

Ab-Initio Calculation of the Vibrational Influence on Hole-Trapping

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Abstract—Within the theory of non-radiative multi phonon (NMP) transitions the reaction rate for an electronic transition is proportional to the product of the corresponding electronic matrix element and the line-shape function. The theory is discussed for the case of oxide traps in MOS structures. A simple method for the calculation of reaction rates for atomistic models is derived from approximations to the NMP theory. This method is applied to two selected model defects in the context of negative bias temperature instability (NBTI).

I. INTRODUCTION

One of the most critical degradation effects observed in p-MOSFETs is the negative bias temperature instability (NBTI) [1], [2]. It is usually observed at elevated temperatures when a large negative bias is applied to the gate contact with all other terminals grounded.

We have recently suggested a model for NBTI that can explain detailed experimental data [3], and explains the behavior of small-scale MOSFETs under NBTI stress observed by the time-dependent defect spectroscopy (TDDS) [4]. This model explains the occurring degradation as a set of electrochemical reactions of oxide defects as illustrated in Fig. 1. The exchange of electrons and holes between the defect and the channel is described within the framework of non-radiative multiphonon (NMP) [5], [6] theory. These transitions require certain features in the adiabatic potential of the defect in its different charge-states. So far, these potentials have been empirically adjusted to fit the experimental data.

This work is a first step towards the analysis of the atomistic roots of the model. We examine the hole-capture process by evaluating atomistic defect structure models for their multiphonon-properties from first-principles density functional theory (DFT). The defects selected for inspection are the oxygen vacancy and the hydrogen bridge. The former has been previously suggested as the defect causing NBTI and other reliability issues such as radiation damage [7], RTN, or 1/f-noise [8]. The hydrogen bridge has been proposed as the defect causing stress-induced leakage current (SILC) [9], [10].

II. VIBRONIC TRANSITIONS

Vibronic transitions, i.e. transitions in molecules or solids where the electronic and the vibrational state change at the

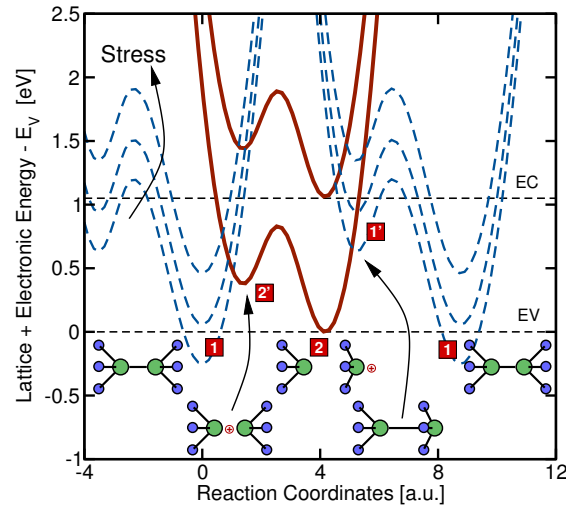


Fig. 1. Schematic energy over configuration diagram for the defect in our model for NBTI including an example illustration using an oxygen vacancy. The dashed curve shows the neutral case, the solid curve is for a captured hole. This work focuses on the transition $1 \rightarrow 2'$

same time, pose an integral part of many different physical and chemical processes [11], [12]. These transitions are usually understood in the framework of the Born-Oppenheimer ansatz for the wave function of the system and a golden rule treatment of the transition. Consequently, the state of the system is described by the electronic wavefunction $|\Phi\rangle$ and the vibrational wave function $|\eta\rangle$. Different electronic states $|\Phi_k\rangle$, give rise to different Born-Oppenheimer potential energy surfaces, so every electronic state has a different set of associated vibrational wavefunctions $|\eta_{k\alpha}\rangle$, as indicated in Fig. 2. The transition rate from an initial vibronic state $|\Phi_i\eta_{i\alpha}\rangle$, i.e. a state that involves electronic and vibrational degrees of freedom, to a final vibronic state $|\Phi_f\eta_{f\beta}\rangle$ is expressed as

$$k_{i\alpha \rightarrow f\beta} = \frac{2\pi}{\hbar} |\langle \eta_{f\beta} | \langle \Phi_f | V' | \Phi_i \rangle | \eta_{i\alpha} \rangle|^2 \delta(E_{f\beta} - E_{i\alpha}), \quad (1)$$

where V' is the perturbation operator, and $E_{f\beta}$ and $E_{i\alpha}$ are the energies of the final and initial state. The usually employed Franck-Condon approximation separates the matrix element in

