Electronic Structure Theory and Mechanisms of the Oxide Trapped Hole Annealing Process

Authors

S. P. Karna, R. D. Pugh, W. M. Shedd
Air Force Research Laboratory
Space Vehicles Directorate, SE, Kirtland AFB, New Mexico

A. C. Pineda
The University of New Mexico – HPCERC
Albuquerque High Performance Computing Center

T. R. Oldham, Sr.
Army Research Laboratory
Adelphi, Maryland
Disclaimer

The High Performance Computing, Education & Research Center (HPCERC) provides a focus for high performance computing and communication at the University of New Mexico (UNM). HPCERC is committed to innovative research in computational and computer science with emphasis on both algorithm development and application. As part of this commitment, HPCERC sponsors this technical report series. The technical reports are subject to internal review by the HPCERC. However, the material, as presented, does not necessarily reflect any position of the HPCERC. Further, neither UNM, nor the AHPCC, makes any warranty or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information contained in this report.

Frank L. Gilfeather, Executive Director, HPCERC
Brian T. Smith, Chief Scientist, HPCERC
John S. Sobolewski, Chief Technologist, HPCERC
Ernest D. Herrera, Associate Director, HPCERC
Susan Atlas, Associate Director, AHPCC Computer Systems Research
Bob Ballance, Associate Director, AHPCC Science & Engineering Research
Electronic Structure Theory and Mechanisms of the Oxide Trapped Hole Annealing Process

Shashi P. Karna, Member, IEEE, Andrew C. Pineda, Member, IEEE, Robert D. Pugh, Member, IEEE, Walter M. Shedd, Member, IEEE, and T. R. Oldham, Sr., Member, IEEE

Abstract—First principles quantum mechanical calculations on model SiO2 clusters support the Lelis model of reverse annealing in the oxide and provide the first electronic structure explanation of the process, suggesting that delocalized holes (E' centers) are annealed out permanently. Localized holes (E' centers) form a metastable, dipolar complex, without restoring the Si–Si dimer bond upon electron trapping. In the presence of an applied negative field, these charge neutral, dipolar complexes, (E' + e−), can readily release the weakly bonded electron, exhibiting a reverse annealing process.

I. INTRODUCTION

M E TAL oxide semiconductor (MOS) devices are known to have a complex time-dependent response to ionizing radiation (see, for example, [1]–[3]). An important component of this response is the build up and annealing behavior of positively charged hole traps in the oxide near the Si/SiO2 interface. Of particular interest has been the so-called “negative bias reverse annealing” (NBRA) [3]–[11]. High temperature, biased anneal experiments on irradiated devices indicate that a significant fraction of trapped holes that under positive bias are apparently annealed out via electron capture reappear when the bias is switched to negative polarity [3]–[8]. These experiments suggest the existence of a metastable neutral center where the electron and hole are associated, but do not recombine. Several studies have been performed to understand the physics of this center and of the reverse annealing process [3]–[8]. While some insights into the reversibility of the positive charge annealing process have been achieved, leading to a qualitative model that successfully explains the main experimental observations, the mechanisms underlying the model have not yet been fully explained.

This model, originally proposed by Lelis et al. [6], [7], involves the trapping and detrapping of electrons at positively charged E' centers (also sometimes called oxygen vacancy defect centers). E' centers involve an unpaired electron located at a three-fold coordinated tetrahedral Si center and a hole trapped at another, spatially separated, Si atom which can be represented as [Si1+Si] [12], [13]. Here the upward arrow represents an unpaired electron. The E' center has been identified as a radiation-induced trapped hole [14]. Experimentally, Lelis et al. observed that some of the trapped holes near the interface appeared to anneal out completely by capturing an electron, and in the model, it is suggested that this happens because the broken Si–Si bond reforms. It is also proposed in the model, that if the two Si atoms relax to positions too far apart for the bond to reform, then the captured electron goes to the neutral Si atom, and pairs up with the unpaired electron instead of going to the positive Si atom [Si1+Si]. The result is a metastable, electrically neutral, dipolar complex which releases the captured electron under negative bias, restoring the E' center. This proposal accounted very simply for the experimental data by Schwank et al. [4] and by Lelis et al. [6]–[8], and it was also consistent with the spectroscopic data available at the time [14].

