

Diffusion Reaction of Oxygen in HfO₂/SiO₂/Si Stacks

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We study the oxidation mechanism of silicon in the presence of a thin HfO₂ layer. We performed a set of annealing in ¹⁸O₂ atmosphere on HfO₂/SiO₂/Si stacks observing the ¹⁸O distribution in the SiO₂ layer with time-of-flight secondary ion mass spectrometry (ToF-SIMS). The ¹⁸O distribution in HfO₂/SiO₂/Si stacks upon ¹⁸O₂ annealing suggests that what is responsible for SiO₂ growth is the molecular O₂, whereas no contribution is found of the atomic oxygen to the oxidation. By studying the dependence of the oxidation velocity from oxygen partial pressure and annealing temperature, we demonstrate that the rate-determining step of the oxidation is the oxygen exchange at the HfO₂/SiO₂ interface. When moisture is chemisorbed in HfO₂ films, the oxidation of the underlying silicon substrate becomes extremely fast and its kinetics can be described as a wet silicon oxidation process. The silicon oxidation during O₂ annealing of the atomic layer deposited HfO₂/Si is fast in its early stage due to chemisorbed moisture and becomes slow after the first 10 s.

Introduction

High dielectric constant (high- κ) oxides, such as HfO₂, are potential candidates to replace SiO₂ as the gate dielectric in complementary metal oxide semiconductor (CMOS) transistors. The nature and the properties of the interface HfO₂/Si have a number of implications on the electrical and physical properties of the oxides. In particular, the mechanism of atomic exchange at the interface, especially for oxygen, is of particular interest from a fundamental perspective as well as for its technological implications related to the formation of the interfacial oxide that determines the performances of the dielectric stack in the high- κ -based CMOS technology.¹

It is known that oxygen diffusion mechanisms in HfO₂ and SiO₂ are quite different. In HfO₂, oxygen diffusion occurs in atomic form through vacancies,^{2–5} while in SiO₂ atomic oxygen has very low diffusion velocity and the oxidation of silicon implies the reaction–diffusion of molecular oxygen.^{6–8} Therefore, the silicon oxidation process in the presence of an HfO₂ layer can occur either through a complicated oxygen exchange mechanism at the HfO₂/SiO₂ interface or via the diffusion of either atomic oxygen into silicon or molecular oxygen in HfO₂. Very little is known about the oxygen diffusion/oxidation in stacks of materials having different oxygen diffusion mechanisms, and the existing literature deals only with the anodic oxidation processes.^{9,10}

Si oxidation in the presence of a high- κ oxide was shown to proceed with quite different kinetics as compared with bare Si oxidation.¹¹ It has been observed that for short annealing the oxidation kinetics of silicon is much faster in the presence of an HfO₂ layer,^{11,13} while for longer annealing it becomes much slower. Two possible causes can be considered for such anomalous kinetics: (1) Atomic oxygen injected into the Si layer during annealing in the presence of high- κ is more reactive but with a slower diffusion coefficient than the molecular oxygen diffusing during bare silicon oxidation; (2) there is a catalytic effect from film contaminants and in particular moisture. Since

moisture is quickly removed during the process, the oxidation rate of silicon drops after the early stage of annealing.^{14–16}

In this paper, we study the mechanism of oxygen diffusion in SiO₂ in the presence of an HfO₂ layer using the ¹⁸O isotopic tracer in HfO₂/SiO₂/Si stacks. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is used to study the oxygen distribution after annealing.

Experimental Methods

A set of HfO₂ films were deposited, on either *p*-Si (100) substrates or on thermally grown 16.0 nm SiO₂ films on Si, by atomic layer deposition (ALD) using either a F-120 reactor (ASM-Microchemistry) or a Pulsar system (ASM). The nominal film thickness was 10 nm. Prior to deposition, the *p*-Si (100) wafers were cleaned using SC2 (HCl:H₂O₂:H₂O, 1:1:5, 80 °C, 10 min) and the native oxide was removed with diluted HF. The silicon oxide was then regrown, through another SC2 step, to ensure maximal reproducibility of the interfacial oxide thickness. The thermal SiO₂ films were used as received to avoid possible damages of the oxide through cleaning steps. The temperature of the substrate during the growth was 300 °C, whereas the solid precursor (HfCl₄ as the source of Hf) was kept at 160 °C. Oxygen was supplied by injecting H₂O in the reaction chamber using N₂ as the carrier gas.

