ETCH

Selective wet etching of high-*k* materials

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The deposition of blanket films with a subsequent etch after gate patterning remains the leading candidate for integrating high-*k* gate dielectrics at the 70nm node. Early high-*k* material candidates such as BST etched easily in a range of acidic chemistries, but device and materials studies have now converged on the oxides, nitrides, and silicates of Al, Zr, and Hf, and particularly on HfO_2 based compounds [1].

Removal of the high-*k* material from the source and drain regions is required after gate patterning. This removal must be done selectively to the polysilicon gate electrode, to the underlying silicon, to silicon nitride spacers, and to deposited silicon oxide used for shallow trench isolation and spacers. Typical high-*k*:SiO_2 etch selectivity specifications range from 1:1–5:1. Etch rates of 0.5nm/min for batch and 5nm/min for single-wafer processes are desired. The traditional plasma and wet etch chemistries used in the formation of SiO_2/polysilicon gates have thus far been unable to provide the necessary selectivity and etch rate.

Given the numerous integration issues surrounding high-*k* gate dielectrics, and the differing needs of the high-performance and low-power devices, the industry may choose to implement a variety of integration schemes simultaneously. For instance, the more easily etched compounds of Hf and Zr with Si, O, and N may be chosen initially as transition materials, similar to the role of FSG in the evolution to low-*k*, with pure HfO_2 or other materials used in later nodes if needed.

Wet etching

High-*k* etchants are typically fluoride-based. In solution, the HF forms a number of chemical species including H^+, F^-, HF_2^-, $(HF)_2$, and HF. The relative concentration of these species varies with the fluoride concentration, the pH, the nature of the solvent, and the temperature. High fluoride concentrations favor the fluoride-rich species HF_2^- and $(HF)_2$. Low pH favors the neutral species HF and $(HF)_2$. While the etch mechanism and dominant etch species for

high-*k* materials are unknown, it is believed that HF_2^- and $(HF)_2$ are the dominant species in SiO_2 etching [2]. Therefore, the etch rate of SiO_2 can be suppressed by the use of dilute solutions with low pH values.

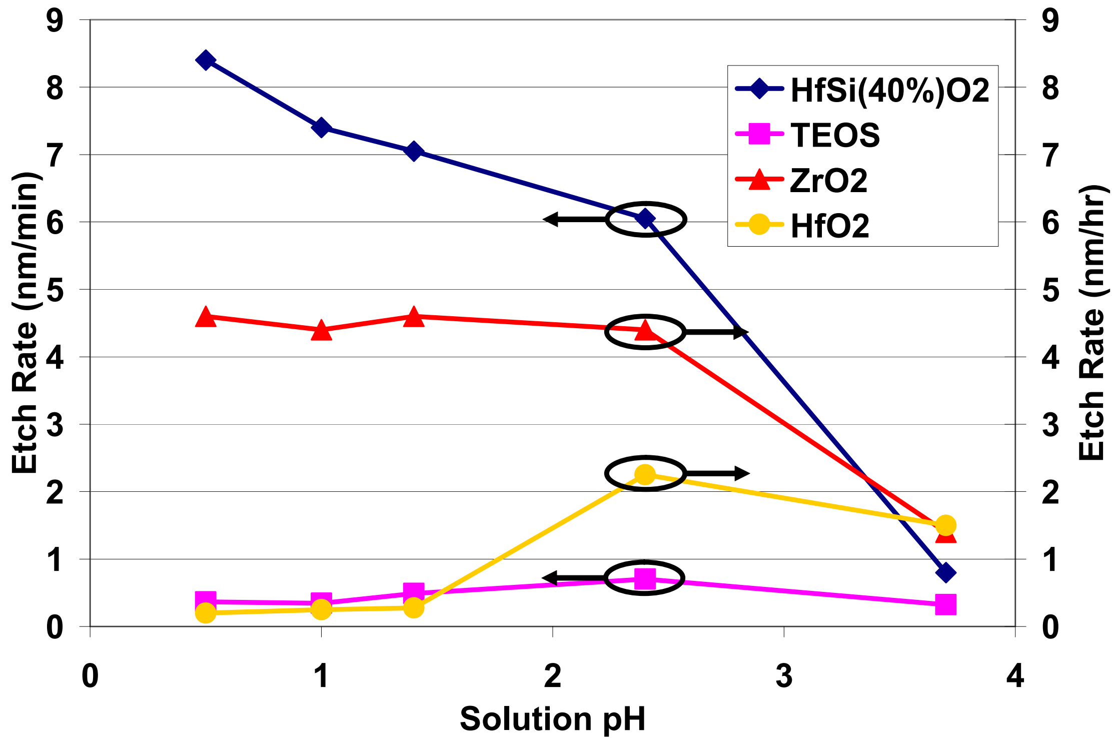

Figure 1. Etch rates of various films in 1000:1 HF at 80°C. The pH is adjusted by the addition of NH_4OH or HCl. Note that HfO_2 and ZrO_2 are plotted on a time axis of nm/hour.