Even so, the idea of a metastable dipole was controversial at first. For one thing, Coulomb repulsion between the two electrons on the negative end of the dipole would make the dipole energetically unfavorable, everything else being equal. This objection was raised most forcefully by Edwards [15]. Lelis et al. speculated that the energy gained from relaxation of the oxide network might be enough to offset the electron-electron interaction, but lacked the analytical capability to calculate any of the energy levels associated with the defect. Other authors have proposed alternative models. Freitag et al. [16], [17] proposed that the experimentally observed charge switching was due to another unknown defect and that E' centers did not account for the charge switching. Fleetwood et al. [18] proposed that while the Lelis et al. model probably accounted for part of the observed charge switching, other defects could also play a role. They suggested several other possible defect structures that could also switch charge.

However, subsequent experiments tended to provide additional support for the Lelis et al. model, culminating with the work of Conley et al. [11], [19]. Conley conducted a series of bias switching experiments, similar to those performed by others, except that he monitored the E' signature with an electron spin resonance (ESR) apparatus. The results showed that E' centers do switch charge, contrary to the conclusions of Edwards and Freitag et al. Furthermore, they switch charge in precisely the manner proposed by Lelis et al., which appeared to rule out the alternative structures proposed by Fleetwood. (Of...
We report calculations on model clusters employing the ab initio Hartree–Fock (HF) method with STO-3G and DZP basis sets. In the HF method, the electronic Schrödinger equation, $H_{\text{elec}}\Psi = E_{\text{elec}}\Psi$, resulting from the Born–Oppenheimer separation of nuclear and electronic motion is solved using a variational principle. The electronic Hamiltonian, $H_{\text{elec}}$, includes the quantum mechanical operators describing the electrons in the system and their interactions with the nuclei and each other. The electronic wavefunctions can then be used to construct potential energy surfaces for the motion of the nuclei and the most favorable arrangement of the atoms can be found by minimization of the total energy of the system. In the HF method, trial wavefunctions are constructed as a Slater determinant of one electron molecular orbitals (MO’s) which are anti-symmetric under the exchange of any pair of electrons as required by the Pauli exclusion principle. These one electron MO’s are written as linear combinations of one electron atomic orbitals, or basis functions, centered on each of the atoms of the system. The variational principle results in a set of one electron equations for the coefficients of the molecular orbital expansion, the Roohan or more generally the Pople–Nesbet equations, that must be solved self-consistently. The degree of sophistication of an HF calculation is determined by the number of basis functions used in the MO expansion and by the degree to which the basis functions approximate the true behavior of atomic wave functions. A minimal basis set calculation, such as that using an STO-3G basis set, uses one basis function for each inner shell and valence shell atomic orbital. The accuracy of HF is significantly improved by performing an extended basis set calculation in which additional basis functions are used to describe each inner shell and valence shell atomic orbital. The accuracy is also improved by adding basis functions (called polarization functions) with higher angular momentum quantum numbers than the maximum angular momentum quantum numbers of the valence shell electrons in the ground state atoms. Extended basis set calculations, such as the double zeta plus polarization (DZP) basis set calculations we report here, allow the atomic orbitals to change in size, shape, and direction as the atoms interact [25], [28]. To speed the evaluation of the required integrals, each basis function is written as a linear combination of Gaussian functions, $\chi_j(\mathbf{r}) = \sum d_{ij}g_j(\mathbf{r})$, where $g_j(\mathbf{r}) \propto \exp(-\alpha_j r^2)$. The coefficients $d_{ij}$ and exponents $\alpha_j$ are determined by variational calculations on single atoms. STO-3G calculations usually give quite good predictions of bond angles and bond distances, but fair poorly on energies. DZP calculations give better results especially for energies, but are much more expensive to do as the computational cost of the calculation rises as the 4th power of the number of basis functions used.