After few weeks of dry air exposure, the films were annealed in a rapid thermal process (RTP) system (JetFirst-Jipelec (France)) in N₂, O₂, and ¹⁸O₂ (¹⁸O₂ isotope enrichment 95.5 obtained from Chemgas – France) at various temperatures and analyzed within 2 days. All the annealings were done in a static atmosphere, without gas fluxes during the process. The annealing chamber was evacuated and filled at the desired pressure with the desired gas. Particular care was taken in avoiding moisture in the annealing chamber, by performing several purging cycles.

ToF-SIMS depth profiles were acquired with an ION-TOF IV operated in dual beam mode. Negative ions generated by a 25 keV Ga⁺ primary source were acquired, while sputtering was accomplished through a 500 eV Cs⁺ ion beam at 45°.

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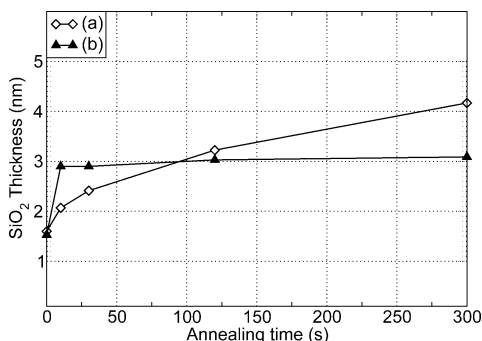


Figure 1. Oxidation kinetics of bare silicon (a) and of silicon capped with an HfO₂ (b), upon annealing at 900 °C in RTP at an O₂ pressure of 100 mbar as shown earlier.¹¹

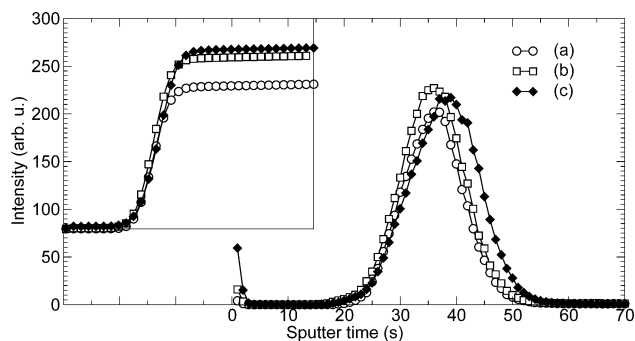


Figure 2. In the main figure, a ToF-SIMS profile of the SiO₂⁻ signal of an HfO₂ grown on a 4.1 nm SiO₂. Profile of the as-grown sample (a) and of samples annealed in O₂ at 900 °C in RTP for 10 s (b) and 300 s (c). The inset reports the integral of the signals reported in the main figure, to show the difference in the SiO₂ thickness.

A methodology to measure SiO₂ interfacial layer thickness by means of ToF-SIMS has been previously developed, and a detailed description is given elsewhere.¹⁷ Briefly, a calibration curve developed on a set of HfO₂/SiO₂/Si stacks with a transmission electron microscopy (TEM) measured interfacial layer is used to translate the SiO₂⁻ peak area into an interfacial layer thickness.

Results and Discussion

Figure 1 shows the oxidation kinetics of silicon with and without a HfO₂ film deposited on top, upon annealing at 900 °C in RTP at an O₂ pressure of 100 mbar as shown earlier.¹¹ We can observe that, while the oxidation kinetics of bare silicon follows a parabolic trend, the presence of an HfO₂ layer on top of silicon causes a sudden increase of the SiO₂ interfacial layer up to 3 nm, but for longer annealing, no measurable further SiO₂ formation is observed.

To verify if the oxidation velocity of Si depends on the interfacial SiO₂ layer thickness, we grew an HfO₂ film on a 4.1 nm SiO₂ and performed an RTP annealing in O₂. The result is shown in Figure 2, where the main graph represents the SiO₂⁻ signal intensity (proportional to the interfacial layer thickness), for as-deposited and annealed for 10 and 300 s, respectively, while the inset shows the integral of the signals with the right-side plateau being proportional to the total SiO₂ thickness. The trend observed is quite similar to the one observed for annealing of HfO₂ layers deposited on native oxide, with an initial fast interfacial layer growth, followed by a slow silicon oxidation process. This experiment demonstrates that the trend observed in Figure 1 does not depend on the interfacial layer thickness but on a variation of the oxidation mechanism occurring after the early stage of annealing.

