

## Exponential ionic drift: fast switching and low volatility of thin-film memristors

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**Abstract** We investigate the exponential dependence of switching speeds in thin-film memristors for high electric fields and elevated temperatures. An existing nonlinear ionic drift model and our simulation results explain the very large ratios for the state lifetime to switching speed experimentally observed in devices for which resistance switching is due to ion migration. Given the activation barriers of the drifting species, it is possible to predict the volatility and switching time for various material systems.

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In the past decade, the interest in resistance switching of thin film devices has been revived primarily because of the possible slowing of the rate of progress in semiconductor electronic circuits [1]. Indeed, hybrid circuits based on transistors integrated with thin film devices in nanowire crossbar structures have the potential to continue the functional improvement of digital systems well beyond the limits of scaled complementary metal–oxide–semiconductor (CMOS) technology and potentially even enable the implementation of hardware-based neuromorphic networks [2, 3].

We have proposed a simple phenomenological model of bipolar resistance switching [4] that can be applied to various material systems, including binary metal oxides and more complex perovskite compounds, various solid state electrolytes, and even organic films, see, e.g., extensive reviews of the switching in these materials in [5, 6].

In that model, we have argued that the motion of mobile atomic species (which could be ions, molecules or vacancies with charged components) can produce dramatic changes in the device resistance. For example, oxygen vacancy movement in transition-metal-oxides has been known for decades [7, 8]. In the particular case of rutile, oxygen vacancies effectively act as dopants with one shallow and one deep level [9]. Since even a relatively minor nonstoichiometry of 0.1% in  $\text{TiO}_{2-x}$  is equivalent to  $\sim 5 \times 10^{19}$  dopants/cm<sup>3</sup>, the modulation of the oxygen vacancy profile has a very strong effect on the electronic transport [10].

Ideally, in digital applications, switching devices should combine long (year-scale) retention times with fast (ns-scale) write speeds. Practically, a smaller dynamic range can be acceptable, e.g., in bio-inspired circuits (with millisecond switching and minute-scale lifetimes). Experimentally, there is an extremely wide range of observed lifetime volatility and switching speeds, with the former extending to years [11] and the latter occurring in microseconds or less [10, 12, 13]. This is possible if the rate of switching is highly nonlinear; for example, Aono et al. reported that the switching time for their  $\text{Ag}_2\text{S}$ -based ‘atomic switches’ [12, 13] depended exponentially on the applied switching bias voltage (a 0.3 V increase in bias increased the switching speed by six orders of magnitude), which they explained with a highly specific model of electrochemical reduction. We explain such broad variations in switching time using a much more general model of nonlinear microscopic drift of charged species in a solid at high fields and temperatures, and describe in general how to simultaneously achieve long state lifetimes and fast switching.

In the model, we assume that one limiting resistance state (either full ON or OFF) of the switch is stable and corresponds to the minimum of the system free energy [14]. When the switch is in the opposite state, the mobile atoms

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will slowly diffuse or drift in the built-in internal field due to space charge or image charge on the metal electrodes towards the equilibrium profile. (For example, using the Poisson–Boltzmann theory, it has been shown that in n-type oxide films positive mobile ions will segregate to the electrodes at equilibrium to form a U-shaped concentration profile [15].) Therefore, we can estimate the switching speed  $\tau_{\text{write}}$  by how fast the charged species can be moved (with the average velocity of the drift  $v$ ) within the active region of the device of length  $L$  by an applied electric field  $E$ , while the volatility  $\tau_{\text{store}}$  is due to the slow diffusion or drift in the built-in internal field.