Three sets of model clusters of increasing complexity and differing network features were employed. Model clusters representing precursors and corresponding hole traps consisted of a) a segment of the oxide without nearby closed ring structures (Fig. 1), b) a segment of oxide with 4 three-member (six-atom) rings (Fig. 2), and c) a segment with 4 six-member (twelve-atom) rings (Fig. 3). A bridging O atom in the clusters, marked as linear combination of Gaussian functions, or basis functions (called polarization functions) with higher angular momentum quantum numbers than the maximum angular momentum quantum numbers of the valence shell electrons in the ground state atoms. Extended basis set calculations, such as the double zeta plus polarization (DZP) basis set calculations we report here, allow the atomic orbitals to change in size, shape, and direction as the atoms interact [25], [28]. To speed the evaluation of the required integrals, each basis function is written as a linear combination of Gaussian functions, $\chi_j(\mathbf{r}) = \sum d_{ij}g_j(\mathbf{r})$, where $g_j(\mathbf{r}) \propto \exp(-\alpha_j r^2)$. The coefficients $d_{ij}$ and exponents $\alpha_j$ are determined by variational calculations on single atoms. STO-3G calculations usually give quite good predictions of bond angles and bond distances, but fair poorly on energies. DZP calculations give better results especially for energies, but are much more expensive to do as the computational cost of the calculation rises as the 4th power of the number of basis functions used.

Three sets of model clusters of increasing complexity and differing network features were employed. Model clusters representing precursors and corresponding hole traps consisted of a) a segment of the oxide without nearby closed ring structures (Fig. 1), b) a segment of oxide with 4 three-member (six-atom) rings (Fig. 2), and c) a segment with 4 six-member (twelve-atom) rings (Fig. 3). A bridging O atom in the clusters, marked
Fig. 3. Defect-free oxide with 4 six-membered rings. The largest atoms are Si, the mid-sized atoms are O atoms, and the smallest atoms are H atoms. The bridging oxygen is removed to form a vacancy site.

Fig. 4. $E_f^2$ Si–Si dimer bond at the vacancy. $V_O$ indicates the location of the missing O atom.

by arrows in Figs. 1–3 is taken as the site for vacancy generation and hole trapping. The oxide network is terminated by H atoms.

III. RESULTS

A. Precursor Clusters

Equilibrium geometries for the model precursor clusters were obtained by *ab initio* Hartree–Fock (HF) energy minimization using atomic basis sets of different sizes. The two smaller clusters were optimized using a double zeta plus polarization (DZP) basis set. The largest clusters were optimized using a minimal STO-3G basis set. Very little change in the geometry was noted between different basis sets. The bond distance and bond angles are in reasonable accord with the corresponding experimental values and very well represent the amorphous nature of SiO$_2$.

B. Neutral Oxygen Vacancy ($V_O^0$)

The neutral oxygen vacancy ($V_O^0$) sites were created by removing one bridging oxygen atom in each cluster. An equilibrium geometry in the $V_O^0$ state for each cluster was obtained by *ab initio* HF energy minimization.

The optimized equilibrium geometry for the $V_O^0$ center obtained from the oxide cluster in Fig. 2 is shown in Fig. 4. The corresponding structure obtained from Fig. 1 is not shown as the resulting effects are very similar.

The main effect of this minimization is the formation of a Si–Si dimer bond with a length of about 2.351 Å for the smallest cluster derived from Fig. 1 and 2.331 Å for the cluster shown in Fig. 4 at the oxygen vacancy [26]. The corresponding Si–Si dimer bond distance for the neutral vacancy derived from Fig. 3, shown in Fig. 5, is 2.438 Å [26]. These distances are substantially smaller by about 0.64 to 0.79 Å than that between the two Si atoms prior to the $V_O^0$ formation. A common feature of all three clusters is that the two Si atoms adjoining the vacancy move inward as noted in previous studies [12], [13], [24]–[28]. The rest of the network experiences marginal changes upon relaxation.

