky, 1983). The problem could be solved by adding BCl_3 that is capable of etch Al_2O_3 (Tokunaga et al., 1981; Keaton and Hess, 1985). As we will see later, the same approach works for high- k dielectrics (at least for those with reasonably volatile chlorides): their etch rates in Cl-based plasmas could be greatly enhanced by addition of BCl_3 .

Cl_2 Plasma

As expected, it was found that Cl_2 plasma alone or with addition of Ar or HBr is not capable of etching high- k dielectrics with acceptable etch rate and selectivity. Etch rates of Hf-based high- k in chlorine plasma was found to be close to that of fluorine plasma (Norasetthekul et al., 2002; Maeda et al., 2004; Chen et al., 2004b). TiO_2 was etched faster by SF_6/Ar than by Cl_2/Ar (Norasetthekul et al., 2001), in line with the relatively high volatility of TiF_4 and higher chemical activity of fluorine. Higher etch rate of Sc_2O_3 was found in the case of Cl_2/Ar plasma (as compared to SF_6/Cl_2 plasma) (Park et al., 2001). The threshold energies for etching in Cl_2 plasma were found to be 12–20 eV for ZrO_2 (Sha and Chang, 2002) and 12–25 eV for HfO_2 (Sha et al., 2003). Since the threshold energy for Si etch in Cl_2 plasma is around 4 eV (Sha and Chang, 2004), it is difficult to obtain selectivity over the Si substrate. In all reports the Si etch rate is significantly higher than the high- k etch rate.

The studies of the high- k surface composition after Cl_2 plasma exposure reveal that there is a limited amount of chlorine present. No Cl was detected by atomic emission spectroscopy (AES) on the surface of Sc_2O_3 (Park et al., 2001) and TiO_2

(Park et al., 2001). XPS analysis of Hf-based dielectric (HfO_2 , HfAlO , HfON , HfSiO) surface showed significantly lower Cl content (1.0–2.2%) after exposure to Cl_2 plasma than F content after exposure to CF_4 plasma (20.9–37.8%) (Chen et al., 2004b). TOFSIMS analysis didn't reveal any chlorides (HfCl_4 , AlCl_3) on the surfaces of the aforementioned Hf-based dielectrics (Chen et al., 2004b). No change in binding energies of Hf and Zr was observed by XPS upon exposure of ZrO_2 and HfO_2 to Cl_2 plasma (Sha et al., 2002, 2003), as shown in Figure 7, while small increase of Cl 2p peak was observed.

Analysis of the volatile etch products shows the presence of metal chlorides. When ZrO_2 is etched by Cl_2 , ZrCl_2 , ZrCl_3 , and ZrCl_4 are identified as main etch products by mass spectrometry (Sha et al., 2002). ZrCl_2 is the least abundant etch product and constitutes several percentages of the total amount of chlorides. At low ion energy ZrCl_3 is the main etch product, while at high ion energies (more than 120 eV) ZrCl_4 becomes the dominant etch product, as shown in Figure 8. It should be noted that no optical emission spectroscopy (OES) emission of Zr or its compounds was observed during the etching.

Similar results were observed for HfO_2 etching in Cl_2 plasma (Sha et al., 2003). No HfCl or HfCl_2 was observed by mass spectrometry, while the main etch products were identified as HfCl_3 and HfCl_4 . As for ZrO_2 etch, HfCl_3 is the dominating etch product at low ion energies, while HfCl_4 becomes the dominating species at high ion energies. Again, no emission from Hf-containing species was observed by OES. In both cases (ZrO_2 and HfO_2) ClO was observed in the mass spectra of the etch products. That allowed the authors to conclude that the main etching reactions during ZrO_2 and HfO_2 etching by Cl_2 plasma are:

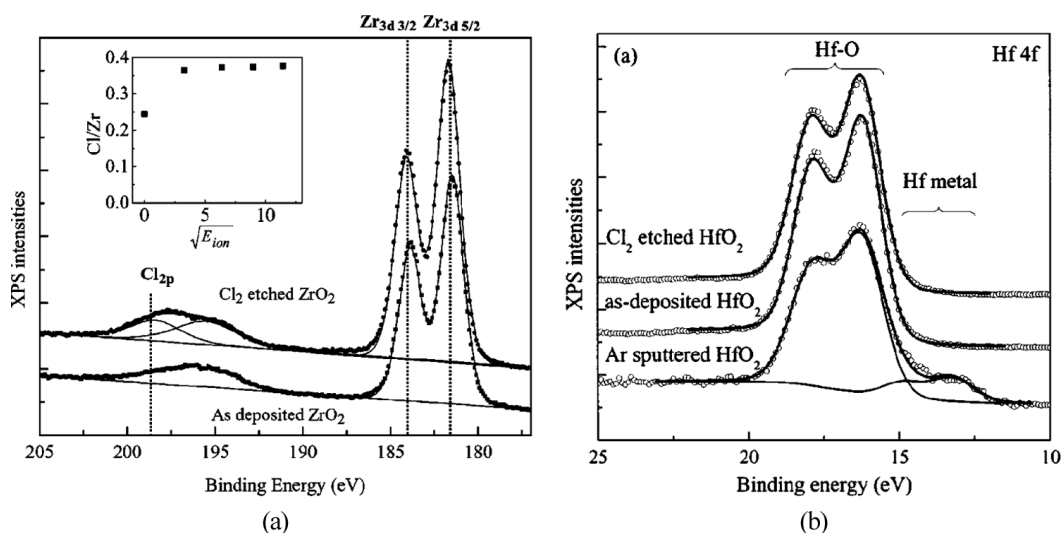
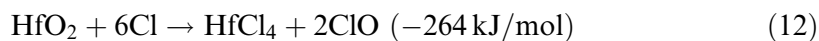
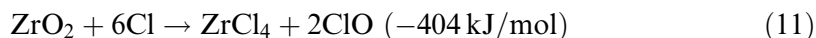


Figure 7. XPS spectra of ZrO_2 (a) (Sha et al., 2002) and HfO_2 (b) (Sha et al., 2003) after exposure to Cl_2 plasma at 3 mTorr, 500 W. Reproduced with permission.

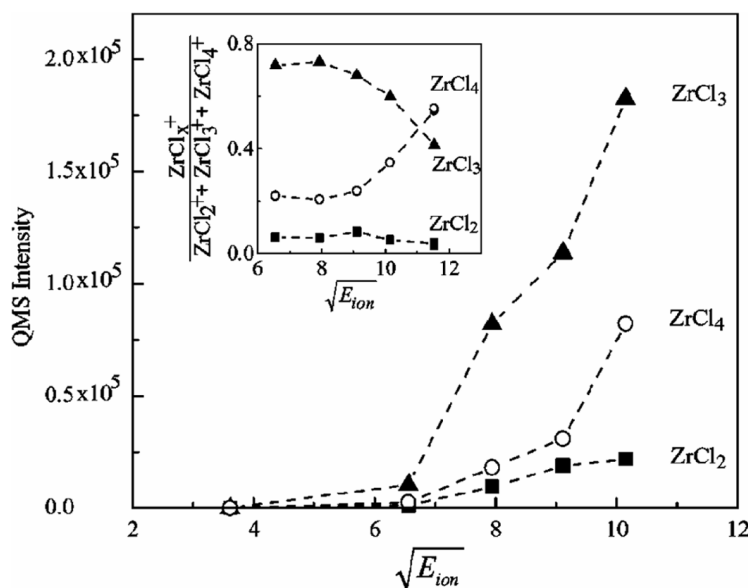


Figure 8. QMS-detected ion intensities as a function of ion energy at 3 mTorr and 500 W, with their relative abundance shown in the inset (Sha et al., 2002). Reproduced with permission.

where both reactions are exothermic. While there is no reported heat formation for HfCl_3 and ZrCl_3 , the authors concluded that formation of those products is highly probable under ion bombardment conditions since those products were observed in the etch experiments.

Etching of HfO_2 by Cl_2/CO plasma at elevated temperature was reported by Hélot et al. (2006). According to the thermodynamic study they performed, the presence of carbon could facilitate formation of HfCl_4 with CO_2 as etch by-product when the surface temperature exceeds 400 K. They performed etching of HfO_2 and SiO_2 by Cl_2/CO plasma mixture at 625 K substrate temperature and found that the selectivity of HfO_2 over SiO_2 could be as high as 20 at zero substrate bias and 2.5 at 25 W substrate bias. It was concluded that the main etch mechanism is chemical interaction, with little effect of ion bombardment. The main disadvantage of this approach is the need for an etch chamber equipped with a high-temperature chuck.

Summarizing the data reviewed above we can see that unlike fluorine plasma, chlorine plasma results in formation of reasonably volatile products, leaving almost no chlorine on the etched surface. The limiting factor in chlorine plasma is, apparently, low reaction probability of Cl_2 with metal oxides. This results in rather low etch rates even if the etch products are volatile enough. At the same time, Si etch rate in pure Cl_2 plasma is quite high, which creates issues with selectivity over the substrate. In order to solve the selectivity problem, etch rate of high- k dielectrics should be increased, while the Si etch rate should be decreased. As will be shown below, this could be achieved using BCl_3 plasma.

BCl_3 Plasma

As was mentioned above, addition of BCl_3 to Cl_2 was used since the 1980s in order to facilitate etching of native Al_2O_3 oxide (Bruce and Malafsky, 1983; Tokunaga et al., 1981; Keaton and Hess, 1965). The main idea of adding BCl_3 is to use boron to

reduce metal oxides facilitating the formation of volatile chlorides. Indeed, it was observed that addition of BCl_3 to Cl_2 plasma significantly increases the etch rate of ZrO_2 (Sha et al., 2003), Al_2O_3 (Jeong et al., 2002), $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (An et al., 2000), $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.9}\text{Ti}_{0.1}]\text{O}_3$ (Jang et al., 2000), $\text{Zr}_{1-x}\text{Al}_x\text{O}_y$ (Pelhos et al., 2001), and HfO_2 (Sha et al., 2003). Etch rate data for HfO_2 , ZrO_2 , SiO_2 , and Si as a function of BCl_3 content in Cl_2/BCl_3 mixture are summarized in Figure 9.

We obtained similar results for etching of hafnium silicates ($\text{Hf}_x\text{Si}_{1-x}\text{O}_2$) with different Si/Hf ratio in BCl_3/Cl_2 plasma (Shamiryan et al., 2006). The only difference is that in pure BCl_3 the etch rate of SiO_2 decreases, while the etch rate of HfO_2 does not. The etch rates of silicates in pure BCl_3 fall in between those of SiO_2 and HfO_2 , with Hf-rich silicates closer to HfO_2 and Si-rich silicates closer to SiO_2 (Figure 10).

One can see that in pure Cl_2 plasma the etch rate of the high- k dielectrics is the lowest, while the Si etch rate is the highest, thus selective etch of high- k is impossible. However, with addition of BCl_3 the high- k etch rate increases, while the Si etch rate monotonously decreases, and in pure BCl_3 plasma etch rates become comparable. In order to understand etch rate behavior we should consider changes introduced by BCl_3 addition to the plasma itself and on the etching surface.

Plasmas of Cl_2/BCl_3 mixture have been extensively studied. Early studies were performed in parallel-plate capacitively coupled reactors where a lot of understanding was obtained on fundamental electron cross sections (Stockdale et al., 1972; Petrovic et al., 1990), negative ion formation (Overzet and Luo, 1991; Gottscho and Gaebe, 1986), metastable chlorine ion characteristics (Hebner, 1996a; Nakano et al., 1992), electron density and temperature (Miller et al., 1995), and laser-induced fluorescence (LIF) measurements of plasma species (Scheller et al., 1988; Hebner, 1997). Of more interest, however, are later studies performed in inductively coupled plasma (ICP) reactors, which are widely used for gate etching in general and high- k etching in particular. An extensive study of Cl_2/BCl_3 plasma in ICP reactors

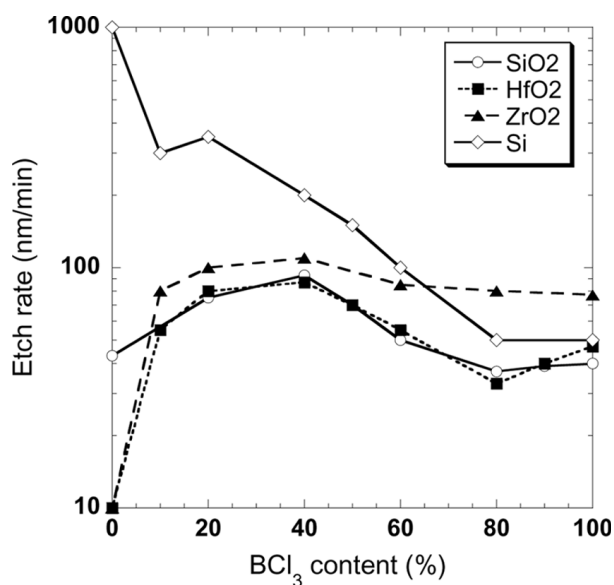


Figure 9. Etch rate of Si (Sha et al., 2003), HfO_2 (Sha et al., 2003), ZrO_2 (Sha and Chang, 2003), and SiO_2 (Sha and Chang, 2004) vs. BCl_3 content in Cl_2/BCl_3 plasma. The etch conditions are 5 mTorr, 300 W TCP power, and ion energy of 75 eV.

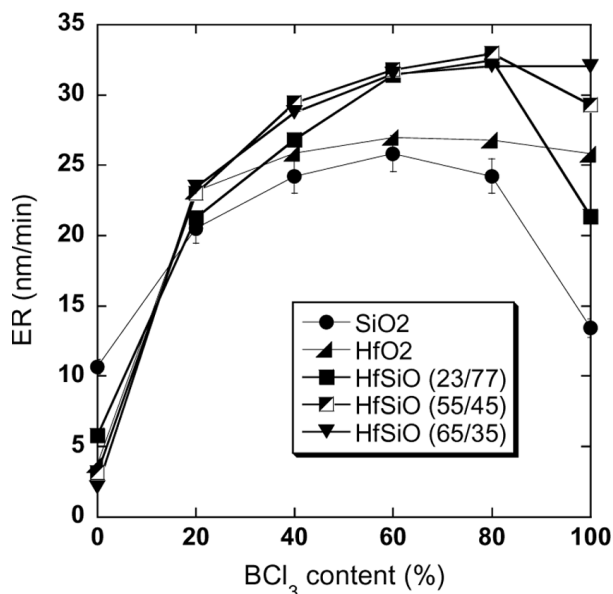


Figure 10. Etch rate of SiO₂, HfO₂, and hafnium silicate with different Hf/Si ratios in BCl₃/Cl₂ plasma as a function of BCl₃ content (Shamiryan et al., 2006).

was performed by Hebner and coworkers. They studied metastable ion kinetics (Hebner et al., 1997), relative density of BCl (Fleddermann and Hebner, 1998) and atomic chlorine (Hebner and Fleddermann, 1998) species, and the influence of surface material on BCl density (Hebner et al., 1999). It was found that there is no interaction between BCl₃ and Cl₂ in the plasma. The electron density has been shown to be constant over the range of BCl₃/Cl₂ ratios. It was shown by LIF measurements that the relative Cl intensity decreases by a factor of 3 and metastable chlorine ion density by a factor of 4 as the mixture changes from pure Cl₂ to pure BCl₃. This is explained by the fact that the dissociative energy of B-Cl is higher than that of Cl-Cl (see Table III). The results are in agreement with simulations performed by Meeks et al. (1998), as illustrated in Figure 11.

Relative BCl intensity measured by LIF linearly increases with increase of BCl₃ content in the BCl₃/Cl₂ mixture (Fleddermann and Hebner, 1998). The results

Table III. Bond strength of species that might be present in Cl₂/BCl₃ plasma used for etching of Si/high-*k* (for bond strength of metal oxides refer to Table VIII in the appendix)

Bond	Strength (kJ/mol)
Cl-Cl	241.2
Cl-O	268.9
B-Cl	530.7
BCl-Cl	328.0
BCl ₂ -Cl	463.1
Si-B	288.3
B-O	808.8

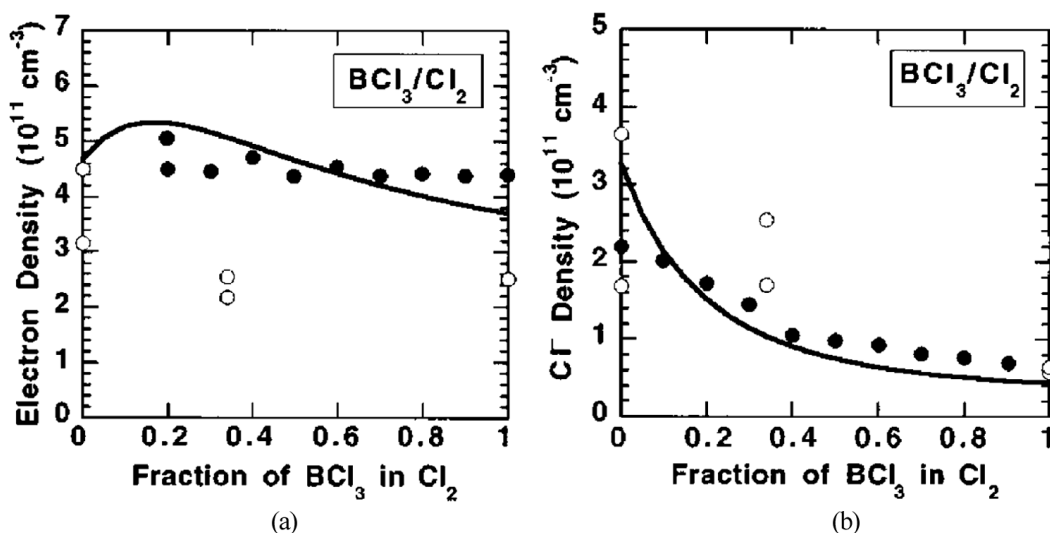


Figure 11. Comparison of model prediction (curve) (Meeks et al., 1998) and data of Hebner et al. (Hebner, 1996b; Fleddermann and Hebner, 1997) (points), 300 W power, 20 mTorr pressure for electron density and Cl^- density. Reproduced with permission.

suggest that Cl_2 acts just as a diluent to BCl_3 and there are no interactions between Cl_2 and BCl_3 .

The mass spectrometry study of BCl_3/Cl_2 plasma revealed that the dominant ionic species are BCl_2^+ and Cl_2^+ (Sha et al., 2003; Sha and Chang, 2004). This is in agreement with the actinometry study performed by Wang and Donnelly (2008), who concluded that the dominant neutral species is BCl_3 with BCl_2^+ as the predominant ion since BCl_3^+ is unstable. With addition of BCl_3 , the Cl_2^+ intensity drops while BCl_2^+ reaches a maximum at about 40% BCl_3 and then also drops, as shown in Figure 12. No Cl_2 emission was observed in pure BCl_3 plasma (Wang and Donnelly, 2008).

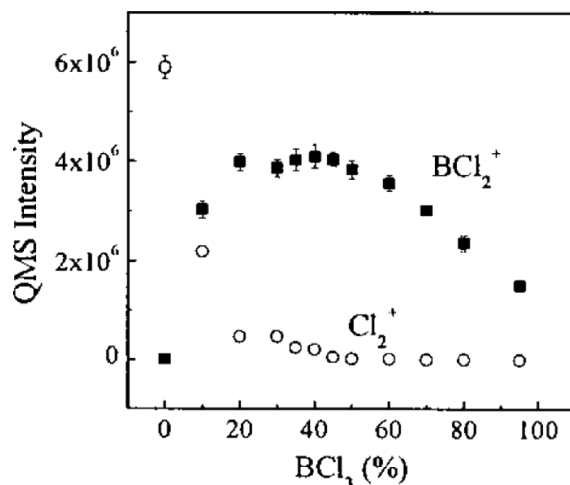
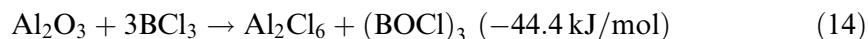


Figure 12. QMS-detected ion intensities of the dominant ionic species Cl_2^+ and BCl_2^+ as a function of BCl_3 percentage (Sha and Chang, 2003). Reproduced with permission.

It is believed that the main mechanism of metal oxide etch in BCl_3 plasma is reduction of the oxide by boron and formation of a volatile metal chloride and trichloro-boroxine (BOCl_3). Trichloro-boroxine is a stable volatile compound with large negative heat of formation (see Table IV).

Examples of the high-*k* etch reactions in BCl_3 -containing plasma are as follows:



From the facts that reactions of metal oxides with BCl_3 are exothermic, B-O bond is stronger than the metal-oxide bonds (see Tables VIII and III), and stable volatile compounds are formed as etch products one could explain higher high-*k* etch rates in BCl_3 -containing plasma.

The mass spectrometry of etch products in BCl_3/Cl_2 plasma indeed shows the presence of $\text{B}_x\text{O}_y\text{Cl}_z$ compounds (Sha and Chang, 2003), such as $(\text{BOCl})_3$, B_2OCl_3 , $\text{B}_3\text{O}_3\text{Cl}_2$, and B_2OCl_4 . It should be noted that those compounds were observed even in the absence of the high-*k* samples, implying that BCl_3 plasma etches the quartz bell jar enclosing the etch reactor. The observed ionic species, including B_2OCl_3^+ , B_3OCl_4^+ , and $\text{B}_3\text{O}_2\text{Cl}_4^+$, are likely produced from the neutrals listed above. When the high-*k* samples were etched, the authors observed an increase in B_2OCl_3^+ , B_3OCl_4^+ , and $\text{B}_3\text{O}_2\text{Cl}_4^+$ signals. No metal chlorides were detected due to overlap of their signals with the strong background signal from etching of the quartz bell jar. However, some metal- and boron-containing etch products as $\text{ZrB}_2\text{Cl}_7^+$, $\text{ZrB}_2\text{OCl}_7^+$ (for etching of ZrO_2) (Sha and Chang, 2003, 2004), and HfBOCl_4^+ (etching of HfO_2) (Sha et al., 2003) were detected.