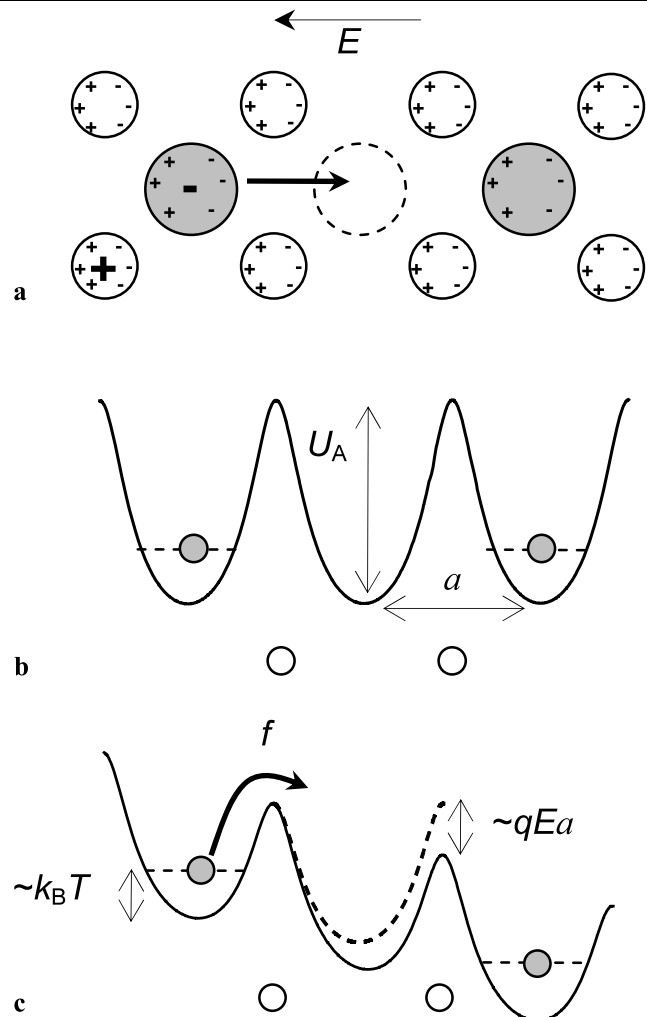
Assuming standard ionic drift with mobility  $\mu$ , the switching speed will be  $\tau_{\text{write}} \approx L/(\mu E)$ . On the other hand, even without any voltage bias across the device or net internal field, it will take  $\tau_{\text{store}} \approx L^2/D$ , where  $D$  is the diffusion constant, for the device to lose its state because of diffusion. Hence, applying the Einstein–Nernst formula between the mobility and the diffusion constant, the volatility/switching speed ratio is

$$\tau_{\text{store}}/\tau_{\text{write}} \sim EL\mu/D = qEL/(k_B T), \quad (1)$$

providing a ratio of not larger than three orders of magnitude assuming room temperature, reasonable bias voltages, and  $L \sim 10$  nm. (Here  $k_B$ ,  $T$ , and  $q$  are the Boltzmann constant, temperature and charge of the electron, respectively.) For comparison, the store-to-write ratio is  $\sim 10^{12}$  in commercial NAND flash memories and even larger than  $10^6$  in volatile DRAMs [16].

Obviously, the observed ten or more orders of magnitude for the ratio of volatility to switching times in oxide devices cannot be explained by the simple picture of macroscopic drift-diffusion. However, with typical applied voltages of the order of a few volts and films a few tens of nanometers thick, the applied electric field in the active region of a device can be extremely high, i.e., exceeding 1 MV/cm. Such a strong field can significantly reduce the activation barrier for migration inside the solid, and hence it is natural to suspect there might be strongly nonlinear ionic transport. Significant increases over the linear drift law have been experimentally confirmed for the rapid high-potential growth kinetics of anodic oxides [17], and more recently for lithium ion drift in silica glasses [18].

