Characterizing the charge trapping across crystalline and amorphous Si/SiO\textsubscript{2}/HfO\textsubscript{2} stacks from first principle calculations

Yue-Yang Liu\textsuperscript{1,2}, Feilong Liu\textsuperscript{1}, Runsheng Wang\textsuperscript{3}, Jun-Wei Luo\textsuperscript{1,4}, Xiangwei Jiang\textsuperscript{1,*}, Ru Huang\textsuperscript{3}, Shu-Shen Li\textsuperscript{1} and Lin-Wang Wang\textsuperscript{2,‡}

\textsuperscript{1}State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China.
\textsuperscript{2}Joint Center for Artificial Photosynthesis and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.
\textsuperscript{3}Institute of Microelectronics, Peking University, Beijing 100871, China.

Abstract
The complexity of charge trapping in novel semiconductor devices such as high-k MOSFETs is increasing as the devices themselves become more complicated. To facilitate the research on such charge trapping issues, here we propose an optimized simulation framework that is composed of density functional theory (DFT) for electronic structure calculation and Marcus theory for charge trapping rates calculation. The DFT simulations are either carried out or corrected by HSE hybrid functional. Using this framework, the hole trapping characteristics along multiple paths in Si/SiO\textsubscript{2}/HfO\textsubscript{2} stacks are investigated, and the relative importance of each path is revealed by calculating its exact hole trapping rate. Besides the study on crystalline stacks, we also create an amorphous stack, which is more realistic compared to experiments and real devices, to reveal more active trapping centers and to study the statistical feature of charge trapping induced by structural disorder. In addition, to seek effective measures for relieving these charge trapping problems, the effects of hydrogen (H) and fluorine (F) passivations are discussed, and physical insights for improving the performance of high-k MOSFETs are provided.
I. INTRODUCTION

Charge trapping from semiconductors to the coated oxide/nitride/high-k layers is a very important quantum mechanical process in semiconductor physics and applications. On the one hand, charge trapping can be utilized to store information in semiconductor-oxide-nitride-oxide-semiconductor (SONOS) capacitor structures to form non-volatile memory devices [1,2]. On the other hand, charge trapping is a severe problem that needs to be solved to improve the reliability of MOSFETs [3,4], especially high-k MOSFETs, which replace the conventional SiO$_2$/SiO$_x$N$_y$ gate dielectrics with high-k materials to reduce gate leakage currents during continuous size scaling [5-7]. Desirable in one case and problematic in the other case, the charge trapping is definitely a key physical process that must be well understood in order to control it in different situations. However, in both cases, as shown schematically in Fig.1, the charge trapping process can happen across multiple interfaces, such as Si/SiO$_2$, SiO$_2$/Si$_3$N$_4$, and SiO$_2$/HfO$_2$ interfaces, which makes the physics complicated and difficult to comprehend, especially if one tries to find out the results merely from fitting to experimental device performance. It will thus be very useful if the problem can be studied by first principle calculations, and different cases can be classified according to their distinct physical behaviors.

The charge trapping phenomenon in MOSFETs is a general process in which carriers in the semiconductor channel are transferred into the gate dielectrics by crossing single or multiple interfaces, and finally trapped in the defective or intrinsic trapping centers in the dielectric oxides. Static defect properties related to the charge trapping process have been investigated widely by using first principles calculations, e.g. the trap energy levels and wave functions, formation/transition energies etc. [8-14]. However, studies on the entire charge trapping process including the whole heterostructure and the related charge transfer dynamics all at ab initio level is much scarcer. One possible reason for such situation is that charge trapping phenomenon in MOSFETs has not been paid sufficient attention until Grasser et al. emphasized its importance to the bias temperature instability (BTI) in recent years [4,15-17]. Another reason is that such simulations on the whole heterostructures are often beyond the capability of the previous ab initio calculations methods and codes, and there are also other technical issues, ranging from interface structure, amorphous structure to how to calculate the charge transfer rates.

As discussed in one of our previous studies on charge trapping across Si/SiO$_2$ interfaces [18], the accurate atomistic simulation of the charge trapping process is possible only after a few technical challenges have been overcome. These include realistic interface structures, correct theoretical band alignment, and the application of adequate charge transfer theories. Undoubtedly, the existence of multiple interfaces will make the calculation even more challenging. First, the construction of atomistic models with multiple interfaces is difficult due to lattice mismatch of different materials. Second, the computational cost could be very high because a system with multiple interfaces is usually very large. Third, the increase of material types and interface numbers will greatly enhance the amount of possible defect candidates, including the defects in each material and the defects at each interface. A systematic study taking into account all the above factors will be a tall order. On the other hand, since the parameters needed to carry out a charge transfer calculation, e.g., the electron-electron coupling, the reorganization energy, and the WKB decay length, are much less well known in multi-junction cases than the simple interface cases, this call for the development of a first principle calculation paradigm to solve this problem.
In this work, we combine the methods we have developed before into an optimized simulation framework, which is able to simulate the charge trapping process in most multiple interface systems, and then we apply it to the Si/SiO$_2$/HfO$_2$ gate stacks to investigate the hole trapping process along different paths in high-k gate transistors.