Figure 1 shows the variation in etch rate as a function of pH for four films. As expected, the etch rate of TEOS decreases with decreasing pH. The hafnium silicate etch rate, however, increases with decreasing pH. This indicates that the etch mechanisms or dominant etch species differ between the two films. The unary oxides etch 50–100× more slowly than do the silicates, with ZrO_2 trending with the silicate as a function of pH and HfO_2 trending with the TEOS.

Figure 2 shows the variation in etch rate of various films as a function of HF concentration. While the etch rate of all films decreases with decreasing HF concentration, the TEOS etch rate drops more quickly than that of the high-*k* films. This results in increased selectivity with decreasing HF concentration (Fig. 3).

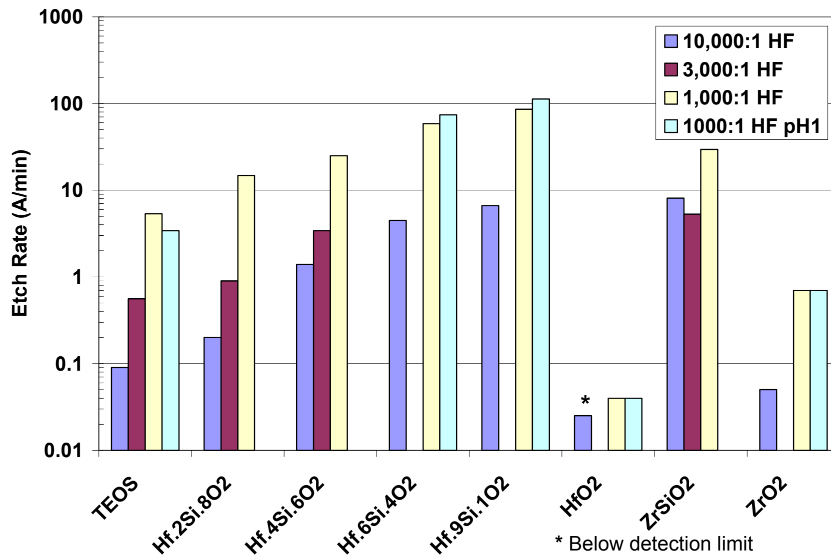

Figure 2. Etch rates of various films in dilute HF at 80°C. The pH is adjusted with HCl.

For use in production, a process must have both sufficient selectivity and a practical high-*k* etch rate. Acidifying the solution to a pH = 1 serves both needs by suppressing the etching of SiO_2 and generally enhancing the etch rate of the high-*k* film. Other work has shown that the activation energy for the high-*k* etches is higher than that of SiO_2 etches [3]. Elevated temperatures increase both the high-*k* etch rate and the high-*k* to SiO_2 selectivity.

Another striking feature is the thousand-fold range in etch rates between various high-*k* films (Fig. 1). The wide range of etch rates has been a consistent issue in developing an etch process. The etch rate depends strongly on the film's stoichiometry, growth method, and thermal history. Figure 4 shows the reduction in etch rate of HfO_2 films after a thermal treatment.

Barnett noted that heat treatment causes the films to crystallize [4]. It appears the key parameter is the crystallinity of the film. Pure, annealed, dense, crystalline films of unary oxides are very difficult to etch with wet chemistries; any disorder in the film greatly increases the etch rate. The film can be disordered for two reasons. First, the film can be structurally disordered, having a stoichiometric ratio of metal and oxygen atoms, but with the atoms arranged randomly and not as a periodic crystal. Second, there can be additional atoms

present that either prevent or slow the crystallization of the film, or result in a crystal that is stressed at the atomic level and is vulnerable to chemical attack.