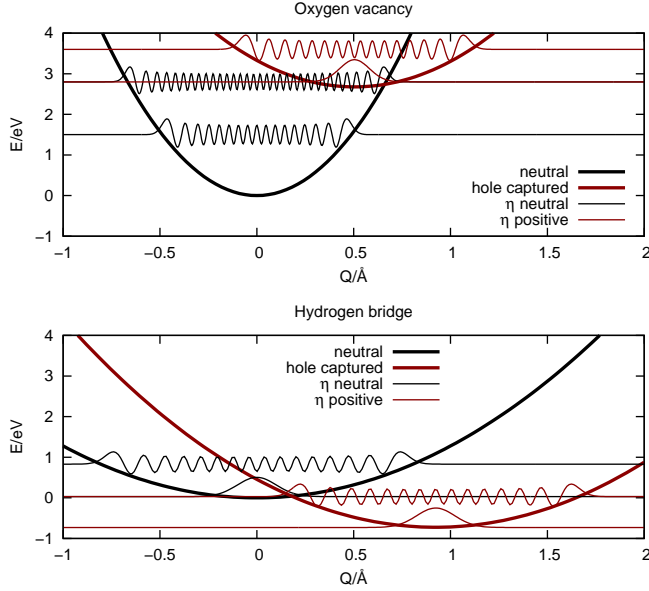


Fig. 2. One dimensional potentials and examples of vibrational wavefunctions for the oxygen vacancy and the hydrogen bridge as extracted from DFT using the method of section IV. The hole energy is set to the silicon valence level. Q is the reaction coordinate. In the high-temperature regime, a transition will take place at the crossing points of the potentials.

(1) into the electronic matrix element $|\langle \Phi_f | V' | \Phi_i \rangle|^2$ and the Franck-Condon overlap factor $|\langle \eta_{f\beta} | \eta_{i\alpha} \rangle|^2$.

The total transition rate from $|\Phi_i\rangle$ to $|\Phi_f\rangle$ is now obtained by considering *all* transitions between the associated vibronic states. Obeying the fact that the vibrational system is under constant random perturbation that leads to a thermal equilibrium with the environment, one has to thermally average over all initial vibrational states and sum over all final vibrational states. Examples for the thermally weighted overlap factors are given in Fig. 3. The resulting expression for the electronic transition reads

$$k_{if} = A_{if} f \quad (2)$$

$$A_{if} = \frac{2\pi}{\hbar} |\langle \Phi_f | V' | \Phi_i \rangle|^2 \quad (3)$$

$$f = \text{ave}_\alpha \sum_\beta |\langle \eta_{f\beta} | \eta_{i\alpha} \rangle|^2 \delta(E_{f\beta} - E_{i\alpha}). \quad (4)$$

This theory has been initially developed in the context of optical spectroscopy [13]. There the quantity f describes the broadening of absorption peaks and is called *line shape function*. Usually, a change in the electronic state of a system requires a number of vibrational quanta to be absorbed or emitted, which is why these transitions are called multi-phonon transitions.

