

Differences Between Charge Trapping States in Irradiated Nano-Crystalline HfO_2 and Non-Crystalline Hf Silicates

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Abstract—This paper provides an explanation for qualitative differences between radiation-induced charge trapping states in nano-crystalline HfO_2 and non-crystalline Hf silicate alloys in high- κ gate stacks by combining electrical measurements with spectroscopic studies and theory. Differences in the observed electrical response to X-ray and γ -ray irradiation are consistent with fundamental differences in electronic structures between high- κ dielectrics that are nano-crystalline and have a film thickness in excess of 4 nm, and high- κ dielectrics that are non-crystalline and devoid of grain boundaries. Oxygen vacancy and interstitial defects are shown to be natural candidates for the electron and hole traps in these high- κ dielectrics.

Index Terms—Charge trapping, electron traps, high- κ dielectrics, hole traps, metal-oxide-semiconductor (MOS) devices, oxide-trap charge.

I. INTRODUCTION

PREVIOUS work (e.g., [1] and [2]) has identified qualitatively different hole and electron trapping in irradiated metal-oxide-semiconductor (MOS) capacitors that incorporate either nano-crystalline HfO_2 films at least 4 nm thick, and non-crystalline Hf silicate alloys, such as $(\text{HfO}_2)_x(\text{SiO}_2)_{1-x}$, with $x \sim 0.5$. When these experiments were performed, little was known about local bonding arrangements at potential trapping sites in HfO_2 , or in Hf silicate alloys. Considerable progress has been made that has extended the understanding of bonding in these oxides and alloys, including the identification of intrinsic defects in HfO_2 that result in localized states within the forbidden band gap. Recent theoretical studies using conven-

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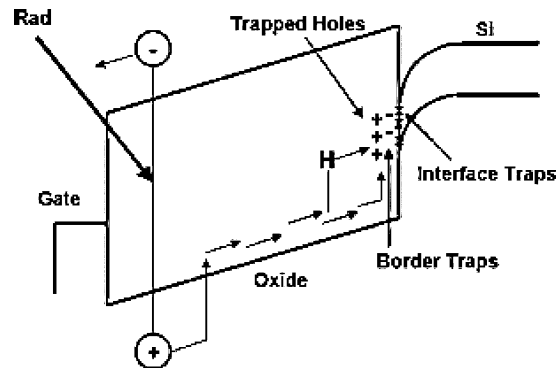


Fig. 1. Energy band diagram: ionizing radiation creates electron-hole pairs in a SiO_2 film for a MOS capacitor under positive bias (after [14] and [15]).

tional solid state approaches [3], [4], complemented by molecular orbital calculations on small clusters using quantum chemistry methods [5], [6], provide a framework for analyzing the transition metal d-state features in the highest lying valence bands and the lowest conduction bands of HfO_2 [7]. More recently, based on theory [8]–[10] and spectroscopic studies [7], the local bonding arrangements at the intrinsic bonding defects in nano-crystalline HfO_2 have been identified [11].

In this paper we review electrical measurements that identify differences in trapping states for electrons and holes in irradiated MOS capacitors with HfO_2 and Hf silicate gate dielectrics. Combining these results with the spectroscopic studies and theory in [7]–[11], we offer a microscopic explanation for the qualitative differences between trapping states in nano-crystalline HfO_2 and non-crystalline Hf silicate alloys that have been reported in the literature [1], [2], [12], [13].

II. ELECTRICAL MEASUREMENTS

We first briefly review studies in which Hf silicate MOS capacitors with 4.5 nm equivalent oxide thickness gate insulators were irradiated with 10-keV X-rays, and then similar studies on HfO_2 capacitors fabricated with or without an oxygen post-gate processing annealing treatment. These establish qualitatively different trapping efficiencies for electrons and holes in the two kinds of Hf-based alternative high- κ dielectrics subjected to X-ray irradiation [1], [2], [12], [13].