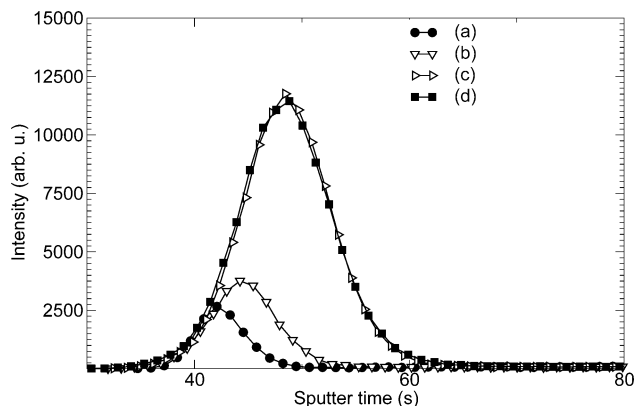


Figure 3. SiO₂⁻ signal of HfO₂ on silicon annealed in different conditions at 900 °C in RTP: (a) as-deposited, (b) annealed for 10 s in N₂, (c) annealed for 10 s in O₂, and (d) annealed for 10 s in N₂ followed by O₂ for 10 s.

We also considered the possibility that the variation in the oxidation velocity is due to the crystallization process taking place in the HfO₂ film during the early stage of the annealing process leading to a decrease in the oxygen diffusion velocity. Crystallization was induced in-situ through a preannealing at 900 °C in N₂ just before the oxidation. Indeed it is known that at such temperature the crystallization of thin HfO₂ films proceeds quickly.¹² The result is shown in Figure 3, where the ToF-SIMS profile of the SiO₂⁻ signal for a series of films annealed in various conditions is reported. It can be observed that there is no effect of the preannealing on the final SiO₂ layer thickness. The interfacial layer grows slightly upon annealing in N₂, increasing further during the O₂ step. The final interfacial layer thickness is the same irrespective of the preannealing step.

Annealing in ¹⁸O₂ for 10 s was done either on as-grown samples or on samples that were previously annealed for 10 s in either N₂ or natural O₂ in the RTP system in-situ (in-situ preannealing). The ¹⁸O concentration after annealing was obtained using the formula

$$C_{18O}^{18} = \frac{I_{18O}^{18}}{I_{16O}^{16} + I_{18O}^{18}}$$

where I_{16O}^{16} and I_{18O}^{18} are the intensities of the ¹⁶O and ¹⁸O peaks, respectively.

Figure 4 shows the ¹⁸O diffusion profiles of a bare SiO₂ layer (a) and of the SiO₂ capped with HfO₂ (b), annealed for 10 and 300 s in ¹⁸O₂. In the bare SiO₂, the ¹⁸O isotope accumulates at the SiO₂/Si interface as expected^{6,8} (Figure 4a).

The degree of ¹⁸O incorporation into the HfO₂ layer is above 50% (Figure 4b) in the sample annealed for 10 s, but its concentration increases only slightly with increasing annealing time. In addition, there is no concentration gradient into the layer even in the sample annealed for the shortest time. We explain this behavior considering that the HfO₂ film is polycrystalline and that the oxygen diffusion velocity is very high in the grain boundaries and low in the crystallites. Therefore, the exchange of the ¹⁶O with the ¹⁸O one in the crystallites from the grain boundaries (and/or from the amorphous fraction) occurs homogeneously in the HfO₂ film. For annealing times longer than 300 s and up to 900 s, no further measurable increase in the ¹⁸O concentration in HfO₂ is observed. The reason might be a decrease of the ¹⁸O₂ concentration in the annealing chamber caused by the ¹⁶O₂ outgassing of the system as noticed previously.¹¹ This might cause a reduced ¹⁸O incorporation for longer annealing.