III. CAPTURE AND RELEASE AT DEFECT SITES

The multi-phonon theory has been used for the description of non-radiative capture and release of charge carriers at defect sites in semiconductors and at oxide-semiconductor interfaces [5], [6], [14], [15]. For oxide traps, one has to

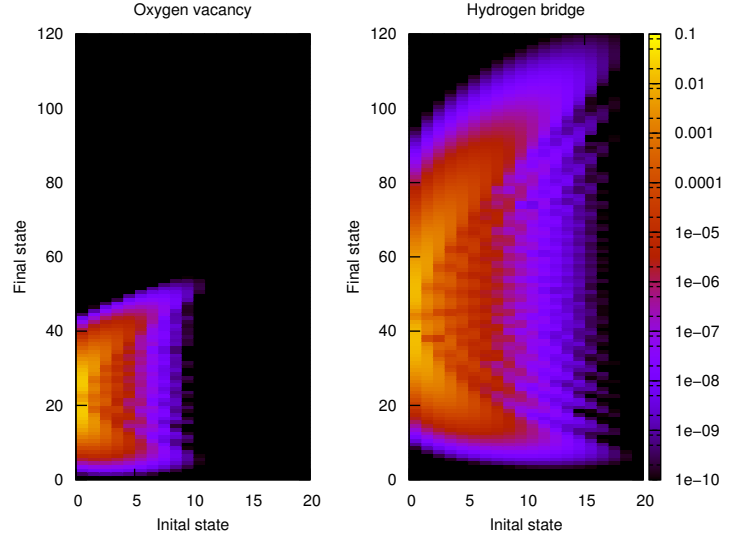


Fig. 3. Thermally weighted overlap factors as extracted from our calculations. The lower spring constant of the hydrogen bridge allows for more initial states to have non-negligible occupation probability.

consider the whole system including the vibrational states of the defect, as well as the electrons in the gate, the defect and the semiconductor. The defect is assumed to have one relevant state to be occupied by an electron. In the limit of non-interacting electrons, the hamiltonian of this system is written as [5]

$$\hat{H} = E_d \hat{n}_d + \sum_k E_k \hat{n}_k + V_{eN}(Q) \hat{n}_d + \hat{H}_N(Q), \quad (5)$$

where the \hat{n}_i are the number operators for the electronic states, k runs over all single-electron states in the gate and the semiconductor, V_{eN} is the binding potential of the electron, and \hat{H}_N is the vibrational hamiltonian. The vector Q in principle contains the coordinates of all atoms in the system but can be usually reduced to the atoms in the direct vicinity of the defect.

During a hole capture transition, the electron residing in the single electron state $|\phi_d\rangle$ is transferred to the state $|\phi_j\rangle$, which was previously unoccupied. The electronic matrix element for this transition is defined by the matrix element $|\langle \phi_d | V' | \phi_j \rangle|^2$ of the single electron wave functions. The perturbation operator for non-radiative processes is found in the non-adiabatic off-diagonal elements of the Born-Oppenheimer hamiltonian [11], [12].

The vibrational wavefunctions and energies for the initial and final state are obtained from

$$(E_d + \sum_k n_k E_k + V_{eN} + \hat{H}_N) |\eta_{i\alpha}\rangle = E_{i\alpha} |\eta_{i\alpha}\rangle \quad \text{and} \\ (\sum_k n_k E_k + E_j + \hat{H}_N) |\eta_{f\beta}\rangle = E_{f\beta} |\eta_{f\beta}\rangle. \quad (6)$$

The energies and vibrational wavefunctions can now be used to calculate the line-shape function f according to (4). E_d and E_j influence the energy eigenvalues, but do not change the functional form of the vibrational wave functions. They can thus be removed from the eigensystem and reinserted in the line shape function expression to give

$$f(E_j) = \text{ave}_\alpha \sum_\beta |\langle \eta_{f\beta} | \eta_{i\alpha} \rangle|^2 \delta(E_{f\beta} - E_{i\alpha} + E_j - E_d). \quad (7)$$

Consequently, the line shape function for non-radiative hole capture is a function of the hole energy. It is calculated from the potential energy surfaces of the defect in its different electronic states which can be obtained from methods of quantum chemistry.

IV. THE CALCULATION OF HOLE CAPTURE RATES FOR ATOMISTIC BULK DEFECT MODELS

Density functional theory (DFT) is a popular method for the atomistic modeling of point defects in materials. The usually employed models are periodic supercell structures. By setting the number of electrons in the system, different charge states of the defect structure can be studied. The evaluation of (2) requires to calculate both A_{if} and $f(E)$, as explained in the previous section.