For reference, radiation-induced charged defect generation and trapping in SiO_2 gate dielectrics are illustrated in the energy band diagram in Fig. 1. Under positive radiation bias, elec-

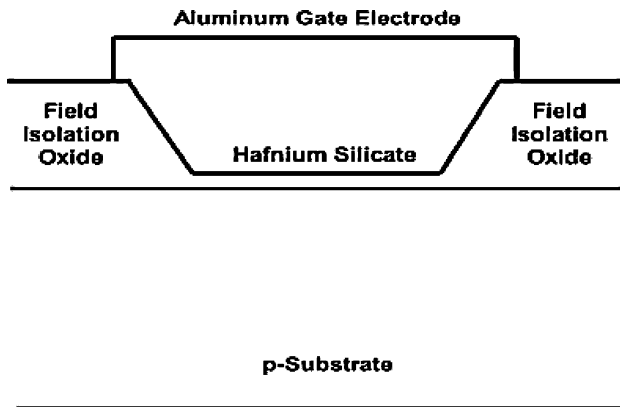


Fig. 2. Schematic cross-sectional diagram of the Hf silicate devices in [1].

trons are swept out at the gate electrode, while holes are transported to the Si/SiO₂ interface [14]. A fraction of these holes are trapped within the oxide, typically leading to a net positive oxide-trap charge density, along with an increase in border traps [15]. Additionally, protons are released from the network SiO₂ during hole transport and trapping, and are transported to the Si/SiO₂ interface [16], [17]. Interactions between these protons and hydrogen-passivated dangling bonds lead to radiation-induced interface-trap formation in devices with SiO₂ gate oxides [17]–[19]. Although Fig. 1 emphasizes hole trapping within the bulk of the oxide layer, alternative thin film high- κ gate dielectrics can also trap a significant density of electrons [2], [12], [20], [21]. In spite of this, the net radiation-induced oxide-trap charge in SiO₂, as well as in most alternative high- κ dielectrics, is generally net positive [2], [14].

Figs. 2 and 3 show the gate stack structure, which includes a thin (~ 0.6 nm) interfacial SiO₂ layer, a Hf silicate film, and an Al gate electrode, and capacitance-voltage (C-V) characteristics that show the buildup of trapped charge after exposure to X-ray irradiation. The negative midgap and flatband voltage shifts, ΔV_{mg} and ΔV_{fb} , in these devices, displayed in Fig. 3, show an excess of trapped positive oxide-trap charge in the as-deposited Hf silicate devices studied in [1]. The concentrations of these defects are significantly larger than for the same X-ray dose for a device quality, thermal SiO₂ gate oxide device of similar electrical thickness. There is no experimental evidence in these figures (e.g., a positive shift or significant inflection in either the midgap or flatband voltage as a function of dose) that would indicate significant electron trapping in the Hf silicate [1].

In a second set of experiments on a different set of devices that are described in detail in [2], it was shown that, for Al₂O₃ and HfO₂ gate dielectric stacks, the density of oxide trapped charge depends strongly on the film thickness and processing conditions, generally displaying a nonlinear dependence on dose, as shown in Fig. 4. Here we plot ΔV_{mg} for MOS capacitors with 7.5 nm nano-crystalline Al₂O₃ or HfO₂ layers deposited onto 1.1 nm interfacial non-crystalline Si oxynitrides. The HfO₂ gate dielectrics in [2] have effective trapping efficiencies that are up to 15 to 20 times larger than those of thermal SiO₂ of equivalent electrical thickness. As shown in Fig. 4, midgap voltage shifts depend strongly on device processing, and exhibit oxide-trap charge buildup that is significantly more non-linear with dose