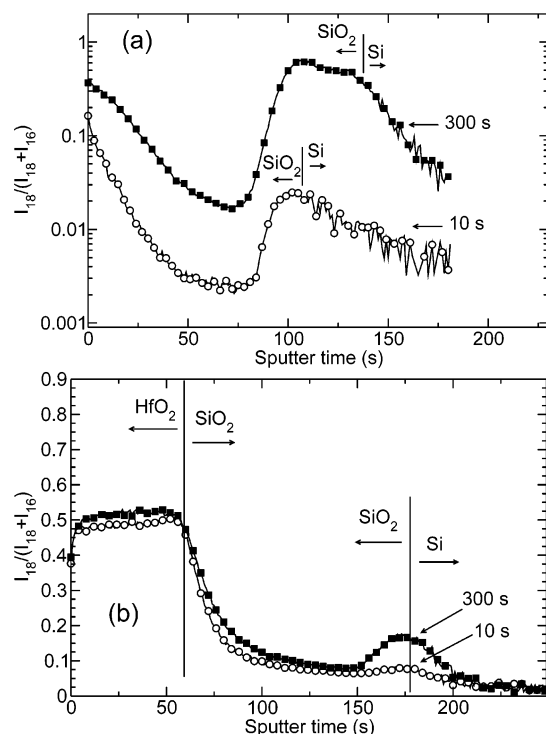


Figure 4. (a) ¹⁸O profiles in bare 16.0 nm SiO₂ films annealed in ¹⁸O₂ at 900 °C in RTP. (b) Same annealing performed on a HfO₂/16.0 nm SiO₂/Si stack.

The identification of the “true” ¹⁸O profile in the SiO₂ underneath the HfO₂ with ToF-SIMS is difficult due to the measurement artifacts. Indeed, inhomogeneities in the sputtering process taking place during the measurement are particularly strong for HfO₂/(SiO₂)/Si systems¹⁸ causing poor depth resolution of the oxygen signal. Figure 4b suggests that the total amount of ¹⁸O uptake in the SiO₂ layer underneath the HfO₂ is very limited (in agreement with the observation of the limited SiO₂ growth in this condition) and accumulates at the SiO₂/Si interface as in the case of bare SiO₂. This is quite surprising, since such behavior suggests that molecular ¹⁸O₂ takes part in the diffusion process in the HfO₂/(SiO₂)/Si stack as shall be discussed in detail later.

The effect of in-situ preannealing is shown in Figure 5. On bare SiO₂ (Figure 5a), the preannealing has little or no effect. The in-situ preannealing has no effect on ¹⁸O uptake into the HfO₂ layer (see Figure 5b). This is in disagreement with data previously published by another group,²⁴ who observed that the preannealing inhibits ¹⁸O incorporation. It must be noted nevertheless that in that particular paper O₂ annealing was performed at lower temperature, where the oxygen diffusion velocity might be more significantly affected by the polycrystalline structure of the film.

In the SiO₂ layer underneath the HfO₂ film, the natural O₂ preannealing prevents further ¹⁸O from diffusing into the SiO₂ layer. This confirms the previous observation that the oxygen diffusion into the SiO₂ layer occurs exclusively in the early stage of annealing. Such variation is not due to a diminished oxygen permeability of the HfO₂ layer to oxygen. We shall also notice that the inhibition of the interfacial layer growth occurs only upon oxygen preannealing, whereas nitrogen preannealing at the same temperature has the opposite effect, causing an increase of the oxygen adsorption into the SiO₂ layer.

The mechanisms occurring during O₂ annealing can therefore be divided in two stages, the first one (stage 1) is already complete after 10 s, whereas the second one (stage 2) starts