A_{if} cannot be obtained using the described models, as both the perturbation operator and the true single-electron states of the system are not present in a DFT calculation. Thus, they have to be estimated from a device simulation [6], [15]. A reasonable estimate is obtained from

$$|\langle \phi_d | V' | \phi_j \rangle|^2 \propto |\langle x_d | \phi_j \rangle|^2, \quad (8)$$

where x_d is the location of the defect. This turns the evaluation of the matrix element into a tunneling expression that can be easily implemented into a device simulation [3], [4].

The calculation of the line shape function from DFT is principally possible. However, approximations have to be made to reduce the complexity of the problem. To make the extraction as simple as possible, we apply the harmonic approximation to the potential energy surface and assume single-mode coupling, i.e.

$$\hat{H}_N(Q) = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial Q^2} + \frac{M\omega_i^2}{2} Q^2, \quad \text{and} \quad (9)$$

$$V_{eN}(Q) = \frac{M(\omega_f^2 - \omega_i^2)}{2} Q^2 + M\omega_f^2 Q_s \left(\frac{Q_s}{2} - Q \right) + E_s, \quad (10)$$

where M is the modal mass. The neutral and the positive state of the defect are now represented by two one dimensional harmonic oscillators with the frequencies ω_i and ω_f displaced by Q_s and E_s . The overlap integral becomes

$$\langle \eta_{f\beta} | \eta_{i\alpha} \rangle = \langle \omega_f, \beta | \omega_i, \alpha \rangle, \quad (11)$$

where $|\omega, i\rangle$ is the i -th eigenvector of the harmonic oscillator of frequency ω . For the evaluation of this integral a number of different analytical expressions have been published in literature. However, most of them are difficult to evaluate

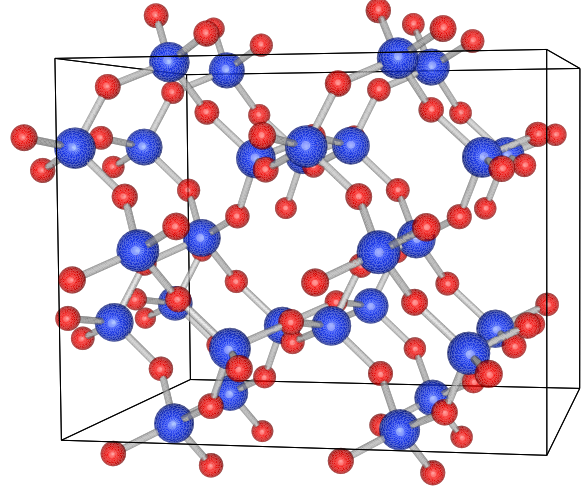


Fig. 4. The alpha-quartz supercell used in this work. The wave functions are expanded in a plane-wave basis-set up to 800 eV. The core electrons are represented using the PAW method.

for large quantum numbers, so we obtained the overlaps by numeric integration of the analytic harmonic oscillator wavefunctions.

To obtain the required parameters from DFT, the defect total energy has been obtained for the neutral and the positive state of the defect in the neutral and positive optimum configuration (see Fig. 5). From these energies and the assumption of single-mode coupling, all parameters can be obtained in a straight forward way. For the calculations in the present work, the electronic structure is described with density functional theory (DFT) using the PBE functional. The calculations have been performed using the Vienna ab initio simulation program (VASP) [16].

The host lattice is an orthorhombic alpha-quartz supercell structure [10], [17], [18] containing 72 atoms. Alpha-quartz was chosen because it is a well studied reference system for amorphous silica [10], [19], [20]. The determination of defect energies relative to the silicon bands follows the method of Blöchl [10], where the DFT-energies of the silicon bands are determined by fixing the (+/-)-transition level of hydrogen to 0.2 eV above the silicon midgap.

