

# On the Microscopic Limit of the Reaction-Diffusion Model for the Negative Bias Temperature Instability

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**Abstract**—It has recently been proposed that the inability of the reaction-diffusion model for the negative bias temperature instability to properly predict the experimentally observed recovery transients is due to the incomplete description of atomic motion in the one dimensional macroscopic formulation of the theory. In order to investigate this claim, we develop a microscopic formulation of the reaction-diffusion model and simulate it using the kinetic Monte Carlo algorithm. The results of the macroscopic and the atomistic formulation are compared. It shows that the recovery behavior predicted by the RD theory is not affected by the change of the formulation. However, differences arise for the degradation behavior, which, as the microscopic formulation is assumed to be the physically more accurate description, raise questions regarding the physical relevance of the reaction-diffusion theory.

## I. INTRODUCTION

The negative bias temperature instability (NBTI) is one of the most critical degradation effects observed in p-channel metal-oxide-semiconductor (pMOS) transistors. Since its suggestion in 1977, the reaction-diffusion (RD) model [1] has been the most popularized explanation for NBTI. The model assumes that hydrogen is released from the interface and subsequently diffuses into the bulk of the oxide. While the reaction at the interface is assumed to be fast and in quasi-equilibrium, it is the diffusion of the hydrogenic species which controls the degradation. During the last decade the model has gone through a number of refinement stages [2]–[4]. The current version assumes that long-term degradation and recovery is dominated by H<sub>2</sub> diffusion. While this version of the RD model could successfully be calibrated to constant-bias degradation data, striking contradictions began to emerge when researchers started to look at the detailed features of recovery [5]–[9].

It has recently been speculated that the failure of the RD theory to explain the experimentally observed long relaxation tails could be due to the fact that the model uses macroscopic rate equations together with the solution of the one-dimensional diffusion equation [10]. The stochastic three-dimensional motion of the diffusing atoms has been suggested to lead to a longer effective diffusion path than what is obtained from a one-dimensional diffusion model. According to the authors of [10], this could explain the experimentally observed long recovery tails, while leaving the degradation

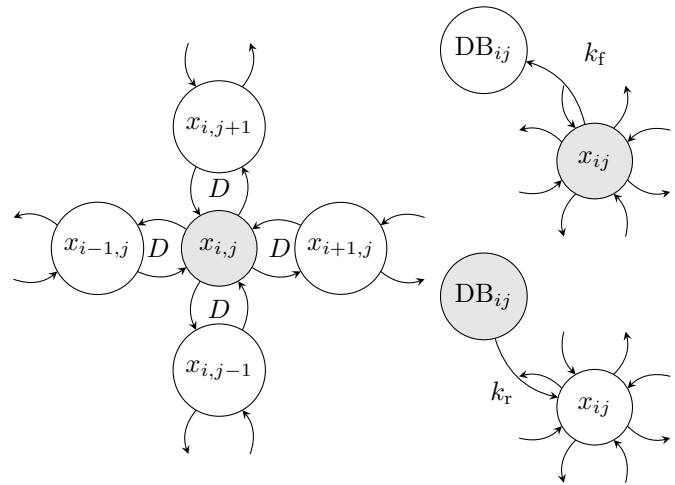


Fig. 1. Reaction channels available to the hydrogen atoms (occupancy is indicated by the gray fill). Within the bulk SiO<sub>2</sub> (left), the atoms are allowed to jump to all neighboring sites in the three-dimensional orthogonal grid with a constant hopping rate. At the interface, some nodes also offer a bonded state to the hydrogen atom (right top). If a bonded state is already occupied the corresponding bonding reaction channel is removed (right bottom).

behavior unchanged. In their paper, they correct the one-dimensional RD model by including a reduced diffusion coefficient during recovery.

In the following we will develop a suitable stochastic formulation of the RD theory to investigate these claims. To keep the model as simple as possible, we restrict ourselves to describing atomic hydrogen diffusion. As our main interest lies in the recovery behavior this simplification is not expected to change the relevant results, as the H and the H<sub>2</sub> version of the RD model give identical recovery behavior [7].