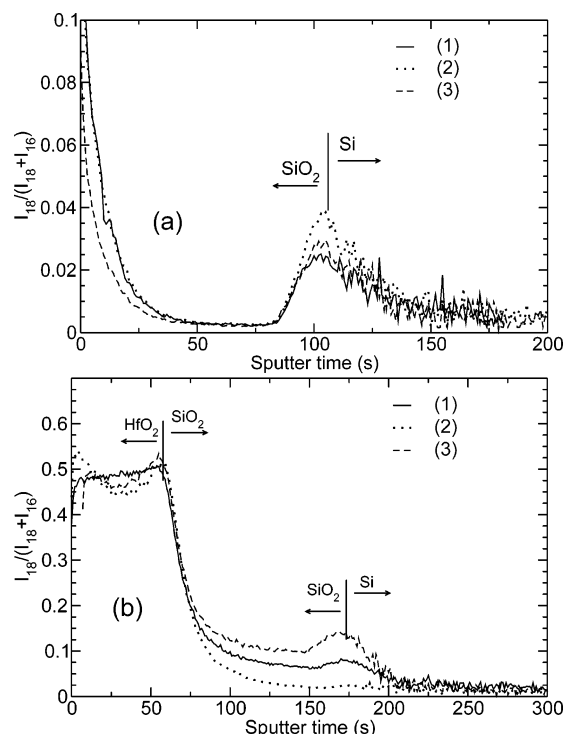


Figure 5. (a) ¹⁸O profiles in an SiO₂ 16.0 nm thick layer annealed at 900 °C in RTP in ¹⁸O₂ for 10 s (1), in ¹⁶O₂ for 10 s and in ¹⁸O₂ for 10 s (2), and in N₂ for 10 s in ¹⁸O₂ for 10 s (3). (b) An HfO₂ film on top of a 16.0 nm SiO₂ layer annealed in the same conditions as before.

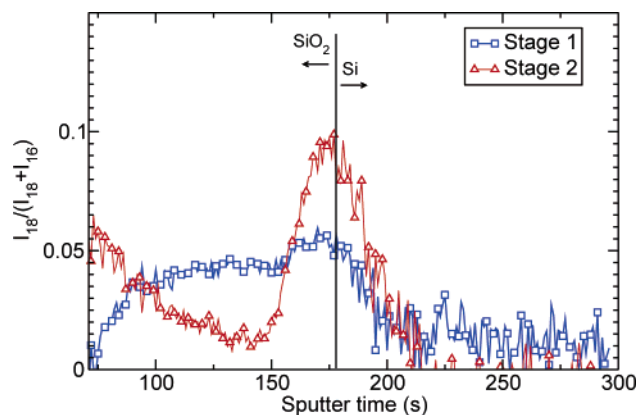


Figure 6. ¹⁸O concentration profiles of early oxidation stage (stage 1) and late oxidation stage (stage 2). The profiles were offset by placing HfO₂/SiO₂ at the origin. (See text for a detailed explanation.)

afterward and follows a much slower kinetics. We determined the ¹⁸O profiles in the capped SiO₂ layer of stage 1 and stage 2, by estimating the ¹⁸O ToF-SIMS profiles differences of various samples. The ¹⁸O profile of the O₂ preannealed sample provides a sort of instrumental function, and its subtraction from the profiles of the other samples allows for the elimination or at least reduction of the effects of the measurement artifacts. Therefore, the ¹⁸O profile upon stage 1 oxidation was obtained by subtracting the ¹⁸O profile obtained after 10 s ¹⁸O₂ annealing preannealed in ¹⁶O₂ from the ¹⁸O curve obtained after 10 s annealing. To obtain the stage 2 oxygen diffusion profile, we subtracted the profile from a 300 s ¹⁸O₂ annealing sample from the one obtained after a 600 s annealing. The results are shown in Figure 6. We can see that after stage 1 oxidation the resulting ¹⁸O distribution is almost flat throughout the SiO₂ layer. The dip in proximity of the HfO₂/SiO₂ interface is a measurement artifact. The ¹⁸O profile for the stage 2 oxidation on the other

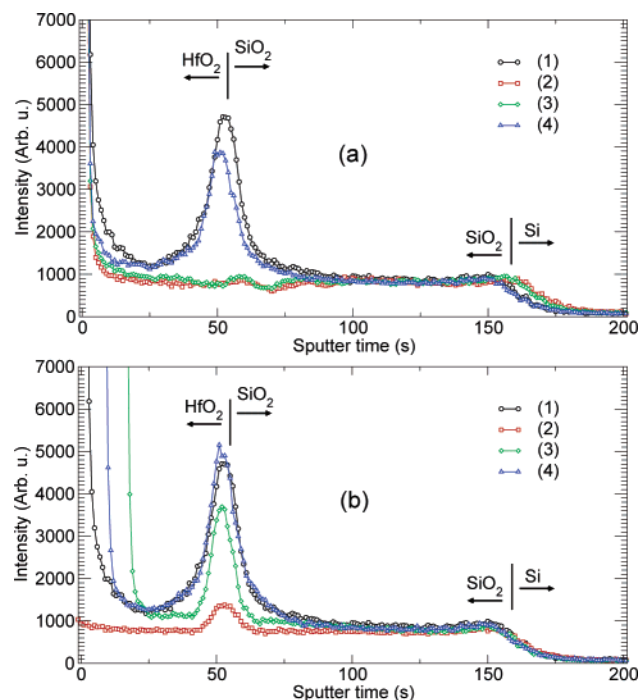


Figure 7. OH signal of O₂ (a) and N₂ (b) annealed samples. Samples as-deposited (1 (black)) and annealed at 900 °C (2 (red)), 700 °C (3 (green)), and 500 °C (4 (blue)). OH signals give indirect information on moisture adsorbed in the HfO₂ film. While for O₂ annealing, 700 °C is sufficient to eliminate excess moisture at the interface, in N₂ excess OH is found even in the sample annealed at 900 °C.

hand is surprisingly similar to the ¹⁸O profile of the annealed bare SiO₂.