V. RESULTS AND CONCLUSION

The extracted potential energy surfaces for the oxygen vacancy and the hydrogen bridge are shown in Fig. 2, the calculated line-shape functions are shown in Fig. 6. For the oxygen vacancy, the calculation predicts a peak capture cross section approximately 1eV above the SiO₂ valence band and a thermal activation barrier of approximately 2.8eV for holes at the silicon valence level when no bias is applied. A considerably different behavior is found for the hydrogen bridge, where the positive state of the defect is predicted to be more stable than the neutral state with a very small activation barrier. The capture cross section is largest approximately 1eV

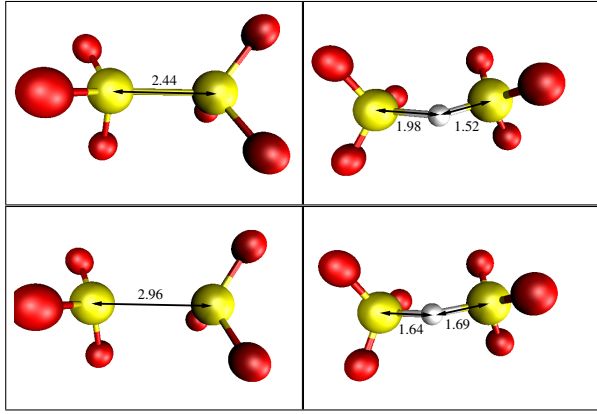


Fig. 5. Optimized structures for the neutral (top) and positive (bottom) charge states of the O vacancy (left) and the hydrogen bridge (right). Distances are given in Ångströms. The structures were relaxed until the forces dropped below $10^{-2} \text{eV}/\text{Å}$.

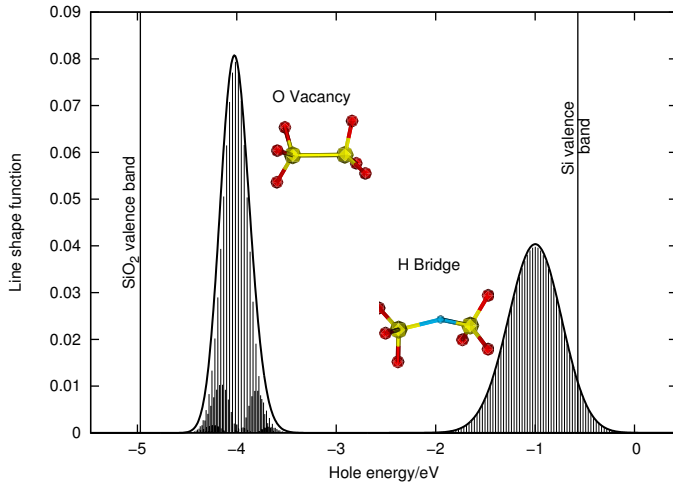


Fig. 6. Line-shape function at 300K. The plain solution of Eq. 4 is a series of Dirac impulses as indicated. Life-time broadening [5] has been simulated by smearing with a normal distribution of spread $k_B T$.

below the silicon valence level, indicating an efficient hole trap.

Parametrization of our model against experimental data indicated that the hole capture process is temperature activated with an activation energy of approximately 0.6 – 1.2eV, the neutral state of the defect being stable when no bias is applied. Obviously, neither of the two investigated defects exactly shows this behavior. Our results for the oxygen vacancy are in good agreement with earlier studies using different functionals, where this defect is shown to act as an efficient trap for holes from the SiO₂ valence band. Especially for the hydrogen bridge, an estimate of its relevance for NBTI is difficult based on our data, when considering the uncertainty immanent in DFT calculations. Further investigation is required eventually using more sophisticated functionals and different alignment methods. For a more detailed study of the trapping dynamics,

the extracted line-shape functions will be fed to a device simulation.