For charge trapping in HfO$_2$ dielectrics, it was demonstrated that oxygen vacancies (V$_{O\delta}$) should be the main charge traps because of their lower formation energies and closer energy levels with Si band edge [19,20]. While such conclusion is intuitively reasoned, it lacks a rigorous verification through quantitative calculations. The charge trapping from Si to HfO$_2$ in real high-k gate transistors is much more complicated. First, the high-k gate transistors always contain a thin SiO$_2$ interlayer between Si and HfO$_2$ so that the interface quality can be improved. Consequently, the energy level of oxygen vacancies in the Si/SiO$_2$/HfO$_2$ stacks will vary significantly depending on their locations, e.g. at the SiO$_2$ layer, at the SiO$_2$/HfO$_2$ interface, or at the HfO$_2$ layer, instead of being a constant [21]. Experiments have shown that there are different defect levels in HfO$_2$ gate stacks [22,23]. It has also been reported that double V$_O$ could contribute more than single V$_O$ to the random charging/discharging in HfO$_2$ [24]. Second, the energy barrier between defect level and the Si band edge is not the only factor that determines the charge trapping rate. The coupling strength between the two states also plays an important role [17,25]. It has been proved that the coupling strength is especially important when the initial state and final state are close in energy [18]. Third, the energy level of charge trapping defect in the dielectric layer depends greatly on the applied gate voltage, and so does the energy difference between these defect levels and the Si band edge. Finally, the Hydrogen(H) or Fluorine(F) passivation of the oxygen vacancy must be carefully considered because gas annealing is an indispensable process in transistor manufactory.

The framework proposed here will take all the important factors of charge trapping process into consideration, including atomistic interfaces, trapping energy barriers, coupling strength, electron-phonon interaction, oxide electric fields, and H/F passivation. With this framework, we manage to present the distinct hole trapping characteristics along different paths in the Si/SiO$_2$/HfO$_2$ stacks, and then reveal the mechanistic details of the charge trapping process, including which quantity controls the trapping rate most, what role the multiple interfaces and various passivation play, and where the dominant traps locate under different magnitudes of electric field. Different with our previous work given in the conference [26], here we spend additional efforts on studying the Si/SiO$_2$ interface defects, and the effect of H and F passivation on all the V$_O$ defects at Si/SiO$_2$ interface, SiO$_2$ bulk, SiO$_2$/HfO$_2$ interface, and HfO$_2$ bulk. We have
also created an amorphous Si/SiO$_2$/HfO$_2$ interface stacks, which is more realistic compared with experiments and actual microelectronic devices to investigate the influence of structural disorder. These information are of great concern for industrial engineers, and have not been studied systematically. We have also provided much more details on Marcus theory and DFT calculations according to our systems. These theories and results will surely deepen our understanding on the charge trapping issue in high-k MOSFETs, and thus facilitate the solution of charge trapping problems in high-k MOSFETs and improve the integration of high-k materials in silicon CMOS technology.

II. THEORY AND SIMULATION

A. Marcus charge transfer theory

The charge trapping probability is determined by multiple factors, including the energy barrier between the initial and final state, the electronic coupling strength between the two states, and electron-phonon interactions. A well-recognized formula to describe such state-to-state charge transfer rate is the one proposed by R. A. Marcus in 1950’s [27,28], which is able to take all the factors mentioned above into consideration:

\[
\nu = \frac{2\pi}{\hbar} |V_c|^2 \sqrt{\frac{1}{4\pi\lambda k_B T}} \exp \left[ \frac{(\Delta G + \lambda)^2}{4\lambda k_B T} \right]
\]

Fig. 2. The energy diagrams in configuration space for hole trapping from Si to the oxygen vacancy trap in (a) SiO$_2$, (b) SiO$_2$/HfO$_2$ interface trap1, (c) SiO$_2$/HfO$_2$ interface trap2, and (d) HfO$_2$. The three key factors in Marcus theory are marked in each case. The two SiO$_2$/HfO$_2$
interface defects are marked and distinguished in Fig. 3.

The schematic description of Marcus theory and the charge trapping process is shown in Fig. 2, in which the horizontal axis represents structural configuration, and the vertical axis is the energy of different configurations. According to the relative magnitude of $G_t$ and $G_c$, and the relative magnitude of $\Delta G$ and $\lambda$, the energy diagram of Marcus charge transfer theory can be divided into different situations. The four schematics shown in Fig. 2 represents the charge trapping process from Si to SiO$_2$, SiO$_2$/HfO$_2$ interface and HfO$_2$ respectively, and all of them are results by the DFT calculations conducted in this work, which will be shown later. For the following conceptual discussion, any one of the four schematics can be used as the reference. At the beginning of the hole trapping process, a hole lies on the valence band maxima of Si ($VBM_{Si}$), and the energy of the system can be written as

$$G_i = E_0 - VBM_{Si} - \lambda_{Si}$$

where $E_0$ is total energy of the charge neutral system, and $\lambda_{Si}$ is the reorganization energy caused by structural relaxation when $VBM_{Si}$ is occupied by the hole. Then the hole transfers to the defect by crossing the energy barrier between $VBM_{Si}$ and the defect level ($E_{defect}$). Such a transition is induced by the coupling constant ($V_C$) between $VBM_{Si}$ and $E_{defect}$. After the hopping, the atomic positions will experience a structural relaxation due to the occupation of the defect level by a hole, and the final energy of the system becomes

$$G_f = E_0 - E_{defect} - \lambda_{defect}$$

where $\lambda_{defect}$ is the reorganization energy caused by the structural relaxation of atoms around the defect.