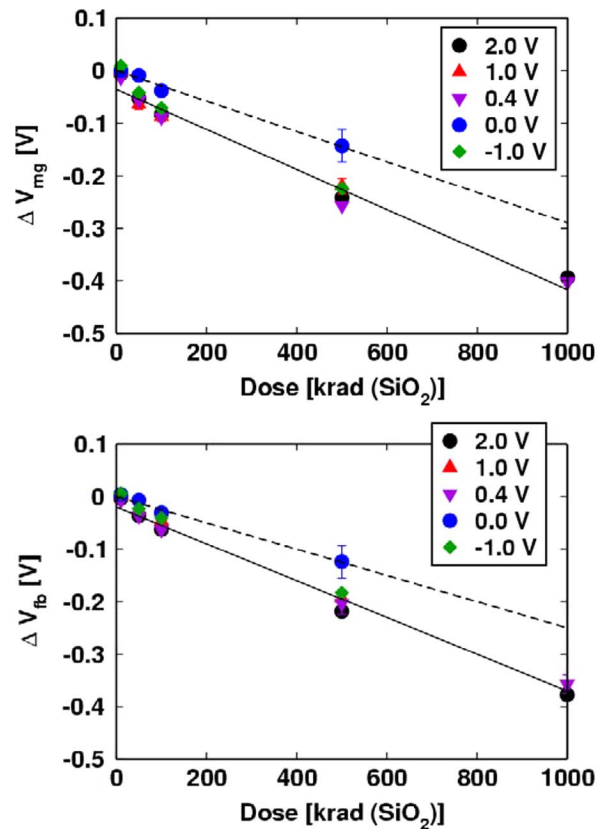


Fig. 3. (Top) Midgap voltage and (bottom) flatband voltage shifts for total dose irradiations of Hf silicate capacitors with 4.5 nm effective oxide thickness gate dielectrics, as a function of radiation bias. The 0 V irradiations are denoted by a dashed line; other biases are as marked in the legend. (After [1].)

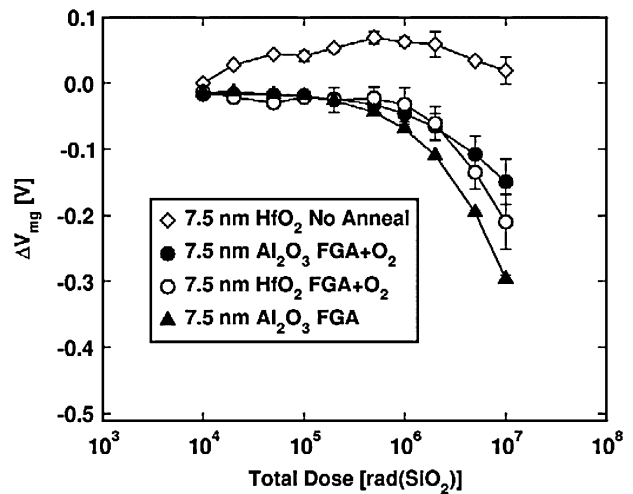


Fig. 4. Midgap voltage shifts versus dose for 7.5 nm HfO₂ and Al₂O₃ ALD dielectrics on 1.1 nm Si oxynitride interfacial layers for different post gate oxidation annealing conditions (after [2]).

than for the Hf silicate devices of Fig. 3. The HfO₂ and Al₂O₃ dielectrics and their interfaces have either been subjected to forming gas anneal (FGA), an O₂ anneal followed by a FGA, or no annealing after the atomic layer deposition (ALD) of the high- κ dielectric.

The HfO₂ devices in Fig. 4 that received no anneal show only small positive shifts (at most ~ 0.1 V) in ΔV_{mg} up to doses as

high as 10 Mrad(SiO₂), while the annealed devices exhibit significantly larger negative shifts, ~ -200 mV. The HfO₂ devices in Fig. 4 also display C-V hysteresis that is process dependent, and similar to what has been reported for Al₂O₃ devices [2]. Unannealed devices show the smallest midgap voltage shifts as a result of the charge compensation in Fig. 4, but have the highest C-V hysteresis (an indication of shallow electron traps or border traps [15], [22]–[24]), and were found in [12] and [20] to exhibit extremely large radiation-induced charge trapping after combined irradiation and bias-temperature stress under worst-case bias conditions. We now discuss the microscopic origins of the qualitative differences in charge trapping between Hf silicate (Fig. 3) and HfO₂ (Fig. 4).