C. The Positively Charged Oxygen Vacancy ($V_O^{+1}$)

In the present study, the oxide trapped holes are represented by the $V_O^{+1}$ centers. The $V_O^{+1}$ centers were generated by removing an electron from the $V_O^0$ centers described above. After the creation of the positive charge, each model cluster was allowed to totally relax to give a minimum energy configuration.

In the case of the cluster shown in Fig. 4, the two Si atoms forming the dimer bond moved slightly away from each other, by 0.32 Å. For the smallest cluster, not shown, the two Si atoms similarly moved apart by 0.35 Å. Marginal changes were noted in the remaining structure of these clusters. Even after repeated geometry optimization, the two central Si atoms in these clusters ($V_O^{+1}$) retained their symmetric configuration. We have calculated the $^{29}$Si hyperfine coupling constants of the two Si atoms. The calculated value ranged from 87 to 99 Gauss in excellent agreement with the corresponding experimental value (100 G) [21]–[23], which has been found from quantum mechanical calculations [24], [27] to be a trapped hole shared between two Si atoms. It is important to note here that the $E_f^2$ center represented by a hole trapped on the smaller vacancy structures, in which the hole and the unpaired electron are equally shared between the two Si atoms adjoining the vacancy, does not represent the precursor to the dipolar complex of the Lelis model [6].

In contrast to the smaller clusters, the cluster shown in Fig. 5, immediately distorted upon removing an electron. The resulting structure is shown in Fig. 6. One of the Si atoms moved far away from its original position, by about 1.33 Å, forming a Si–O bond with another O atom in the back ring. The other Si atom experienced a small relaxation, but essentially remained in its original.
position. The back-bonded Si–O distance is much larger (about 1.76 Å) compared to a normal Si–O bond which has a length of approximately 1.62 Å. In this case, the unpaired electron spin is completely localized on the undisturbed, three-fold coordinated Si atom. The distorted, back bonded Si atom has practically no spin density. This model represents the $E'_4$ center [12], [13], the precursor [Si$^{1+}$Si] of the Lelis model.

D. Electron Trapping by the Oxide Hole Centers ($V^{+1}_O + e^-$)

Next an electron was added to the $V^{+1}_O$ centers at their respective optimized equilibrium geometries, as shown in Figs. 4 and 6, and the resulting neutral systems were allowed to fully relax to a minimum energy state. The cluster of Fig. 4 representing the $E'_6$ center reached an equilibrium structure restoring the Si–Si dimer bond of the neutral oxygen vacancy centers ($V^{0}_O$). The binding energy of the electron in Fig. 4 was calculated to be approximately 8.90 eV. The electron charge, as expected, is shared nearly equally by the two Si centers forming the dimer. This sharing of the electron charge by the two Si centers is easily seen in the electron charge distribution in the highest occupied molecular orbital as shown in Fig. 7. The cluster with no rings near the vacancy displays similar behavior.

When an electron was added to the [Si$^{1+}$Si] complex shown in Fig. 6, and a geometry optimization was performed, a minimum energy structure was reached after about 25 iterations. In this structure, however, the Si–Si dimer bond of the $V^{0}_O$ is not fully restored. The back bonded Si atom is still separated from its dimer counterpart of the $V^{0}_O$ by about 2.61 Å which is 0.17 Å larger than in $V^{0}_O$.

The system ($V^{+1}_O + e^-$) in this state is about 1.99 eV higher in energy than $V^{0}_O$. (The latter result was computed using the DZP basis set, as STO-3G basis set energies are not very meaningful.) This structure thus represents a metastable state of the charge neutral $V^{0}_O$ center. In this state, the calculated binding energy of the electron, with respect to the equilibrium $V^{+1}_O$ structure is about 7.29 eV (again using the DZP basis set). Also, the electron charge in the case of Fig. 6 is largely localized on the undistorted Si. This readily apparent in the electronic charge distribution of the highest occupied molecular orbital as shown in Fig. 8.