The nonlinear ionic drift equation can be derived from the simple rigid point-ion model illustrated schematically in Fig. 1, and has been understood but seldom applied for 60 years [7, 19]. In solids, an ion hops in the net potential of the constituent ions, which here are assumed to have periodicity  $a$  and activation energy  $U_A$ . The application of an electric field  $E$  will deform the potential well and result in a change of the effective barrier by  $\sim \pm qEa/2$ , aligned with (+) and opposite to (–) the direction of the electric field. Therefore, the overall effect on the average drift velocity



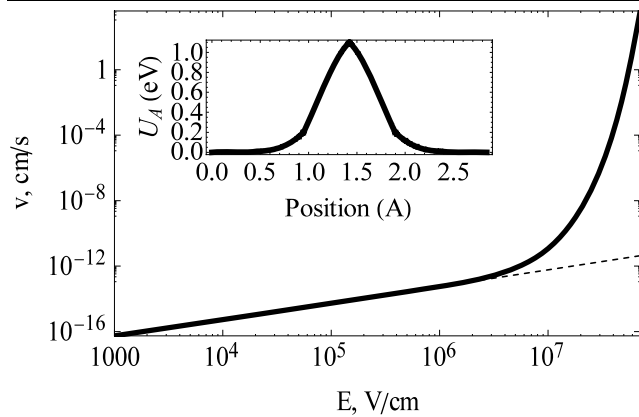
**Fig. 1** Illustration of vacancy diffusion. **a** The rigid point-ion model and corresponding potential energy profile without **(b)** and with **(c)** an applied electric field. The local field acting on the mobile ion at the saddle point of the energy barrier along the migration path can be much larger than the average macroscopic field

can be described by the formula for high-field ionic drift [7, 17, 19]:

$$v \approx f a e^{-\frac{U_A}{k_B T}} \sinh(qEa/2k_B T) = \begin{cases} \mu E & E \ll E_0, \\ \mu E_0 e^{E/E_0} & E \sim E_0, \end{cases} \quad (2)$$

where  $f$  is the frequency of escape attempts, while  $\mu = qfa^2 \exp[-U_A/(k_B T)]/(k_B T)$  is the mobility at small electric fields and  $E_0 = 2k_B T/(qa)$  is the characteristic field for a particular mobile atom in the crystal, which is typically about 1 MV/cm for  $T = 300$  K. Also note the formula is only valid if the net potential barrier  $U_A - qaE/2$  is not negative.

Figure 2 shows the theoretical drift velocity of the oxygen vacancies in ideal crystalline rutile using (2) and simulation



**Fig. 2** Nonlinear (*solid*) and linear (*dashed*) drift velocity of doubly charged oxygen vacancies along the [110] direction in rutile at room temperature, using the activation barrier calculated in [20] (*inset*)

data for the activation energy profile of an oxygen vacancy [20]. Here we have assumed  $f = 10^{13}$  Hz, which was taken from far infrared dielectric dispersion studies [21]. Strongly nonlinear behavior is observed for electric fields larger than  $\sim 10$  MV/cm, with the drift velocity increasing by more than 8 orders of magnitude for a change in the electric field from 10 to 40 MV/cm. Using arguments similar to those used for (1), the ratio of volatility to the switching time is

$$\tau_{\text{store}}/\tau_{\text{write}} \sim L/(2a) \times \exp(E/E_0). \quad (3)$$

Note that even the high electric field required for exponential ion transport may still be much lower than the critical field for dielectric breakdown of the oxide. The local electric field  $E$ , which should be used in (2, 3) for the ionic drift, can be much higher than the average field  $E_A$  that is determined from the applied bias voltage  $V = \int E_A(x) dx$  [7]. For example, in a uniform isotropic dielectric with permittivity  $\chi$  and Lorentz factor  $F$ , the local field experienced by the ion can be as high as  $E = (1 + \chi F)E_A$ . For rutile, the static Lorentz factor is about 0.5 for oxygen ions (or, equivalently, vacancies) along particular directions [22], and the static permittivity  $\chi \approx 100$  [23], yielding a local field  $\sim 50$  times larger than the applied field. The typical applied (or average) electric field that causes breakdown for bulk rutile is close to 2 MV/cm [24]; thus, it is possible to observe strongly nonlinear ion transport with electric fields well below this value. Moreover, in the most accepted theory, electrical breakdown is due to the hot electrons that gain energy more rapidly from the field than losing it to phonons [7]. It is therefore natural to expect that the breakdown field will increase for few-nm-scale films, so that the nonlinear ion transport regime is further extended.