Stage 1 Oxidation. We make the hypothesis that stage 1 oxidation is promoted by moisture adsorbed in the HfO₂ layer. Such moisture is unstable at high temperature during oxygen annealing, therefore its removal causes the oxidation kinetics to change. We monitored OH signal in the ToF-SIMS depth profile to get an indication of the trend of the moisture desorption kinetics as a function of annealing temperature and atmosphere. A ToF-SIMS analysis of a set of samples annealed at 500, 700, and 900 °C for 10 s in O₂ and N₂, respectively, is shown in Figure 7. The OH peak provides an indication of hydrogen in the high- κ layer. We can observe how annealing in O₂ is extremely effective in removing hydrogen. Indeed, the instrumental background level is reached at 700 °C. Moisture is adsorbed preferentially at the interface HfO₂/SiO₂, as can be concluded observing the peak at the interface. For samples annealed in N₂ instead, an OH peak is still present in the sample annealed at 900 °C, demonstrating that N₂ annealing is not effective in moisture removal. This observation correlates well with the one that nitrogen in-situ preannealing is not effective in inhibiting interfacial SiO₂ growth, providing a stronger support on the role of moisture in promoting Si oxidation in the presence of HfO₂ films. An even stronger evidence in support of the role of moisture in the determination of the interfacial SiO₂ growth upon annealing is given by the reconstructed stage 1 ¹⁸O profile in Figure 6 that presents an almost flat oxygen distribution throughout SiO₂. This isotopic oxygen distribution is different from a typical dry oxidation process and was associated with a wet oxidation process.¹⁹ We can therefore refer to stage 1 oxidation as a wet oxidation process. It is well-known that HfO₂ is much more hygroscopic than SiO₂ and also that moisture adsorption is partially irreversible in HfO₂.^{15,16} Since available experimental data for moisture adsorption are mostly related to surface moisture, it is likely

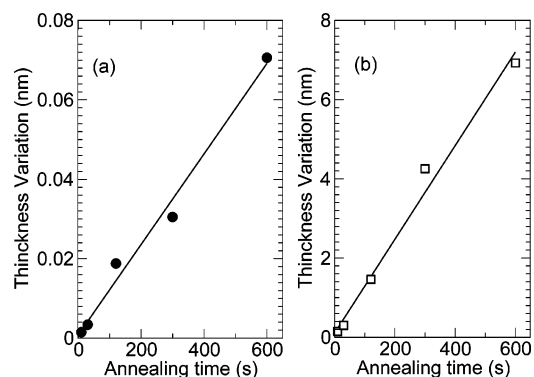


Figure 8. Uptake of ¹⁸O into SiO₂ on a HfO₂/SiO₂ stack (a) and on a bare 16 nm SiO₂ film (b) as a function of the annealing time at 900 °C and a 250 mbar ¹⁸O₂ pressure.

that the OH groups that are buried in the film are bound to the film even more strongly. For an estimation of the stability of moisture in bulk hafnia, only theoretical studies provide information on its stability. A recent work predicts that the activation energy for OH diffusion is 1.4 eV.²⁰ Why moisture removal is more efficient during O₂ annealing as opposed to N₂ annealing is not clear at the moment. We notice that O₂ annealing causes an electrical field in the HfO₂ layer due to the oxygen diffusion process;²¹ this can act as a driving force for the charged OH⁻ species. The most notable study of the oxygen diffusion mechanism in high- κ /Si stacks with similarities with the system studied in this paper was done on the ZrO₂/Si system.⁴ The study reported that the interfacial SiO₂ growth was essentially independent from the annealing time and on the oxygen partial pressure. In addition, it was shown that vacuum preannealing was not significantly affecting the build-up of the SiO₂ interfacial layer. The process can be explained as a stage 1 type of oxidation.