III. DEFECT STATES IN HfO₂ AND Hf SILICATES

The differences in experimental results for Hf silicate devices in Fig. 3 and HfO₂ devices in Fig. 4 derive from intrinsic differences between the band edge electronic states in nano-crystalline HfO₂ and non-crystalline Hf silicate. The non-crystalline Hf silicate dielectrics have defect states that are more similar in nature (although much higher in density [1]) to those in SiO₂ than do the HfO₂ films. The measurements in Fig. 3 [1] are made on as-deposited films that are homogeneous non-crystalline dielectrics. Upon annealing to temperatures of approximately 900 °C, these films chemically phase separate into nano-crystalline HfO₂ encapsulated in a non-crystalline SiO₂ matrix [25], [26]. This phase separation has been confirmed by infrared spectroscopy, X-ray photoemission spectroscopy studies of the O 1s core level spectrum and differentiation of that spectrum, and X-ray absorption spectroscopy that has focused on changes in the conduction band edge Hf d-states between as-deposited and annealed films [25]–[27].

In contrast, the nano-crystalline HfO₂ thin films have grain boundaries between the individual nano-scale crystallites (grains) [26]. These grain boundaries are generally a source of electrically active defects, either intrinsic or due to segregated impurities [11]. Critical to an understanding of the impact of the nano-crystallinity of HfO₂ on its electrical response are the properties of the intrinsic atomic d-states of Hf at the valence and conduction band edges that promote localized trapping states at both band edges [11], [26]. Intrinsic defect states, such as O-atom vacancies [8]–[10] that can cluster on grain boundaries in the HfO₂ or ZrO₂ display a strong atomic d-state character as well [11].

Recently, several important properties of the band edge defects in HfO₂ and other related transition metal oxides have been obtained from spectroscopic studies, as we now summarize. Then, based on theory, we interpret these spectroscopic changes in terms of O-atom defect bonding arrangements, either O-atom vacancies and O-interstitials, or a combination of both [8]–[11]. The resulting discussion of these new results provides significant insight into the microstructure of defects leading to the differences in radiation response illustrated in Figs. 3 and 4.

The electronic structure of nano-crystalline HfO₂ (including the valence and conduction band states and the intrinsic defects) has been determined using advanced spectroscopic techniques. For example, soft x-ray photoelectron spectroscopy, SXPS, at Brookhaven National Laboratory, has been used to study va-

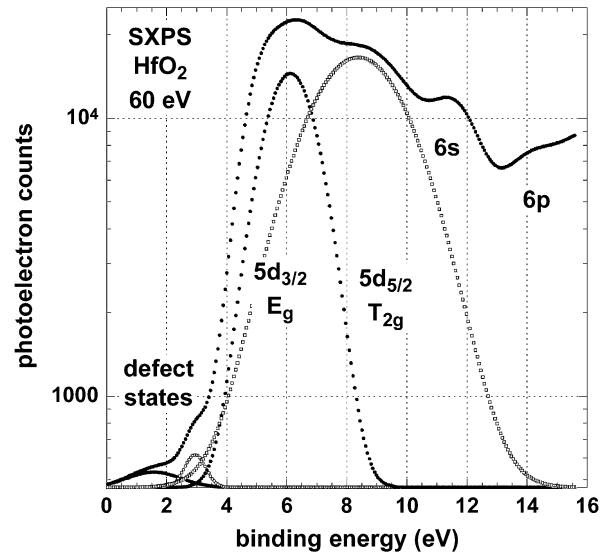


Fig. 5. SXPS valence band spectrum for nano-crystalline HfO₂: 5d-state and defect features are identified.

lence band states, whereas near edge x-ray absorption spectroscopy, NEXAS, has been applied at the Stanford Synchrotron Radiation Laboratory, and vacuum ultra-violet spectroscopic ellipsometry, VUV SE, has been performed at North Carolina State University. The results of these standard materials characterization techniques have been combined to develop a fundamental understanding of the conduction and valence band states and associated defects in HfO₂. Qualitatively similar intrinsic and defect states have been found in nano-crystalline ZrO₂ films, the only difference being a reduction of ~ 0.3 eV in the ZrO₂ optical band gap [6]. Hence, additional insights into the properties of HfO₂ likely can be obtained in the future through comparison with characterization results on ZrO₂ and other transition metal oxides.