In Fig. 2, the results are shown for an ideal crystalline structure, while many experiments are performed with nanocrystalline or amorphous phases. The diffusion of mobile species along grain boundaries is typically much faster

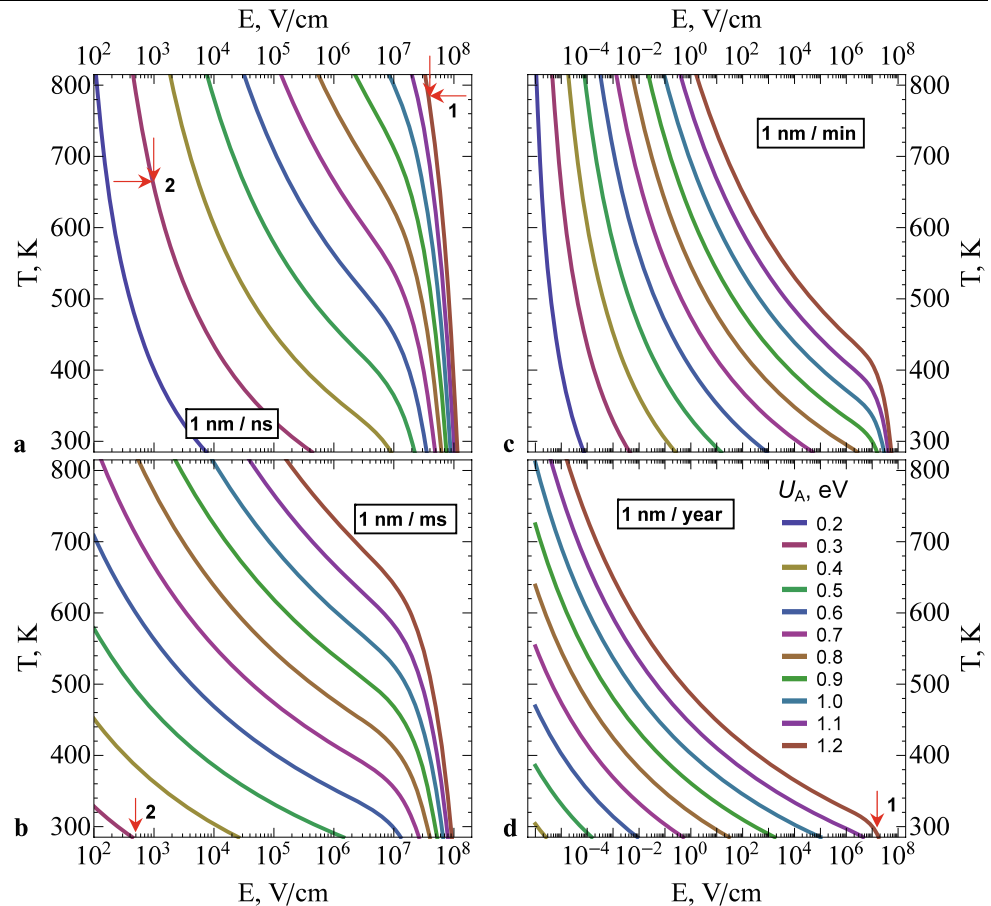
than in the bulk, and hence only these fast diffusion paths may play a role in switching [5, 25]. On the other hand, it is unclear if such paths are always available in practice, since by reducing the lateral dimensions of a device to the nanoscale the number of grains (and the grain edges along the electric field) per device will also decrease dramatically. Statistically, that could lead to large parameter variations of the ionic switches, in a manner similar to the critical electromigration current density in polycrystalline nanowires [26], unless the grain size is also reduced significantly. In such a limiting case, the material will be considered purely amorphous and the model should be adjusted to incorporate the statistical nature of ion or vacancy hopping barriers.

