

LETTER TO THE EDITOR

Novel exchange mechanisms in the surface diffusion of oxides

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Abstract

We use temperature-accelerated dynamics to show the importance of exchange mechanisms in surface diffusion and growth of simple oxides. Such mechanisms can dominate transport processes both on terraces and steps for both homoepitaxial and heteroepitaxial growth. We suggest that the mixing inevitable when an exchange mechanism is present must be considered when attempts are made to grow sharp interfaces in oxide nanostructures.

(Some figures in this article are in colour only in the electronic version)

Published work on surface diffusion in ionic systems has usually assumed that the mechanism involves forming an adsorbed ion pair on the surface which then moves from one surface site to another by a hopping mechanism. In this paper we show the importance of exchange mechanisms in surface diffusion on oxides of the rock-salt structure. Mechanisms of this kind have long been known for metals [1] and their importance highlighted in a recent review [2]. Our results show analogous, but quite distinct, exchange processes. Exchange seems rather general in surface diffusion. Since it implies surface mixing, it is impossible to produce atomically sharp interfaces if the atoms of the uppermost layer exchange with those in the substrate below.

The simulation of diffusion in simple ceramics presents particular problems because energy barriers are often high, of the order of 1.5 eV or more in the bulk oxides. It is therefore impossible to run molecular dynamics simulations for long enough to obtain adequate statistics at temperatures of interest. Kinetic Monte Carlo (KMC) methods can reach the relevant timescales, but they assume that we know *in advance* the rates of *all* relevant mechanisms (but

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Table 1. Short-range interionic potentials $V(r) = A \exp(-r/\rho) - C/r^6$ for rock-salt oxides (the short-range term is ignored for cation–cation interactions).

Interionic interactions	A (eV)	ρ (Å)	C (eV Å ⁶)
Ba ²⁺ –O ²⁻	905.7	0.3976	0.0
Sr ²⁺ –O ²⁻	959.1	0.3721	0.0
O ²⁻ –O ²⁻	22 743.0	0.149	27.88

see [3] for developments in this area). One way to investigate a particular mechanism is to find the activation pathway of a diffusion mechanism by a nudged elastic band method [4]. This requires knowledge of both the initial and final states of the diffusion mechanism.

Voter and co-workers [5, 6] have developed a variety of methods for use where long timescales are required under the general label of ‘accelerated dynamics’. These provide a way of obtaining an *unbiased* calculation of the diffusion rate that does not require prior knowledge of the diffusion mechanism, i.e., without advance information on the configuration of the final state or the trajectory. Temperature accelerated dynamics (TAD) uses simulations performed at high temperature to calculate the evolution of systems at a lower temperature of interest. Unlike crude extrapolations of high-temperature simulations to low temperature, it identifies and extrapolates the rates of individual mechanisms to lower temperatures (using the nudged elastic band method to find the activation energy). It therefore correctly accounts for the different behaviour of the various contributing mechanisms with temperature. The TAD calculation can thus be used as a direct simulation of the diffusion, changing the state of the system according to the fastest mechanism and advancing the simulation clock by the shortest transition time at the required temperature. Alternatively, as here, we use the method to collect an unbiased list of mechanisms together with the appropriate rates as input to a KMC simulation.

The TAD calculations are performed using a rigid-ion model based on [7]. Full ionic charges are used. The short-range potentials between the ions have the form $V(r) = A \exp(-r/\rho) - C/r^6$ where A , ρ and C are parameters of the potential and r is the interionic separation. The model parameters are given in table 1. Models of this kind are known to give excellent results for simple closed-shell ionic surfaces, both for surface energies and structures, defect energies and activation energies for defect mechanisms. Comparisons with quantum calculations show good agreement for processes where electronic rearrangement is not an issue [8].