Fig. 5 shows the SXPS spectrum for HfO₂. This spectrum has been fit with gaussian functions that identify the intrinsic π - and σ -bonding features derived from Hf atomic d-states, as well as defect state features at the valence band edge that have been assigned to intrinsic defects. Qualitatively similar spectra have also been obtained for the other group IVB transition metal oxides, TiO₂ and ZrO₂, reinforcing the generality of this response, and emphasizing that these are generic materials properties, as oppose to lot specific variations. Based on the relative intensities observed in Fig. 5, the defect volume densities are in range of 2×10^{19} to 10^{20} cm⁻³, or 1×10^{13} to 2×10^{13} cm⁻² if projected to a thin-film near-interfacial layer.

Fig. 6 presents the VUV SE ϵ_2 (imaginary part of the complex dielectric constant) spectrum for HfO₂, identifying 2 defect state features below the lowest d-state conduction band edge d-state feature [11]. One of these features overlaps the intrinsic band edge, which extrapolates to an effective band gap, or optical absorption threshold energy of ~ 5.7 eV, and gives an effective trap depth of 0.4 ± 0.2 eV. The second defect state lies deeper within the band gap, ~ 1.8 eV below the lowest energy d-state feature of the conduction band, and does not overlap the tail of the band edge. The photoconductivity and cathodoluminescence spectra for HfO₂ support the intrinsic nature of

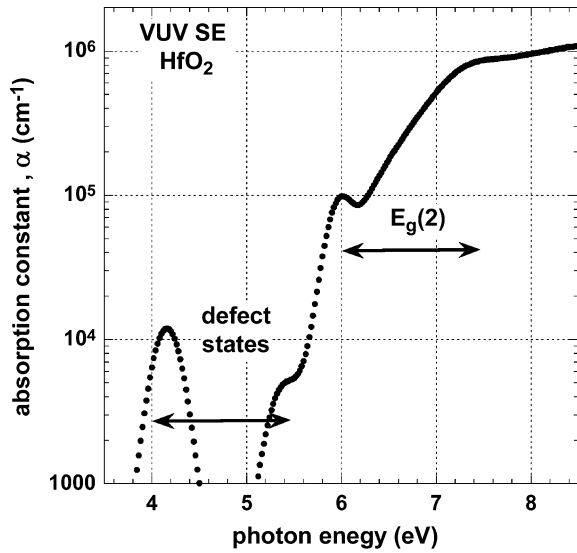


Fig. 6. ϵ_2 spectrum from spectroscopic ellipsometry measurements for nano-crystalline HfO_2 : 5d-state and defect features are identified.

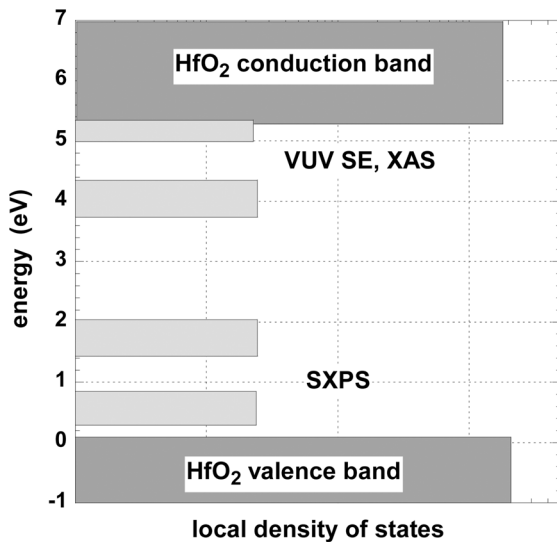


Fig. 7. Schematic representation of band edge states in HfO_2 , including defect states within the forbidden band gap (after [9]).