Electrical power dissipation in the small volume of a device can lead to significant heating, depending on the structure and materials, which in turn will increase the switching speed of a device. In this case, (1) and (3) are multiplied by the factor  $\exp[U_A/(k_B T_{\text{store}}) - U_A/(k_B T_{\text{write}})]$ , where  $T_{\text{write}}$  and  $T_{\text{store}}$  are the temperatures in the active region during switching and storage, respectively. Elevated temperatures (which may be caused by self-Joule-heating of the device) and nonlinear drift combined provide a very wide range of conditions to enable fast switching and long storage lifetimes (Fig. 3).

Virtually all experimental data on resistance switching have been reported for stand-alone devices, whereas the performance of devices integrated in crossbar structures will be affected by the half-select problem [2]. The worst case for the storage lifetime is determined by drift in an electric field that is half the magnitude of that used for switching. Even for such a challenging case, plausible performance metrics can be found from Fig. 3 and used for engineering devices. For example, for mobile species with large activation energies  $U_A > 1.2$  eV, it is possible to have year-scale retention even in the continual presence of an internal field  $E = 15$  MV/cm at 300 K, whereas switching can be as fast as 10 ns at  $E = 30$  MV/cm and 800 K. In such a system, self-heating in the semi-selected devices can be negligible if the electronic transport is strongly nonlinear. Also note that, according to Fig. 3, fast diffusion channels characterized by very low activation energies may not be practical for the crossbar non-volatile memory applications because of poor volatility.

Several issues affecting the accuracy of the model and (2) in particular must be pointed out. Most importantly, the model is best suited for ionic crystals that can be described with point-ions interacting through Coulomb repulsion and van der Waals forces. While for covalent crystals, finding the diffusion barrier using an elastic band approach [27] provides insight into ion mobility, the modulation of the saddle point in the potential barrier may significantly deviate from (2) due to the complex dynamics of electron–electron

**Fig. 3** Temperature and electric field dependence of ionic migration for several values of activation energy and four different values of the drift velocity: **a** 1 nm/10 ns; **b** 1 nm/1 ms; **c** 1 nm/1 min; and **d** 1 nm/1 year. Each curve was calculated from (2) assuming  $f = 10^{13}$  Hz and  $a = 0.15$  nm. The pair of points indicated by red arrows illustrate a possible ratio of retention and switching speed in a system affected by the half-select problem, i.e., 1 year/10 ns for an activation energy  $U_A = 1.2$  eV, which is relevant for oxygen vacancies in  $\text{TiO}_2$ , for example



and electron–ion interactions in the high electric field. Similarly, any electrochemical effect, e.g., electrochemically assisted diffusion of cations in superionic conductors, may not be properly described by the model. In the case of rutile, the bonding is a mixed ionic/covalent hybrid and the point-ion technique gave satisfactory results for the calculation of diffusion barriers in earlier studies [28].

Ions near defects will relax to reduce the local electrical field, so that  $E$  needed for (2) will be somewhat smaller and may not be linearly proportional to  $E_A$ . Moreover, ionic core penetration may further decrease the Lorentz factor [7]. On the other hand, the fact that the apparent jump distances were 10–20 times larger than those that were expected for linear drift for hopping of lithium ions in silica glasses [18] provides at least one system with local field enhancement in saddle point. Finally, the temperature dependences of  $f$  and  $\chi$  should be negligible within the accuracy of our model.

To conclude, very large ratios observed for the state lifetime to switching speed are consistent with the exponential ionic drift model presented here, especially given the effects of both high fields and temperature. With enough information about the activation barriers, Joule heating, and the relation of internal field to applied field, it should be possible to

explicitly design systems that have values of this ratio suitable for digital and bio-inspired applications.

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