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Reduction of hafnium oxide and hafnium silicate by rhenium and platinum

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We report chemical interactions of Hf-based dielectrics with Re and Pt overlayers during annealing. Reduction of the Hf to a suboxide is observed by x-ray photoelectron spectroscopy, along with a decrease in total oxygen content measured by medium-energy ion scattering. For Re, this unanticipated reaction is highly dependent on the premetallization history of the sample. The presence of hydroxyl groups, observed by infrared absorption, is thought to be responsible. In addition, substantial electrostatic core-level shifts are observed, even in the absence of Hf reduction. The electrostatic shifts are symptomatic of altered threshold voltages for devices. © 2006 American Institute of Physics. [DOI: 10.1063/1.2177360]

Conventional Si complementary metal-oxide-semiconductor devices rely on polycrystalline-Si polysilicon as a gate conductor. An improvement in performance can be gained by replacing the polysilicon with a metal, eliminating the gate depletion effect. Metal gates are commonly used in conjunction with metal oxide gate dielectrics, such as HfO₂ and Hf_(1-x)Si_xO₂. This has the added advantage of avoiding unwanted polysilicon/HfO₂ interactions.¹ For successful implementation, the gate metal must be chosen so that it does not undergo an unfavorable chemical interaction with the dielectric. Since the dielectric materials under consideration have been chosen based on thermodynamic stability,² this leaves a wide variety of metals as eligible candidates. In particular, *p*-type metals with large work functions, such as Pt and Re, are known to form relatively unstable oxides, and *should* be stable in contact with HfO₂ and SiO₂.

In this letter, we report unexpected chemical reactions between Re and Pt metallization layers and HfO₂ and Hf_(1-x)Si_xO₂ that lead to the reduction of Hf oxide to a suboxide. The reaction depends on the quality of the metal oxide, and does not take place for well-annealed metal oxides. Even in samples where no reduction of Hf is observed, substantial shifts are seen in the Hf 4*f* and oxygen 1*s* core level due to charged defects. The shifts are electrostatic rather than chemical in origin, and result in changes in the capacitance-voltage characteristics of devices.

The dielectrics used in this study were grown by chemical vapor deposition (CVD) from Hf tert-butoxide precursor on silicon oxynitride and introduced to an ultrahigh vacuum (UHV) analysis system after storage in air. Re was deposited *in situ* by electron-beam evaporation from a Ta crucible at a growth rate of about 1 Å per minute. Pt was also deposited by e-beam evaporation, but in an external system. The oxidation state of the Hf was studied by x-ray photoelectron spectroscopy (XPS) using a Mg *K*α source and an emission angle of 45°. Medium-energy ion scattering (MEIS) measurements were used to determine the oxygen content and morphology of films. All anneals were performed in the same UHV system as Re deposition, XPS, and MEIS.

First, let us examine the Hf 4*f* core level of a HfO₂ film that was briefly degassed at 200 °C prior to Re deposition (Fig. 1). The 4*f* doublet appears at binding energies of 19.4 and 17.7 eV. This is typical of fully oxidized Hf (Hf⁴⁺). As the sample is postmetal annealed, a second Hf peak appears at a binding energy of 15.9 eV, which is indicative of Hf in a suboxide (Hf^{sub}). (A larger shift of roughly 3.7 eV would be expected for fully metallic Hf. It is likely that the peak labeled Hf^{sub} is in a partially oxidized configuration.) The intensity grows with further annealing. Judging from the relative intensity of the Hf peaks and the escape depth of photoelectrons, roughly 2–3 Å of HfO₂ is reduced. Similar behavior is found for Pt.

Reduction of Hf is found for both HfO₂ and Hf_(1-x)Si_xO₂ (Fig. 2). The amplitude of Hf^{sub} relative to Hf⁴⁺ is somewhat smaller for Hf_(1-x)Si_xO₂ than HfO₂, but shows the same trend, increasing for temperatures greater than 550 °C. Evidently, the incorporation of SiO₂ into HfO₂ offers only minor stabilization to Hf_(1-x)Si_xO₂ in contact with Re.