Since the wave function of $VBM_{Si}$ is very delocalized, the structural relaxation caused by hole occupation in $VBM_{Si}$ should be negligible, and thus $\lambda_{Si}$ is treated as zero. On the contrary, the $\lambda_{defect}$ is usually large due to the localized nature of defect states and the strong electron-phonon coupling. Therefore, the Gibbs energy change of the hole trapping process can be written as:

$$\Delta G = G_f - G_i = VBM_{Si} - E_{defect} - \lambda_{defect}$$

The overall $\lambda$ can also be taken as $\lambda_{defect}$ if we ignore $\lambda_{Si}$. With the meanings of $\Delta G$, $\lambda$, and $V_C$ known, the difficulty lies on how to calculate them accurately in a Si/SiO$_2$/high-k system. First, we should build a structure with explicit interface so that the effect of such multiple interfaces can be studied thoroughly. Second, we must conduct high-accuracy DFT calculation on the whole interface system to obtain the correct band gap and band alignment. This is very important for charge trapping simulation because the charge trapping rate depends exponentially on the energy barrier between silicon band and defect levels. For this purpose, we like to use the Heyd-Scuseria-Ernzerhof (HSE) hybrid exchange-correlation functional instead of LDA or GGA, because the latter ones usually underestimate the band gap [31]. Third, a more direct method should be used to obtain the coupling constant accurately, under the realistic atomistic environment, especially with atomistic interfaces taken into considerations. Finally, a hole should be precisely inserted (trapped) to the targeted defect level as to obtain the correct reorganization energy. With all these key quantities obtained, the state-to-state hole trapping rate can be calculated using Eq. (1).
B. Atomistic models

We first construct two Si/SiO$_2$/HfO$_2$ interface models that are shown in Fig. 3(a) and (b), which differs with each other at the thickness of the SiO$_2$ interlayer. The phase of the SiO$_2$ and HfO$_2$ is β-cristobalite and monoclinic, respectively, and the orientation of the structure is (001). The side length of the unit cell is set as 10.86×10.86 Å$^2$, which is the size of the relaxed Si part. The strain of the SiO$_2$ part with respect to the Si and HfO$_2$ part is -6.69% and -2%, respectively. These settings are chosen and determined by carefully referencing previous works [21,32-34]. The effect of strain on defect formation energy can be found in several recent works [35, 36]. The marked oxygen atoms in Fig.3 are the oxygen vacancies that have been studied in this work. Each defect is denoted by a phrase combining defect location with the defect order number. For example, Si/SiO$_2$-1 is the first defect at the Si/SiO$_2$ interface. To reveal the important role of dangling bonds at the Si/SiO$_2$ interface, and in seeking for a solution to weaken the trapping capability of the dominant hole traps, we have also attempted to passivate all the oxygen vacancies by H and F atoms. Lastly, we create an amorphous Si/SiO$_2$/HfO$_2$ structure (cSi/aSiO$_2$/aHfO$_2$) by MD simulations through the melt-quench process, to study the statistical property of charge trapping in disordered system. Six interfacial oxygen vacancies and eight HfO$_2$ oxygen vacancies are sampled and labeled in Fig. 3(c). We note that a metal gate could affect the work function at the metal/HfO$_2$ interface [37], but it will not change the physical picture of charge trapping from Si to the trap states in SiO$_2$ and HfO$_2$ layers.

Fig. 3. (a) and (b) Two (001) oriented Si/SiO$_2$/HfO$_2$ gate stack models with 0.6 and 1.2 nm interlayer, respectively. Oxygen vacancies at different locations, i.e. Si/SiO$_2$ interface, SiO$_2$ interlayer, SiO$_2$/HfO$_2$ interface, and HfO$_2$ high-k layer, are numbered separately. (c) The cSi/aSiO$_2$/aHfO$_2$ stack used for statistical study.
The MD simulation is carried out by the QuantumATK 2018.6 [38,39] (ATK), and the force field is from Ref [40]. Langevin thermostat is adopted in the whole melt-quench process, and a timestep of 1 fs is used. The melt process begins with an enlarged supercell, as references usually do [41,42], to facilitate the bond breaking, and it lasts for 50 ns under the temperature of 5000 K. After that, the supercell is shrunk back and melt for another 50 ns under 5000K. Finally, the system is cooled down linearly from 5000 K to 300 K within 500 ns, i.e. a cooling rate of 9.4 K/s, to get the final structure. One tricking thing is that the SiO$_2$ and HfO$_2$ will mix with each other if we start the melting with the whole crystalline interface structure. To avoid that, we need to begin with a crystalline Si/SiO$_2$ stack and get the crystalline-Si/amorphous-SiO$_2$ first, and then put the crystalline HfO$_2$ into the supercell and melt the HfO$_2$ while keeping the SiO$_2$ part fixed.

The quality of the amorphous HfO$_2$ is confirmed by checking the coordination of each atom and the radial distribution function (RDF) of them, which are shown in Fig. 4. In agreement with previous theoretical and experimental works [43-45], the coordination number of Hf atom is dominated by 6 while accompanied by a few 5 and 7, and that of the O atom is dominated by 3 with a few 2 and 4. The 1-coordinated O atom is the ones at the SiO$_2$/HfO$_2$ interface, who bridge the Si and Hf atoms. Also in consistent with previous works [46-48], the Hf-O RDF peaks at about 2.1 Å, while that of O-O and Hf-Hf distribute around 2.8 Å and 3.5 Å.

![Fig. 4. The coordination number and the radial distribution function of the amorphous HfO$_2$ part.](attachment:fig4.png)

**C. Density-functional theory simulation**

DFT simulations are carried out by the plane-wave package PWmat with GPU acceleration [49,50]. GGA-PBE functional is used for structural relaxation with a convergence criterion of 0.01 eV/Å for the residual force. Hybrid HSE functional is used in all the self-consistent field (SCF) calculations to obtain the correct band alignment and defect levels. HSE functional is also used in calculating the reorganization energy to correct the PBE results. The SG15 norm-conserving pseudopotentials are adopted with an energy cutoff of 50 Ry. Single Gamma point is sampled considering the large superlattices and large number of atoms in each model. HSE parameters are set separately with a mask function for different materials to obtain their correct band gaps simultaneously [51]. The parameter sets for bulk Si, SiO$_2$, and HfO$_2$ are determined by reproducing their reported band gap of 1.12 eV, 8.5 eV, and 5.8 eV, respectively. With these parameters, the band alignment of the Si/SiO$_2$/HfO$_2$ interface structure are obtained and shown in

7
Fig. 5. It can be seen that the band gaps that agree well with experiment values are realized simultaneously. Besides, it is found that the interface transition regions are not atomically sharp. Therefore, the local atomic nature of interfaces must be considered in a realistic simulation of the multi-interface gate stacks.