The surface analysis of high-*k* samples etched in BCl_3 -containing plasma at -110 V substrate bias reveals presence of boron and chlorine. An XPS spectrum of ZrAlO is shown in Figure 13. One can see the presence of boron (a peak at 195.1 eV) as well as chlorine (peak at 201.3 eV). Similar results were obtained by Kim et al. (2004) for Al_2O_3 films exposed to BCl_3 plasma.

Study of Si surface exposed to BCl_3 plasma revealed that it is covered by a B-containing protective film (Sha and Chang, 2003; Pelhos et al., 2001). An XPS signal of B from Si surface exposed to BCl_3 plasma at zero bias is shown in Figure 14.

Table IV. Enthalpies of formation of some B-containing compounds

Compound	Enthalpy of formation $\Delta_f H^\circ$ (kJ/mol)
BCl_3	-402.6
BO	25
BO_2	-300.4
B_2O_3	-1273.5
$(\text{BOCl})_3$	-1630.2

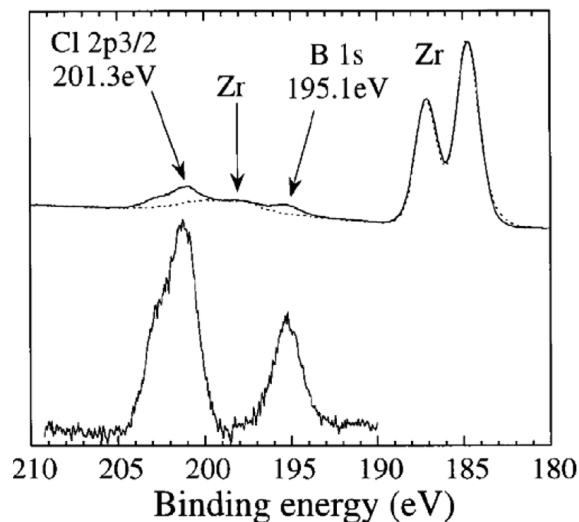


Figure 13. XPS spectrum of B from $\text{Zr}_{1-x}\text{Al}_x\text{O}_y$ sample etched in BCl_3 plasma. A before-etch spectrum is subtracted to show Cl and B peaks (bottom curve) (Pelhos et al., 2001). Reproduced with permission.

One can see significant presence of B on the Si surface as compared with the high- k surface (see Figure 13). It should be noted, however, that the high- k was etched at -100 V bias, while no bias was applied to the Si sample. When exposure time in pure BCl_3 plasma at zero bias is prolonged, a film is deposited that is thick enough to completely screen the XPS signal from the substrate (Nakamura et al., 2006; Kitagawa et al., 2006; Nakamura et al., 2009). The film consists of boron, oxygen, and chlorine (Nakamura et al., 2006; Shamiryan et al., 2007) in roughly equal amounts, with oxygen probably coming from the air exposure between plasma exposure and XPS measurements. It was found that the deposition depends on pressure: the deposition was observed at 5 mTorr, but not at 10 mTorr for pure BCl_3 plasma (Nakamura et al., 2006; Kitagawa et al., 2006). An example of XPS spectra

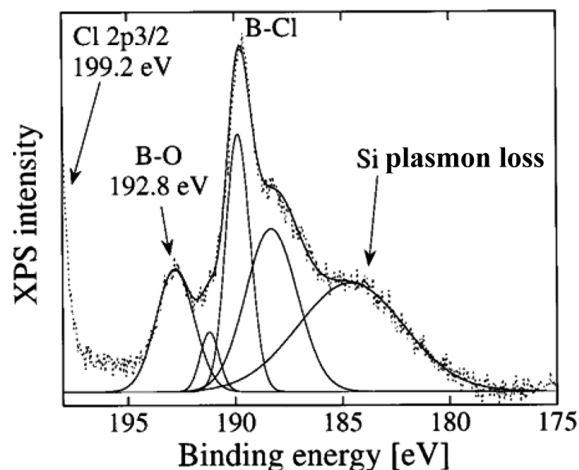


Figure 14. Boron XPS signal from an α -Si sample etched in BCl_3 plasma (Pelhos et al., 2001). Reproduced with permission, revised July 2009.

of Hf 4f, Cl 2p, B 1s, and O 1s on top of HfO₂ and Si exposed to BCl₃ plasma at different conditions (with or without deposition) is shown in Figure 15.

One can see that the Hf peak almost disappears when deposition conditions are used (Figure 15(a)) but is almost unaffected when the etch conditions (10 mTorr) are used. Chlorine and boron peaks appear on both Si and HfO₂ surfaces under deposition conditions, while under the etch conditions only a small Cl 2p peak is observed. Oxygen peaks from HfO₂ remain unchanged after etching, but shift to higher binding energies in the deposited film, possibly indicating the presence of B-O bond.

It is important to note that the deposition of a B-Cl film depends not only on pressure but also on the presence of additives to the BCl₃ plasma. When O₂ is added, first the deposition is suppressed and only etching is observed, then, as O₂

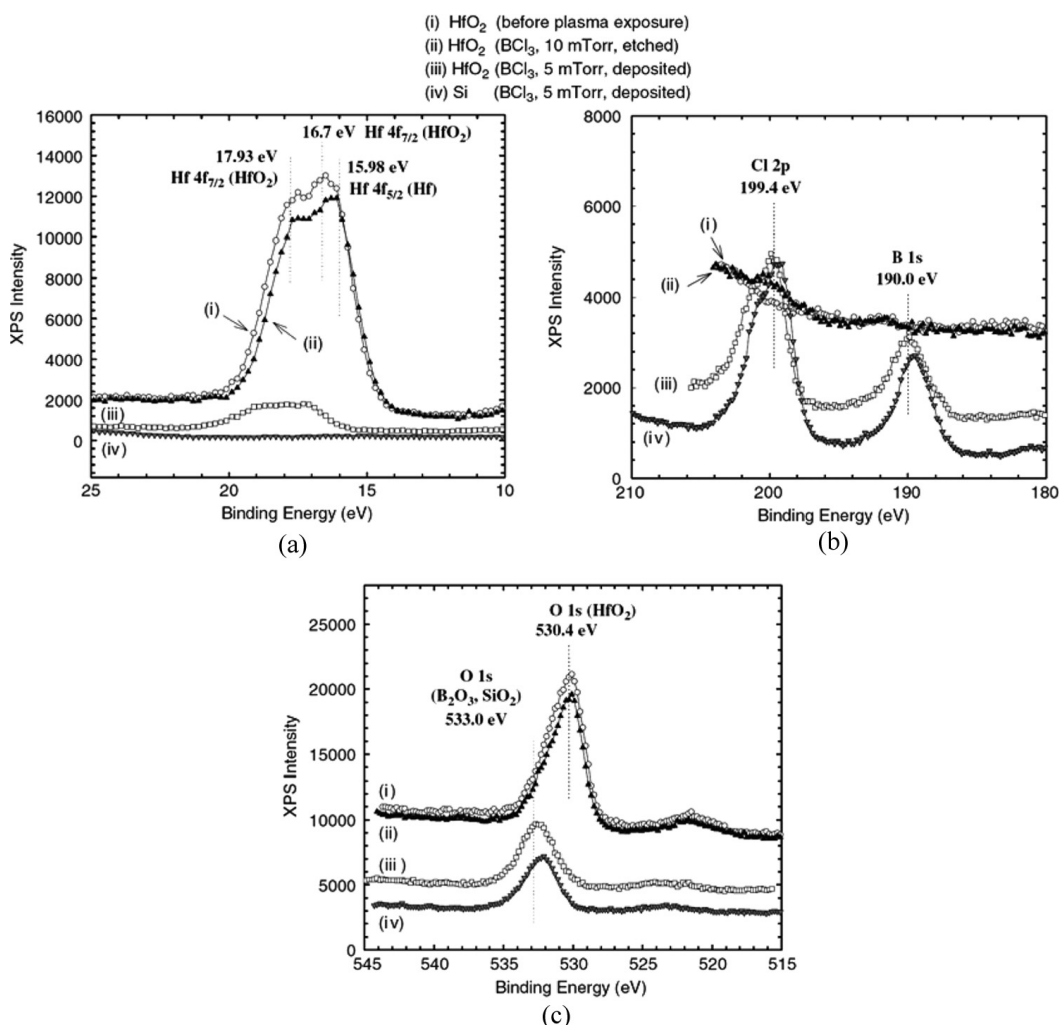
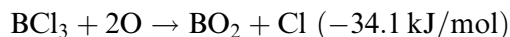
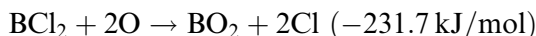
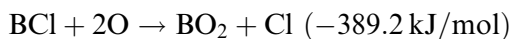
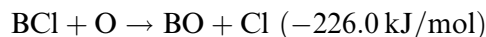


Figure 15. XPS spectra of (a) Hf 4f_{7/2} and Hf 4f_{5/2}, (b) Cl 2p and B 1s, and (c) O 1s, obtained from HfO₂ and Si sample surfaces under three different conditions: (i) HfO₂ surface before plasma exposure, (ii) HfO₂ surface exposed to BCl₃ plasma during 5 min without RF biasing at 600 W power and pressure of 10 mTorr (etched), and (iii) 5 mTorr (deposited); (iv) the spectrum obtained from Si surface exposed to BCl₃ at deposition conditions (Nakamura et al., 2006). Reproduced with permission.

concentration exceeds 30%, deposition is observed again (Kitagawa et al., 2006), as shown in Figure 16.

Apparently, boron reacts with oxygen in the plasma, producing BO_x species. Strong optical emission of BO_2 and BO was observed when 5% O_2 was added to BCl_3 plasma (Shamiryan et al., in press), as illustrated by Figure 17.

Banjo et al. (1997) observed BO_2 by mass spectrometry as O_2 concentration in BCl_3/O_2 exceeded 5%, Baek et al. (1999) reported increase of emission intensity of BO and BO_2 species with increase of O_2 concentration. However, no B_xO_y was found on the etched surface (Baek et al., 1999). We can suppose that as O_2 is added to BCl_3 plasma, less boron is available for film deposition due to reaction with oxygen in the plasma through the following possible exothermic reactions (Baek et al., 1999):



When a lot of O_2 is added (more than 30%), B_2O_3 is likely to form and to be deposited on the wafer (Kitagawa et al., 2006).

Addition of nitrogen produces a different effect. Breithbarth (1992) studied production of BCl and atomic B in BCl_3/N_2 plasma afterglow using plasma-induced emission and concluded that energy transfer from long-lived N_2 energy level could

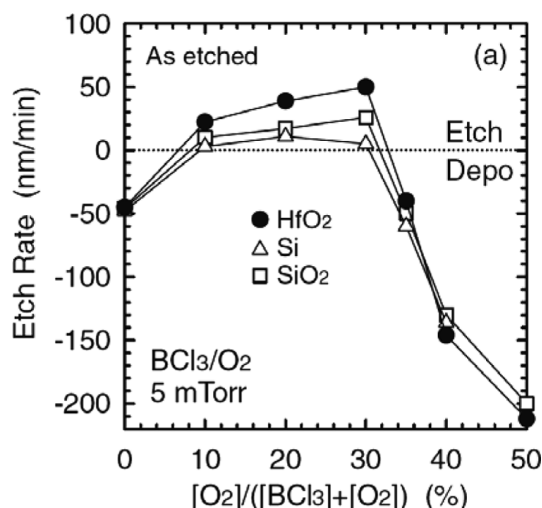


Figure 16. Etch rates of HfO_2 , Si , and SiO_2 in BCl_3/O_2 plasma (Kitagawa et al., 2006). Reproduced with permission.

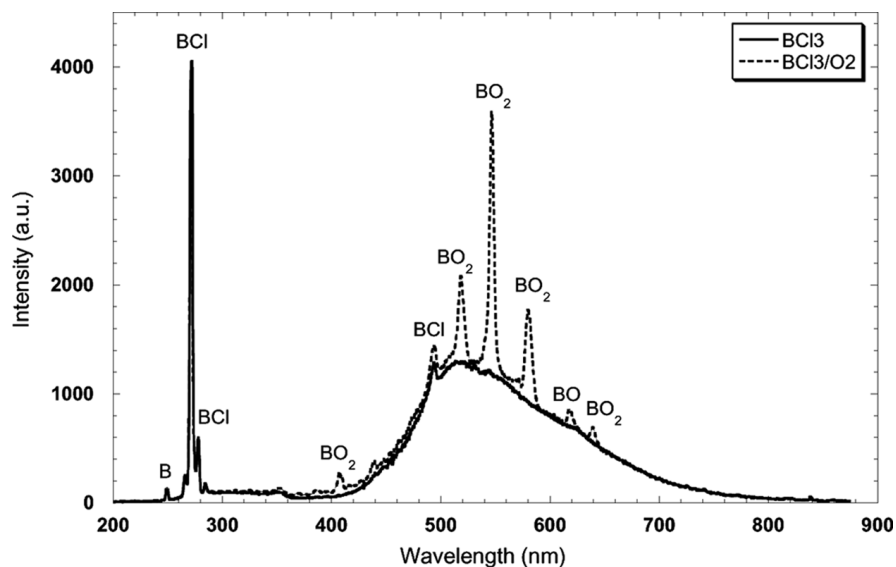
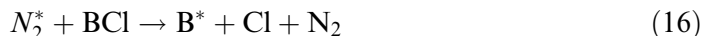


Figure 17. Optical emission spectra of pure BCl_3 plasma (solid curve) and BCl_3 plasma with 5% O_2 (dotted curve). Pressure is 5 mT, TCP power 450 W (Shamiryan et al., in press).

result in dissociation of BCl_3 . For example, vibrationally excited N_2 can dissociatively excite boron from BCl (Breitbarth, 1992):



Nordheden and Sia (2003) reported increased electron density and dissociation rate of BCl_3 as N_2 was added to the plasma, and Fleddermann and Hebner observed increase in the chlorine negative ion density and the Cl metastable ion density, attributed to increased dissociation of BCl_3 by collision with N_2 quasi-metastables (Hebner et al., 1997; Fleddermann and Hebner, 1997). They, however, didn't observe any changes in electron density over the range of BCl_3/N_2 ratios.

The increased dissociation of BCl apparently results in more pronounced deposition of the B-containing film. The film composition changes, as chlorine in the film is replaced by nitrogen. At 50% N_2 in BCl_3 plasma the deposition rate is tripled, and almost no Cl (around 1%) is found by XPS (Shamiryan et al., 2007). Fourier transform-infrared (FT-IR) spectra of the deposited film show appearance of BN peak as N_2 percentage in plasma increases, as illustrated in Figure 18.

When a small amount of N_2 is added, we observed that etch rate of Si and SiO_2 decreases faster than that of HfO_2 (Shamiryan et al., in press), as shown in Figure 19. Wang and Donnelly found that addition of 0.5% of air (which is essentially a mixture of 78% nitrogen and 21% oxygen) (*CRC Handbook of Chemistry and Physics*, 2004–2005) to BCl_3 plasma enhances the film formation on Si, but not on HfO_2 . The film on Si becomes thicker with stoichiometry close to $\text{B}_3\text{O}_4\text{Cl}$.

There are somewhat contradictory results on Ar addition to BCl_3 plasma. Scheller et al. (1998) reported that addition of Ar can result in enhanced production of BCl in capacitively coupled plasma (CCP). Hebner et al. (1997) didn't observe any effect of Ar on BCl_3 plasma in an ICP reactor except dilution, which was explained by differences in plasma density between CCP and ICP. Recently, however, Kim

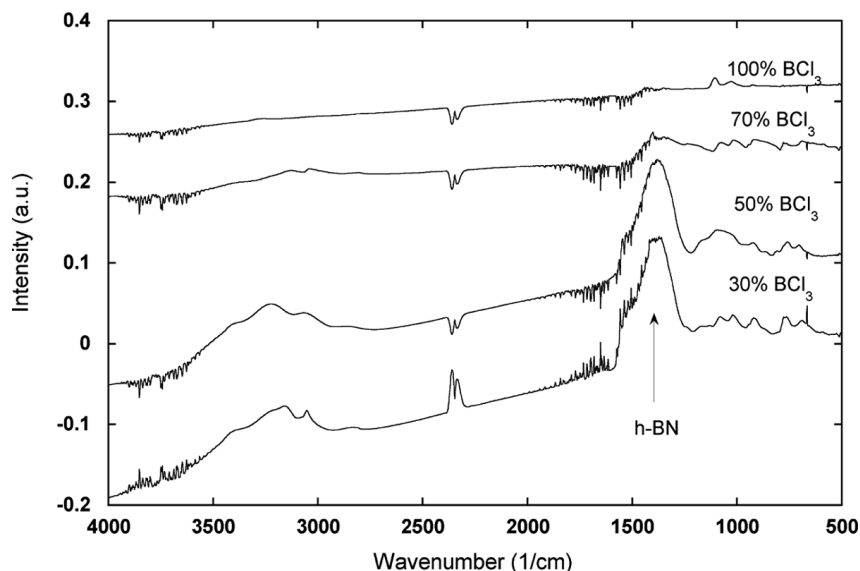


Figure 18. FT-IR spectra (shifted for clarity) of films deposited from BCl_3/N_2 plasma with different gas ratios. The plasma power is 450 W, pressure is 10 mT, and wafer temperature is 60°C (Shamiryan et al., 2007).

et al. (2008a) reported nonlinear etch behavior of ZrO_2 in BCl_3/Ar plasma with a peak in etch rate at about 30% of Ar added, as illustrated in Figure 20.

They correlated the etch behavior to the changes of both densities and fluxes for Cl , BCl_2 , and BCl_2^+ with addition of Ar to BCl_3 plasma in an ICP reactor. They found that electron temperature increases with addition of Ar, while the densities of Cl atoms and BCl_2 radical decrease, according to the simulation results. Density

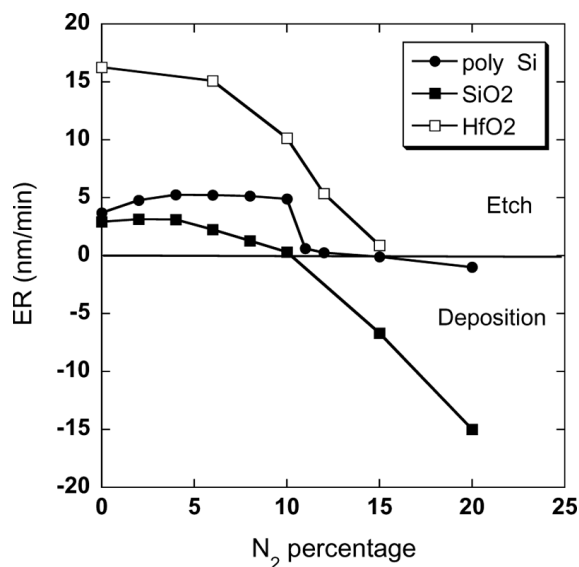


Figure 19. Etch rate of HfO_2 , SiO_2 , and Si in BCl_3/N_2 plasma mixture as function of N_2 content. The total flow is kept constant at 200 sccm, pressure is 10 mTorr, and ICP power is 450 W (Shamiryan et al., in press).

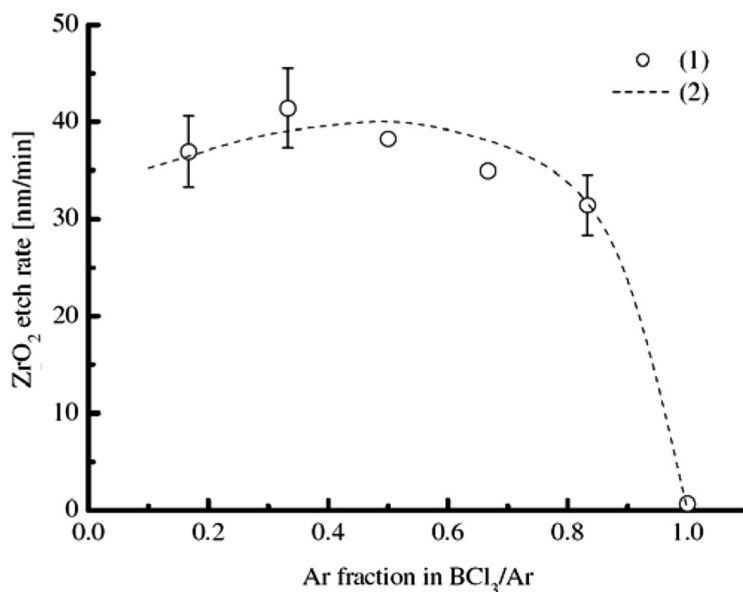


Figure 20. Experimental (1) and model-predicted (2) ZrO_2 etch rate as function of BCl_3/Ar mixing ratio. The plasma conditions are: pressure 4 mTorr, flow 60 sccm, ICP power 500 W, bias power 100 W (Kim et al., 2008a). Reprinted with permission.

of BCl_2^+ has a peak at about 60% of Ar, as shown in Figure 21. The discrepancy between the simulated and measured results is within the experimental error that allowed the authors to conclude that their model provides an adequate description of ZrO_2 etch in BCl_3/Ar plasma.