IV. DISCUSSION

The calculations on neutral $V^{0}_O$ centers reveal that regardless of the complexity in the oxide network surrounding the vacancy, the network relaxes in such a way that the two Si atoms adjacent to it move toward each other when the vacancy is first formed. However, trapping of a hole leads to different responses in the network depending upon the atomic structures around the vacancy. For an oxygen vacancy located at a site with no rings or between small (stiff) rings, a trapped hole is shared between dimer Si atoms. These structures lead to the formation of $E'_5$ species. For an oxygen vacancy located between large, flexible rings, hole trapping results in preferential distortion of the SiO$_2$ ring adjacent to the vacancy. In this case, the hole is localized at a single Si atom, which tends to distort and form a dipolar bond with an O atom in the back of the flexible (six-member) ring. The electron is localized on an essentially undisturbed Si atom. This complex represents the $E'_5$ center.

The type of $E'_5$ center formed is intimately related to the local structure of $V^{0}_O$. Open structures with no back oxygen available


Fig. 8. Contour plot of the highest occupied molecular orbital for the largest positively charged oxygen vacancy using a DZP basis set. The phase (sign) of the molecular orbital is denoted by solid and dashed lines, which represent positive and negative values, respectively. Note that the electron is largely localized on the undistorted Si atom.

for bonding and small, inflexible rings both lead to a symmetric relaxation following the hole trapping, whereas large ring structures have both a flexible network and back oxygen atoms available for bonding. Thus, the first two types of local structures result in the formation of $E'_\delta$ while structures with properties similar to the third result in the formation of $E'_\gamma$ centers upon hole trapping.

In both the $E'_\delta$ and $E'_\gamma$ configurations, the one electron energy level corresponding to the orbital in which the unpaired electron is localized is lower in energy by more than 10 eV than the next empty orbital. These levels are referred to as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. The HOMO and LUMO in the case of isolated clusters as used in this study loosely correspond to the top of the valence band (VB) and the bottom of the conduction band (CB), respectively, of bulk SiO$_2$. The HOMO-LUMO energy difference for the $E'_\delta$ and $E'_\gamma$ configurations shown in Figs. 4 and 6 are listed in Table I. An added electron, when captured by the $V^{+1}_{O}$ center, goes into the previously singly occupied, lower energy level, which in this case is the HOMO. In the case of the $E'_\delta$ centers, where the HOMO wavefunction has equal contributions from the two Si centers (Fig. 7), the added electron is shared by the two Si atoms and restores a covalent bond between them. However, in the case of the $E'_\gamma$ centers the HOMO wavefunction is highly localized on a single Si atom (Fig. 8), so the added electron is localized there. This gives rise to the dipolar complex of the Lelis model. In this state, due to increased Coulomb repulsion between the two electrons in a small volume of space and a reduced electron-nuclear attraction, the system becomes metastable. The added electron in the metastable state has considerably smaller binding energy than that in a stable, dimer structure. Therefore, by overcoming the smaller binding energy, the system can relax by releasing the extra electron. This results in the regeneration of the trapped hole ($E'_\gamma$) center.

It should be noted that further work is needed to access the relative stability of the metastable configuration, and the degree to which polarization of the surrounding oxide, neglected in our cluster approximation, might further stabilize the metastable configuration.

V. Conclusions

The present calculations have provided a detailed electronic structure explanation of the reverse annealing process of oxide trapped holes. The results demonstrate that upon electron capture, a hole shared between two Si atoms ($E'_\delta$) completely anneals out by restoring a Si–Si dimer bond. However, a localized hole ($E'_\gamma$) forms a metastable, dipolar complex, without restoring the Si–Si dimer bond upon electron trapping. In the presence of an applied negative field, these charge neutral, dipolar complexes, ($E'_\delta + e^{-}$), can readily release the weakly bonded electron, exhibiting a reverse annealing process.

Acknowledgment

The authors would like to thank the University of New Mexico (UNM) for access to the resources of their Albuquerque High Performance Computing Center (AHPCC) and Maui High Performance Computing Center (MHPCC).

References