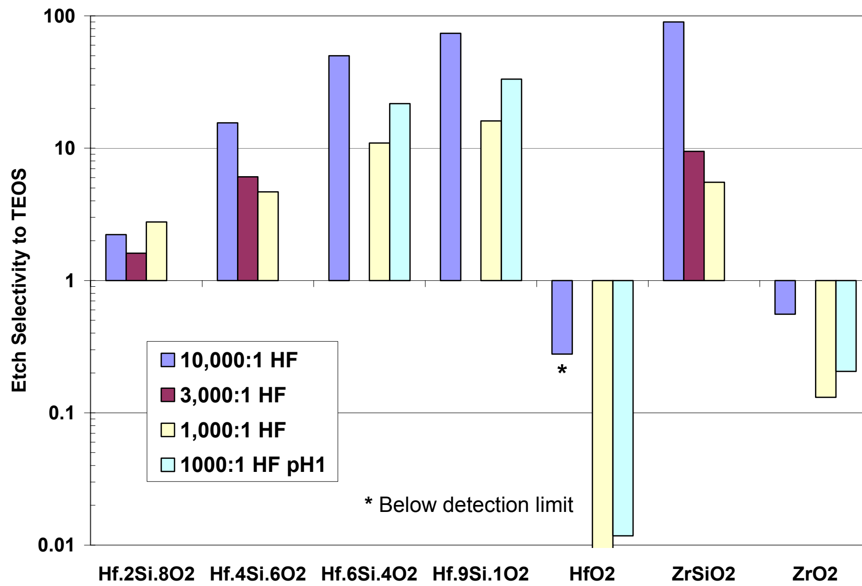

Figure 3. Etch selectivity of dilute HF at 80°C. The pH is adjusted with HCl.

All films with disorder tested to date have been successfully etched with the hot, acidified, dilute HF (HADHF) chemistries listed in Fig. 2. Recent electrical results indicate that amorphous films may have electrical advantages as well. The grain boundaries between crystals form regions of highly enhanced diffusion, providing a path for dopants or metals from the gate to reach the channel. The crystals also act to reduce the electron mobility through Coulomb scattering [5]. It has been suggested that amorphous, nitrided HfO_2 may be the best long term high-*k* material [6].

While HADHF chemistries provide an etch solution for current disordered films, it is possible that other chemistries will be required for future films. Work continues on improving the selectivity of fluoride chemistries. For example, by choosing solvents with varying dielectric constants, the balance between the various “HF species” (HF vs H^+, F^-…) is strongly affected. Working on the hypothesis that the dominant etching species for HfO_2 and SiO_2 differ, Watanabe, et al., investigated the performance of anhydrous HF in different solvents [7]. They found that using concentrated HF in an organic solvent with a low dielectric constant provided acceptable high-*k* etch rates and simultaneously reduced the etch rate of the SiO_2 sufficiently to give a SiO_2:HfO_2 selectivity of 0.8:1.

While perhaps not yet ready for use in production, these HF:solvent results are superior to any aqueous results on annealed HfO_2 that have been widely reported. But there are still many more techniques of traditional chemistry that have yet to be fully explored. Preliminary testing in some of these areas has yielded very promising results [8].

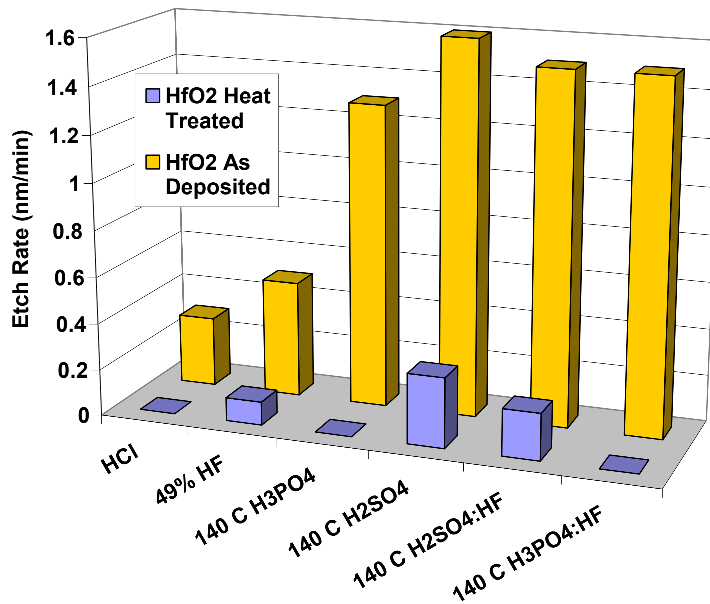

Figure 4. Etch rates of ALD HfO_2 films as deposited and after a 120 min, 550°C thermal cycle simulating the deposition of polysilicon.

Disorder ion implant

Disordered films etch more rapidly than do crystalline films (Fig. 4). It may be possible to create sufficient disorder in a crystalline film by the dislocation of atoms during ion implantation. Barnett, et al., reported a 3× increase in the etch rate of annealed, MOCVD HfO_2 films after a 1×10^{15} atoms/cm^2 implant of Ar, As, Ge or Si ions at 10–15keV [4]. The etch rate enhancement could be eliminated by a brief anneal, indicating that crystal damage was the primary mechanism.