Stage 2 Oxidation. The interpretation of the diffusion process during stage 2 oxidation should explain an apparent contradiction of the presented data. Indeed, on one hand, we observed that the oxygen exchange rate into HfO₂ is extremely fast, while on the other hand, it appears that HfO₂ constitutes a formidable barrier for the oxidation of the underlying silicon. As it was shown in Figures 4 and 6, stage 2 oxidation can be assimilated to a classical dry silicon oxidation process, with the accumulation of ¹⁸O at the SiO₂/Si interface, suggesting that the oxidizing species of silicon is molecular oxygen as in the case of bare SiO₂. To elucidate the oxygen exchange mechanism at the HfO₂/SiO₂ interface, it is therefore instructive to observe the dependence of the oxidation velocity on the annealing time, pressure, and temperature and to compare it with the one of bare SiO₂. Stage 2 oxidation was studied by performing an in-situ preannealing in ¹⁶O₂ at 900 °C for 10 s before carrying out the ¹⁸O₂ ones. In Figure 8, we compare the oxidation velocity of silicon starting from a 16 nm thick SiO₂ with (a) and without (b) the HfO₂ capping layer. For HfO₂ samples given the difficulties related to the measurement of the “real” ¹⁸O profile in the SiO₂ layer with ToF-SIMS, we measured the variation of the ¹⁸O depth profile as a function of the annealing time obtained as a difference of the various ¹⁸O₂ annealed samples. The HfO₂ capped oxide shows a growth rate approximately 2 orders of magnitude lower than the uncapped one. The pressure dependence of the oxidation kinetics is shown in Figure 9. For both bare SiO₂ and the HfO₂/SiO₂ stack, there is a linear dependence of the oxidation velocity on the ¹⁸O₂ pressure in agreement with the Deal and Grove model in the range of thickness considered.

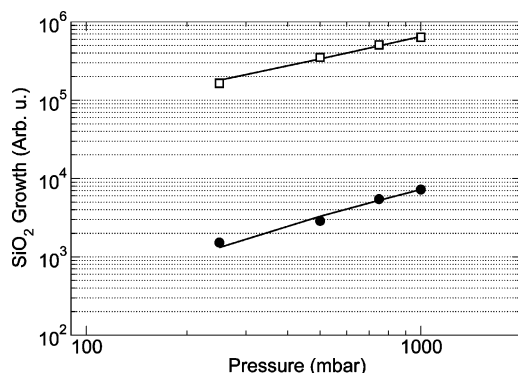


Figure 9. Uptake of ¹⁸O into SiO₂ on a HfO₂/SiO₂ (close circles) stack and on a bare SiO₂ (open squares) films as a function of ¹⁸O₂ pressure for a 900 °C RTP annealing for 600 s.

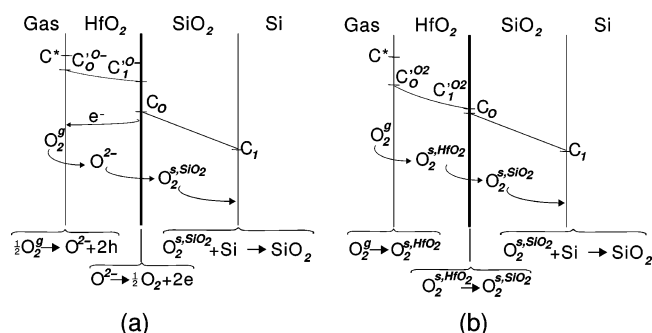


Figure 10. (a) Silicon oxidation model in the presence of a high- κ layer assuming an oxygen exchange model where atomic-charged oxygen in the HfO₂ is transformed into neutral-molecular oxygen in SiO₂. The rate-determining step is the oxygen exchange at the HfO₂/SiO₂ interface. (b) A model where the molecular oxygen is the diffusing species throughout the whole HfO₂/SiO₂ stack. The rate-determining step is the oxygen exchange at the HfO₂ surface.