The reorganization energy $\lambda$ for each defect is obtained by inserting a hole into the defective system, and then relax the system and record the energy change. Since this relaxation is a local effect, we can calculate it based on a pure bulk SiO$_2$ and HfO$_2$, or with the SO$_2$/HfO$_2$ interface system without Si. This has the advantage that the defect level will be inside the band gap, thus will not hybridize with the Si inside-band states, which can make the charged defect atomic relaxation intractable. More specifically, we first relax the atomic structure with defect at its neutral state ($N$ electrons) and obtain an atomic structure $R_0$. Then, we remove an electron from the $R_0$ structure ($N-1$ electrons), and without relaxation the atomic positions, carry out an electronic structure self-consistent calculation to obtain the total energy $E(R_0, N-1)$. The electron is in fact removed from the defect level, because the defect level lies at the band gap and is the highest occupied level. After that, we relax the atomic structure with $N-1$ electrons to obtain its minimum energy $E(R_1, N-1)$. The energy differences between these two atomic configurations (both with $N-1$ electrons) is the reorganization energy:

$$\lambda = E(R_0, N-1) - E(R_1, N-1)$$

Note, since both energies have $N-1$ electron, they both have electrostatic image energies, thus there is no need for image interaction correction. The uncertainty caused by this electrostatic image interaction for the calculation of $\lambda$ should thus be much smaller than the typical defect level calculations where $E(N+1)$ and $E(N)$ are subtracted.

The Gibbs free energy change $\Delta G$ can be obtained straightforwardly according to Eq. (4) once the band alignment, defect levels and reorganization energy are known. The most difficult but important task is to calculate the coupling constant $V_C$. In previous literatures, the $V_C$ is often obtained by using the WKB approximation [16,17]:

![Graph showing band alignment and reorganization energy calculation](image-url)
where $\Delta E$ is a tunneling barrier, $m_t$ is the tunneling effective mass and the parameter $k_t$ can only be obtained by calibration with experiments. Such approximation treats the coupling of two states as the tunneling of one state to the other, and it is not capable of taking into account the explicit atomic environment. Moreover, the WKB approximation has only been used in single-interface systems such as Si/SiO$_2$, and its validity in multiple-interface systems is quite questionable (as the wave function can be bounced by at the interface). Even in single-interface Si/SiO$_2$ system, our previous work has shown that the WKB approximation can underestimate the coupling strength of two states [18].

In our more accurate approach, $V_C$ will be obtained by direct DFT calculations. Considering a two-state system with coupling constant $V_C$ that is subjected to an external field, we can write down the Hamiltonian of the system by denoting the original energy difference of the two levels as $\Delta \varepsilon_0$, and the field induced potential change as $F$:

$$H = \begin{pmatrix} -\Delta \varepsilon_0 / 2 + eF & V_C \\ V_C & \Delta \varepsilon_0 / 2 - eF \end{pmatrix}$$

Diagonalizing this 2x2 Hamiltonian, we can obtain the eigen energies of these two states as:

$$\varepsilon_{\pm} = \pm \sqrt{V_C^2 + \left(\frac{\Delta \varepsilon_0}{2} - eF\right)^2}$$

It can be seen that the two levels will get closer to each other under certain field, but they will never cross each other due to their coupling. The minimum energy gap of the two levels is found to be exactly two times of the coupling constant $V_C$. Guided by this theory, we intentionally apply an electric field to the Si/SiO$_2$/HfO$_2$ structure, and to drive the VBM$_{Si}$ and $E_{defect}$ close to each other until the anti-crossing (avoid crossing) phenomenon occurs.

In summary, the theoretical simulation framework contains two steps. First, carrying out DFT calculations to obtain the parameters needed by Marcus theory, and then input them into the Marcus charge transfer formula to get the exact trapping rate. The work flow of this scheme is shown in Fig. 6. With this framework, we can now investigate the charge trapping process in any multilayered structures.
III. RESULTS AND DISCUSSION

From Eq. (1), it can be seen that the hole trapping from $VBM_{Si}$ to a defect in the dielectric layer is more likely to happen when the defect level is close to the $VBM_{Si}$, and when the coupling constant between the two states is large. However, as we will show below these two conditions are usually against each other, hence it is difficult to be satisfied at the same time. The balance between these two factors dominates the story of hole charge trapping in the Si/SiO$_2$/HfO$_2$ system.

A. Defect level and Si band edge alignment

Fig. 7 summarizes the defect level alignment of multiple-source V$_0$ centers with respect to the Si band edge. Obviously, the V$_0$ defects at different positions produce distinct defect levels. First, we find that the V$_0$ defects at the Si/SiO$_2$ interface will not induce any local defect states near the $VBM_{Si}$ unless a hydrogen atom is introduced. Second, the V$_0$ defects inside the SiO$_2$ interlayer are deeply below the $VBM_{Si}$, indicating that they are rarely able to trap holes. Third, those at the SiO$_2$/HfO$_2$ interface also lie below $VBM_{Si}$ but are much closer to $VBM_{Si}$ in energy, which means that they are more advantageous in hole trapping. Last, the V$_0$ defects at the HfO$_2$ layer lie very slightly above $VBM_{Si}$, making them the most energetically favorable hole traps. Nevertheless, it is worth mentioning that all the defect levels will be raised up by negative bias temperature instability (NBTI) stresses for a p-type FET where the hole trapping takes place. So the hole trapping capability will change according to the gate electric field amplitude.

Fig. 6. The flowchart of the theoretical simulation framework, including the sophisticated DFT calculations, and the Marcus charge trapping theory.
The defect level alignments of multiple-source $V_0$ centers with respect to the Si band edge. The $V_0$ defect state at the Si/SiO$_2$ interface is not local unless an H atom is induced.