Using MEIS, we observe a decrease in the oxygen content of the film when the HfO₂ is reduced by Re. A slight

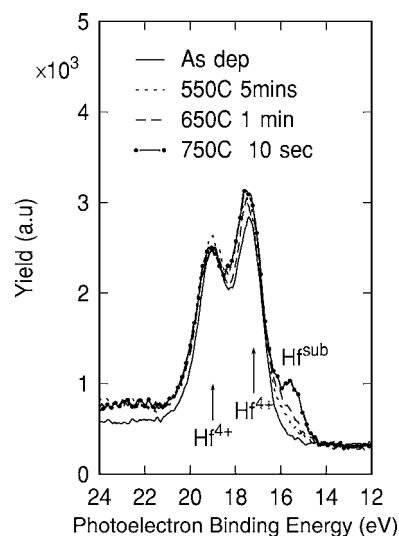


FIG. 1. X-ray photoemission spectra of Re metallized HfO₂/SiO₂N_y/Si samples with various postmetal anneals. The Hf 4*f* peaks are shown. Positions for oxidized Hf (Hf⁴⁺) and Hf suboxide (Hf^{sub}) are indicated. A peak due to Hf suboxide grows with increasing annealing temperature.

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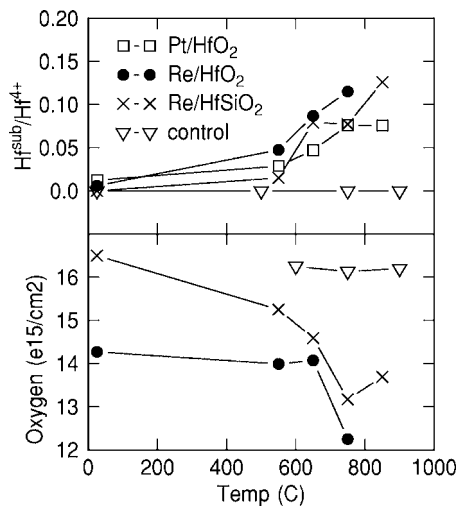


FIG. 2. Relative intensity of partially oxidized Hf (Hf^{sub}) normalized to fully oxidized Hf (Hf^{4+}) detected by x-ray photoemission (top). The total oxygen content of the film measured MEIS decreases as the Hf^{sub} signal increases (bottom). Results are shown for Re and Pt metallized HfO_2 and Re metallized $\text{Hf}_{(1-x)}\text{Si}_x\text{O}_2$ as well as uncapped HfO_2 .

increase in oxygen appears above 900 °C, but we believe it is not significant. The drop in oxygen intensity shows that oxygen is lost from the sample, rather than merely transferred to the Re. Furthermore, the Re 4f core level shows no evidence of oxidation (not shown), although some low concentration of oxygen could remain dissolved in the Re. It is noteworthy that samples without Re showed no oxygen loss between 600 °C and 950 °C, indicating that uncapped $\text{HfO}_2/\text{SiO}_x\text{N}_y/\text{Si}$ structures are stable in the temperature regime relevant to device processing. (Ultimately, at higher temperatures, the HfO_2 will react with the underlying substrate to form a silicide, as has been observed for ZrO_2 and HfO_2 samples without a Re overlayer.)³⁻⁵

So far, we have only discussed films that have undergone minimal thermal cycling prior to deposition. Much different results are found for Re metallization of films that have been densified by *in situ* UHV anneals (Fig. 3). A 5 min premetal anneal at 500 °C strongly suppresses the formation of the