these defect states derived from the x-ray and VUV spectra [11]. The photoconductivity spectrum displays a sub-bandgap feature that extends from the intrinsic band edge at ~ 5.7 eV to ~ 5.1 eV, and the cathodoluminescence spectrum yields a peak at 4.2 eV, which is the energy of the deeper defect state relative to the top of the valence band. Note that the defect states shown spectroscopically in Figs. 5 and 6 and summarized schematically in Fig. 7 are pre-existing defects [27] found in thin film dielectrics that were not subjected to either electrical or radiation stress. The defects in HfO_2 are indicated in Fig. 7 as two states below the conduction band edge in the upper half of the forbidden bandgap, and two above the valence band edge in the lower half of the bandgap. These defects serve as direct precursors to the defects in irradiated or stressed films, much in the same way that a simple O vacancy serves as a precursor to the

well known E' center in irradiated SiO_2 [24], [28]–[31]. Calculations in [8]–[10] focus on electronic states associated with O-vacancies and O-interstitials in HfO_2 [8]–[10]. Experimental work in [7], [11], and [32] shows that these are present in relatively high concentrations in HfO_2 and ZrO_2 . O-atom vacancy defect states with different charge states are found in [8]–[10] to lie in the upper half of the forbidden bandgap within ~ 2 eV of the conduction band edge, and O-atom interstitial defect states are located in the lower half of the bandgap, within about 1–2 eV of the valence band edge. Based on the equivalence of O vacancies and sub-oxide bonding [11], we conclude that O vacancies are logical candidates to function as electrically active defects in irradiated or stressed HfO_2 .

We should also point out that the relatively high density of pre-existing trapping states, i.e., as high as $\sim 10^{13}$ cm^{-2} in areal density, or equivalently $> 3 \times 10^{19}$ cm^{-3} in volume density, is expected to be significantly enhanced by O vacancies and/or interstitials that are clustered preferentially at the grain boundaries that are intrinsic to nano-crystalline dielectrics [7], [11]. This is reinforced by SE studies that show a decrease in effective defect densities with increasing annealing temperature [33]. This decrease is consistent with increases in crystallite size as a function of post-deposition annealing (e.g., Fig. 4) at increasingly high temperatures, along with a corresponding reduction in O vacancy and interstitial density. Similar defects are also reported in hafnium oxynitrides [34]. O vacancies have been known to be important to the radiation response of SiO_2 for more than 20 years [24], [28]–[31], but a significant role for O interstitials in MOS radiation response appears unique to these high- κ dielectrics. Other intrinsic electron traps in these systems typically are also present because of the Jahn–Teller term splitting of the Hf (or other group IVB transition metal) bonding site, which induces defects similar to those shown schematically in Fig. 7 [7], [35], [36]. Processing techniques (e.g., ultra-thin HfO_2 annealed in N_2 or NH_3 at 700 °C and Zr/Hf Si oxynitrides that can be scaled to effective oxide thickness values of 0.7–0.8 nm) are being developed to reduce these effects [36]–[38]. These new results suggest that more advanced high- κ dielectrics may show properties that are even more favorable for potential applications in a radiation environment than ones investigated to date.

IV. CONCLUSION

New spectroscopic evidence, combined with theoretical calculations and experimental studies, show significant differences in the charge trapping properties of amorphous Hf silicate and nano-crystalline HfO_2 gate dielectrics. The increased electron trapping in the nano-crystalline HfO_2 thin films likely is associated primarily with O vacancies and O interstitials that are enhanced by grain boundaries in these structures, as well as the Jahn–Teller term splitting of the Hf bonding site. These typical defects in crystalline films are not present in Hf silicate devices, which respond much more similarly to SiO_2 , although with significantly enhanced defect densities. These results reinforce that qualitatively different types of dominant charge trapping mechanisms can exist in high- κ gate dielectrics owing to inherent differences in their microstructures, and point to promising approaches for reducing the charge trapping in these materials.

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