**B. $VBM_{Si}$-$E_{\text{defect}}$ coupling**

Fig. 8 depicts the coupling and anti-crossing energy curves between $VBM_{Si}$ and two $V_0$ defects. The two $V_0$ defects vary in location and their distance from Si, and thus couple with different strength with $VBM_{Si}$. For the first defect at the SiO$_2$ interlayer, as is shown in Fig. 8(a), it can be seen that the wave function of the $E_{\text{defect}}$ is significantly localized at the oxygen vacancy before a strong coupling, and $VBM_{Si}$ is much more delocalized at the Si atoms. With further approaching of the two energy levels, their wave functions begin to overlap with each other, and they localize at the same position when they couple the most. After that, these two states separate apart, and the characters of $VBM_{Si}$ and $E_{\text{defect}}$ state will be switched. From the minimum gap of these two curves, one can obtain the $2V_c$ amplitude. The second defect shown in Fig. 8(b) is a defect at the HfO$_2$ layer. The coupling process is nearly the same as that in Fig. 8(a), but the coupling constant is much smaller in value. This is because the $V_0$ defect at HfO$_2$ is farther away from silicon, and there is an interface in between.

**Fig. 8.** The coupling process of $VBM_{Si}$ with $V_0$ defect in (a) SiO$_2$ interlayer, and (b) HfO$_2$ high-k layer
The coupling constants of \( VBM_{Si} \) with all the other \( V_O \) defect levels are obtained by the same procedure and are shown in Fig. 9. Obviously, the coupling constants decrease monotonically with the distance of the defects from the Si substrate. However, it is also evident that the decay behavior of \( V_C \) can be divided into three types according to the \( V_O \) defect locations. First, it can be seen from Fig. 9(b) that the \( V_C \) decay at the SiO\(_2\) interlayer follows a good exponential trend with a decay length of 1.58 Å. However, it will experience a sharp drop when encountering the SiO\(_2\)/HfO\(_2\) interface. If we put the interface defects of the two models together, as is seen in Fig. 9(c), we can also see an exponential trend but with a different scaling length (1.92 Å). More importantly, we find from Fig. 9(a) that the \( V_C \) decay in the high-k HfO\(_2\) layer doesn’t follow a simple exponential law. These results mean that the coupling constant decay in a single interface system, e.g. Si/SiO\(_2\), can be qualitatively described by a simple exponential function such as WKB approximation, but the \( V_C \) decay in multi-interface high-k stacks, e.g. Si/SiO\(_2\)/HfO\(_2\), is more complicated, and it can’t be described by a simple exponential function.

![Fig. 9.](image)

**Fig. 9.** The decay of coupling constant with the distance of \( V_O \) defect from Si substrate.

### C. Reorganization energy

The effect of electron-phonon interaction is included in the reorganization energy, i.e. the energy change caused by structural relaxation after charge trapping. Fig. 10 illustrates the reorganization process for three typical \( V_O \) defect locations. There is a common feature that all the atoms around the vacancy defect will depart more from each other after hole trapping. However, the reorganization energy value differs because of the different local environment. By using PBE functional, it is found that the \( V_O \) defect at the SiO\(_2\) interlayer has the reorganization energy of 0.31 eV, while the SiO\(_2\)/HfO\(_2\) interface, and HfO\(_2\) \( V_O \) defects have values around 1 eV.

Although these DFT results are expected to be relatively correct, it is always puzzling us that whether the choice of functional (e.g. PBE and HSE) will affect the calculation of the reorganization energy, especially because the level of charge localization and polaronic energy depend on the functional used, and sometimes PBE gives delocalized solutions when the physically correct picture is that of a localized charge.
To answer this question, we build two smaller models containing 96 atoms, of which one is crystalline HfO$_2$ and the other one is SiO$_2$, so that the structural relaxation by HSE functional is available. Then we sampled two V$_0$ defects (3-coordinated and 4-coordinated) in HfO$_2$ and one V$_0$ defect in SiO$_2$ to calculate the reorganization energy with PBE and HSE functional, respectively. See Fig. S1-S3 in the Supplemental Material for the models and detailed comparison results [52]. It is found that the HSE functional generally produces larger reorganization energy than the PBE functional. For both kinds of V$_0$ defects in HfO$_2$, the HSE result is larger than the PBE result by a factor of about 1.4. For the V$_0$ defect in SiO$_2$, when we calculated the electronic structure using PBE functional under the neutral defect atomic positions, but occupying it with one hole (thus making it a “+” charged state), due to state hybridization with VBM state, after SCF steps, the hole is not staying in the localized defect state as the one shown in Fig.10(a), instead it occupies a delocalized state, which changes the physical meaning for reorganization energy. To correct this problem, we have forced the hole in the original localized defect state (from the neutral state SCF calculation) in a constraint DFT scheme, and keep the hole state unchanged during SCF iterations. The atomic relaxed “+” charged state does not have this problem, thus can be calculated in more conventional way. The so calculated PBE reorganization energy is 0.99 eV, which is also about 1.4 times smaller than the corresponding HSE result (1.38 eV). We have also tested the effect of functional on the H-passivated V$_0$ defects, and found a slightly different ratio between PBE and HSE results. See Fig. S4-S5 in the Supplemental Material for the simulation results [52].

In summary, the PBE function always produces smaller reorganization energy than the HSE functional probably due to larger wave function delocalization, but the PBE results can be approximately corrected by multiplying an amplification factor that depends on the defect type. For V$_0$ defect in SiO$_2$ and HfO$_2$, the correction factor is 1.4, while for Single-H passivated defect, the correction factor is 1.1, and for Double-H passivated defect, the correction factor is 1.3.