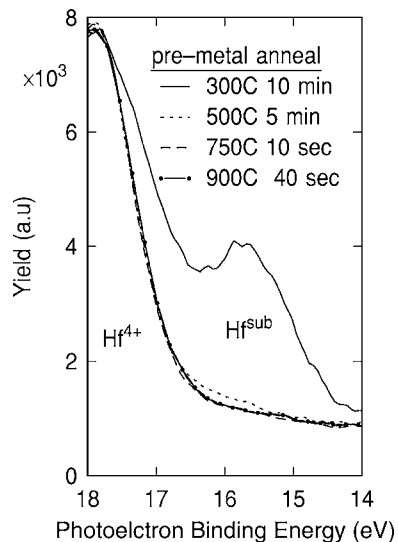


FIG. 3. Effect of premetal anneal on reactivity of HfO_2 with Re. After metallization, all samples received a 10 s 850 °C anneal in UHV. The reactivity is reduced by a premetal anneal.

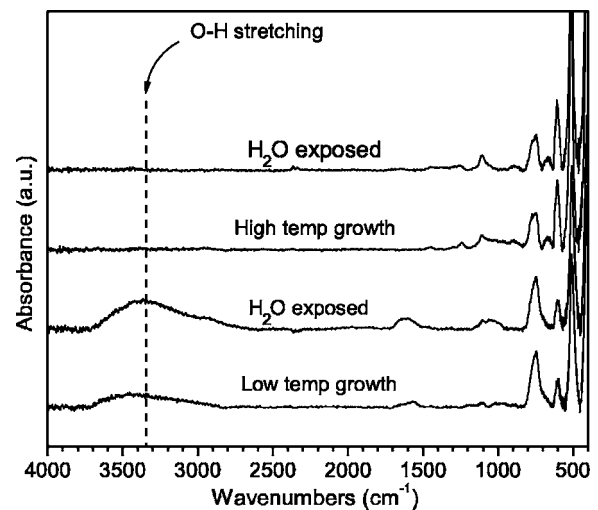


FIG. 4. Infrared absorption spectra for HfO_2 films grown at various temperatures and the effect of H_2O exposure. The feature at 3365 cm^{-1} is assigned to O–H stretching.

Hf^{sub} during postmetal annealing. A sample that has been preannealed at 750 °C for 10 s shows no detectable Hf^{sub} signal. From this, we can conclude that reduction of preannealed HfO_2 by Re is below the detection level of XPS.

Significant changes take place in HfO_2 during premetal annealing that may explain differences in the reactivity. It is likely that the combination of impurity elimination and crystallization improves the resistance of HfO_2 to oxygen removal. Crystallization has been observed at high temperatures,⁶ and it is likely that an amorphous or highly defective film will have both greater hydroxyl uptake as well as susceptibility to chemical attack. Some evidence of carbonates has been found in HfO_2 films⁷ and hydroxyls have been found in Y_2O_3 .⁸ To clarify the role of impurities, samples were exposed to H_2O by immersion for 24 h at room temperature prior to Re deposition. This was found to significantly increase suboxide formation, compared to storage in a dry ambient. Thus, we believe that hydroxyl groups are mainly responsible for the instability.

Direct evidence of hydroxyl groups was found in 1000 Å thick CVD HfO_2 films by infrared absorption spectroscopy (IRAS) (Fig. 4). For low-temperature growth, where poorer crystallinity is expected, a broad hydroxyl peak was observed centered at 3365 cm^{-1} . In addition, the hydroxyl intensity increased with H_2O exposure by immersion. On the other hand, no hydroxyl peak is observed on films grown at higher temperature, even after exposure to H_2O . This demonstrates that hydroxyl uptake can take place in HfO_2 , and that the extent depends on the details of film deposition. Since hydroxyls will desorb during premetal annealing, they are likely to be greatly reduced in densified samples. Thus, the IRAS results are in keeping with the observation that preannealed films are less susceptible to chemical reaction with Re.