## II. THE MICROSCOPIC RD MODEL

In the conventional macroscopic atomic hydrogen RD model the kinetic equation describing the interface reaction



is assumed to be of the form [11]

$$\frac{\partial N_{it}}{\partial t} = k_f(N_0 - N_{it}) - k_r N_{it} H_{it}, \quad (2)$$

where  $N_{it} = [\text{Si}\cdot]$  is the interface state density,  $N_0 = [\text{Si-H}]_0$  the initial density of passivated interface defects,  $H_{it}$  the hydrogen concentration at the semiconductor-oxide interface, while  $k_f$  and  $k_r$  are the reaction rates for depassivation and passivation, respectively. The motion of the hydrogen atoms in the bulk  $\text{SiO}_2$  is described by a simple diffusion law.

$$\frac{\partial H}{\partial t} = -D\nabla^2 H, \quad (3)$$

where  $H = [H](x, t)$  and  $D$  is the diffusion coefficient.

Both (2) and (3) have a well-defined microscopic form. This microscopic view is established by treating the atomic motion as hopping transport between interstitial sites and the passivation/depasivation as bonding/bond breaking reaction (see Fig. 1). In the following, the interstitial sites are assumed to form a regular and orthogonal three-dimensional grid and the hopping rate  $D$  is assumed to be constant in accord with the isotropic and non-dispersive diffusion underlying the conventional macroscopic RD model [12]. The distance between the interstitials is assumed to be  $4\text{\AA}$ , which corresponds well with calculations on atomistic silica models [13]. Additionally, a hopping rate of  $65\text{s}^{-1}$  is assumed, leading to a macroscopic diffusion coefficient of  $1.04 \times 10^{-13}\text{cm}^2/\text{s}$ , which lies within the range of published values for RD diffusion coefficients [2], [14]. Although in the real  $\text{SiO}_2$  of a MOS transistor the amorphous structure will lead to a random network of interstitial sites [13] with a variety of hopping rates and a more complex topology, these variations are assumed to be unimportant in the RD model [15].

The Si/SiO<sub>2</sub>-interface is represented by an array of special interstitial sites at the bottom of the simulation box. The density of interface states used in macroscopic descriptions is realized by giving selected interface sites the ability to bond or release a diffusing hydrogen atom as illustrated in Fig. 1. For example, a typical  $N_0$  of  $10^{12}\text{cm}^{-2}$  [14], [16] can be modeled by selecting 16 interface interstitials of a simulation box with a lateral extension of  $100 \times 100$ . This corresponds to an average distance of the interfacial sites of 10nm.

### III. THE STOCHASTIC SIMULATION ALGORITHM

Our description of the RD problem is based on the theory of stochastic chemical kinetics [17]. In this framework, the system under consideration is treated as a stochastic process  $\vec{X}(t)$  that exists in one of a countable set of states  $\vec{x}_i$ . Transitions between those states occur instantaneously through a set of  $M$  reaction channels, each characterized by its propensity function  $a_j(\vec{x})$  and state-change vector  $\vec{v}_j$ . The transient evolution of this system is described by the master equation [17]

$$\frac{\partial P(\vec{x}, t)}{\partial t} = \sum_{j=1}^M [a_j(\vec{x} - \vec{v}_j)P(\vec{x} - \vec{v}_j, t) - a_j(\vec{x})P(\vec{x}, t)] \quad (4)$$

where  $P(\vec{x}, t) = P(\vec{X} = \vec{x}, t | \vec{x}_0, t_0)$  is the probability that the stochastic process  $\vec{X}(t)$  equals  $\vec{x}$  at time  $t$ , given  $\vec{X}(t_0) = \vec{x}_0$ .

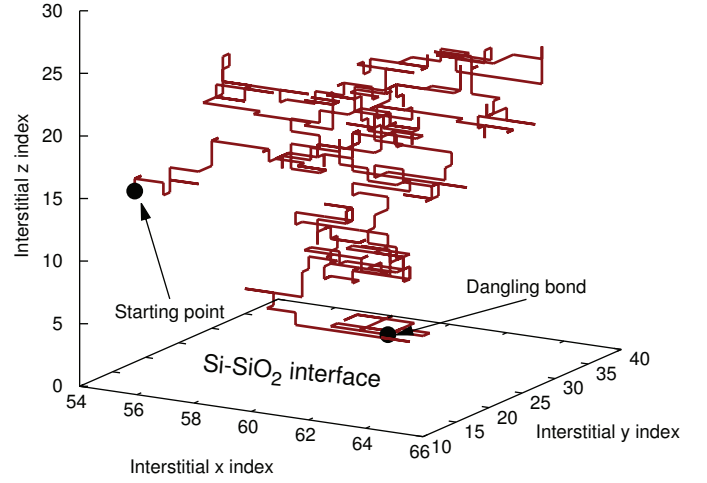


Fig. 2. Final part of the trajectory of a hydrogen atom during recovery calculated using the stochastic simulation algorithm (SSA). The motion clearly proceeds in a three-dimensional stochastic fashion as requested by [10].