D. Hole trapping rates

Fig. 10. The structural relaxation after hole trapping and the reorganization energy for V$_0$ defects at (a) SiO$_2$, (b) SiO$_2$/HfO$_2$ interface, and (c) HfO$_2$. All the values are corrected by HSE functional calculations.
With all the decisive parameters obtained, the hole trapping rates can be calculated by using Eq. (1). The trapping rates to the $V_O$ defects at SiO$_2$ interlayer are too small to be shown here, so there are only data for $V_O$ defects at SiO$_2$/HfO$_2$ interface and the HfO$_2$ layer in Fig. 11. First, we can discuss the case when gate voltage is zero. It can be seen that the trapping rates to the HfO$_2$ layer $V_O$ defects are very high, but not always the highest, even though these $V_O$ defects are closest to $VBM_{Si}$ in energy. This is because they are very far away from the Si substrate, thus their coupling with $VBM_{Si}$ is very weak. On the contrary, the $V_O$ defects at the SiO$_2$/HfO$_2$ interface couple much stronger with $VBM_{Si}$ due to smaller distance with Si, so their hole trapping capability can be stronger even though their energy barrier with $VBM_{Si}$ is less favorable for hole trapping. These results manifest well in the balance between coupling constant and energy barrier in controlling the charge trapping rate. Overall, the energy barrier between $VBM_{Si}$ and $E_{defect}$ is more dominant because it appears at the exponential component in Eq. (1).

In a MOSFET, the hole trapping is always electric field-dependent. The oxide electric field will change the alignment of the defect level with respect to the $VBM_{Si}$, and thus also change the energy barrier

$$\Delta G = VBM_{Si} - (E_{defect} + F_{OX} \cdot d) - \lambda_{defect}$$  \hspace{1cm} (9)

where $F_{OX}$ is the electric field induced by negative gate voltage, and $d$ is the distance between Si substrate and the $V_O$ defect. Taking this re-alignment into account, the $F_{OX}$-dependent hole trapping rates are calculated and also shown in Fig. 11. Since all the defect levels will be raised up by the NBTI stresses, the interfacial $V_O$ defects will get closer to $VBM_{Si}$ and become more energetically favorable for hole trapping. As a result, their trapping capability will become stronger. On the contrary, because the $V_O$ defects at the HfO$_2$ are already higher in energy than $VBM_{Si}$ at zero electric field, the NBTI stress will further drag the energy level away from $VBM_{Si}$, which eventually enters the Marcus inverted region so their trapping capability will be decreased [53]. Nevertheless, the $V_O$ defects in HfO$_2$ layer will always stay effective because the electric field in high-k layer is usually very weak.

![Fig. 11. The $F_{OX}$ dependent hole trapping rate for different $V_O$ defects in the case of model-I and model-II.](image)
E. Complicated effect of H and F passivation

The effect of Hydrogen (H) and Fluorine (F) passivation on defect charge trapping is very complex and interesting. On the one hand, it is widely known that proper passivation is able to reduce defect state density so to relieve the charge trapping phenomenon [54-56]. On the other hand, it is also found that the forming and breaking of Si-H bond at the Si/SiO\(_2\) interface play an important role in charge transfer and BTI [57,58]. Moreover, the F passivation is reported to be different from H passivation in relieving charge trapping in high-k MOSFETs [59-61]. These phenomena naturally give rise to many questions such as why H passivation is not as good as F in relieving charge trapping? Why H atoms are important for charge trapping at the Si/SiO\(_2\) interface? In addition, is the effect of passivation the same for defects that locate at different part of multilayer high-k gate stacks? We will like to use our theoretical simulations to help to answer these questions.

![Fig. 12. PDOS and wave function of oxygen vacancies at the Si/SiO\(_2\) interface. (a) No vacancy, (b) 1\(^{st}\)-Vo type with no passivation, (c) 1\(^{st}\)-Vo type with single H passivation, (d) 1\(^{st}\)-Vo type with double H passivation, and (e)-(g) 2\(^{nd}\)-Vo type.](image)

First, we take a look at the effect of H atoms on the Vo defects at the Si/SiO\(_2\) interface. It can be seen from the models in Fig. 3 that there are two kinds of Vo defect at the Si/SiO\(_2\) interface according to their local bonding environment. The first Si/SiO\(_2\) Vo defect lies between two Si atoms that belong to the bulk silicon, and the second Vo defect lies between bulk Si and SiO\(_2\). The energy levels of these two defects before and after H passivation are all obtained by checking the partial density of states (PDOS) of the atoms around the defect, and are shown in Fig. 12. As mentioned in part III-A, there are no strongly local defect states inside or near the band gap when the defect is not passivated, as is seen in Fig. 12(b). Two strong PDOS peaks slightly above the Si CBM might indicate defect states. However, a closer investigation of the actual states near those energy shows that not only they have strong charge at the defect site, but they also have charge density in the Si. It is possible the defect state is hybridized strongly with bulk Si state. The case of Vo defects with double H passivation is also similar, as shown in Fig. 12(d). For the double H passivation, the PDOS peaks are far below the VBM, indicating the passivation has pushed them all the way from conduction band into valence band. In contrast, for the Vo with only one H, the
defect state has been pushed down, from above CBM into the band gap, but not all the way into the VB, as shown in the PDOS of Fig. 12(c). As a result, the corresponding wave function is very localized. Such phenomenon has also been observed in the second Si/SiO₂ interface defect, as is shown in Fig. 12(e)-(g). All these show a complicated story of H passivation at the Si/SiO₂ interface.