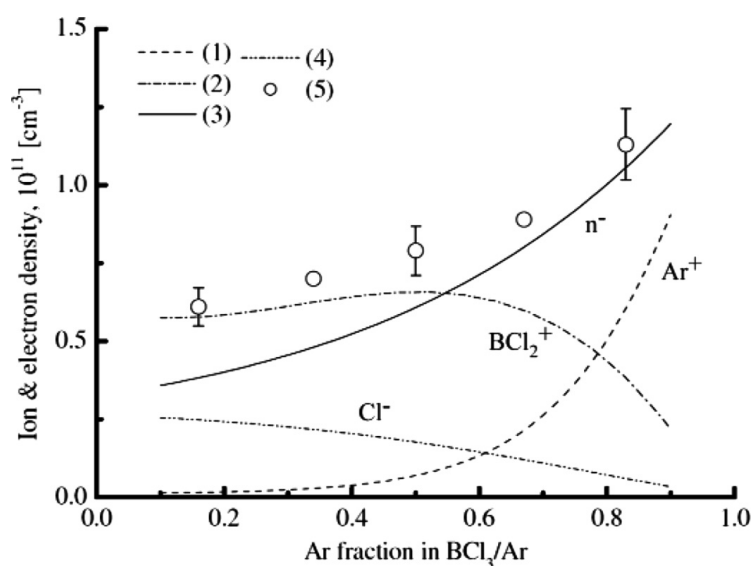


Figure 21. Model predicted (1)–(4) and measured (5) densities of charged species as functions of BCl_3/Ar mixing ratio: (1) Ar^+ , (2) BCl_2^+ , (3) electrons, (4) Cl^- , and (5) total density of positive ions. The plasma conditions are: pressure 4 mTorr, flow 60 sccm, ICP power 500 W, bias power 100 W (Kim et al., 2008a). Reprinted with permission.

Studying film deposition from BCl_3 plasma in an ICP reactor, we observed that the deposition rate is enhanced by addition of Ar, as shown in Figure 22, which also contradicts a simple dilution theory.

As reported by Kim et al. (2008b), addition of He to BCl_3 plasma increases etch rate of ZrO_2 from 36 to 57 nm/min as He concentration increases from 0 to 83%. Using simulations in conjunction with Langmuir probe diagnostic they found that with addition of He the electron temperature rises from 2.66 eV (pure BCl_3) to 5.13 eV (83% He). The rise in electron temperature leads to an increase in positive ion density as measured by Langmuir probe. The simulations show an increase in Cl^+ and BCl^+ ion densities, as shown in Figure 23.

Since densities of neutral species, according to the model prediction, decrease with increase of He content, while ZrO_2 etch rate follows the increase in ion densities, the authors concluded that the limiting stage of the etch reaction is the ion-stimulated desorption of the etch products. Even though etch of ZrO_2 and HfO_2 cannot be compared directly, it is interesting to note that Wang and Donnelly (2008) concluded that desorption of the etch products cannot be the limiting step of the etch reaction as activation energies of HfO_2 etching in BCl_3 plasma of 0.8–4.2 kJ/mol were found to be much lower than the heat of vaporization of HfCl_4 (100.4 kJ/mol).

Addition of H_2 to BCl_3 plasma was found to enhance deposition of a B-containing film (Wang and Donnelly, 2006). The idea behind addition of H_2 to BCl_3 plasma is that because H_2 is efficient in removal of B-contamination from the Si surface (as will be shown below), BCl_3/H_2 plasma would combine etching and cleaning in one step. However, addition of H_2 to BCl_3 plasma produced a thicker film on HfO_2 . The XPS analysis of B (1s) showed appearance of strong peaks indicating BO and BOCl_x , as illustrated in Figure 24.

Having reviewed all the data collected on BCl_3 -based plasma behavior one can see that selectivity of high- k etch over Si substrate could be achieved through two mechanisms: increasing etch rate of the high- k and decreasing etch rate of Si. The

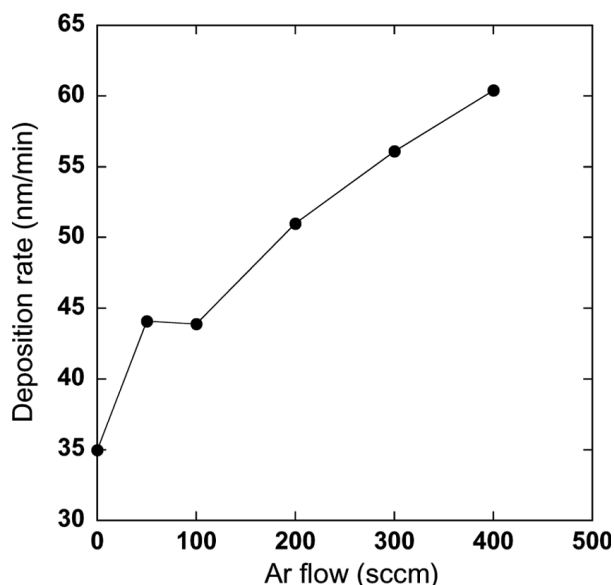


Figure 22. Deposition rate of a film in BCl_3/Ar plasma as function of Ar flow. The BCl_3 flow is kept constant at 200 sccm, pressure is 10 mTorr, ICP power is 450 W.

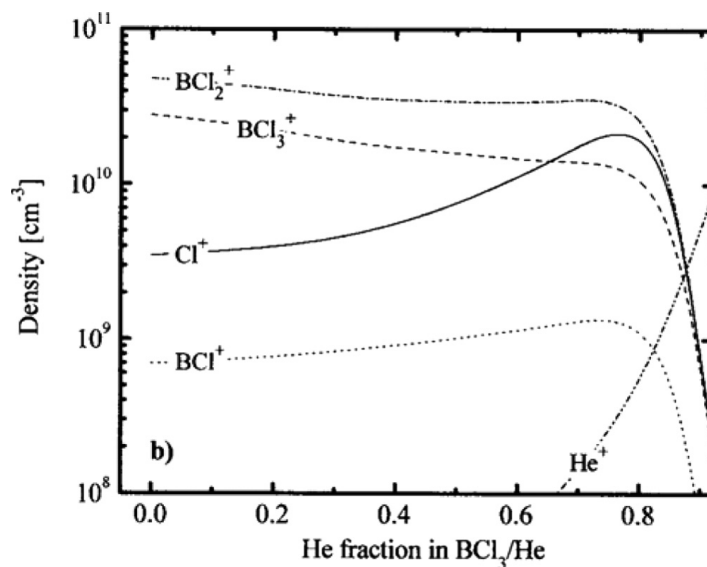


Figure 23. Model-predicted ion densities in BCl_3/He plasma as function of He fraction. Pressure 4 mTorr, total flow 60 sccm, ICP power 500 W, DC power 100 W (Kim et al., 2008b). Reprinted with permission.

increase of high- k etch rate is caused by boron reduction of metal oxides, while the sharp decrease of the Si etch rate is caused, first, by decrease of chlorine content in BCl_3 plasma and, second, by preferred formation of a protective boron-containing film on the Si surface.

Analysis of the etching threshold energies (E_{th}) in Cl_2 and BCl_3 plasma shows significant increase of E_{th} of Si etch in BCl_3 plasma as compared to Cl_2 plasma, while

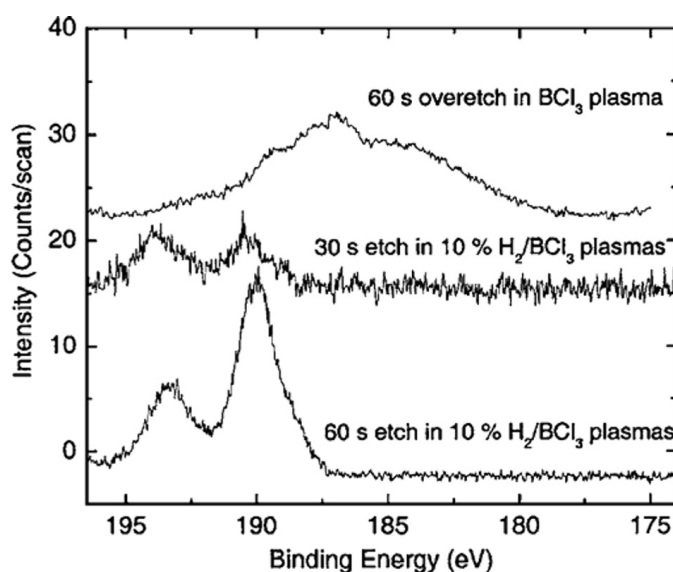
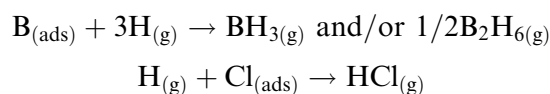


Figure 24. B(1s) XPS spectra, top: over-etching in a BCl_3 -plasma (total etching time 130s, 10 mTorr, 10 sccm, 190 W); middle: 30s exposure to a 10% H_2 - BCl_3 plasma (same plasma conditions); bottom: 60s exposure to the same plasma (Wang and Donnelly, 2006). Reprinted with permission.

E_{th} for high- k remains almost the same. The increase of the Si etching threshold energy in the BCl_3 plasma could be attributed to the formation of the B-containing passivation film. The etching threshold energies for Si, SiO_2 , and two high- k materials, ZrO_2 and HfO_2 , are summarized in Table V. One can see that among fluorine, chlorine, and BCl_3 plasmas only the latter allows development of selective etching of high- k over the Si substrate.

A potential issue in etching of high- k dielectrics in BCl_3 plasma could be the presence of boron on the Si surface after the processing. Boron is a p -type dopant for Si and therefore preferably should be removed from the surface. Wang and Donnelly (2005, 2006) studied boron removal using H_2 or Ar/H_2 plasma after high- k etch. They found that hydrogen can remove boron and chlorine from the Si surface, likely through the following reactions:



The XPS spectra of boron and chlorine before and after hydrogen plasma treatment are shown in Figure 25. The author found that pure hydrogen plasma etches Si with the rate of 220 nm/min. However, in Ar/H_2 plasma (1% Ar) the Si etch rate was reduced to less than 10 nm/min without losing boron cleaning efficiency. Ar/I_2 plasma was also found to be efficient in boron removal, but more Si was etched than in Ar/H_2 plasma. BCl_3/H_2 plasma deposited a thick B-containing layer instead of combining of cleaning and etching.

The authors also found that cleaning of the chamber walls is important, as boron deposited on the chamber walls was apparently re-sputtered on the Si substrate, leading to much longer cleaning times required to remove all boron from the Si surface.

The influence of chamber walls condition on the high- k etch process was studied by the group of Joubert (Le Gouil et al., 2006; Ramos et al., 2007). They deliberately coated the chamber walls with either fluorocarbon polymers deposited from $\text{CH}_2\text{F}_2/\text{HBr}$ plasma (Cunge et al., 2005) or with SiOCl resulting from etching of a blanket Si wafer by Cl_2/O_2 plasma (Joubert et al., 2004). It was found that the deposition of B-Cl film is enhanced in a polymer-coated chamber, probably due

Table V. Etching threshold energies of different materials in halogen plasmas

Material	Etching threshold energies, eV		
	Cl_2	BCl_3	F-based
Si	4 ^a	29 ^a	2–4 (SF_6 , NF_3) ^b
SiO_2	20 ^a	32 ^a	2–4 (SF_6 , NF_3) ^b
HfO_2	12–25 ^c	25 ^c	79 (CHF_3) ^d
ZrO_2	12–20 ^e	21 ^a	n/a

^aSha and Chang, 2003.

^bGray et al., 1993.

^cSha et al., 2003.

^dWang et al., 2006.

^eSha et al., 2002.

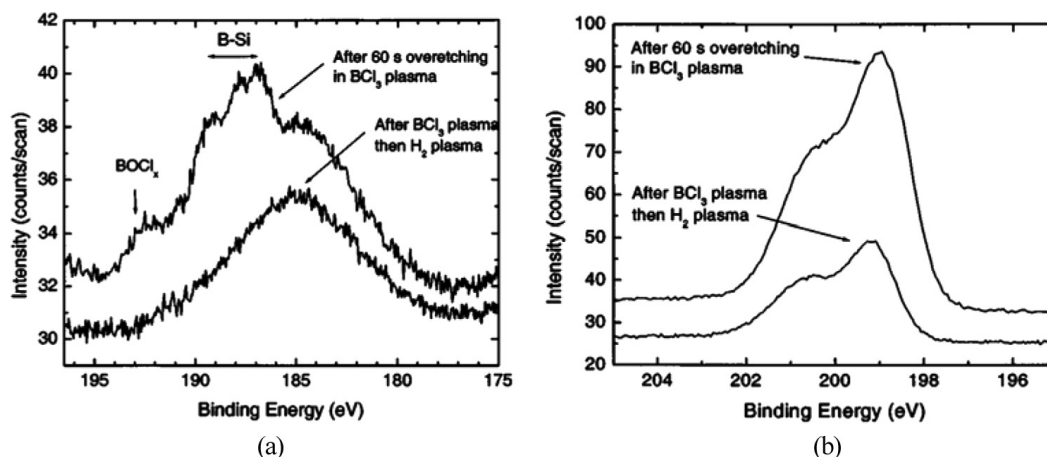


Figure 25. XPS spectra of B(1s) (a) and Cl(2p) (b) of the residue on Si surface. Top: after a 60s over-etching period in a BCl_3 plasma (total etching time 130s, 10 mTorr, 10 sccm, 195 W). Bottom: after cleaning in a H_2 plasma for 60s (10 mTorr, 10 sccm, 185 W) (Wang and Donnelly, 2005). Reprinted with permission.

to hydrogen that could be released from the polymer and can assist in the film deposition, as was observed by Wang and Donnelly (2006). As a result of enhanced film deposition on Si, increased selectivity of HfO_2 etching over the Si substrate was obtained in a polymer-coated chamber (Ramos et al., 2007).

Summarizing data on chlorine-based plasma etch we can conclude that the most promising dry removal candidate is BCl_3 plasma, possibly with some additives. Cl_2 alone is not efficient, due to low high- k etch rate (Cl_2 has difficulties in breaking metal-oxygen bonds) on one hand and high Si etch rate on the other hand. The BCl_3 plasma allows selective removal of high- k dielectrics due to a two-fold impact of boron: first, it reduces metal oxides by forming a volatile $(\text{BOCl})_3$ compound making metals available to form chlorides; second, it forms a passivating B-Cl film on the Si surface. The BCl_3 plasma and, consequently, the film deposition are sensitive to addition of other gases, for example, addition of oxygen prevents film deposition since boron forms BO_x compounds in plasma, and addition of H_2 or N_2 enhances film deposition; in the latter case the film composition changes from B-Cl to B-N. It might be possible to tune the etch process for maximum selectivity using additives to BCl_3 plasma. The boron contamination from the Si surface after high- k etch with BCl_3 plasma can be removed using Ar/ H_2 plasma.

Other Plasmas

Attempts were made to etch high- k with other plasmas, but no success was achieved. Norasetthekul and coworkers (Norasetthekul et al., 2001, 2002; Park et al., 2001) tried to etch TiO_2 , HfO_2 , and Sc_2O_3 with $\text{CH}_4/\text{H}_2/\text{Ar}$ plasma aiming at formation of volatile metal organics/hydrides but found that the etch rate of the mentioned high- k dielectrics in this plasma mixture is even lower than in pure Ar plasma, possibly due to polymer formation from CH_4 plasma. HBr plasma was reported to etch HfO_2 faster than CF_4 (Chen et al., 2004a), which is expected from the higher volatility of metal bromides than that of fluorides (see Table X in the appendix). However, as the metal-bromine bond is weaker than the metal-chlorine bond (see

Table VIII in the appendix) and the metal bromides are less volatile than chlorides (see Table X in the appendix), HBr plasma is even less efficient in etching of high- k than Cl_2 plasma.

Conclusions for Dry Removal

From the data on dry (plasma) high- k removal we can see that BCl_3 -plasma is the most viable solution for the selective removal. Fluorine plasma could form fluorides, but their volatility is very low. Moreover, as fluorine readily etches Si, obtaining selectivity to Si substrate seems extremely difficult. Metal chlorides are substantially volatile, but pure chlorine cannot form them since it cannot break a strong metal-oxygen bond, resulting in a very low etch rate of high- k . Again, as in the case of fluorine, achieving selectivity over the Si substrate is difficult as chlorine easily etches it. Addition of boron in the form of BCl_3 increases the high- k etch rate by removing oxygen through a reduction reaction and decreases etch rate of Si through formation of a passivating B-containing film. As a result, a selective removal of a high- k film over the Si substrate could be achieved. The BCl_3 plasma etch, however, works only if the metal chlorides are volatile enough to be evaporated at the etch temperatures. As most of the conventional etch reactors work at temperatures below 100°C , vaporization of products with boiling temperatures above 500°C (at atmospheric pressure) will be almost impossible even at 5 mTorr (see Figure 4). It means that, for example, rare earth cannot be etched in a conventional plasma reactor even if chlorides are successfully formed using BCl_3 plasma. In that case, besides etching at elevated temperatures, the only option for high- k removal is wet etch or a combination of dry etch and wet etch. These approaches will be reviewed below.

Wet Removal

In this section we will (1) discuss the possible etch mechanism of Hf-based high- k layers in HF aqueous solutions, reviewing the most important factors that improve the selectivity towards an oxide layer; (2) continue with HF semi-aqueous solutions for Hf-based high- k layers to complete the group of HF based etchants; (3) examine the annealing effect and high- k layer damage, which are being considered as standard treatments of the high- k layers; (4) provide a short summary of other non-HF wet solutions; and (5) mention other high- k layers not used very often.

High- k Etchants Based on HF

As was presented above, nowadays the dry etch process is considerably improved and can be applied to remove high- k layers of 2–3 nm. Still, small amounts of Hf residues might be present at the end of the process, and they will be removed only by a wet process. The alternative might be dry removal of the high- k layers at elevated temperatures, but this requires “etchers” having high temperature electrostatic chuck. As a consequence, there was and still is a high interest in combining the dry-wet processes or even wet only for removal of the high- k layers. As will be shown below, considering only the wet option is closely linked to the type of high- k , more specifically to its structure, amorphous or crystalline.

Looking at the stacks where the high- k layers are being introduced it is obvious that the “design” of these wet mixtures is quite challenging. Besides keeping the

selectivity towards the SiO_2 they have also to be selective towards many other pre-patterned layers that are present in the stack. Both front side removal for pattern definition and backside cleaning for avoiding cross-contamination are important issues to be accounted for.

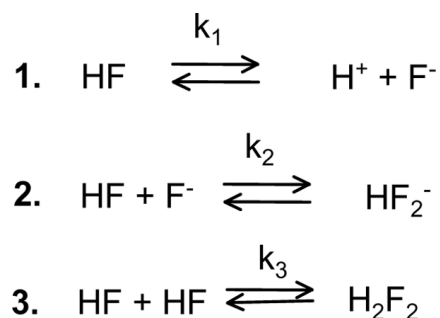
There are many screening tests done, starting with simple acidic solutions that will provide the best selectivity towards an oxide layer and ending with 49% HF, which has no practical application. From all reported trials it is obvious that the HF-based mixtures performed the best by far. Most of the time, the etch rate was much too low to have any future from a production point of view. Also, the hard conditions (high temperatures using strong acids) and the impossibility of removing the last high- k monolayer at the interface with Si “pushed” HF-based solutions as a first candidate, one of the easiest, simplest, and oldest mixtures. These solutions will be reviewed after discussion of HF-based mixtures.

Aqueous HF Solutions for Removing Hf-Based High-k Layers

As was shown above, the HfO_2 -based layers represent the most prominent high- k class. There are a lot of variations in thickness, annealing conditions, mixing with Si/Al, doping with different elements (Dy) (Lee et al., 2001), or capping with other layers, but the major component still remains HfO_2 . For this reason the main wet etch part will refer to this layer. In some paragraphs we will still refer to other types of high- k layers when the comparison is relevant.

The advantage of using HF-based mixtures comes from the fact that they are used in most manufacturing facilities and can be implemented directly. Still, we have to keep in mind that these mixtures were initially optimized to remove an oxide layer and now have to be used to remove high- k layers as selectively as possible over an oxide layer. Although there are a few published studies of high- k removal with concentrated HF solutions, the lack of selectivity with respect to SiO_2 removed this option. Instead, diluted HF solutions were considered and generally “adopted.” Looking at the current high- k thickness, even less than 2 nm, it is more advantageous to have an etch rate of 0.1 nm/min providing an etch process that is highly selective.

Most of the work reported until now has been done using aqueous HF-based solutions. This is a relatively simple system where behavior of HF is well studied. Very briefly, we may say that in water-based solutions the HF dissociates, forming different chemical species, mostly H^+ , F^- , HF_2^- , HF, and $(\text{HF})_2$ (Scheme 1). Other higher polymeric species may exist, but they do not really play a role in the etch mechanism. Equilibrium constants for these reactions at 25°C are already published (IUPAC, 1982). They are corrected for zero ionic strength. Because in diluted HF solutions the ionic



Scheme 1. HF dissociation in aqueous solutions.

strength is very low these values can be used. Also, the calculations can be done using concentrations instead of activities. Their composition is calculated using, besides these three reactions, the mass low and the charge low conservation. Their relative concentration depends mainly on three factors: pH of solution, fluoride concentration, and temperature. While the mechanism for etching SiO_2 with HF is well understood, and the species responsible have been already identified/controlled, HF^{2-} and H_2F_2 (Knotter, 2000) for etching Hf-based high- k layers were totally unknown.