Several evidences that oxygen diffusion in hafnia occurs through doubly charged vacancies are reported,^{2,20,21} nevertheless our ¹⁸O diffusion studies demonstrate that the species responsible for stage 2 oxidation is molecular oxygen. If the oxygen leading to stage 2 derives from the HfO₂ lattice, then there must be an oxygen exchange process at the HfO₂/SiO₂ interface transforming charged-atomic oxygen into neutral-molecular oxygen. A diffusion process based on this mechanism is depicted in Figure 10a. C^* is the activity coefficient of the gaseous O₂, C_o^{02-} is the oxygen O²⁻ concentration at the HfO₂ interface, C_i^{02-} is the concentration of oxygen at the HfO₂/SiO₂ interface, while C_o and C_i are the O₂ concentration in SiO₂ at the interface with hafnia and with silicon, respectively. Given the high oxygen exchange rate into the HfO₂ matrix, the difference between C^* and C_o^{02-} as well as the one between C_i^{02-} and C_o^{02-} should be small. Therefore, the rate-determining step of the diffusion process should be the process of formation of O₂ at the HfO₂/SiO₂ interface. Alternatively, we can make the hypothesis that a small concentration of molecular O₂ diffuses into the HfO₂ layer and causes the oxidation of SiO₂ as depicted in Figure 10b. In this case, molecular oxygen diffuses into HfO₂, exchanges at the HfO₂/SiO₂ interfaces, and follows the conventional diffusion-reaction path. In this hypothesis, the oxygen responsible for the oxidation of silicon is no longer related to the amount of ¹⁸O in the HfO₂ layer measured in the profiles presented, and the effectiveness of HfO₂ as an oxygen diffusion barrier can be better understood. Figure 11 shows the Arrhenius plot of the oxidation velocity for the two considered systems. We can see that the slope of the two lines is the same, suggesting

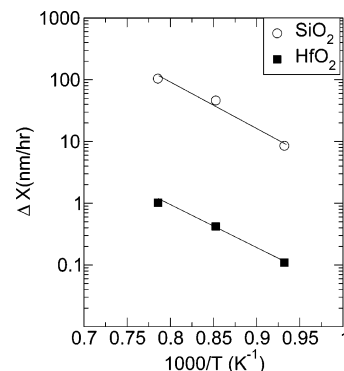


Figure 11. Arrhenius plot of the oxidation velocity of SiO₂ in an HfO₂/SiO₂ (close circles) stack and on bare SiO₂ (open squares) films as a function of temperature.

that the activation energy for the oxidation process is the same for HfO₂/SiO₂ and bare SiO₂ indicating that the rate-determining step for the oxidation is the same in the two cases. We therefore conclude that stage 2 oxidation is the result of molecular oxygen diffusion and that the atomic oxygen moving fast into the HfO₂ lattice cannot exchange with the SiO₂ at the interface as depicted in the model of Figure 10b. The lack of charged-atomic oxygen diffusion into capped SiO₂ can be explained considering that charged defects are unstable in SiO₂, given the covalent nature of SiO₂ that makes charge stabilization difficult, in addition, migration of a charged species requires electrons to move in the opposite direction in the SiO₂ layer, but given the high band gap of silica, this process is energetically unfavored.²² Therefore, for a diffusion process to take place, the oxygen species should be neutralized before they can diffuse into the interfacial SiO₂ layer. In addition, the limited mobility of atomic-oxygen species in SiO₂ is well-known. Indeed, according to theoretical calculation, the activation energy for the diffusion of atomic O[•] is above 1.3 eV,²³ while the activation energy for molecular oxygen is as low as 0.3 eV.^{22,23} The formation of molecular O₂ in the solid phase is on the other hand unlikely.

Conclusion

We have shown that the oxidation process in HfO₂/SiO₂/Si stacks is a two stage process. Stage 1 occurs during an early phase of annealing (10 s), is promoted by the moisture chemisorbed in the HfO₂ layer, is extremely fast, and leads to a relatively thick SiO₂ layer in a very short time. The removal of the chemisorbed moisture requires high temperatures in an oxygen atmosphere. Therefore, from the point of view of CMOS technology, the control of the moisture contamination of HfO₂ is extremely important to prevent interfacial SiO₂ formation.

Stage 2 oxidation on the other hand is 2 orders of magnitude slower than bare silicon oxidation, despite the fast atomic-oxygen exchange occurring in the HfO₂ layer during annealing. It was demonstrated that stage 2 oxidation is caused by molecular O₂ diffusion throughout the entire HfO₂/SiO₂ stack. Such a diffusion process is limited by the low O₂ solubility in HfO₂. HfO₂ is therefore a formidable diffusion barrier for molecular oxygen, preventing SiO₂ growth effectively.

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