Following the framework shown in Fig. 6, the hole trapping rates from VBMₜₙ to these Single-H passivated Si/SiO₂ interface defects are obtained and shown in Fig. 13(a). In comparison with the main hole trapping centers shown in Fig. 11, we find that these Si/SiO₂ interface defects are weaker in hole trapping under NBTI stresses. The reason is multifold. First, the energy barrier of H passivated Si/SiO₂ interface defects is much larger than those at the HfO₂ layer, as can be seen in Fig. 7. Second and more importantly, the reorganization energy of H passivated Si/SiO₂ interface defects are found to be very small, as is shown in Fig. 13(b) and (c). They are only 1/3 to 1/2 of those unpassivated Vo at SiO₂/HfO₂ interface and HfO₂ layer. Moreover, their trapping capability is further weakened by the NBTI stresses because the defect levels lie above VBMₜₙ, which will be raised up, further increase the energy barrier.

![Fig. 13. (a) Comparison of hole trapping rate from VBMₜₙ to Vo defects at SiO₂/HfO₂ interface, HfO₂, and H-passivated Si/SiO₂ interface; (b) and (c) The reorganization of the two kinds of Vo defects at the Si/SiO₂ interface, both with single H passivation.](image)

In contrast to the Si/SiO₂ interfacial Vo defects, the Vo defects in other locations will directly induce a very localized defect state near the VBMₜₙ, as has been shown in Fig. 7 and Fig. 10. Therefore, the effect of passivation on these locations is supposed to be very different from that on Si/SiO₂ interface. Along with the purpose to distinguish the effect of H and F passivation, we carry out study on H and F passivation on Vo defects in all locations.

Fig. 14(a) shows the energy alignment of Si band edge and the H passivated Vo defects at different locations. Both Single-H passivation and Double-H passivation are studied. Compared with the defect levels without passivation (denoted by gray star-lines), it can be seen that Single-H passivation will push all the Vo defect levels upwards while Double-H passivation will pull them down. Besides, the localized defect state will disappear when the Vo defects at SiO₂ are passivated
by double H atoms. Nevertheless, neither Single-H passivation nor Double-H passivation is able to completely eliminate the hole trapping problem. For Single-H passivation, the SiO_2 V_O defect and the 2nd SiO_2/HfO_2 interface V_O defect are close to VBM_{Si}, and thus are effective traps. The Double-H passivation is better in relieving hole trapping, but the 1st SiO_2/HfO_2 interface V_O defect and the HfO_2 V_O defect are still not far from VBM_{Si}, and thus are likely to be effective traps. We next calculated the coupling constants and reorganization energy of each defect, which are shown in Fig. 14(b). The resulting hole trapping rate under different magnitude of electric field are shown in Fig.14(c). Under negative gate voltages, it can be seen from Fig. 14(c) that the Vo-1H at the SiO_2 layer and the Vo-2H at the SiO_2/HfO_2 interface will both be active hole trapping centers.

The effect of F passivation is found to be very different from H passivation. It can be seen from Fig. 15(a)(b)(c) that a single F atom can perfectly replace the O atom regardless of the location at the SiO_2 layer, the SiO_2/HfO_2 interface, or the HfO_2 layer. This is a bit surprising since one might think a single F anion cannot replace an O^{2-} anion. Since there is no dangling bond with F passivation, there is also no obvious defect energy near the Si band edge, as is seen in Fig. 15(d). The defect levels induced by a Single-F passivation is far from the Si band edge, and thus will not be able to trap holes according to Eq. (1). The Double-F passivation present several different features. First, the relaxed locations of F atoms are different with Single-F passivation. Second, the two F atoms will induce two localized states that close in energy, as can be seen in Fig. 15(e). The two states differ at the charge density distribution. Despite these differences, we can clearly see the common feature that no localized state that close to Si band edge will be induced by F passivation. Consequently, the hole trapping problem can be greatly relieved by F passivation, which is in consistent with experimental observation [60].

![Fig. 14. (a) the energy alignment of V_O defects and the Si band edge before and after passivation, (b) the coupling constant and reorganization energy of each V_O defect, (c) the electric field dependent hole trapping rate from VBM_{Si} to four V_O defects that most likely to be traps.](image-url)
Fig. 15. The relaxed structures of F passivated V\textsubscript{O} defects and their PDOS. (a)(b)(c) Single-F passivation in SiO\textsubscript{2}, SiO\textsubscript{2}/HfO\textsubscript{2} interface, and HfO\textsubscript{2}, respectively. (f)(g)(h) Double-F passivation in each position. (d) The PDOS of the Single-F atom at SiO\textsubscript{2}/HfO\textsubscript{2} interface. (e) The PDOS of the two F atoms at HfO\textsubscript{2}.

F. Charge trapping variation in amorphous Si/SiO\textsubscript{2}/HfO\textsubscript{2} stack

Although we have pointed out the distinct charge trapping characteristics of defects at SiO\textsubscript{2}, HfO\textsubscript{2}, and their interfaces, respectively, one could still concern what happens in more complicated but more realistic amorphous Si/SiO\textsubscript{2}/HfO\textsubscript{2} stacks. The local environment in amorphous ones could be very different even for the same kind of defects in the same material, not to mention the interfaces. We note that the defect level of oxygen vacancy in an amorphous Si/SiO\textsubscript{2}/HfO\textsubscript{2} stack was reported before [62], but no further study on charge trapping or statistical study on the defect level variation was carried out. Therefore, we create the amorphous Si/SiO\textsubscript{2}/HfO\textsubscript{2} stack shown in Fig. 3(c) to reveal the charge trapping variation in disordered system, and to look for the information that can not be extracted from crystalline ones. As marked in Fig. 3(c), we sampled six interface V\textsubscript{O}S defects and eight HfO\textsubscript{2} bulk V\textsubscript{O}S. We have also created a puckered V\textsubscript{O} defect in SiO\textsubscript{2}, as is shown in the inset of Fig. 16, which has been proved to be exist in amorphous silica [63,64]. Then we calculate their defect levels, coupling constant with VBM\textsubscript{Si}, reorganization energy, and finally the hole trapping rates under different magnitude of electric fields.