We have found that the species responsible for etching of HfO_2 layer are not the same as for SiO_2 and that their concentration can be well controlled by tuning the main parameters listed above (Claes et al., 2003). Two types of high- k dielectrics have been studied in detail, atomic layer deposition (ALD) HfO_2 as deposited and ALD HfO_2 implanted with BF_2 , after a post-deposition anneal (PDA) process at 500°C in O_2 (Paraschiv et al., in press). The purpose of the implantation was to break the crystalline structure of HfO_2 and will be discussed below.

pH Influence. Dissociation of HF is highly dependent on pH of the solution. Its influence, at constant HF concentration (0.5 mole/L), on removal of SiO_2 , as-deposited, and BF_2 -implanted HfO_2 samples was checked between pH -1 and 4.5 , as illustrated in Figure 26. Experimental results have been compared with theoretical calculations (Verhaverbeke et al., 1994) for the different HF species formed in aqueous solutions as a function of pH (only in the pH range where the ionic strength tends towards zero).

It was found that the highest selectivity towards a SiO_2 layer is obtained at pH values between 0 and ~ 2 . According to the theoretical calculation of the different HF species, using the standard equations and dissociation constants described in Scheme 1, in this pH range the HF_2^- concentration decreases, moreover, HF and H_2F_2 concentrations show similar trends to the etch rate of as-deposited HfO_2 .

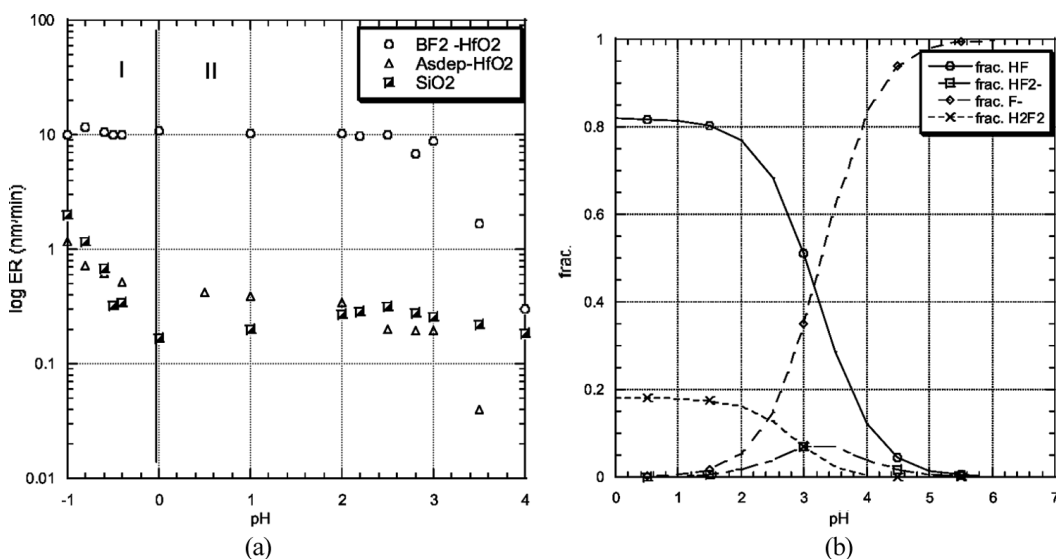


Figure 26. Comparison of the theoretical calculation of fraction α of each species in an HF solution with the experimental etch rates, measured as a function of pH: (a) experimental etch rates determined for thermally grown SiO_2 , as-deposited HfO_2 , and BF_2 -implanted HfO_2 at 25°C ; total fluoride concentration was fixed at 0.05 mole/L; ER are plotted in a log scale; (b) theoretical trends for different species (a) present in an HF solution.

Between pH 2 and 4 the HfO_2 etch rates (ER) start to decrease, whereas the oxide ER reaches a maximum around pH 3. The same increase is observed from the theoretical calculation for HF_2^- . Undissociated HF and H_2F_2 shows a trend similar to that of HfO_2 , decreasing significantly.

For pH values higher than 3, the F^- concentration increases, while the HfO_2 ER is decreasing. This suggested that F^- is not playing any important role in the wet etch of HfO_2 .

At pH lower than 0 the ER of both oxide and as-deposited HfO_2 are considerably increased. Most probably, as it was already suggested by Knotter (2000) for oxide layers, in this range the etch process is controlled by the protonation process, $-\text{OH}_2^+$ formation, and not by concentration of different HF species. The behavior is different for the implanted sample where the ER is constant between pH -1 and 2. The high ER of the implanted layer suggested that the physical damage canceled out all the other effects.

HF Concentration. Studying the ER as a function of HF concentration and comparing the experimental results with the theoretical calculation of HF dissociation as a function of HF concentration, it was found that HF, and not H_2F_2 , is the most probable species responsible for the HfO_2 etch (Figure 27). The observation that the HF concentration follows the same trend as HfO_2 ER strongly suggests that this is the main species responsible for etch.

Effect of Solution Temperature. The temperature was found to be an important factor that helps in improving the selectivity towards SiO_2 . The highest temperature effect was observed for as-deposited HfO_2 . The high activation energy, $E_a = 11.5$ kcal/mol, obtained for as-deposited HfO_2 seems to indicate that the rate-limiting etch step is determined by the adsorption/desorption of the reactive species towards and/or from the surface (Abramson and King, 1939). The same behavior was not

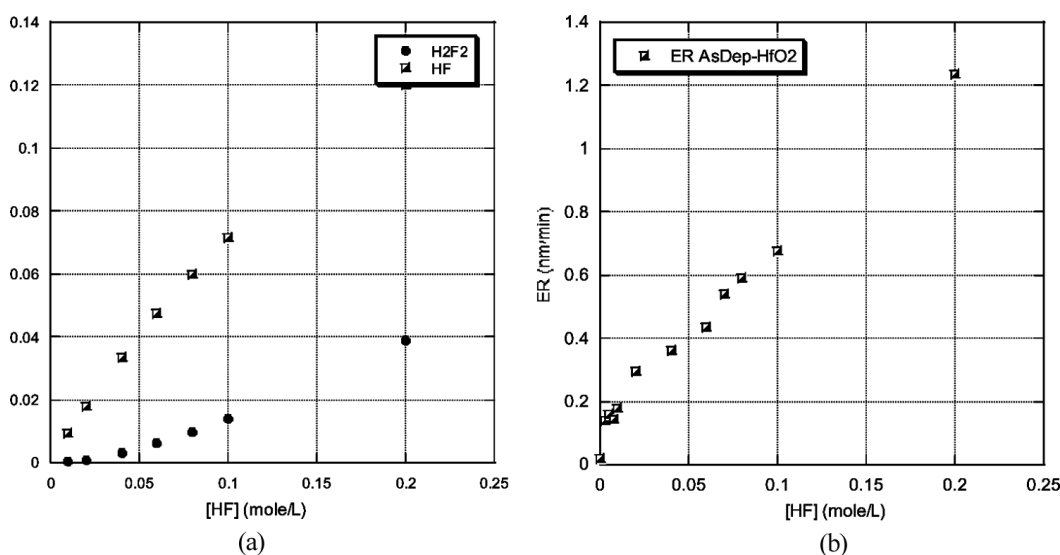


Figure 27. Variation of HF and H_2F_2 concentration vs. total fluoride concentration. Comparison of the theoretical calculation with the experimental etch rate for as-deposited HfO_2 : (a) theoretical trends for HF and H_2F_2 species present in an HF solution; (b) experimental etch rates measured for as-deposited HfO_2 at 25°C ; pH = 1.

observed for BF_2 -implanted samples where the low $E_a = 2 \text{ kcal/mol}$ points more towards a diffusion-controlled etch process.

Same improved selectivity (20:1) over TEOS in diluted HF solutions was also obtained for HfSiO_x layers by increasing the temperature to 80°C (Christenson, 1980a). Si content was 40%.

The best results have been obtained by working at a pH between 0 and 2, temperatures between 40° and 60°C , and low HF concentrations, 0.03–0.05 mol/L. Christenson et al. (1980b), based on activation energy measurements for HfO_2 and HfSiO_x layers, reached the same conclusion that increasing the solution temperature will increase the selectivity towards SiO_2 . The high activation energy obtained in HKE-110 (generic name given to a fluoride-based solution) suggested a temperature of 200°C for obtaining adequate selectivity.

All these results point to the etch mechanism similar to that of SiO_2 with only one change: HF is the active species. In Figure 28(a) we propose a mechanism in which the HF is coordinated by O of $-\text{OH}$ group. Even in its protonated form, the oxygen still has a pair of free electrons that are available to coordinate the hydrogen. In this way the F is brought closer to Hf. Elimination of $-\text{OH}$ group is closely coupled with addition of F (Figure 28(a)). After the $-\text{OH}$ is replaced by F the next nucleophilic substitution can go easier because this time the nucleophilic reactants can reach Hf easily from the side opposite to the leaving group (Figure 28(b)). In this way the surface is again OH functionalized, whereas the first HfO_2 molecule has now two F atoms already in place.

The better selectivity in this pH range should be linked not only to the control of HF dissociation but also to the fact that the HfO_2 surface is much more protonated than SiO_2 . The point of zero charge of HfO_2 is ~ 7.5 , whereas for SiO_2 is only 3.7. This means that more active sites, $\text{Hf}-\text{O}(\text{H})^+-\text{X}$ ($\text{X} = \text{Hf}$ or H), are available for complexing the HF molecule, allowing an easier attack.

The same behavior has been reported by Lowalekar and Raghavan (2004) in the case of ZrO_2 . The selectivity was improved by using low HF concentration, high solution temperatures, and relatively low pH = 3. The authors explained this phenomena also considering the $-\text{OH}$ sites' acidity for ZrO_2 ($\text{pK}_a = 6.7$) and SiO_2 .

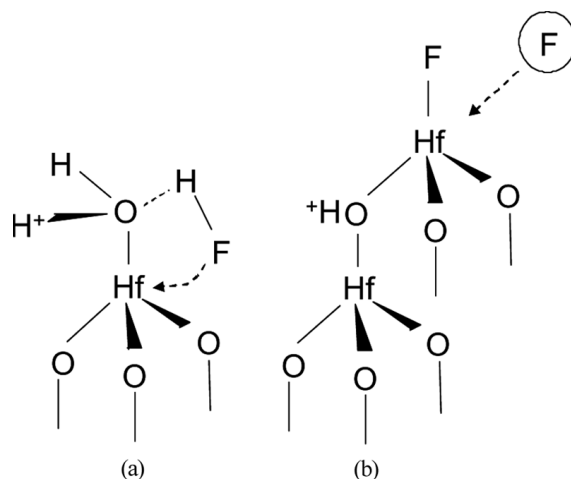


Figure 28. Etch mechanism proposed for HfO_2 etch in HF-based solutions.

Chen et al. (2006) analyzed the HfO_2 surface after exposure to diluted HF by XPS. From the F (1s) XPS signal found at 682–686 eV it was concluded that F represents inorganic fluoride. Hence, F should be bound to Hf and not to O. Also the calculated thickness of the fluoride layer, ~ 0.3 nm, which corresponds roughly to one monolayer, indicated that these are not residues but most probably Hf-F chemical species. This finding agrees very well with the previous scenario.

Lowalekar and Raghavan (2004) constructed Pourbaix diagrams for Zr-F- H_2O and Hf-F- H_2O systems to calculate their solubilities as a function of pH. Depending on the pH, the complexes could be cationic, $\text{ZrF}_2^{2+}/\text{HfF}_2^{2+}$, or anionic, $\text{ZrF}_6^{2-}/\text{HfF}_6^{2-}$. HfO_2 might form an insoluble compound, HfF_4 . Still, the fact that the HfO_2 ER wasn't decreased points to the assumption that HfF_4 is formed in the bulk solution. The solubility of HfF_4 increases with decreasing pH. Based on these studies they were able to achieve selectivity of 60, 16.5, and 2 for metal-organic chemical vapor deposition (MOCVD) ZrO_2 , HfO_2 , and HfSiO_x (80% SiO_2) respectively. HF concentration was 0.01% (at room temperature) and the reference was the TEOS layer. They also observed that significant increase of ZrO_2 ER, heat-treated, can be achieved by increasing the solution temperature. Still, the selectivity wasn't improved due to the fact that the TEOS ER was increasing faster. Although, as with SiO_2 , the ER of ZrO_2 increased with HF concentration, at lower HF concentrations the selectivity over SiO_2 was considerable improved.

Semi-Aqueous HF Solutions for Removing Hf-Based High-k Layers

Besides the three aforementioned factors that control the HF dissociation we may consider the fourth one: ionization constant of the HF solution. This is important when a soluble organic solvent is added to the aqueous solution. HF dissociation can be changed by adding an alcohol. Isopropanol, ethanol, or even ethylene glycol, characterized by low dielectric constants, reduce the HF dissociation driving the equilibrium (Scheme 1) to the left (Kezuka et al., 1999). Removing the ionic species from the solution has a high impact on SiO_2 ER and implicitly on selectivity over HfO_2 . By replacing the H_2O with pure ethanol, the HF dissociation constant decreased by more than two orders of magnitude (Garrido et al., 1996). Reduction of HF dissociation depends on the dielectric and ionization constant of the applied solvent (Luxenburg and Kim, 1980). As can be seen from Table VI, most of the usual mixtures of polar solvents with different dielectric constants and HF (0.05 mole/L at 25°C) were quite inert to both as-deposited HfO_2 and thermally grown SiO_2 layers.

If for thermally grown SiO_2 this behavior was expected, then for HfO_2 , counting on the fact that HF is supposed to be the main etchant species, it was unexpected. A possible explanation could be the low solubility of the reaction products in such non-aqueous media. More work has been done using ethanol/water mixtures. Increasing the ethanol concentration decreases both the thermally grown SiO_2 and as-deposited HfO_2 ER (Figure 29). Still, this behavior is not linear, and a good selectivity is obtained for mixtures containing $\sim 80\%$ ethanol.

Based on the k_1 and k_2 values, determined by Luxenburg and Kim (1980) for different water/ethanol ratios for HF-based mixtures, it is easy to model variations of all HF species (Quevedo-Lopez et al., 2002). Comparing the experimental results with the modeled HF species present in water/ethanol mixtures it is indeed confirmed that the etch rate dependence for HfO_2 does not correspond with the active species concentration evolution of HF_2^- or F^- . Thus, HfO_2 etching is not due to the ionic species present in solution, but due to the HF and/or H_2F_2 species.

Table VI. ER of as-deposited HfO₂ and thermally grown SiO₂ films with different solvent/HF mixtures ([HF] = 0.05 mole/L; T = 25°C)

Solvent	Thermally grown SiO ₂ ER (nm/min)	As-deposited HfO ₂ ER (nm/min)
H ₂ O	0.472	0.3
DMSO	0.02	0.09
DMF	0.14	0
CH ₃ CN	0.156	0.15
CH ₃ OH	0.05	0.13
Ethanol	0	0.08
2-Propanol	0	0.11
Acetone	0	0.2

Watanabe et al. (2003) also tried mixtures of organic solvents, HF (25 wt.% HF) and water to etch as-deposited and heat-treated MOCVD HfO₂ films. ERs varied from 0.21 to 1.43 nm/min for as-deposited samples and from 0.17 to 1 nm/min for heat-treated samples. The best achieved selectivity was ~0.3.

Annealing Effect

Although Hf is soluble in HF, the ERs of HfO₂ and Hf_xSi_{1-x}O₂ in HF solutions decrease drastically after thermal treatment (Balog et al., 1977; Quevedo-Lopez et al., 2002; Chen et al., 2004c; Onsia et al., 2002; Chambers et al., 2001). It is

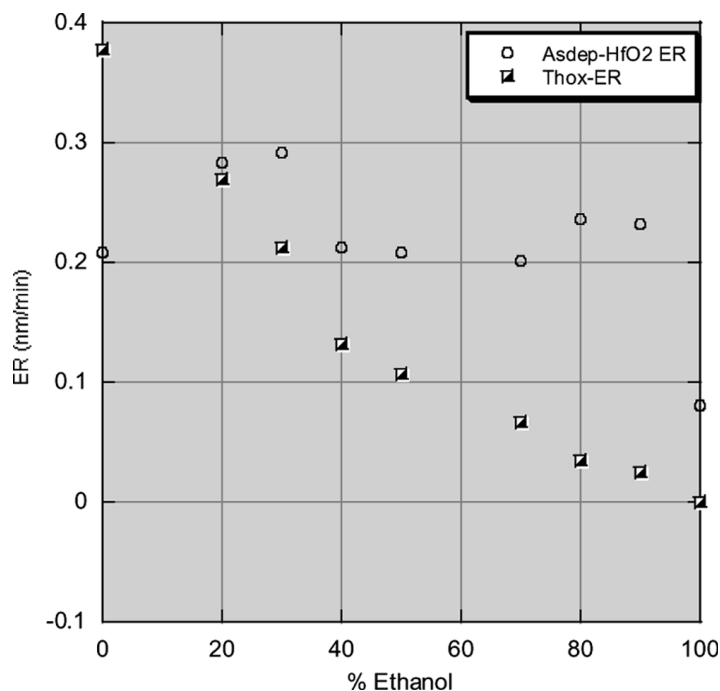


Figure 29. As-deposited HfO₂ and thermally grown SiO₂ ER variation as a function of the percentage of ethanol in the HF/H₂O/ethanol mixture ([HF] = 0.05 mole/L; T = 25°C).

reported that the quality of the layer is highly improved after an annealing process. A lower defect density ($<10^9$) can be correlated with improved electrical performance of the high- k layer (Claes et al., 2004). A thermal annealing process carried out in the presence of nitrogen is beneficial because it reduces the boron penetration (Quevedo-Lopez et al., 2003), increases resistance to crystallization and phase separation (Visokaym et al., 2002; Lysaght et al., 2003), and improves electrical properties (Joel et al., 2001; Visoka et al., 2002; Onishi et al., 2001). Crystallization and densification due to thermal treatment are the main responsible factors for lower dissolution of Hf-based layer in different aqueous solutions (Quevedo-Lopez et al., 2002). The effect is directly dependent on Hf concentration (Chambers et al., 2001) in the case of HfSiO_x layers.

It is not the purpose of this article to review all the publications that deal with optimization of the annealing conditions and engineering of the high- k /Si interface. We are aiming to compare most general methods applied for a nitridation step and describe/compare their effect on the wet etch behavior. As the incorporation of nitrogen in the high- k layers (uniformity across the layer and its chemical state) is highly dependent on the precise annealing conditions and deposition method (and Hf/Si ratio in the case of HfSiO_x), it will be hard to generalize their behavior. The results presented below should be taken as particular cases.

There are mainly two very general approaches to carrying out nitridation: (1) rapid thermal annealing in different ambients containing nitrogen (NH_3 , N_2 , NO , NO_2), and (2) using a plasma nitridation where N_2 and N_2O are the carrier gases. As will be shown below the type of nitridation has a strong impact on the etch behavior (Claes et al., 2005). Figure 30 shows the remaining thickness as a function of etch time for thick ALD HfSiO_x (containing 60% Hf) layer nitridated with NH_3 or by a decoupled plasma nitridation (DPN) in N_2 . An increase in initial etch rate after nitridation treatment was observed. HfSiO_x layers with 60% Hf etched much faster after a NH_3 nitridation than with a DPN treatment. The bulk etch rate for as-deposited and DPN-treated Hf-silicates was similar but rather low compared to

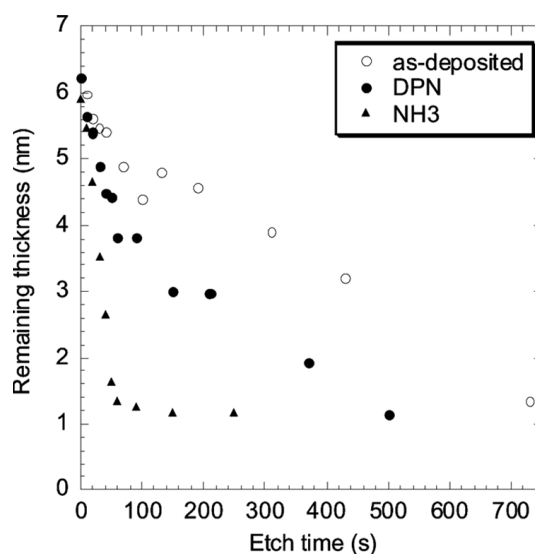


Figure 30. Remaining thickness as a function of etch time for ALD HfSiO_x (60% Hf) as-deposited, NH_3 , and DPN treated (etch solution: 0.01 M HF/HCl at RT).

that after the NH_3 -based nitridation process. It seems that NH_3 nitridation modified the complete layer, while a DPN anneal only altered the top part of the layer without affecting the bulk part of it. In order to understand the behavior the authors performed further characterization of the layers. Surprisingly, the layer density (determined by X-ray reflectometry) increased after thermal treatment but the ER also increased. This pointed out that the layer undergoes a chemical modification and not just a physical change; it was confirmed by TOFSIMS and angle resolved X-ray photoelectron spectroscopy (AR-XPS). N incorporation into the layer and formation of HfN , HfON , and SiN supported the idea that the layer was chemically modified. Layer nitridation was different and less for DPN-treated samples. The amount of N incorporated into the layer increased with the Hf concentration.

Bulk etch rate for both as-deposited and annealed Hf silicates was dependent on Hf content. Initially it increases with Hf content and then after more than 50% Hf the ER decreases (Figure 31).

The etch behavior was also dependent on layer thickness. Figure 32 shows the etch behavior for thin (~ 2 nm) and thick (~ 5 nm for ALD and ~ 8 nm for MOCVD) HfSiO_x layers. Thin (2 nm) HfSiO_x layers were almost completely removed within the first 10 s of etching. Thick HfSiO_x layers show a two-step process: the top part (2 nm) etched faster than the bulk part. One explanation the authors gave was the difference in thermal budget seen during deposition. As a consequence, the top surface could be less dense. Etch rates suggested similar properties for the top part of a thick layer and a thin layer itself. Both ALD and MOCVD Hf-silicate layers showed similar etch behavior.