The physics are contained in the propensity functions  $a_j$  and the state-change vectors  $\vec{v}_j$  for the  $M$  reaction channels.

For our application, the state vector  $\vec{x}$  is chosen such that it contains the interstitial positions and bonding states of all hydrogen atoms. In this formulation, the propensity functions reduce to the simple hopping and bonding rates and the occupation dependence of (2) is realized by removing the bonding reaction channels for already occupied dangling bond sites, as illustrated in Fig. 1. The thus formulated master equation is straight-forward to solve using the stochastic simulation algorithm (SSA) [17], also known as the kinetic Monte Carlo method.

The stochastic description of the system (4) matches the equation applied in [18]. However, it has to be noted that Panagopoulos et al. used a tau-leaping-like algorithm [19] instead of the SSA for the solution of the master equation. Their algorithm introduces an additional simulation parameter, the time step, that is not present in the SSA and that may influence the results in [18]. It has to be stressed that the SSA does not have any algorithmic parameters and is a mathematically exact description of the system defined by the states and reaction channels [17].

### IV. RESULTS

As shown in Fig. 2, the random three-dimensional motion of the diffusing hydrogen is obtained from this description as suggested in [10]. Test calculations in two and three dimensions have shown that all relevant features of the microscopic RD model are already present in a two-dimensional system, so for reasons of computational efficiency all degradation and recovery calculations were performed on an ensemble of two-dimensional systems. The distance between two dangling bonds in our two dimensional model is 4nm (one dangling bond every 10 interstitials).

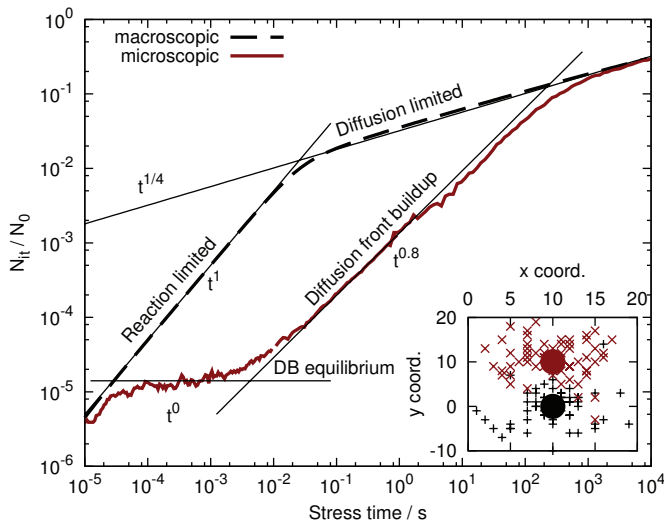


Fig. 3. A typical degradation transient as obtained by our microscopic RD implementation. Four main regimes can be defined, which are indicated in the figure. (inset) Snapshot of an ensemble of 1000 equivalent systems in the early stages of diffusion.

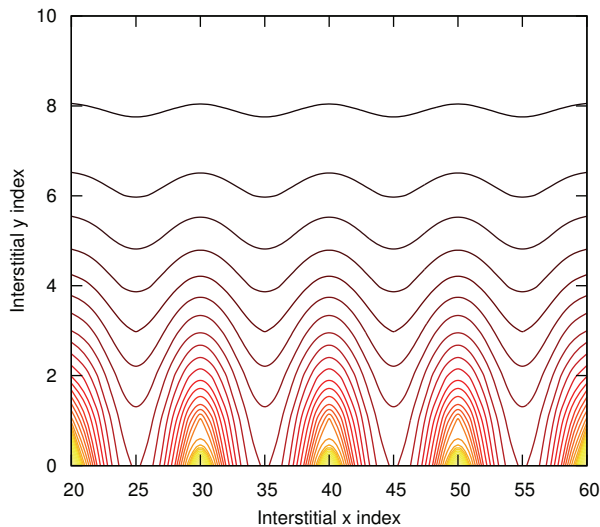


Fig. 4. Only after the individual diffusion fronts originating from separate dangling bonds have united to a common diffusion front will the system enter the diffusion-limited regime.

### A. Diffusion Front Buildup

A typical degradation curve as generated by our RD implementation is displayed in Fig. 3. It shows that the degradation behavior of the microscopic RD model strongly deviates from the macroscopic version. Instead of the three regions which arise from the macroscopic RD model — reaction limited, intermediate plateau and diffusion-limited — the microscopic description shows four regimes.