The reduction of HfO_2 is not anticipated by thermodynamic considerations. The reaction of HfO_2 with a noble metal (Me)



should not occur, since the formation energy of HfO_2 is greater than that of Re or Pt oxide. Alternatively, we may

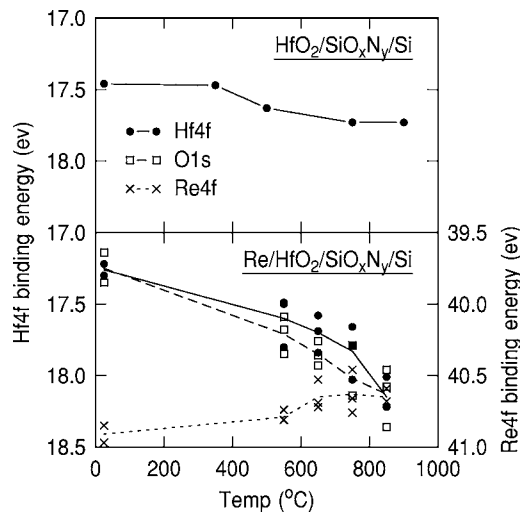


FIG. 5. Effect of annealing on core-level binding energies of HfO_2 samples. An uncapped sample (top) shows a much reduced shift compared to Re capped samples (bottom). For the Re capped samples, the Re $4f$ and oxygen $1s$ binding energies are also shown. The oxygen $1s$ binding energy has been shifted to allow plotting on the same scale.

consider the catalytic decomposition of HfO_2 with additional OH impurities:



In this case, not only is the HfO_2 destabilized by the presence of OH, but we also have the possibility that the presence of Re may assist in HfO_2 decomposition by stabilizing the formation of charged oxygen vacancies. Since both Re and Pt have large work functions, they can act as a sink for electrons thereby lowering the formation energy of charged defects.^{9,10} Even in samples which have been thoroughly preannealed we still see indirect (electrostatic) evidence of charged defects. This suggests that some level of oxygen vacancy formation takes place even without hydroxyl groups present.

Indirect evidence of charged defects can be observed by electrostatic shifts in XPS. In the spectra shown so far, the binding energy has been shifted to align the Hf^{4+} peaks. Binding energy shifts during postmetal anneals are observed for both the Hf $4f$ and oxygen $1s$ core lines on Re metallized samples that have been preannealed to avoid detectable reduction of the HfO_2 (Fig. 5). Both core levels shift by 0.7 to 0.8 eV toward higher binding energy after postmetal anneals to 850 °C. At the same time, the Re $4f$ core level undergoes a much smaller change of 0.2 to 0.3 eV toward lower binding energy. The Re shift is most likely due to agglomeration of the metal, which is observed with MEIS. This allows us to rule out sample charging as the origin of the shifts. Electrostatic shifts have previously been reported for *uncapped* HfO_2 layers,¹¹ with a larger magnitude, but the same direction. In Ref. 11, the shifts were attributed to excess oxygen in the metal oxide. We observe only 0.3 to 0.4 eV shifts in

uncapped samples. We believe that the larger metal-induced shifts have a different origin, described below.

Significant shifts in threshold voltages have been observed for *p*-type metal/ HfO_2 structures annealed in reducing ambients, ascribed to dangling Hf bonds¹² or oxygen vacancies.^{9,10,13} In light of this, we suggest the following interpretation of electrostatic shifts of the metal-oxide core levels. On samples capped with high work function metals, creation of charged defects near the metal/dielectric interface is highly facile, and the Fermi level is driven from its initial position near the valence band toward the conduction band. This is observed as a shift of the Hf $4f$ and oxygen $1s$ levels toward greater binding energy. Indeed, capacitance-voltage data for preannealed samples confirm that there is significant movement of the Fermi level after an 850 °C postmetal anneal in UHV. These results are supported by Fermi-level measurements using pulsed laser photoemission spectroscopy.¹⁴

In summary, two types of interactions are observed for Re metallized $\text{HfO}_2/\text{SiO}_x\text{N}_y/\text{Si}$ structures. On air exposed samples, chemical reduction of the Hf takes place during postmetal annealing in UHV. The instability is enhanced by the presence impurities, most likely hydroxyls. In addition, we observe significant electrostatic shifts due to charged defects, tentatively thought to be oxygen vacancies.

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