The Hf/Si ratio impacts not only the wet etch process but also the surface topography. It is believed that during annealing the layer segregates in silica and polycrystalline HfO_2 (Ramanathan et al., 2003). This results in formation of island-shaped grains after annealing and dip in HF. AR-XPS confirms that after annealing and HF dip the surface layer becomes Hf rich (the segregated silica is removed), whereas the surface and bulk compositions of the as-deposited film were the same even after HF dip (Chen et al., 2006).

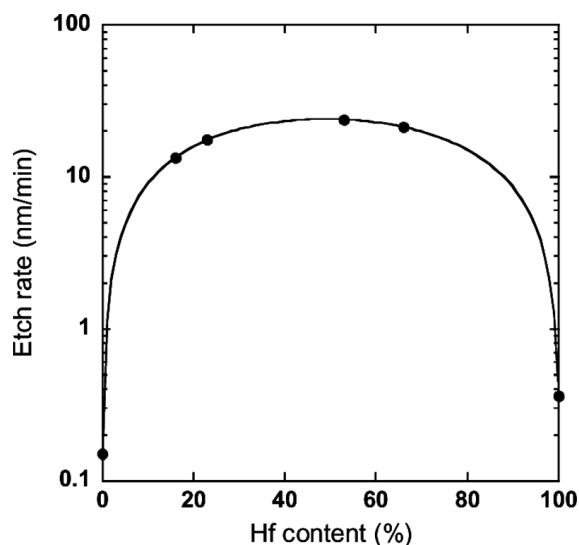


Figure 31. ER of as-deposited ALD HfSiO_x as a function of Hf content. (pH = 0.5; [HF] = 0.03 m/L, 55°C; 5s).

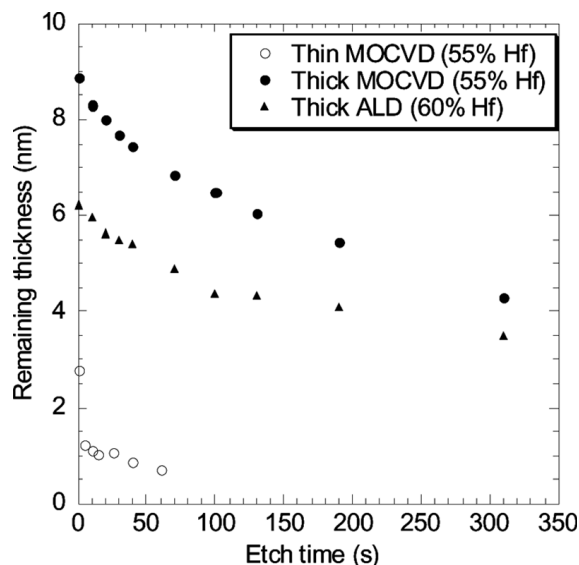


Figure 32. Remaining thickness as a function of etch time for thin/thick MOCVD and ALD HfSiO_x (55–60% Hf) on 1 nm SiO_2 interface layers etched in 0.01 M HF/HCl at room temperature.

Saenger et al. (2003a) have been able to remove the as-deposited atomic layer chemical vapor deposition (ALCVD) HfO_2 with an ER of 8 nm/min in 10:1 HF. After annealing at 700°C, it became almost unetchable. The same behavior has been reported by M. Balasubramanian et al. (2004) for MOCVD HfO_2 , which after annealing at 1000°C for 1 s in N_2 ambient became unetchable.

In the case of ALD HfO_2 when the precursor was $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_3$ [OC(CH₃)₃] the film was still etchable even after an annealing for 1 min in N_2 at 800°C (Seo et al., 2006). After analyzing the microstructure of the annealed film the authors discovered that the film was still amorphous.

J. Chen et al. (2006) also looked at the annealing effect on layer microstructure and its etch behavior in HF. After annealing at 700°C or 1000°C (1 min in N_2) the ER of HfAlO_x , HfO_2 , HfSiO_x , and HfON deposited by chemical vapor deposition (CVD) or physical vapor deposition (PVD) in 1% HF dropped by different amounts. A 7 nm layer of HfAlO_x (Hf:Al = 7:3) was removed in 10 s, whereas HfO_2 of the same thickness couldn't be removed at all. HfON was completely removed but the ER varied as a function of thickness. After annealing the layer at 1000°C the ER of HfAlO_x dropped from tens of nm/min to 0.08 nm/min and HfON became unetchable. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) analysis of the HfO_2 after deposition and annealing at 700°C and 1000°C, respectively, revealed that the layer changed from amorphous to partially crystallized and finally fully crystallized. After a wet HF treatment the AFM measurements revealed also: (1) a smooth surface for the amorphous layer, (2) a rough surface characterized by the presence of islands of 10–20 nm (grain size of HfO_2 crystal was 10–20 nm) for the film annealed at 700°C, and (3) formation of groove-like structures due to the etch of the grain boundaries, when the anneal was carried out at 1000°C (Figure 33). In the case of HfAlO_x the layer was crystallized only at 1000°C (Figure 34).

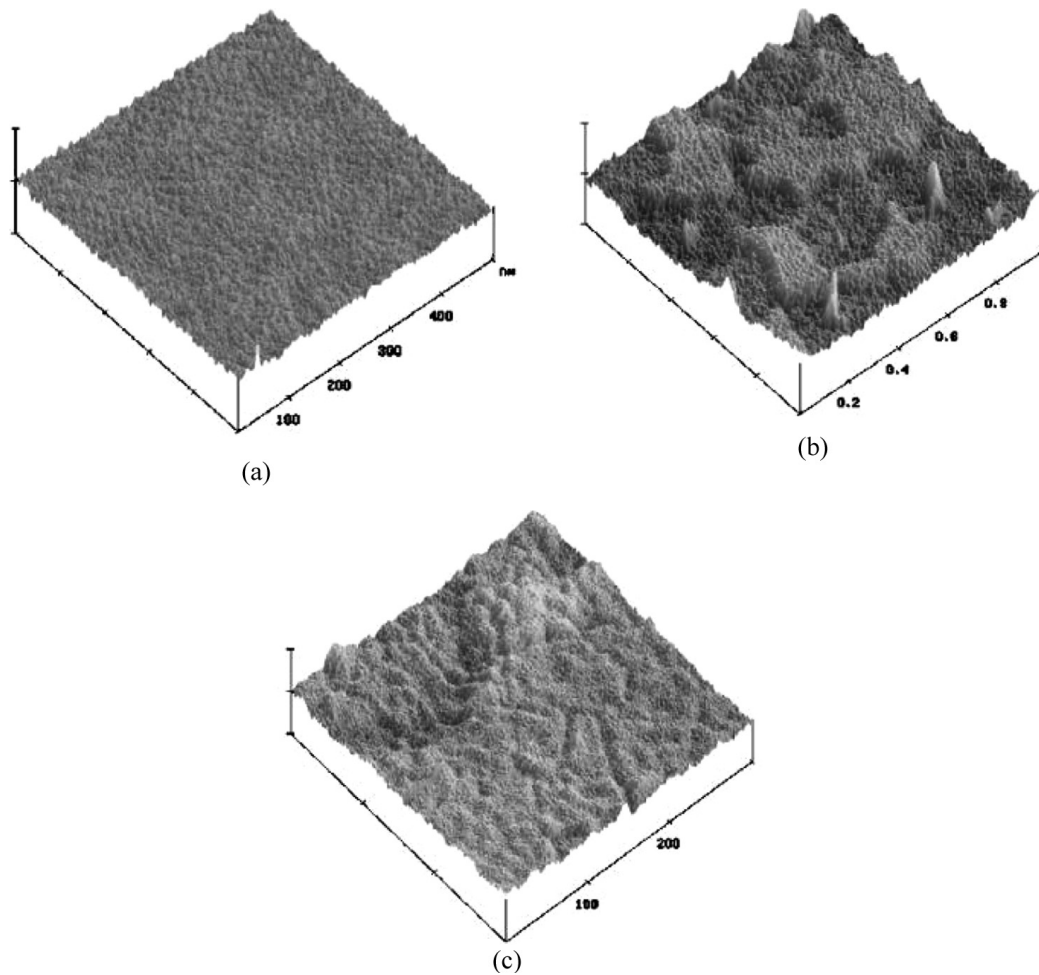


Figure 33. AFM analyses after etching in 10% HF for 1 min, on the HfO_2 surfaces of (a) as-deposited film, (b) after PDA at 700°C for 1 min in N_2 , and (c) after PDA at 1000°C for 1 min in N_2 . (Chen et al., 2006) Reprinted with permission.

Effect of Ion Implantation

In device applications, the high- k layers are mostly thermally treated, for reasons mentioned before. This makes them very difficult to be removed by a wet selective process towards an oxide layer. Improved selectivity might be achieved with an appropriate pretreatment of the annealed HfO_2 layer prior to wet etching. This can be carried out either by a plasma damage or by ion implantation. It is known that ion implantation damage can increase the wet etch rate of SiO_2 (Liu et al., 1996).

An increase of the ER after implantation has been reported by Balasubramanian et al. (2004) after implanting an MOCVD HfO_2 layer with As, BF_2 , B, or P. Best results were obtained for BF_2 and As implants when the implant energy was 5 keV. Still, only the first 4 nm were removed in the diluted HF solution (1:50). After this critical depth the ER became negligible. Increasing the implant energy to 20 keV did not help. Two explanations have been provided for this effect: (1) the projected range was larger than the HfO_2 thickness, and (2) a self-annealing process may occur during the implantation due to temperature rise. It should be mentioned that As and

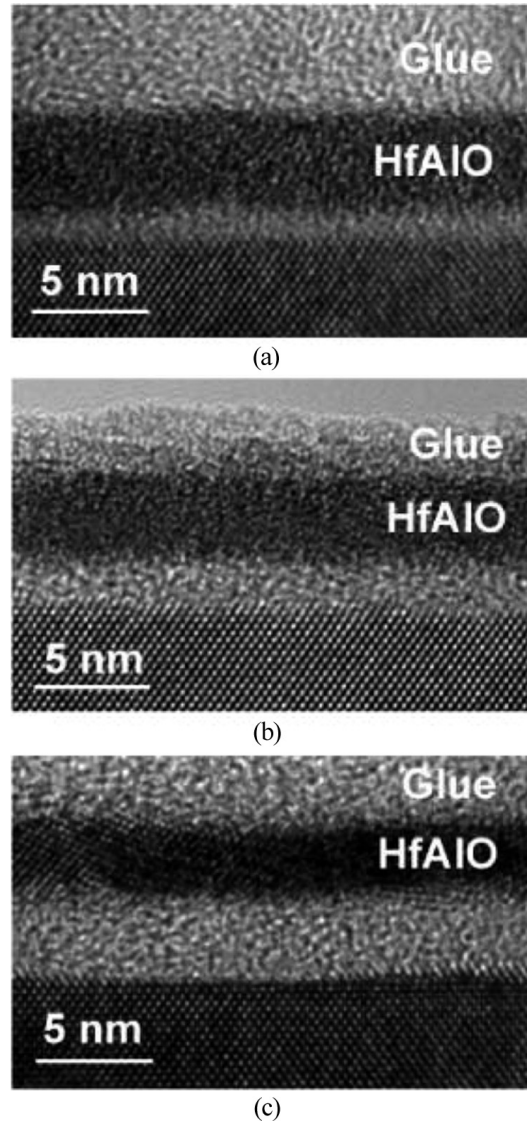


Figure 34. Cross-sectional TEM images of (a) as-deposited HfAlO film, (b) HfAlO film annealed at 700°C for 1 min in N₂, and (c) HfAlO film annealed at 1000°C for 1 min in N₂. (Chen et al., 2006) Reprinted with permission.

BF₂ implanted samples have shown reasonably high ER even after annealing for 1s at 1000°C. This may suggest that under these conditions the layer itself undergoes physicochemical changes that are not recovered during annealing. This contradicts results reported by Barnett et al. (2003a) that show that the ER of an MOCVD HfO₂ film is again negligible after a brief annealing. In the last case this suggests more a physical damage mechanism, crystallization damage. No effect has been observed for B and P implants, possibly due their small atomic size and out diffusion through the HfO₂ grain boundaries (Suzuk et al., 2003). An implant dose of 10¹⁵ atoms/cm² increased the ER of HfO₂ in H₃PO₄ (155°C) from 0.04 to 0.15 nm/min (Barnett et al., 2003b).

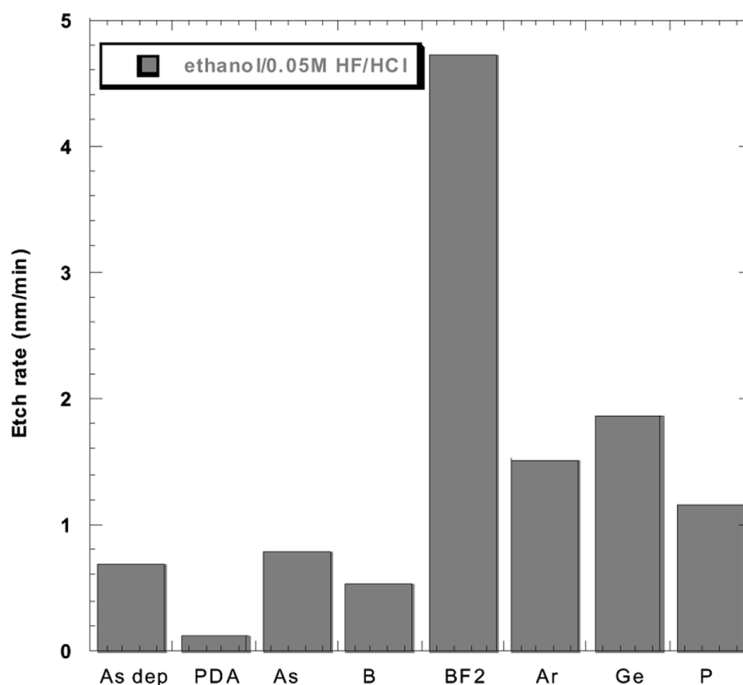
A wide range of implants, As, Ar, Ge, P, B, BF₂, and GeF₂, for high- k damage has been also screened by Claes et al. (2003) (Table VII).

Table VII. Overview of implant elements under study with their implant energies and doses

Implant element	Implant energy (keV)	Implant dose (10^{15} at/cm ²)
As	2	1
Ar	1	1
	4	1 or 3
Ge	2	1
	5	1 or 3
P	2	1
B	0.5	1
BF ₂	2	2
GeF ₂	4	1
	7	1

The implanted thickness was targeted for 4–5 nm ALD HfO₂ (total thickness of the high-*k* layer). As can be seen from Figure 35, the BF₂ implant gave the best result.

Still, this implanting process can have an impact on electrical performance, i.e., shifts in sheet resistance, when integrated in downscaled devices. Some tailing of the implant profile in the Si substrate cannot be avoided. Therefore, nonreactive ions or molecules are preferred. HfO₂ damaging was also obtained by exposing the thermally treated HfO₂ to an ion bombardment from an Ar plasma. High-*k* was sputtered until around 1 nm of HfO₂ was left on the substrate. This remaining layer was etched away with the optimal etch solution (Figures 36(a) and (b)).

**Figure 35.** Etch rate of thermally treated ALD HfO₂ after implantation with different ions when etched in an ethanol/0.05 M HF/HCl solution.

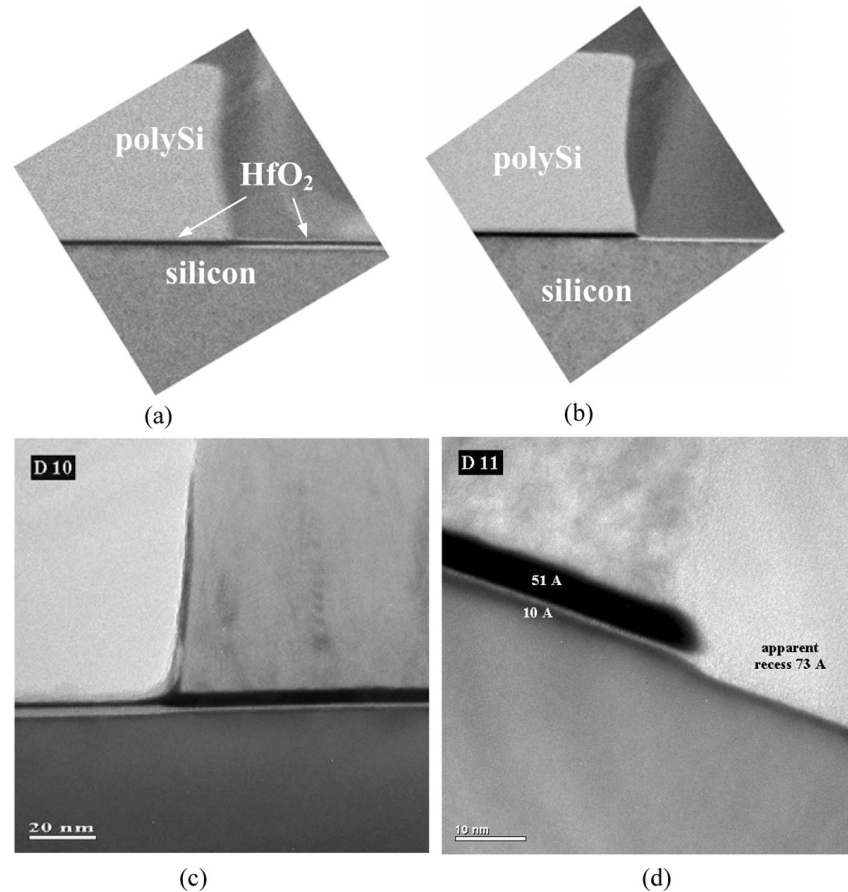


Figure 36. TEM micrographs of thermally treated ALD HfO_2 after: (a) polysilicon etch and Ar bombardment of high- k ; (b) followed by wet removal with 80% ethanol/0.05 M HF/HCl for 5 min; (c) polysilicon etch and BF_2 implantation of high- k ; (d) after wet removal with 80% ethanol/0.05 M HF/HCl for 5 min.

In Figures 36(c) and (d) are presented the results of the high- k removal process before and after a BF_2 implantation or after a partial dry etch process.

Non-HF-Based High- k Etchants

H_2SO_4 , H_2O_2 , 49% HF, TMAH, HCl, H_3PO_4 , HNO_3 , KOH, and NH_4OH used at temperatures between 20° and 150°C (Christenson et al., 2003a) were found to be unsuccessful in removing HfO_2 , ZrO_2 , ZrSi_xO_y , or HfSi_xO_y layers providing enough selectivity towards the SiO_2 . Metallic Hf is soluble in H_2SO_4 or H_3PO_4 but in order to remove an Hf layer first the native oxide had to be removed in HF (Chen et al., 2006). HfSi_xO_y layers were removed in so-called HKE (fluoride-based family) at 80°C, but this solution was unsuccessful for HfO_2 and ZrO_2 . Based on activation energy measurements it was possible to conclude that by playing with the temperature, at least for HfSi_xO_y layers, it would be possible to obtain reasonable selectivity towards oxide layers. The huge decrease in ER between HfSi_xO_y (20% Si) and HfO_2 indicates the effect of the sample crystallinity on the etch behavior.

The deposition method also impacts HfO_2 ER. In their study Chen et al. (2006) used CVD and PVD deposition systems to deposit HfO_2 and HfSiO_2 . All the acids

tested (HF, HCl, HNO₃, H₂SO₄, H₃PO₄) were able to etch the PVD HfO₂ with low ER, but only HF solutions were able to etch the CVD HfO₂. Comparing their results with the theoretical calculation done by Lowalekar and Raghavan (2004), it is obvious that the HfF₄ solubility is much higher (Figure 37), the compound being soluble at room temperature in H₂O or acidic solutions.

The saturation solubility of HfF₄ measured in HCl (15%), H₃PO₄ (85%), and H₂SO₄ (80%) solutions by inductively coupled plasma optical emission spectroscopy were 0.87 mol/L, 4.73×10^{-2} mol/L, and 2.15×10^{-2} mol/L. The low solubility in H₃PO₄ was easily explained by analyzing the HfO₂ after H₃PO₄ exposure. A phosphate layer of ~3 nm was detected on the HfO₂ surface (P 1s recorded at 132–136 eV) (Paraschiv et al., in press).

No significant etch for HfO₂ (ALCVD and MOCVD) or ZrO₂ in SC1 (NH₄OH:H₂O₂:H₂O = 1:2:100) was reported by Bellandi et al. (2003). HfAl_xO_y and ZrAl_xO_y were etched faster, the values being proportional with the alumina content. For HfSiO_x the ER were found to be closed to the SiO₂ reference.

We have tried a combination of HF (0.05 mole/L) and different acids (Paraschiv et al., unpublished). For solutions with a pH higher than zero, the effect of different acids on etch behavior of BF₂-implanted HfO₂ was negligible. In the case of H₃PO₄ the ER was a bit lower, agreeing with the hypothesis that a phosphate layer might block the etch. HCl and HNO₃ gave similar ERs for both thermally grown SiO₂ and as-deposited HfO₂. In the case of H₂SO₄ the thermally grown SiO₂ ER increased to as high as 4 nm/min.