- The earliest degradation times ( $t < 2 \times 10^{-5}$  s in this case) are dominated by the depassivation of dangling bonds. This regime is similar to the reaction-limited regime in macroscopic RD calculations.

- After the passivation and depassivation has reached an equilibrium between  $k_f$  and  $k_r$  separately for each Si—H, the fraction of depassivated dangling bonds remains constant until the diffusion of the hydrogen atoms becomes dominant.
- As more and more hydrogen atoms leave their initial position, the degradation is determined by the buildup of the diffusion front along the Si-SiO<sub>2</sub> interface and the equilibration between the dangling bonds, see Fig. 4. This regime is a direct consequence of the physical picture behind the RD theory and shows a strong increase in the power-law exponent that is not experimentally observed.
- Finally, the well-known diffusion-limited behavior is obtained. The stress time after which this regime is observed depends on the relation between the average distance between two dangling bonds and the diffusion coefficient.

It is interesting to note that the observation of the diffusion-limited regime after a certain degradation time in this simple formulation sets a lower boundary for the diffusion coefficient. This lower bound requires the diffusion front to extend several microns into the oxide or polysilicon gate in order to avoid saturation, which is certainly curious, considering the dimensions of modern gate stacks. There exists no comparable criterion for the macroscopic model.

To make the microscopic RD theory compatible with the macroscopic version, we consider first-principles calculations that have shown a lowering of diffusion barriers for hydrogen (molecules) along the Si/SiO<sub>2</sub>-interface as compared to the bulk SiO<sub>2</sub> [20]. These findings indicate that the motion of hydrogen might proceed at a much higher rate at the interface, which aids the equilibration between the dangling bonds and therefore reduces the required bulk diffusion coefficient. To account for this in our microscopic model, we applied different diffusion coefficients  $D_I$  and  $D_B$  in the interface region and in the bulk, respectively.

### B. Stress and Recovery in the Microscopic Model

As can be seen in Fig. 5, the increase of the interface diffusion coefficient reduces the effect of dangling bond equilibration significantly. To get a reasonable match between the microscopic RD model and the macroscopic version, an increase of approximately three orders of magnitude is required. While a diffusion coefficient of this magnitude may be hard to justify from a physical point-of-view, it is still closer to the physical reality than the assumption of immediate equilibration along the Si-SiO<sub>2</sub>-interface that is inherent to the usually employed one-dimensional macroscopic RD model. A perfect match between the microscopic and the macroscopic version of the RD model is only obtained in the limit  $D_I \rightarrow \infty$ .

Interestingly, the three-dimensional stochastic motion of the hydrogen atoms *does not influence* the recovery behavior of the system, which contradicts the predictions of [10]. The recovery in the microscopic model matches the macroscopic version, which is incompatible with experimental data [5]–[7], independently of the choice of interface acceleration.

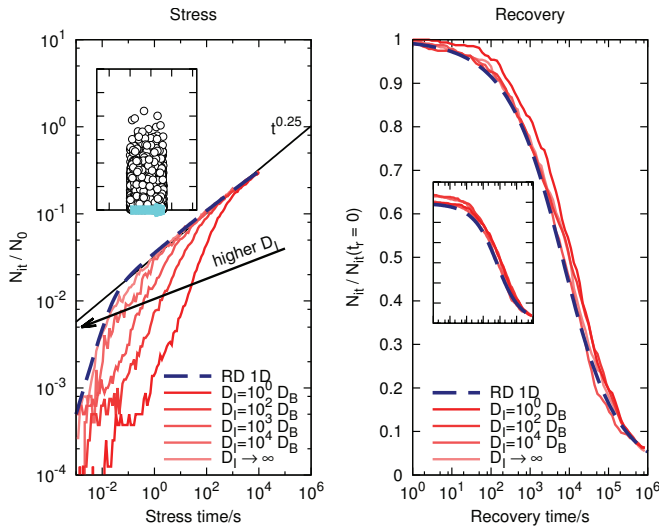


Fig. 5. Stress (left) and recovery (right) traces as predicted by our microscopic RD model and the influence of an increased interface diffusion coefficient  $D_I$ . **Degradation:** The increase of  $D_I$  reduces the equilibration time between the dangling bonds. The newly observed diffusion front build up regime becomes less pronounced in the degradation curve, leading to almost perfect agreement with the macroscopic model for  $D_I \rightarrow \infty$ . **Inset:** The simulation box is laterally limited (the cyan line marks the interface region), which gives similar results to a periodic boundary system and mimics an infinitely extended interface. The boundary conditions force the atomic motion into a straight path leading to a laterally invariant and thus effectively one-dimensional behavior. **Recovery:** Contrarily to the claims in [10], the recovery behavior of the three-dimensional stochastic RD model perfectly resembles the one-dimensional macroscopic recovery.