The relatively small increase in etch rate after this implant is somewhat surprising. Ion trajectory calculations with SRIM predict that the implanted film should be completely amorphous, and hence etch 10–100× faster than a crystalline film [9]. The phenomenon of "self-annealing," the restoration of crystal structure due to the temperature rise during

implant, is known to happen in silicon. It is possible that the high-*k* film self-annealed during the implant. Cooling the wafer during the implant can reduce self-annealing and would potentially leave the film susceptible to wet chemistries.

Damage can also occur by the addition of implant species that act as chemically active contaminants in the lattice. Barnett saw little variation in etch rate when varying the implant species, indicating the chemical effects of the implant species used in the experiment were negligible. This is reasonable as a 10keV ion will cause many damage sites in the crystal as it decelerates, but will only contribute one site with a chemically active species. Further, a dose of 1×10^{15} atoms/cm^2 only represents 1% of the atoms in a 20nm film, which may be insufficient to cause a significant change in the etch rate due to the chemistry of the crystal. Also, the implant of a more chemically active species such as fluorine might have more impact on the etch rate.

Plasma etch

While no acceptable plasma-etch process with sufficient selectivity to all other exposed films has been reported, promising results have been obtained with a partial plasma etch of the high-*k* film followed by a wet etch process. In tests, 16nm HfO_2 films were thinned by 3nm with a plasma etch, after which another 6nm could then be easily removed with HADHF [10]. The plasma apparently damages a small thickness of the remaining high-*k* film sufficiently so that it can be selectively etched by wet chemistries. A less aggressive plasma/wet process — that removes a 4nm HfO_2 film and leaves the polysilicon gate and underlying silicon electrically undamaged — may be possible.

The plasma approach has a number of benefits. The film can be partially etched, reducing the thickness that must be removed by wet chemistries. Further, plasma exposure involves a very high dose of low energy ions. The remaining film can be both thoroughly disordered and doped at the percent level with a chemically active species.

Conclusion

Hot, acidic, dilute HF chemistries have been shown to be effective in etching disordered high-*k* films including silicates of Hf and Zr. Further development is underway on wet chemistries to etch the crystalline films of the unary oxides. Until these chemistries are developed, the

combination of partially etching the film with a nonselective plasma, followed by a selective wet chemistry is the most promising approach currently available. The required etch varies greatly with the nature of the high-*k* film. Only after the electrical parameters of the film are optimized, and the nature of the film fixed, can the final etch process be determined. ■

Acknowledgments

The author thanks International SEMATECH for providing samples and Steve Nelson for assistance with experimental work and data analysis.

References

1. H. Iwai et al., "Advanced Gate Dielectric Materials for Sub-100 nm CMOS," *2002 IEDM Conf., IEDM Digest,* p. 625-628, 2002.
2. D.M. Knotter, "Etching Mechanisms of Vitreous Silicon Dioxide in HF-Based Solutions," *J. Amer. Chem. Soc.,* 122(18), 4345-4351, 2000.
3. K. Christenson, et al., "Selective Wet Etching of High-*k* Dielectrics," 2002 UCPSS Conf., to be published.
4. J. Barnett, et al., "Wet Etch Enhancements of HfO_2 Films by Implant Processing," 2002 UCPSS Conf., to be published.
5. T. Yamaguchi, et al., "Additional Scattering Mechanism for Mobility Degradation in Hf-silicate Gate MISFETs," 2002 IEDM Conf., *IEDM Digest,* p. 621-624, 2002.
6. M. Koyama, et al., "Effects of Nitrogen in HfSiON Gate Dielectric on Its Excellent Electrical and Thermal Characteristics," 2002 IEDM Conf., *IEDM Digest,* p. 849-852, 2002.
7. D. Watanabe, et al., "Selective Wet Etching for High-*k* Material by Organic Solvent Containing Hydrofluoric Acid," 2003 SPWCC, Semiconductor Pure Water and Chemicals Conference, M. Balazs, Ed., Los Altos, CA, p. 117.
8. FSI internal tests, to be published.
9. Calculated with SRIM 2000, www.srim.org.
10. FSI internal tests.

Kurt Christenson received his BA in physics from Bethel College in St. Paul, MN, and received his MS and PhD degrees in physics from the University of Illinois in Champaign-Urbana. He performed post-doctoral studies in e-beam lithography at IBM's Watson Research Center in Yorktown Heights, NY. Christenson is a senior member of the technical staff at FSI International, 3455 Lyman Blvd., Chaska, MN 55318; ph 952/448-8047, fax/952-361-7393, kurt.christenson@fsi-intl.com

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