Alternative High-k Materials

ZrO₂ is/was a promising high-*k* candidate. It has a dielectric constant of 20–25, is thermodynamically stable in contact with silicon (Hubbard and Schlom, 1996), has a large energy band gap of 5.1 eV (Kralik et al., 1998), and has a lattice mismatch

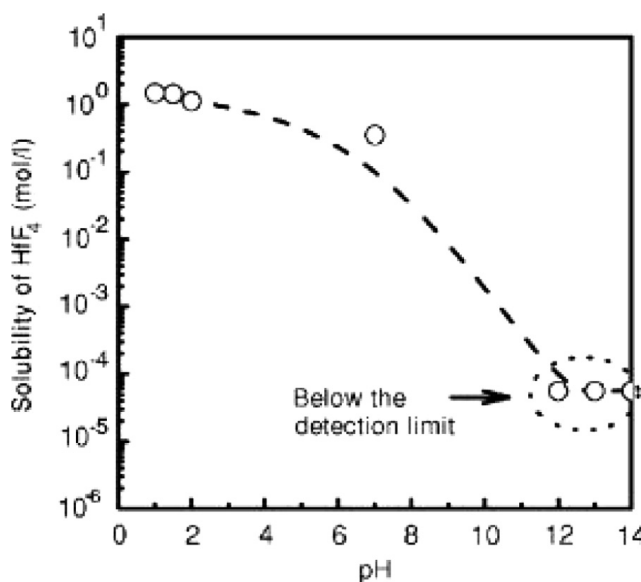


Figure 37. Solubility of HfF₄ in solutions with various pH values. HF and NH₄OH were used to acquire various pH values. The symbols are the experimental data and the dashed line is the fitting of experimental data using the cubic spline approach (Lowalekar and Raghavan, 2004). Reproduced with permission.

of 2.1% with Si (100). The best etch chemistries are the same mixtures as for Hf-based high- k layers. As in the case of Hf-based layers the ER is dependent on the annealing temperature and gas ambient (Hu and Tay, 2001). As-deposited PVD and rapid thermal chemical vapor deposition (RTCVD) ZrO_2 shows two etching regimes (HF etchant (1:100), a slow etch regime, incubation time, at the beginning followed by higher removal rate. These two regime processes were more pronounced for samples annealed in different ambient (N_2 , O_2 , wet H_2 , wet O_2) and at different temperatures (400° to 800°C). The incubation time increased with the annealing temperature (Figure 38). Layer thickness has been measured by spectroscopic ellipsometry. For the as-deposited ZrO_2 , a one-layer model has shown a good fit for the calculated and experimental results. However, for the films annealed at high temperatures, a two-layer model with a topmost layer composed of ZrO_2 and voids and with an interface layer composed of ZrO_2 and SiO_2 underneath gave the best fit. High ERs

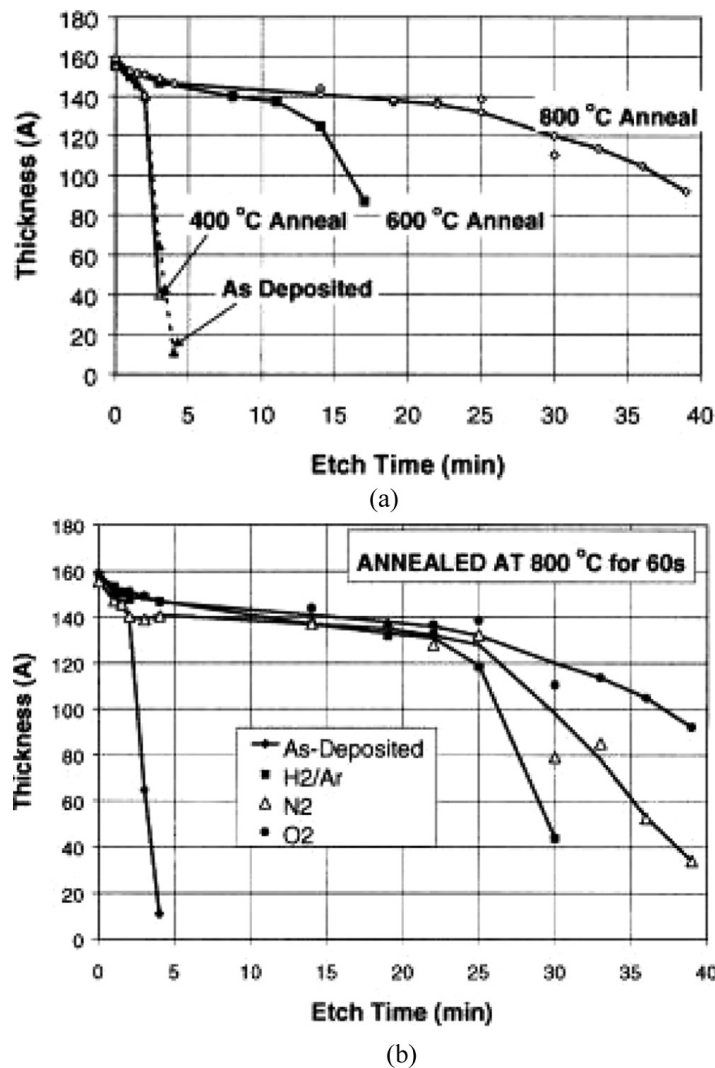


Figure 38. Rapid thermal processing (RTP) anneal effect on etching of ZrO_2 films in 1:100 HF solution at 45°C: (a) annealing temperature effect for samples annealed in O_2 at 400°, 600°, and 800°C for 60s; (b) gas ambient effect for samples annealed in forming gas, N_2 , O_2 at 800°C for 60s (Pelhos et al., 2001). Reprinted with permission.

have been obtained only when the annealing temperature was lower than 400°C (38–39 Å/min). For higher annealing temperatures the ER decreases to as low as 3.3 Å/min (800°C anneal in O₂ for 60s). Besides the temperature, the annealing ambient also had an impact on ZrO₂ removal. ER of 1, 6, and 2.9 Å/min have been obtained after annealing the samples at 800°C for 60s in forming gas or O₂, respectively. All these treatments influenced not only the wet removal but also had a big impact on the EOT and leakage current (the worst was for N₂ anneal at 800°C).

As was mentioned before, the same two-step etch process has been also observed for Hf-based layer with the difference that the first step proceeds faster than the second one.

Sputtered deposited ZrO₂ has been removed at a rate of 0.7 nm/min and 0.6 nm/min in 200:1 and 100:1 HF solutions respectively, at 21°C. ALCVD ZrO₂ was reported to be etched with 1.6 nm/min in 10:1 HF solution using a spin process tool (Agarwal et al., 2002).

Other etchants have also been tried without too much success. The ALCVD ZrO₂ layer was found to be stable in SC1, SC2, SPM, RCA, and 20% KOH (Agarwal et al., 2001). Relatively low solubility was found in 10:1 HF (4.39 Å/min), hot H₃PO₄ (11.5 Å/min), HF/HCl (7:1) (11.85 Å/min), and hot concentrated H₂SO₄ (0.583 Å/min) (Lee et al., 2001). Higher ER was obtained for HF (10:1) when, instead of using static solutions, a spin process was applied (16.71 Å/min) (Lee et al., 2001).

ZrSiO_x. Quevedo-Lopez et al. (2003) published a detailed study regarding the etch properties of ZrSiO_x and HfSiO_x as deposited or annealed (furnace annealing or rapid thermal annealing (RTA) in N₂ ambient) in HF solution. Rutherford backscattering spectroscopy (RBS) and XPS were the two techniques used to characterize the complete removal of the high-*k* layers. ZrSiO_x (11% Si, 22% Zr) was deposited by CVD, whereas HfSiO_x (19% Si, 14% Hf) was deposited by PVD. Surprisingly, the layer did not show a two-step etch process, as in case of ZrO₂. In both cases in diluted HF a low remaining Zr or Hf concentration has been observed, even for long etch time. This was observed only using RBS with a 3.8 μm Mylar absorber). The remaining Zr concentration was always higher than the Hf concentration. Although it was already reported that Zr interdiffusion into Si substrate occurs during high RTA N₂ annealing (Quevedo-Lopez et al., 2001) the fact that most of the Zr is located in the first 0.6 nm of the Si indicated an incomplete removal of the ZrSiO_x layer. No real difference in the etch behavior between RTA and furnace annealing has been observed. As deposited, both layers were amorphous, whereas after annealing they were crystalline. More efficient in removal were highly concentrated (49%) HF solutions. Still, in the case of HfSiO_x even after 20s HF dip for both samples, as-deposited and annealed, a remaining Hf concentration was detected. In contrast, for ZrSiO_x the as-deposited sample was clean. One explanation for the different behavior of the as-deposited Hf and Zr samples was the deposition method. Regarding the behavior of the annealed samples it was suggested that beside the crystallization an increased concentration of the metal, near the Si interface, may occur (Wei et al., 1996).

La₂O₃ is also considered as high-*k* but it has a major problem, its hygroscopic nature. Lanthanide metal atoms have large ion radius and low electro-negativity. Increasing the atomic number will increase the electronegativity of the element. This phenomenon is well correlated with a decrease of the reactivity with water (Jeon and Hwang, 2003). Still, nowadays it is being used in conjunction with other high-*k* as capping layers (Ragnarsson et al., 2007) in order to tune the work function of metal gates. In this case HF is not suitable for removing La, with LaF₃ being insoluble.

As can be seen from Figure 12, increasing the HF concentration decreases the ER, most probably due to formation of insoluble LaF_3 . The removal rate is increased by increasing pH of the solution. In most of the cases, using only HF-based solutions to remove high- $k/\text{La}_2\text{O}_3$ layers resulted in redeposition of large particles. Better results have been obtained using acidified solutions or, even better, using a two-step cleaning approach: first diluted HCl to remove the La_2O_3 and then HF/HCl/ H_2O to remove the Hf-based underlying high- k layer (Figure 39) (Paraschiv et al., in press).

Dy_2O_3 is similar to La_2O_3 and almost the same procedure has been used to remove it (Figure 40).

Al_2O_3 can be considered as a high- k gate dielectric. Still, besides that it provides only a moderate increase of the k value, 9–11 (Manchanda et al., 2001; Buchanan et al., 2000), due to the large negative fixed charge incorporated in the film ($10^{12}/\text{cm}^2$), the threshold voltage becomes rather high (Buchanan et al., 2000). It can be used as capping layer, also being easily removed dry or with acidified solutions (*CRC Handbook of Chemistry and Physics*, 1982–1983a).

Pr_2O_3 has a relatively high dielectric constant of 26–30, low leakage currents ($<10^{-8} \text{ A}/\text{cm}^2$), and is thermally stable up to 1000°C in N_2 ambient (Osten et al., 2001). It was removed with a standard RCA clean. High etch rates have been reported in H_3PO_4 and HCl solutions (a 0.75% HCl solution gave ER of 28 nm/min) (Schwalke et al., 2002). In H_2O -diluted HNO_3 mixtures (1:400) the layer has been removed with an ER of 1.8 nm/min (Mane et al., 2005). This dielectric is sensible to moisture (Jeong and Wang, 2003). To overcome this problem, alloys with TiO_x have been tried (Jeon and Hwang, 2002). These alloys were found to be stable against moisture. Their dielectric constant was dependent on Pr/Ti ratios (Wenger et al., 2004). Aqueous HF-based solutions, generally used to remove the high- k materials, were not efficient in dissolving the $\text{Pr}_{2-x}\text{Ti}_x\text{O}_3$ layers, most probably because PrF_3 and TiF_3 , TiF_4 have poor solubility in H_2O (*CRC Handbook of Chemistry and Physics*, 1982–1983b). Also diluted HNO_3 mixtures were not able to attack the layer. Better results have been reported when H_2SO_4 has been used as etchant (Mane et al., 2005). This acid was able to remove both types of layers, Pr_2O_3 and $\text{Pr}_{2-x}\text{Ti}_x\text{O}_3$. Still, the optimized mixtures used different etching conditions. If Pr_2O_3 was etched with a reasonable ER (3 nm/min) at room temperature in $\text{H}_2\text{SO}_4:\text{H}_2\text{O}$ (1:400) mixture in the case of $\text{Pr}_{2-x}\text{Ti}_x\text{O}_3$, the temperature had to be increased to 65°C in order to achieve a similar rate removal. In both cases the removal rate can be controlled by changing either acid concentration or solution temperature. The higher solubility of Pr_2O_3 than

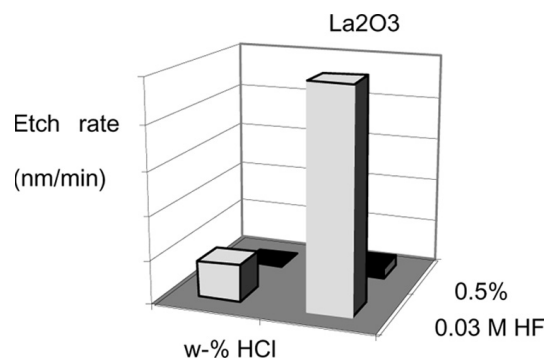


Figure 39. La_2O_3 removal in HF/HCl/ H_2O mixtures.

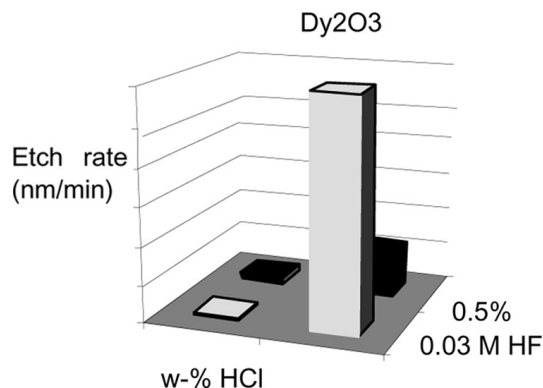


Figure 40. Dy₂O₃ removal in HF/HCl/H₂O mixtures.

Pr_{2-x}Ti_xO₃ might be explained by the difference in solubility between Pr₂O₃ and TiO_x compounds (Greenwood and Earnshaw, 1997).

Gd₂O₃ ($k = 14$) and, even better due to absence of magnetic ions in the oxide (Gurvitch et al., 1989), Y₂O₃ ($k = 18$) have also been used as high- k layers. Both were soluble in acidic media and in both cases the fluorides were insoluble in water (*CRC Handbook of Chemistry and Physics*, 1982–1983c). This property renders the usage of HF media for layer removal inappropriate.

Sm₂O₃ is insoluble in H₂O but moderately soluble in strong acidic media. HF-based solutions can be used to dissolve this layer, as SmF₃ is soluble in H₂O or in strong mineral acids (*CRC Handbook of Chemistry and Physics*, 1982–1983a).

Conclusions for Wet Removal

Hf-based high- k layers are still the most promising candidates for SiO₂ replacement. Wet removal of those layers is possible, but the layers have to be in an amorphous state. This is possible by combining Hf and Si or by damaging the crystalline structure obtained after an annealing step. The most used techniques for amorphizing the layers are ion implantation and different plasma treatments. By these techniques the layers become etchable in diluted HF-based solutions. They provide the best results in terms of ER and complete removal. It is supposed that the active species for etching is the undissociated HF and the etch mechanism is similar to the one for oxide; the HF attack is helped by -OH groups, which coordinate the HF molecule bringing the F closer to Hf. The selectivity towards an oxide layer is obtained by adjusting the pH and temperature and using very diluted HF solutions. Adding an organic solvent improves the selectivity by suppressing the HF dissociation. The Hf-based high- k removal is highly dependent on type of annealing, type of damage (higher ER obtained when BF₂ was used as implant), and layer thickness. Zr-based high- k behaves similarly to Hf-based high- k . All the other standard acid-based solutions or cleaning mixtures used in integrated circuit manufacture were not successful in removing the high- k layers with practical ER. Most nonstandard high- k , like La₂O₃, Pr₂O₃, Gd₂O₃, and Sm₂O₃, do not need HF-based solutions to be removed.

Combination of Dry and Wet Removal

As one can see, neither wet nor dry etch alone could be used as a universal selective high- k removal technique. Wet etch is isotropic and produces undercut on one hand

and is not able to remove crystallized high- k on the other hand. Dry etch is limited by volatility of the etch product, and selectivity to the substrate might be a concern. However, by adding dry and wet removal one could combine the advantages of both methods without suffering from the disadvantages. The combination of dry and wet removal has not received as much attention as dry or wet only removal techniques, but it is worth mentioning in this review as it could bring solutions for otherwise challenging high- k removal. The main idea of the dry/wet combination is modification of the high- k by plasma prior to wet removal. The non-modified high- k cannot be etched wet, while after the modification it becomes etchable. As the plasma modification is anisotropic, the material under the gate is not modified, and lateral attack by wet chemistry is avoided. In this section we will review two approaches: amorphization and chlorination of high- k with subsequent wet removal.

Amorphization of High- k Prior to Wet Removal

As was discussed in the wet removal section, amorphization of high- k by ion implantation increases its wet removal rate. However, high- k can be amorphized not only by ion implantation but also by energetic ions in plasma during gate etch. Since amorphization is an anisotropic process, it does not affect the high- k under the gate and the wet chemistry does not produce any undercut since it cannot etch non-amorphized high- k . The schematic of this process is shown in Figure 41.

The amorphization could be done by nonreactive plasma (e.g., Ar/O₂) (Chang et al., 2007), or reactive BCl₃ plasma etch could be stopped before reaching the substrate and the remaining amorphized high- k could be removed wet (Shamiryan et al., 2005).

Saenger et al. (2003b) reported on high- k layer damaging by ion bombardment supplied by an oxygen plasma in a reactive ion etching tool. However, it is known that oxygen treatments should be avoided in order not to alter high- k layer characteristics by oxygen diffusion.

The same plasma damage by Ar ions followed by wet removal with diluted HF (10%) has been also reported by Chen et al. (2004c) for MOCVD HfO₂ films. Even when the layers have been annealed at 950°C for 30 s in N₂ after an optimized Ar plasma damage, the layer was completely removed. By XRD analysis they observed that the layer it is changed from a monoclinic structure (after annealing) to an amorphous structure (after Ar plasma). Also, in XPS the Hf-related peak is much broader after Ar plasma, indicating the presence of HfO₂, HfO_x, and Hf (Figure 42).

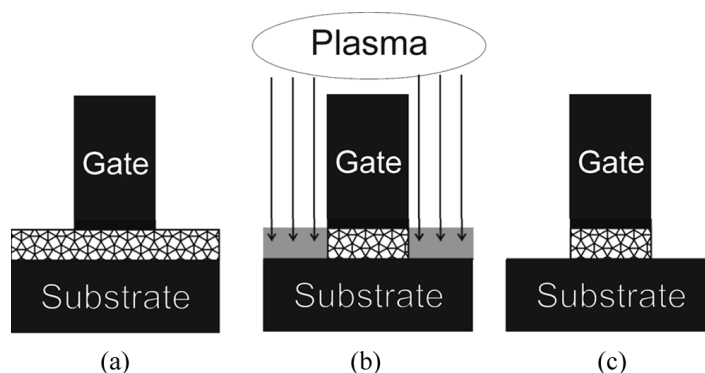


Figure 41. Schematic of high- k amorphization with subsequent wet removal.

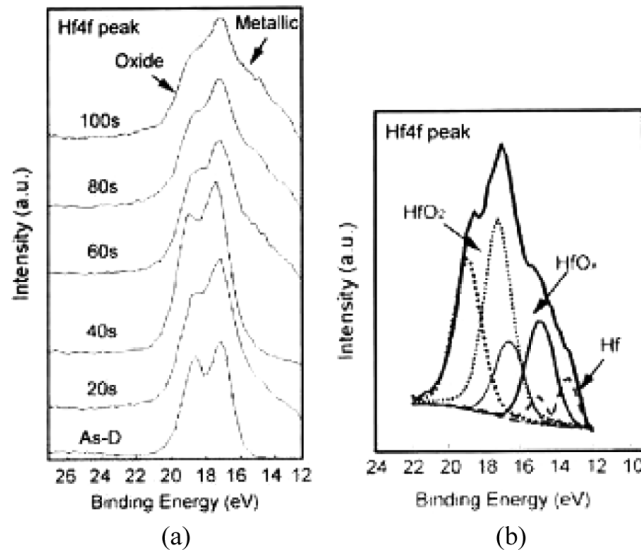


Figure 42. (a) Hf 4f peaks from XPS for Ar-bombarded HfO_2 ; (b) fitting curve of Hf 4f peak from HfO_2 after Ar bombardment for 70s. (Chen et al., 2004c) Reproduced with permission.

A partial dry etch of an annealed HfO_2 using a $\text{HBr}/\text{Cl}_2/\text{O}_2$ based plasma followed by wet clean with diluted HF it is also reported by Mitsuhashi et al. (2003). A more complicated method is proposed by Hobbs and Tobin (2003). Based on the fact that HfCl_4 sublimates at 319°C they propose flowing an anhydrous HCl over a metal oxide while the layer receives heat by radiation. The effective range is $600^\circ\text{--}800^\circ\text{C}$.

Chang et al. (2007) found that upon exposure to Ar/O_2 plasma crystallinity of HfO_2 decreases, as illustrated by Figure 43. An XRD peak at about 27° related to (-111) HfO_2 that is present after annealing at 700°C is significantly reduced after 60s of Ar/O_2 plasma exposure and almost completely disappears after 120s. At the same time, the HfO_2 etch rate in diluted HF (100:1) increases from $0.0012 \text{ \AA/s}$ for annealed sample to $>2 \text{ \AA/s}$ for plasma-exposed samples. It is interesting to note that if the samples were annealed again at 700°C after the plasma exposure, the wet etch rate drops back to $0.0095 \text{ \AA/s}$. The wet removal rate was also found to be dependent on the rf bias applied to the substrate. That allowed the authors to conclude that the wet etch rate increases due to amorphization of HfO_2 by ion bombardment in plasma.