However, as can be seen in the inset of the degradation graph in Fig. 5, the closed lateral boundary conditions in our calculations force the random motion of the diffusing hydrogen atoms into a straight path, therefore creating a laterally uniform distribution of hydrogen atoms which yields an effectively one-dimensional diffusive system.

### C. Open Boundary Conditions

Closed boundary conditions for diffusive motion give the same results as periodic boundary conditions, as long as the dangling bonds are homogeneously distributed throughout the interface. Therefore, the calculations of Fig. 5 mimic the behavior of an infinitely expanded Si-SiO<sub>2</sub> interface. In order to see how a clustering of dangling bonds or very small device dimensions will change the NBTI behavior in our microscopic RD theory, we also apply open boundary conditions in our calculations, see Fig. 6. These boundary conditions are especially easy to realize in our formulation, by not limiting the diffusion of the particles to a simulation box.

When open boundary conditions are applied, the particles diffuse freely in the whole  $z > 0$  half-space. As shown in Fig. 7, this out-diffusion of particles into regions that were forbidden in the closed-boundary case leads to an increase in the power-law exponent of the degradation as the diffusion profile assumes more and more the shape of a line- or point-source diffusion front [21]. In the recovery trace this effective

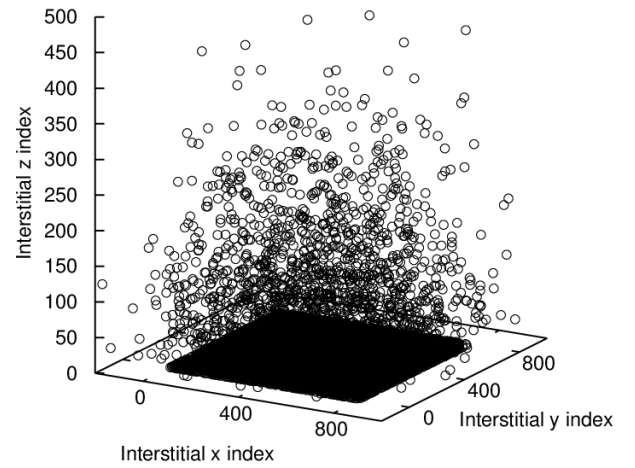


Fig. 6. Open systems are easily modeled using our microscopic formulation of the RD model by not limiting the motion of the hydrogen atoms to a simulation box. The figure shows a snapshot of a three dimensional simulation with 6400 atoms.

loss of particles manifests as a permanent (or slowly recovering) component on top of which the typical, macroscopic recovery occurs, again independently of the selected  $D_I$ . Although the recovering part of the degradation keeps its strong deviation from measured recovery traces, the permanent part may be misunderstood as being compatible with experimental observations [22]. However, it has to be stressed that this slowly returning fraction of atoms can only be observed in combination with the increased power-law during degradation, which has never been reported from any measurements.

## V. CONCLUSION

We report on a stochastic three-dimensional implementation of the reaction-diffusion model for NBTI. The model is theoretically well-founded on the theory of stochastic chemical kinetics and is understood as a consequent realization of the physical picture behind the reaction-diffusion theory.

The degradation predicted by the microscopic model features a new regime which is dominated by the lateral equilibration of dangling bonds. This regime features a strongly increased power-law exponent and is not observed experimentally. Further, it cannot be obtained from the usual macroscopic one-dimensional RD models, which *inherently assume* an *instant equilibration along the interface*. The effect can only be reduced in a physically meaningful way by a strong increase of the diffusion coefficient along the interface.

Recent claims that a stochastic three dimensional description of the atomic diffusion could explain the long relaxation tails observed in NBTI experiments while leaving the degradation untouched have been disproved by our calculations. The shape of the recovery arising from the reaction-diffusion theory is shown to be independent of the dimensionality and atomistic occupation effects by our calculations. Moreover, the microscopic description itself questions the physical relevance of the usually employed RD model. Especially its implicit assumption on the equilibration between the dangling bonds