Fig. 16 The defect levels of the oxygen vacancies in cSi/aSiO\textsubscript{2}/aHfO\textsubscript{2}. 

18
The defect level of each \( V_O \) sample is shown in Fig. 16. Compared with the results in crystalline stacks, the consistent phenomenon is obvious, i.e. the defect levels induced by \( SiO_2 \) \( V_O \) defects and \( SiO_2/HfO_2 \) interface \( V_O \) defects are all below the VBMSi, and those induced by \( HfO_2 \) \( V_O \) defects are mostly above the VBMSi. On the other hand, several new phenomena are also easily noticed. First, the puckered \( V_O \) defect in \( SiO_2 \) is much closer to VBMSi compared with the common dimer ones in crystalline \( SiO_2 \). Second, there are several 4-coordinated \( V_O \) defects in the a\( HfO_2 \) whose defect level is slightly below the VBMSi instead of inside the Si band gap. Third, the defect levels at each material exhibit strong variation, which is accessible considering the disordered local environment in amorphous structures.

![Coupling constant and reorganization energy](image)

Fig. 17 (a)The coupling constant of each defect level with VBMSi, (b) the reorganization of each defect after hole trapping. All the reorganization data are corrected by HSE functional calculation.

The variation also shows itself in the coupling constants and reorganization energy of each defect in Fig. 17. For the coupling constants shown in Fig. 17(a), we can still see a decrease trend with the increasing distance of defect from Si, which is consistent with the case in the crystalline stack, but the trend is not strictly followed by every point. For the reorganization energy, the fluctuation is also obvious even though the magnitude is less than one order.

![Electric field dependent hole trapping rate](image)

Fig. 18 The electric field dependent hole trapping rate of each defect in the amorphous Si/\( SiO_2/HfO_2 \) stack.
Finally, we calculate the hole trapping rate of each defect in the cSi/aSiO$_2$/aHfO$_2$ stack, and their dependence on external electric field. Obviously, there are four kinds of defects in Fig. 18, i.e. the SiO$_2$/HfO$_2$ interface $V_{OS}$ whose hole trapping capability increases monotonically with the electric field, the common HfO$_2$ $V_{OS}$ (2- and 3-coordinated) whose hole trapping rates decrease monotonically, the 4-coordinated HfO$_2$ $V_{OS}$ whose trapping rate increase first and then decrease after certain field strength, and the puckered SiO$_2$ $V_O$ defect who is always a strong trapping center due to its closeness to Si in real space and its closeness to VBMSi in energy. In comparison with the results in crystalline Si/SiO$_2$/HfO$_2$ stacks, two new phenomena need to be pointed out. First, the strong hole trapping rates of puckered $V_O$ defect in SiO$_2$ overturns the previous conclusion that VO defects in the SiO$_2$ part are not effective hole trapping centers compared with those in HfO$_2$ and interface. Second, although some SiO$_2$/HfO$_2$ interface defects are very effective in hole trapping, most of them are not as effective as the defects in HfO$_2$. In other words, the amorphous Si/SiO$_2$/HfO$_2$ stack shows us a more complete picture of hole trapping in high-k gate stacks.

IV. CONCLUSIONS

In conclusion, we have proposed an optimized theoretical simulation framework to study the charge trapping across multiple interfaces. By applying this framework to crystalline and amorphous Si/SiO$_2$/HfO$_2$ stacks, we manage to elucidate the hole trapping mechanism for multiple trapping paths in the structure and identify the dominant hole trapping centers by calculating the exact hole trapping rates under different magnitudes of gate electric field. Results show that the dominant hole trapping centers are neither located at a single material nor limit themselves as a single type. On the contrary, the strong hole trapping center could be a puckered $V_O$ defect or Single-H passivated dimer $V_O$ defect at the SiO$_2$, some $V_O$ defects at the SiO$_2$/HfO$_2$ interface, or most $V_O$ defects inside the bulk HfO$_2$. Moreover, we find that H passivation is not able to eliminate such hole trapping problem effectively due to the formation of some H-related defects, which are also effective trapping centers. On the contrary, F passivation is found to be more effective in eliminating defect states, and should be paid more attention to. We hope all these conclusions could be instructive in improving the performance of high-k MOSFETs, and the simulation framework could be helpful for studying the charge trapping problems in other semiconductor devices.

Acknowledgement
This work was supported by National Natural Science Foundation of China (grand Nos. 61927901, 11774338, 11574304), China Key Research and Development Program (2018YFA0306101), Chinese Academy of Sciences-Peking University Pioneer Cooperation Team (CAS-PKU Pioneer Cooperation Team), the Youth Innovation Promotion Association CAS (Grand No. 2016109), and project grand No.6J6011000. Y. Y. Liu acknowledges the support from the National Postdoctoral Program for Innovative Talents (No. BX201700231), and the China Postdoctoral Science Foundation (Grant No. 2018M630194). L. W. Wang was funded by the Joint Center for Artificial
Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award number DE-SC0004993.

References


[38] https://www.synopsys.com/silicon/quantumatk.html.


[41] E. A. Chagarov and A. C. Kummel, “Ab initio molecular dynamics simulations of properties of a-$\text{Al}_2\text{O}_3$/vacuum and a-$\text{ZrO}_2$/vacuum vs a-$\text{Al}_2\text{O}_3\text{Ge}(100)(2\times1)$ and a-$\text{ZrO}_2\text{Ge}(100)(2\times1)$ interfaces”, J. Chem. Phys. 130, 124717 (2009).


[52] See Supplemental Material at [URL will be inserted by publisher] for the influence of functional (PBE and HSE) on the reorganization energy.
[62] P. Broqvist, A. Alkauskas, J. Godet, and A. Pasquarello, “First principles investigation of