If the dry removal part contains a reactive plasma, that etches high- k , then the etch can be stopped before reaching the substrate and the rest of the high- k could be removed wet. When the bias during the dry etch is reduced in order to minimize the substrate damage by the energetic ions, the amorphization depth would decrease and the amount of the high- k removed by the dry part should be tuned precisely in order to leave a fully amorphized layer for the wet etch. This is illustrated by experiments on combined BCl_3 plasma/HF-based solution ($\text{HF}/\text{HCl}/\text{H}_2\text{O}$, $[\text{HF}] = 0.03 \text{ m/L}$, $\text{pH} = 1$) removal of HfO_2 (Shamiryan et al., 2006). To simulate the real metal gate/high- k stack, a layer of TaN (15 nm) was deposited on top of the high- k . The TaN was removed in two steps: main etch (ME) and over etch (OE). The ME consists of BCl_3/O_2 (5% of oxygen is added for gate profile control and was found to produce little difference on high- k etch), and the OE (which is at the same time a high- k

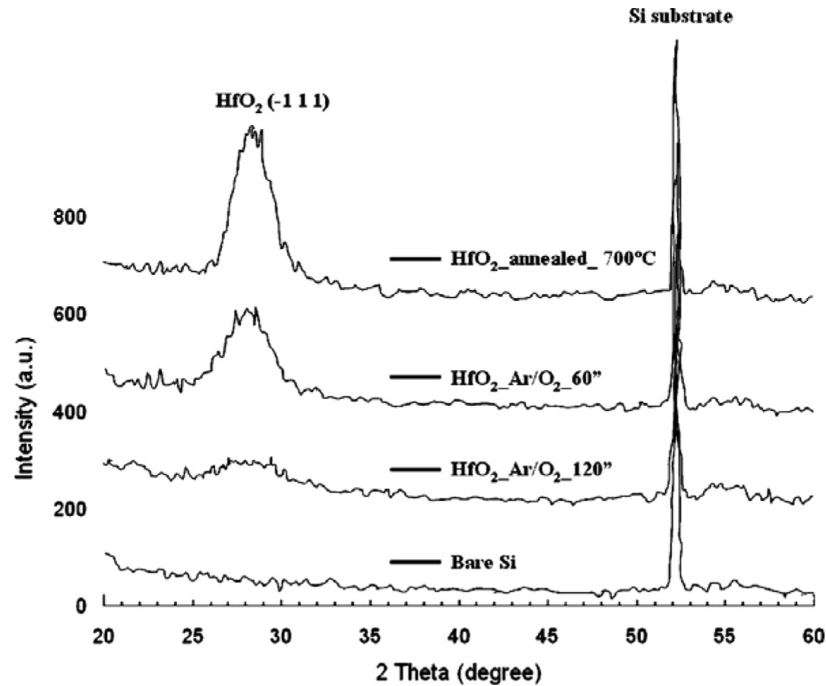


Figure 43. XRD intensity ratio analysis of HfO_2 after Ar/O_2 bombarded treatment. (Chang et al., 2007) Reproduced with permission.

removal step) consists of pure BCl_3 . The high- k thickness as measured by spectroscopic ellipsometry (SE) after dry/wet etch is shown in Figure 44.

First, 10s of ME was applied followed by 7s OE. It was found by SE that the TaN is not completely removed by the ME (not shown in the figure), and

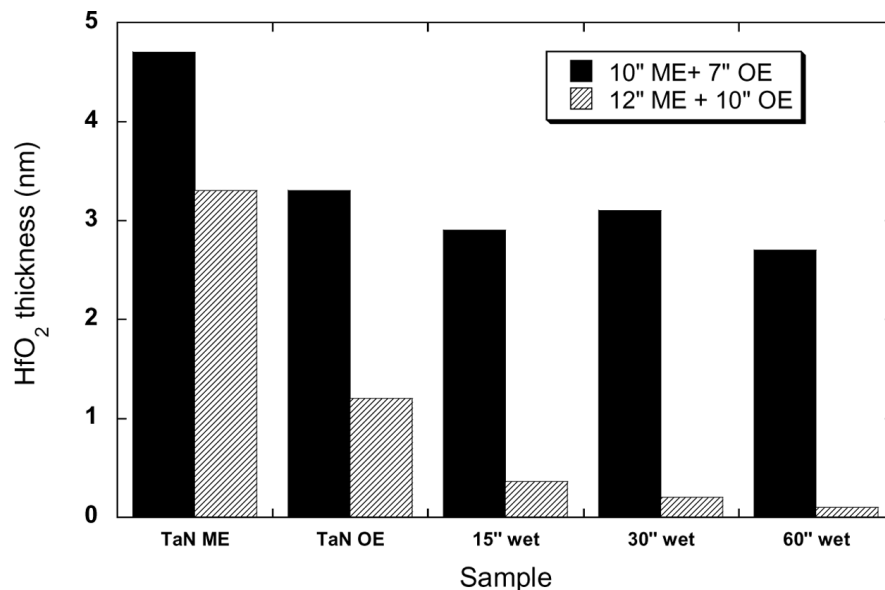


Figure 44. Thickness of the annealed high- k (measured by spectroscopic ellipsometry) after different dry and wet removal steps.

approximately 3 nm of the high- k is left after the OE. The subsequent wet removal was not efficient for etching away the remaining high- k : even after 60s of the treatment by the HF/HCl water solution the thickness didn't decrease significantly, with no clear trend observed. It can be concluded that plasma damage for the remaining 3 nm of the high- k was not high enough to amorphize the whole layer and facilitate the wet removal. As the etch time was increased (ME to 12s and OE to 10s), only 1 nm of the high- k layer was left after the dry etch. This remaining layer appears to be sufficiently damaged as it was readily removed by the same mixture. The 12s ME plus 10s OE was selected as the dry part of the removal process. The high- k removal was confirmed by total reflection X-ray fluorescence (TXRF) results (Hf concentration was below the detection limit of 10^{10} cm^{-2}).

A special method was assisted excimer photon irradiation etch of HfO_2 . Although this method produces rather low ER, due to selectivity towards the SiO_2 layer, it is interesting to use it to remove the HfO_2 residues after a dry etch process. The etchant is H_3PO_4 . The ER becomes noticeable, $\sim 0.27 \text{ nm/min}$, only when the layer is previously exposed to an excimer UV irradiation (172 or 222 nm wavelengths). It is speculated that during this irradiation the photon energy excites the electrons from the valence band to the conduction band and breaks the Hf-O bond. As a consequence the oxygen atoms are released and metallic Hf atoms are dissolved from the surface in H_3PO_4 solution (Hf solvent) (Kume et al., 2003).

Chlorination of High-k Prior to Wet Removal

It was shown in the section dedicated to dry high- k removal that some high- k cannot be removed dry as the boiling temperatures even of the most volatile chlorides are still too low to provide enough volatility of the etch products. However, metal chlorides are usually soluble in water. Therefore, the following scheme could be used for removal of high- k with nonvolatile chlorides: first, the chlorides are formed in plasma, and then, second, the chlorides are removed by water. The scheme is similar to that depicted in Figure 41, but instead of just a physical interaction between plasma and high- k (amorphization) the plasma also produces chemical changes in the high- k layer.

Such dry/wet combination was applied to removal of dysprosium scandate (DyScO_3) high- k material (Shamiryan et al., 2009). Neither Dy nor Sc form chlorides that are volatile enough to be etched at 60°C . However, as both chlorides are water soluble, some part of the high- k can be removed by water rinse after exposure to chlorine-containing plasma, as shown in Figure 45.

After plasma exposure, the DyScO_3 thickness decreases when exposed to Cl_2 plasma, indicating very low etch rate typical for rare earth (Park et al., 2001). The total thickness of the high- k increases in BCl_3 , indicating the presence of B-Cl film (the formation of this film was discussed in the previous section). After water rinse the high- k thickness decreased in both cases, indicating possible removal of the chlorides (in the case of Cl_2 exposure) as well as the B-Cl film and the chlorides (in the case of BCl_3). Total thickness loss is about 2–3 nm, which is comparable to the typical thickness of the high- k dielectric, which makes the process suitable for selective high- k removal.

A similar approach was used for dry etching of poly-Si gates doped with ytterbium (Demand et al., 2007). As Yb does not volatile halides, its presence in the Si gates poses a considerable challenge, leaving residues after etch when Yb atoms masked the Si etch. As Yb doping was made by ion implantation, when no annealing is applied the Yb atoms are localized in a plane beneath poly-Si surface. In order to

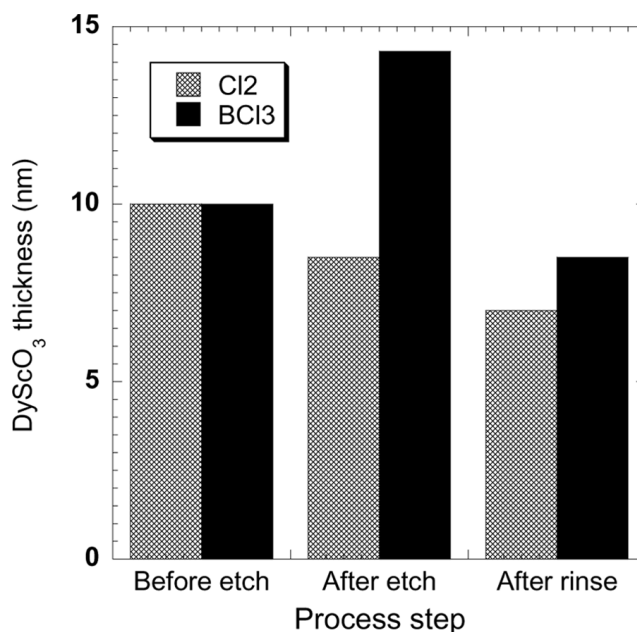


Figure 45. DyScO₃ thickness (measured by spectroscopic ellipsometry) after the steps in the dry/wet removal process. Plasma parameters are: pressure 10 mT, TCP power 450 W, bias −30 V, gas flow 100 sccm, wafer temperature 60°C, exposure time 30s. Water rinse is 10 min at room temperature in deionized water.

remove the Yb, the etching of poly-Si (using Cl₂/HBr chemistry) stopped when the Yb-containing plane was reached. After that a water rinse was applied that was targeted to remove any YbCl₃ and/or YbBr₃ that might have formed. Then the poly-Si etch was continued. As one can see from the scanning electron microscopy (SEM) images in Figure 46, intermediate water rinse prevents residue formation.

In conclusion, even though there are not too many reports available on dry/wet combination for wet removal, it is a promising approach when one needs to improve selectivity over the substrate or remove a layer that cannot be removed only by wet (crystallized high-*k*) or dry (too low volatility of the etch products). The dry/wet

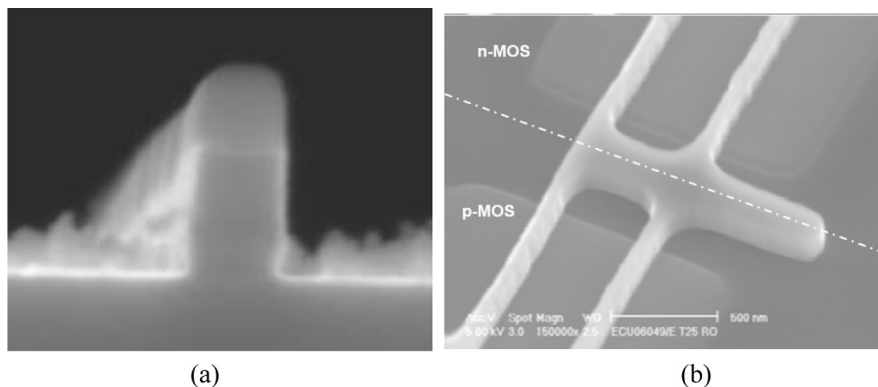


Figure 46. X-SEM image of a Yb-doped Si gates after dry etch without intermediate water rinse (a) and tilted top-down SEM image after the same gate etch but with intermediate water rinse (b). The n-MOS area is doped with Yb.

approach combines high selectivity of the wet chemistry with directionality of the plasma etch, allowing high selectivity without creating an undercut.

Conclusions

Depending on the nature of the high- k dielectric, its selective removal could be achieved by plasma etch, wet etch, or their combination. When the metal chlorides are volatile enough, plasma etch could effectively remove high- k when BCl_3 -based chemistry is used. Neither fluorine nor chlorine plasma is suitable for high- k removal. Fluorine forms metal fluorides, but their volatility is low, and moreover, selectivity over the Si is unacceptably low since fluorine readily etches Si. Metal chlorides are volatile, but chlorine, apparently, cannot break the metal-oxygen bonds in the high- k in order to form those chlorides. As a result, the etch rates are low, as well as selectivity since chlorine etches Si. The role of boron in BCl_3 -based plasma is two-fold. First, it reduces the metal oxides by forming volatile BOCl_x compounds, making metals available for reactions with chlorine to produce volatile chlorides. Second, a B- and Cl-containing film is formed in BCl_3 -based plasma that passivates the Si surface through formation of Si-B bonds. The passivation reduces Si etch rates. As a result, high- k etch is enhanced while Si etch rate is suppressed, which allows selective high- k removal. More research is required in order to improve understanding of the B-Cl film formation. It is known that the deposition strongly depends on plasma composition, e.g., addition of O_2 prevents film formation, while addition of N_2 converts the B-Cl film to B-N like. It might be possible to tune the chemistry and plasma condition to form the film on Si and not on high- k to reach the highest selectivity. The main limitation of plasma high- k removal is volatility of the etch product.

Wet removal of high- k dielectrics is possible on the condition that they remain in amorphous state. This can be achieved by increasing the crystallization temperature (e.g., by using Hf silicates instead of pure HfO_2) or by amorphization (using ion implantation or plasma treatment). The best results in wet removal of Hf-based high- k dielectrics are achieved using diluted HF solutions. It is supposed that the active species for etching is the undissociated HF and the etch mechanism is similar to that of silicon dioxide; the HF attack is helped by -OH groups, which coordinate the HF molecule bringing the F closer towards Hf. The selectivity towards an oxide layer is obtained by adjusting the pH and temperature and using very diluted HF solutions. Selectivity over SiO_2 could be increased by adding organic solvents that increase HF dissociation. The main limitations of the wet high- k removal is strong dependence on the high- k processing conditions and lateral etch of high- k under the gate due to isotropic character of wet etching.

The most promising approach is combination of dry (plasma) and wet removal. In this approach plasma modifies high- k , making it susceptible to wet etch. The modification could be physical (amorphization of a crystalline high- k) or chemical (converting the top layer to chloride). The modified high- k is then removed by wet chemistry, which could not etch the unmodified layer. Since the plasma effect is anisotropic, the high- k layer under the gate is not modified and, therefore, is not attacked by the wet chemistry. The dry/wet combination allows very selective removal when the plasma etch is stopped before reaching the Si substrate and the remaining plasma-damaged layer is removed wet, as well as removal of high- k , which forms not volatile but soluble etch products. In the latter case the chlorides formed on the top high- k surface could be removed, e.g., by water rinse.

Acknowledgments

The authors would like to thank Dries Dictus and German Aksenov for fruitful discussions.

Appendix

Table VIII. Bond strengths of high-*k* materials (bond metal-oxygen) and the corresponding halides

Element	Bond strength (kJ/mol)			
	-O	-F	-Cl	-Br
Si	799.6 ± 13.4	552.7 ± 2.1	406	367.8 ± 10.0
Al	511 ± 3	663.6 ± 6.3	511.3 ± 0.8	429 ± 6
Zr	776.1 ± 13.4	616 ± 15	492.7	n/a
Hf	801 ± 13.4	650 ± 15	497.2	n/a
Ta	799.1 ± 12.6	573 ± 13	544	n/a
Ti	672.4 ± 9.2	569 ± 33	372.8 ± 2.1	439
La	799 ± 4	598 ± 42	n/a	n/a
Dy	607 ± 17	531	n/a	n/a
Y	719 ± 11.3	605.0 ± 20.9	527 ± 84	485 ± 84
Gd	719 ± 10	590.4 ± 27.2	n/a	n/a
Sc	681.6 ± 11.3	589.1 ± 13	331	444 ± 63

The data are taken from the *CRC Handbook of Chemistry and Physics* (2004–2005).

Table IX. Standard molar enthalpy (heat) of formation at 298.15 K for crystalline materials

Element	$\Delta_f H^\circ$ (kJ/mol)			
	Oxide	Fluoride	Chloride	Bromide
Si	−910.7	−1615.0 (g)	−687.0 (l) −657.0 (g)	−457.3 (l) −415.5 (g)
Al	−1675.7	−1510.4	−704.2	−527.2
Zr	−1100.6	−1911.3	−980.5	n/a
Hf	−1144.7	−1930.5	−990.4	n/a
Ta	−2046.0	−1903.6	−859.0	−598.3
Ti	−944.0	n/a	−804.2 (l) −763.2 (g)	−616.7
La	−1793.7	n/a	−1072.2	n/a
Dy	−1683.1	n/a	−1000.0	−836.2
Y	−1905.3	−1718.8	−1000.0	n/a
Gd	−1819.6	−1297.0 (g)	−1008.0	n/a
Sc	−1908.8	−1629.2	−925.1	−743.1

If the enthalpy for crystalline material is not known, then the enthalpy for gas (g) or liquid (l) phase is listed (*CRC Handbook of Chemistry and Physics* (2004–2005)).

Table X. Melting points and boiling points of the metal halides that could be halogen plasma etch products (*CRC Handbook of Chemistry and Physics* (2004–2005))

Halide	Fluoride		Chloride		Bromide	
	MP, °C	BP, °C	MP, °C	BP, °C	MP, °C	BP, °C
SiF ₄ , SiCl ₄ , SiBr ₄	−90.2	−86	−68.74	57.65	5.39	154
AlF ₃ , AlCl ₃ , AlBr ₃	2250	1276 ^a	192.6	180	97.5	255
ZrF ₄ , ZrCl ₄ , ZrBr ₄	932	912 ^a	437	331 ^a	450	360 ^a
HfF ₄ , HfCl ₄ , HfBr ₄	>970	970 ^a	432	317 ^a	424	323 ^a
TaF ₅ , TaCl ₅ , TaBr ₅	95.1	229.2	216	239.35	265	349
TiF ₄ , TiCl ₄ , TiBr ₄	284	subl	−24.12	136.45	39	230
LaF ₃ , LaCl ₃ , LaBr ₃	1493	n/a	859	n/a	788	n/a
DyF ₃ , DyCl ₃ , DyBr ₃	1154	n/a	680	n/a	879	n/a
YF ₃ , YCl ₃ , YBr ₃	1150	n/a	721	n/a	904	n/a
GdF ₃ , GdCl ₃ , GdBr ₃	1231	n/a	609	n/a	770	n/a
ScF ₃ , ScCl ₃ , ScBr ₃	1515	n/a	967	n/a	969	n/a

^aSublimation point.

References

- Abramson, M. B. and King, C. B. (1939). *J. Am. Chem. Soc.*, **61**, 2290.
- Agarwal, A., Freiler, M., Lysaght, P., Perrymore, L., Bergmann, R., Sparks, C., Bowers, B., Barnett, J., Riley, D., Kim, Y., Nguyen, B., Bersuker, G., Shero, E., Lim, J. E., Lin, S., Chen, J., Murto, R. W., and Huff, H. R. (2002). Challenges in integrating the high-*k* gate dielectric film to the conventional CMOS process flow, in: *Gate Stack and Silicide Issues in Silicon Processing II*, ed. S. A. Campbell, L. A. Clevenger, P. B. Griffin, and C. C. Hobbs, K2.1.1, Materials Research Society, Warrendale, Penn.
- An, T.-H., Park, J.-Y., Yeom, G.-Y., Chang, E.-G., and Kim, C.-I. (2000). *J. Vac. Sci. Technol. A*, **18**, 1373.
- Baek, K. H., Park, C., and Lee, W. G. (1999). *Jpn. J. Appl. Phys.*, **38**, 5829.
- Baklanov, M., Green, M., and Maex, K., ed. (2007). *Dielectric Films for Advanced Microelectronics*, John Wiley, Hoboken, N.J.
- Balasubramanian, M., Bera, L. K., Mathew, S., Balasubramanian, N., Lim, V., Joo, M. S., and Cho, B. J. (2004). *Thin Solid Films*, **101–102**, 462.
- Balog, M., Schieber, Michman, M., and Patai, S. (1977). *Thin Solid Films*, **41**, 247.
- Banjo, T., Tsuchihashi, M., Hanazaki, M., Tuda, M., and Ono, K. (1997). *Jpn. J. Appl. Phys.*, **36**, 4824.
- Barnett, J., Riley, D., Messina, T. C., Lysaght, P., and Carpio, R. (2003b). Wet etch enhancement of HfO₂ films by implant processing, in: *Ultra Clean Processing of Silicon Surfaces V*, 11, Trans Tech Publications, Enfield, N.H.
- Bellandi, E., Crivelli, B., and Alessandri, M. (2003). In *Ultra Clean Processing of Silicon Surfaces V*, 15–18, Trans Tech Publications, Enfield, N.H.
- Bersuker, G., Gutt, J., Chaudhary, N., Moumen, N., Lee, B. H., Barnett, J., Gopalan, S., Brown, G., Kim, Y., Young, C. D., Peterson, J., Li, H.-J., Zeitzoff, P. M., Sim, J. H., Lysaght, P., Gardner, M., Murto, R. W., and Huff, H. R. (2004). in: *2004 IEEE International Reliability Physics Symposium: Proceedings*, 479, IEEE, 25–29 April 2004, Phoenix, A.Z.
- Breitbarth, F. W. (1992). *Plasma Chem. Plasma Process.*, **12**, 261.
- Britten, J. A., Nguyen, H. T., Falabella, S. F., Shore, B. W., and Perry, M. D. (1996). *J. Vac. Sci. Technol. A*, **14**, 2973.