REFERENCES

- [1] K. O. Jeppson and C. M. Svensson, "Negative bias stress of mos devices at high electric fields and degradation of mnos devices," *J.Appl.Phys.*, vol. 48, no. 5, pp. 2004–2014, 1976.
- [2] D. K. Schroder, "Negative bias temperature instability: What do we understand?" *Microelectronics Reliability*, vol. 47, pp. 841–852, 2007.
- [3] T. Grasser, B. Kaczer, W. Goes, T. Aichinger, P. Hehenberger, and M. Nelhiebel, "A two-stage model for negative bias temperature instability," in *Proc. Intl.Rel.Phys.Symp.*, 2009, pp. 33–44.
- [4] T. Grasser, H. Reisinger, P.-J. Wagner, and B. Kaczer, "The time dependent defect spectroscopy (tds) technique for the characterization of the bias temperature instability," in *Proc. Intl.Rel.Phys.Symp.*, 2010, pp. 16–25.
- [5] C. H. Henry and D. V. Lang, "Nonradiative capture and recombination by multiphonon emission in gaas and gap," *Physical Review B*, vol. 15, no. 15, pp. 989–1016, January 1977.
- [6] S. Makram-Ebeid and M. Lannoo, "Quantum model for phonon-assisted tunnel ionization of deep levels in a semiconductor," *Physical Review B*, vol. 25, no. 10, pp. 6406–6424, May 1982.
- [7] C. J. Nicklaw, Z.-Y. Lu, D. Fleetwood, R. Schrimpf, and S. Pantelides, "The structure, properties, and dynamics of oxygen vacancies in amorphous sio₂," *IEEE Transactions on Nuclear Science*, vol. 49, pp. 2667–2673, 2002.
- [8] D. Fleetwood, H. Xiong, Z.-Y. Lu, C. Nicklaw, J. Felix, R. Schrimpf, and S. Pantelides, "Unified model of hole trapping, 1/f noise, and thermally stimulated current in mos devices," *IEEE Transactions on Nuclear Science*, vol. 49, no. 6, pp. 2674–2683, 2002.
- [9] P. E. Blöchl and J. H. Stathis, "Hydrogen electrochemistry and stress-induced leakage current in silica," *Physical Review Letters*, vol. 83, no. 2, pp. 372–375, July 1999.
- [10] P. E. Blöchl, "First-principles calculations of defects in oxygen-deficient silica exposed to hydrogen," *Physical Review B*, vol. 62, no. 10, pp. 6158–6178, September 2000.
- [11] K. Huang and A. Rhys, "Theory of light absorption and non-radiative transitions in f-centers," *Proc. Roy. Soc. A*, vol. 204, pp. 406–423, 1950.
- [12] K. Mikkelsen and M. Ratner, "Electron tunneling in solid-state electron-transfer reactions," *chemrev*, vol. 87, pp. 113–153, 1987.
- [13] T. H. Keil, "Shapes of impurity absorption bands in solids," *Physical Review*, vol. 140, pp. A601–A617, 1965.
- [14] A. Schenk, "An improved approach to the shockley-read-hall recombination in inhomogeneous fields of space-charge regions," *J.Appl.Phys.*, vol. 71, pp. 3339–3349, 1992.
- [15] A. Palma, A. Godoy, J. A. Jemènez-Tejada, J. E. Carceller, and J. A. Lòpez-Villanueva, "Quantum two-dimensional calculation of time constants of random telegraph signals in metal-oxide-semiconductor structures," *Physical Review B*, vol. 56, no. 15, pp. 9565–9574, October 1997.
- [16] G. Kresse and J. Furthmüller, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set," *Physical Review B*, vol. 54, no. 11, pp. 11 169–11 186, 1996.
- [17] E. Calabrese and W. Fowler, "Electronic energy-band structure of α quartz," *Physical Review B*, vol. 18, no. 6, pp. 2888–2896, 1978.
- [18] J. Glinnemann, H. E. King, H. Schulz, T. Hahn, S. J. L. Placa, and F. Dacol, "Crystal structures of the low-temperature quartz-type phases of sio₂ and geo₂ at elevated pressure," *Physical Review B*, vol. 41, no. 12, pp. 8313–8317, 1990.
- [19] J. K. Rudra and W. B. Fowler, "Oxygen vacancy and the e'_1 center in crystalline sio₂," *Physical Review B*, vol. 35, no. 15, pp. 8223–8230, 1987.
- [20] A. S. Mysovsky, P. V. Sushko, S. Mukhopadhyay, A. H. Edwards, and A. L. Shluger, "Calibration of embedded-cluster method for defect studies in amorphous silica," *Physical Review B*, vol. 69, no. 8, p. 085202, 2004.