- Bruce, R. H. and Malafsky, G. P. (1983). *J. Electrochem. Soc.*, **130**, 1369.
- Buchanan, D. A., Gusev, E. P., Cartier, E., Okorn-Schmidt, H., Rim, K., Gribelyuk, M. A., Mocuta, A., Ajmera, A., Copel, M., Giha, S., Bojarczuk, N., D'Emic, C., Kozlowski, P., Chan, K., Fleming, R. J., Jamison, P. C., Brown, J., and Arndt, R. (2000). 80 nm poly-silicon gated n-FETs with ultra-thin Al_2O_3 gate dielectric for ULSI applications, *Tech. Dig. Int. Electron Devices Meet.*, 223–226.
- CRC Handbook of Chemistry and Physics, 63rd ed. (1982–1983a). B-74, CRC Press, Boca Raton, Fla.
- CRC Handbook of Chemistry and Physics, 63rd ed. (1982–1983b). B-138, B-160, CRC Press, Boca Raton, Fla.
- CRC Handbook of Chemistry and Physics, 63rd ed. (1982–1983c). B-101, B-163, CRC Press, Boca Raton, Fla.
- CRC Handbook of Chemistry and Physics, 85th ed. (2004–2005).
- Chambers, J. J., Rotondaro, A., Bevan, M., Visokay, M. and Colombo, L. (2001). Abstract 1434, in: *ULSI Process Integration II: Proceedings of the International Symposium*, Electrochemical Society, Pennington, N.J.
- Chang, W.-T., Hsieh, T.-E., and Lee, C.-J. (2007). *J. Vac. Sci. Technol. B*, **25**, 1265.
- Chen, J., Tan, K. M., Wu, N., Yoo, W. J., and Chan, D. S. H. (2004a). *J. Vac. Sci. Technol. A*, **21**, 1210.
- Chen, J., Yoo, W. J., Tan, Z. Y. L., Wang, Y., and Chan, D. S. H. (2004b). *J. Vac. Sci. Technol. A*, **22**, 1552.
- Chen, J., Yoo, W. J., Chan, D. S. H., and Kwong, D.-L. (2004c). *Electrochem. Solid-State Lett.*, **7**, 18.
- Chen, J., Yoo, W. J., and Chan, D. S. H. (2006). *J. Electrochem. Soc.*, **153**, G483.
- Christenson, K., Schwab, B., Wagener, T., Rosengren, B., Riley, D., and Barnett, J. (2003). Selective wet etching of high-k gate dielectrics, *Solid State Phenomena*, **92**, 129.
- Claes, M., Paraschiv, V., Boutkabout, H., De Gendt, S., Richard, O., Lindsay, R., Boullart, W., and Heyns, M. (2003). in: *Physics and Technology of High-k Gate Dielectrics II: Proceedings of the Second International Symposium on High Dielectric Constant Materials*, ed. S. Kar, Electrochemical Society, Pennington, N.J.
- Claes, M., De Gendt, S., Witters, T., Kaushik, V., Conard, T., Zhao, C., Manabe, Y., Delabie, A., Rohr, E., Chen, J., Tsai, W., and Heyns, M. M. (2004). *J. Electrochem. Soc.*, **151**(11), F269.
- Claes, M., Paraschiv, V., Dictus, D., Conard, T., Boullart, W., Vanhaelemeersch, S., and De Gendt, S. (2005). Wet etch characteristics of Hf-silicates, paper presented at 208th ECS Meeting, 16–21 October, Los Angeles.
- Cunge, G., Pelissier, B., Joubert, O., Ramos, R., and Maurice, C. (2005). *Plasma Sources Sci. Technol.*, **14**, 599.
- Demand, M., Paraschiv, V., Shamiryan, D., Veloso, A., Vrancken, C., Brus, S., and Boullart, W. (2007). in: *Proceedings of the 29th International Symposium on Dry Process*, 289, Tokyo, Japan, 13–14 November 2007.
- Fleddermann, C. B. and Hebner, G. A. (1997). *J. Vac. Sci. Technol. A*, **15**, 1955.
- Fleddermann, C. B., and Hebner, G. A. (1998). *J. Appl. Phys.*, **83**, 4030.
- Garrido, B., Monserrat, J., and Morante, J. R. (1996). *J. Electrochem. Soc.*, **143**(12), 4059.
- Gottsch, R. A. and Gaebe, C. E. (1986). *IEEE Trans. Plasma Sci.*, **PS-14**, 92.
- Gray, D. C., Tepermeister, I., and Sawin, H. H. (1993). *J. Vac. Sci. Technol. B*, **11**, 1243.
- Greenwood, N. N. and Earnshaw, A. (1997). *Chemistry of the Elements*, Butterworth, London.
- Gurvitch, M., Manchanda, L., and Gibson, J. M. (1989). *Appl. Phys. Lett.*, **55**, 360.
- Gusev, E. P., Cabral, Jr., C., Copela, M., D'Emica, C., and Gribelyuk, M. (2003). *Microelectron. Eng.*, **69**, 145.
- Hebner, G. A. (1996a). *J. Appl. Phys.*, **80**, 3215.
- Hebner, G. A. (1996b). *J. Vac. Sci. Technol. A*, **14**, 2158.
- Hebner, G. A. (1997). *J. Appl. Phys.*, **81**, 578.

- Hebner, G. A. and Fleddermann, C. B. (1998). *J. Appl. Phys.*, **83**, 5102.
- Hebner, G. A., Fleddermann, C. B., and Miller, P. A. (1997). *J. Vac. Sci. Technol. A*, **15**, 2698.
- Hebner, G. A., Blain, M. G., and Hamilton, T. W. (1999). *J. Vac. Sci. Technol. A*, **17**, 3218.
- Hélot, M., Chevolleau, T., Vallier, L., Joubert, O., Blanquet, E., Pisch, A., Mangiagalli, P., and Lill, T. (2006). *J. Vac. Sci. Technol. A*, **24**, 30.
- Hobbs, C. C. and Tobin, P. J. (2003). U.S. Patent 6,818,493.
- Hu, Y.-Z. and S.-P Tay, S.-P. (2001). *J. Vac. Sci. Technol. B*, **19**(5), 1706.
- Hubbard, K. J. and Schlom, D. G. (1996). *J. Mater. Res.*, **11**, 2757.
- IUPAC. (1982). *Stability Constants of Metal Ion Complexes*; part A, 188, Pergamon Press, Oxford.
- JANAF Thermochemical Tables, 1985 Supplement 1. (1985). *J. Phys. Chem. Ref. Data*, **14**.
- Jang, J. W., Lee, Y. H., Lee, Y. J., Lee, J., and Yeom, G. Y. (2000). *Surf. Coat. Technol.*, **131**, 252.
- Jeon, S. and Hwang, H. (2002). *J. Appl. Phys.*, **81**, 4856.
- Jeon, S. and Hwang, H. (2003). *J. Appl. Phys.*, **93**(10), 6393.
- Jeong, C. H., Kim, D. W., Bae, J. W., Sumg, Y. J., Kwak, J. S., Park, Y. J., and Yeom, G. Y. (2002). *Mater. Sci. Eng. B*, **93**, 60.
- Joel, S., Choi, C.-J., Seong, T.-Y., and Hwang, H. (2001). *Appl. Phys. Lett.*, **79**, 245.
- Joubert, O., Cunge, G., Pelissier, B., Vallier, L., Kogelschatz, M., and Pargon, E. (2004). *J. Vac. Sci. Technol. A*, **22**, 553.
- Keaton, A. L. and Hess, D. W. (1985). *J. Vac. Sci. Technol. A*, **3**, 962.
- Kezuka, T., Itano, M., and Ohmi, T. (1999). in: *Proceedings of the Sixth International Symposium on Cleaning Technology in Semiconductor Device Manufacturing*, 244–260, Electrochemical Society, Pennington, N.J.
- Kim, D.-P. Yeo, J.-W., and Kim, C.-I. (2004). *Thin Solid Films*, **459**, 122.
- Kim, M., Min, N.-K., Yun, S.-J., Lee, H. W., Efremov, A., and Kwon, K.-H. (2008a). *Microelectron. Eng.*, **85**, 348.
- Kim, M., Min, N.-K., Yun, S. J., Lee, H. W., Efremov, A., and Kwon, K.-H. (2008b). *J. Vac. Sci. Technol. A*, **26**, 344.
- Kitagawa, T., Nakamura, K., Osari, K., Takahashi, K., Ono, K., Oosawa, M., Hasaka, S., and Inoue, M. (2006). *Jpn. J. Appl. Phys.*, **45**, L297.
- Knotter, D. M. (2000). Etching mechanisms of vitreous silicon dioxide in HF-based solutions, *J. Am. Chem. Soc.*, **122**(18), 4345.
- Kralik, B., Chang, E. K., and Louie, S. G. (1998). *Phys. Rev. B*, **57**, 7027.
- Kume, S., Nishimori, H., Sugahara, H., Hishinuma, N., and Arikado, T. (2003). in: *Proceedings of 2003 IEEE International Symposium on Semiconductor Manufacturing*, September 30–October 2, 2003, San Jose, California, 179, IEEE, New York.
- Le Gouil, A., Pargon, E., Cunge, G., Joubert, O., and Pelissier, B. (2006). *J. Vac. Sci. Technol. B*, **24**, 2191.
- Lee, H., Jeon, S., and Hwang, H. (2001). *Appl. Phys. Lett.*, **79**, 2615.
- Liu, L., Pey, K. L., and Foo, P. (1996). HF wet etching of oxide after ion implantation, in: *1996 IEEE Hong Kong Electron Devices Meeting: Proceedings, 29 June 1996*, Institute of Electrical and Electronics Engineers, New York.
- Lowalekar, V. and Raghavan, S. (2004). *J. Mater. Res.*, **19**(4), 1149.
- Luxenburg, P. and Kim, J. I. (1980). *J. Phys. Chem.*, **121**, 87.
- Lysaght, P., Foran, B., Stemmer, S., Bersuker, G., Bennet, J., Tichy, R., Larson, L., Huff, H. R. (2003). *Microelectron. Eng.*, **69**, 182.
- Maeda, T., Ito, H., Mitsuhashi, R., Horiuchi, A., Kawahara, T., Muto, A., Sasaki, T., Torii, K., and Kitajama, H. (2004). *Jpn. J. Appl. Phys.*, **43**, 1864.
- Manchanda, L., Busch, B., Green, M. L., Morris, M., van Dover, R. B., Kwo, R., and Aravamudan, S. (2001). High K gate dielectrics for the silicon industry, in: *Extended*

- Abstracts of International Workshop on Gate Insulator: IWGI 2001*, 56–60, Business Center for Academic Societies Japan, Tokyo.
- Mane, A. U., Wenger, C., Schroeder, T., Zaumseil, P., Lippert, G., Weidner, G., and Mussig, H. J. (2005). *J. Electrochem. Soc.*, **152**(6), C399.
- Mantenieks, M. A. (1997). in: *Proceedings of the 25th International Electric Propulsion Conference*, August 24–28, 1997, Cleveland, Ohio.
- Meeks, E., Ho, P., Ting, A., and Buss, R. J. (1998). *J. Vac. Sci. Technol. A*, **16**, 2227.
- Miller, P. A., Hebner, G. A., Greenberg, K. E., Pochan, P. D., and Aragon, B. B. (1995). *J. Res. Natl. Inst. Stand. Technol.*, **100**, 427.
- Mitsubishi, R., Kubota, M., and Hayashi, S. (2003). U.S. Patent 6,667,246.
- Moore, G. E. (1965). *Electronics*, **38**, 114.
- Nakamura, K., Hamada, D., Ueda, Y., Eriguchi, K., Baklanov, M. B., and Ono, K. (2009). *Appl. Phys. Express*, **2**, 016503.
- Nakamura, K., Kitagawa, T., Osari, K., Takahashi, K., and Ono, K. (2006). *Vacuum*, **80**, 761.
- Nakano, T., Sadeghi, N., Trevor, D. J., Gottscho, R. A., and Boswell, R. W. (1992). *J. Appl. Phys.*, **72**, 3384.
- Norasetthekul, S., Park, P. Y., Baik, K. H., Lee, K. P., Shin, J. H., Jeong, B. S., Shishoda, V., Lambers, E. S., Norton, D. P., and Pearton, S. J. (2001). *Appl. Surf. Sci.*, **185**, 27.
- Norasetthekul, S., Park, P. Y., Baik, K. H., Lee, K. P., Shin, J. H., Jeong, B. S., Shishoda, V., Norton, D. P., and Pearton, S. J. (2002). *Appl. Surf. Sci.*, **187**, 75.
- Nordheden, K. J. and Sia, J. F. (2003). *J. Appl. Phys.*, **94**, 2199.
- Onishi, K., Kang, L., Choi, R., Dharmarajan, E., Gopalan, S., Joen, Y., Kang, C., Lee, B., Nieh, R., and Lee, J. C. (2001). *Tech. Dig. Int. Electron Devices Meet.*, 131.
- Onsia, B., Hellin, D., Claes, M., Maes, A., De Gendt, S., and M. Heyns, M. (2003). *Solid State Phenomena*, **92**, 19.
- Osten, H. J., Liu, J. P., Gaworzewski, P., Bugiel, E., and Zaumseil, P. (2001). High-k gate dielectrics with ultra-low leakage current based on praseodymium oxide, *Tech. Dig. Int. Electron Devices Meet.*, 653.
- Overzet, L. J. and Luo, L. (1991). *Appl. Phys. Lett.*, **59**, 161.
- Paraschiv, V., Claes, M., Boullart, W., De Gendt, S., and Vanhaelemeersch, S. *J. Electrochem. Soc.*, in press.
- Park, P. Y., Norasetthekul, S., Lee, K. P., Baik, K. H., Gila, B. P., Shin, J. H., Abernathy, C. R., Ren, F., Lambers, E. S., and Pearton, S. (2001). *J. Appl. Surf. Sci.*, **185**, 52.
- Pelhos, K., Donnelly, V. M., Kornblit, A., Green, M. L., Van Dover, R. B., Manchanda, L., Hu, Y., Morris, M., and Bower, E. (2001). *J. Vac. Sci. Technol. A*, **19**, 1361.
- Petrovic, Z. L., Wang, W. C., Suto, M., Han, J. C., and Lee, L. C. (1990). *J. Appl. Phys.*, **67**, 675.
- Quevedo-Lopez, M., El-Bouanani, M., Addepalli, S., Duggan, J. L., Gnade, B. E., Wallace, R. M., Visokay, M. R., Douglas, M., Bevan, M. J., and Colombo, L. (2001). *Appl. Phys. Lett.*, **79**, 2958.
- Quevedo-Lopez, M. A., El-Bouanani, M., Wallace, R. M., and Gnade, B. E. (2002). *J. Vac. Sci. Technol. A*, **20**, 1891.
- Quevedo-Lopez, M. A., El-Bouanani, M., Kim, M. J., Gnade, B. E., Wallace, R. M., Visokay, M. R., LiFatou, A., Chambers, J. J., and Colombo, L. (2003). *Appl. Phys. Lett.*, **82**, 4669.
- Ragnarsson, L.-A., Chang, V. S., Yu, H. Y., Cho, H.-J., Conard, T., Kai, M. Y., Delabie, A., Swerts, J., Schram, T., De Gendt, S., and Biesjemans, S. (2007). *IEEE Electron Device Lett.*, **28**, 486.
- Ramanathan, S., McIntyre, P. C., Luning, J., Lysaght, P. S., Yang, Y., Chen, Z., and Stemmer, S. (2003). *J. Electrochem. Soc.*, **150**, F173.
- Ramos, R., Cunge, G., and Joubert, O. (2007). *J. Vac. Sci. Technol. A*, **25**, 290.
- Saenger, K. L., Okorn-Schmidt, H. F., and D'Emic, C. P. (2003a). A selective etching process for chemically inert high-k metal oxides, in *Novel Materials and Processes for Advanced*

- CMOS, ed. M. I. Gardner, S. De Gendt, J.-P. Marin, and S. Stemmer, 29, Materials Research Society, Warrendale, Penn.
- Saenger, K., Okorn-Schmidt, H., and D'emic, C. (2003b). In *Novel Materials and Processes for Advanced CMOS*, 79, Materials Research Society, Warrendale, Penn.
- Scheller, G. R., Gottscho, R. A., Intrator, T., and Graves, D. B. (1988). *J. Appl. Phys.*, **64**, 4384.
- Schwalke, U., Boye, K., Haberle, K., Heller, R., Hess, G., Muller, G., Ruland, T., Tzschockel, G., Osten, J., Fissel, A., and Mussig, H.-J. (2002). in: *Proceedings of the 32nd European Solid State Device Research Conference: ESSDERC*, 24–27 September 2002, 407, Florence, Italy.
- Seo, M., Kim, S. K., Kim, K.-M., Park, T. J., Kim, J. H., Hwang, C. S., and Cho, H. J. (2006). *ECS Trans.*, **1**(5), 211.
- Sha, L. and Chang, J. P. (2003). *J. Vac. Sci. Technol. A*, **21**, 1915.
- Sha, L. and Chang, J. P. (2004). *J. Vac. Sci. Technol. B*, **22**, 88.
- Sha, L., Cho, B.-O., and Chang, J. P. (2002). *J. Vac. Sci. Technol. A*, **20**, 1525.
- Sha, L., Puthenkovilakam, R., Lin, Y.-S., and Chang, J. P. (2003). *J. Vac. Sci. Technol. B*, **21**, 2420.
- Shamiryan, D., Paraschiv, V., Claes, M., and Boullart, W. (2006). In *Defects in High-k Gate Dielectric Stacks*, ed. E. Gusev, 331–338, Springer, Dordrecht.
- Shamiryan, D., Paraschiv, V., Eslava-Fernandez, S., Demand, M., Baklanov, M., Beckx, S., and Boullart, W. (2007). *J. Vac. Sci. Technol. B*, **25**, 739.
- Shamiryan, D., Demand, M., and Paraschiv, V. (2009). U.S. Patent 7,521,369. European patent application EP 1 923 910 A2, patent pending.
- Shamiryan, D., Danila, A., Paraschiv, V. M., Baklanov, M., and Boullart, W., *J. Vac. Sci. Technol. B*, in press.
- Shamiryan, D., Paraschiv, V., Baklanov, M., and Boullart, W., *J. Vac. Sci. Technol. B*, in press.
- Shih, K. K., Chieu, T. C., and Dove, D. B. (1993). *J. Vac. Sci. Technol. B*, **11**, 2130.
- Shul, R. J. and Pearton, S. J., ed. (2000). *Handbook of Advanced Plasma Processing Techniques*, 2, Springer, New York.
- Steinbrüchel, C. (1989). *Appl. Phys. Lett.*, **55**, 1960.
- Stockdale, J. A., Nelson, D. R., Davis, F. J., and Compton, R. N. (1972). *J. Chem. Phys.*, **56**, 3336.
- Stuart, R. V. and Wehner, G. K. (1962). *J. Appl. Phys.*, **33**(7), 2345.
- Suzuki, K., Tashiro, H., Morisaki, Y., and Sugita, Y. (2003). *IEEE Trans. Electron Devices*, **50**, 1550.
- Takahashi, K. and Ono, K. (2006). *J. Vac. Sci. Technol. A*, **24**, 437.
- Takahashi, K., Ono, K., and Setsuhara, Y. (2005). *J. Vac. Sci. Technol. A*, **23**, 1691.
- Timp, G., Agarwal, A., Baumann, F. H., Boone, T., Buonanno, M., Cirelli, R., Donnelly, V., Foad, M., Grant, D., Green, M., Gossman, H., Hillenisu, S., Jackson, J., Jacobson, D., Kleiman, R., Kornblit, A., Klemens, F., Lee, J. T.-C., Mansfield, W., Moccio, S., Murrell, A., O'Malley, M., Rosamilia, J., Sapjeta, J., Sherman, P., Sorsch, T., Tai, W. W., Tennant, D., Vuong, H., and Weir, B. (1997). *Tech. Dig. Int. Electron Devices Meet.*, 930.
- Tokunaga, K., Redeker, F. C., Danner, D. A., and Hess, D. W. (1981). *J. Electrochem. Soc.*, **128**, 851.
- Trouton, F. (1884). *Philos. Mag.*, **5**, 54.
- Verhaverbeke, S., Teerlinck, I., Vinckier, C., Stevens, G., Cartuyvels, R., and Heyns, M. M. (1994). *J. Electrochem. Soc.*, **141**(10), 2852.
- Visokay, M. R., Chambers, J. J., Rotondaro, A. L. P., Shanware, A., and Colombo, L. (2002). *Appl. Phys. Lett.*, **80**, 3183.
- Wang, C. and Donnelly, V. M. (2005). *J. Vac. Sci. Technol. B*, **23**, 547.
- Wang, C. and Donnelly, V. M. (2006). *J. Vac. Sci. Technol. B*, **24**, 41.

- Wang, C. and Donnelly, V. M. (2008). *J. Vac. Sci. Technol. A*, **26**, 597.
- Wang, X., Liu, Y., Xu, X., Fu, S., and Cui, Z. (2006). *J. Vac. Sci. Technol. A*, **24**, 1067.
- Watanabe, D., Momota, H., Kezuka, T., Takashi, K., Mitsushi, I., Riley, D., and Barnett, J. (2003). Selective wet etching for high-*k* material by organic solvent containing hydrofluoric acid, in: *Semiconductor Pure Water and Chemicals Conference Proceedings, 22nd*, 117, SPWCC, Los Altos, Calif.
- Wei, Y., Wallace, R. M., and Seabaugh, A. C. (1996). *Appl. Phys. Lett.*, **69**, 1270.
- Wenger, C., Dabrowski, D., Zaumseil, P., Sorge, R., Formanek, P., Lippert, G., and Muessig, H.-J. (2004). *Mater. Sci. Semicond. Process.*, **7**, 227.
- Wilk, G. D., Wallace, R. M., and Anthony, J. M. (2001). *J. Appl. Phys.*, **89**, 5243.