The calculations were performed within the canonical (NVT) ensemble. The surface was represented by a slab of ions, periodically repeated in three dimensions, but with sufficient space between slabs in the third dimension to prevent inter-slab interactions. The slabs typically contained ≈ 500 ions. The Ewald summation was used for the Coulombic interactions. All short-range interactions were cut off at a distance of 9 Å. The high and low temperatures used were 1200 and 300 K, respectively. The minimum prefactor was set to 5×10^{11} Hz to ensure that all possible escape routes were detected before the lowest was chosen (for an explanation of the use of this criterion see [5, 6]). In a normal TAD calculation this value could be set higher, but the aim here was to provide data for the KMC calculation rather than follow the diffusion directly. Typically boosts of the order of 10^2 – 10^6 were obtained for a given transition.

We have simulated the diffusion of BaO molecules along the (100) surface of a BaO substrate. The TAD calculations clearly show that the diffusion mechanism with the lowest barrier involves exchange with surface ions. Each jump involves one of the ions in the adsorbed molecule exchanging with an ion in the surface while the other one remains overhead, held by

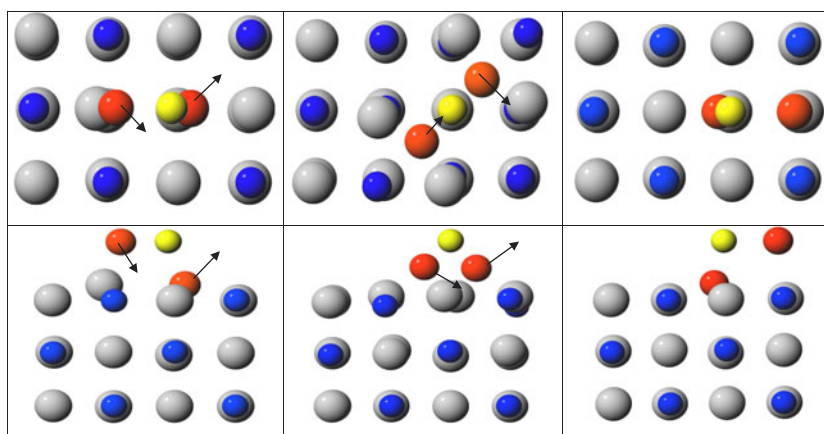


Figure 1. Exchange mechanism for diffusion of an ionic molecule on the (100) surface of BaO (top and side views). Red (O) and grey (Ba) spheres represent the ions in the (100) surface. Green (O) and blue (Ba) spheres denote the ions in the BaO molecule. The yellow sphere is the barium ion displaced by the exchange mechanism.

the Coulombic binding. This reorientates the molecule either by 90° or by 180° , depending on which of the three possible nearest-neighbour adsorption sites are occupied by the exchanged ion. The molecule can then move by exchanging the counter-ion with a counter-ion in the surface. A diagram of the mechanism is shown in figure 1. The migration energies for the two exchanges are very similar: 0.35–0.46 eV for the cation, 0.37–0.44 eV for the anion. This is much less than the activation energy to move the molecule over the surface as a single adsorbed species: about 1.1 eV. Despite the similarity to the metal exchange reaction, there is an important difference—the necessity for the counterion to remain close to the exchanging ion. This makes the extended subsurface diffusion mechanisms suggested for metals [2, 9] unlikely for ionic surfaces.

Motion along a step also proceeds by an exchange mechanism. However, the edge complicates matters because of the drastically reduced symmetry. The second stage of the exchange can move the ion pair towards, away from or parallel to the step. The energy barrier to moving the ion pair away from the step is slightly higher than the barrier to moving towards it, whilst the energy to move along the step is midway between these two. The energy to extract an ion from the step is relatively high (approximately 0.7 eV), whilst the return energy is low (approximately 0.2 eV). Ions in contact with the step edge are therefore bound to the step. They are able to move back and forth along the step by exchanging with ions in the step edge as shown in figure 2. However, no exchange occurs with surface layer ions.

The activation energies for all of these processes have been used as input to kinetic Monte Carlo simulations. The size of the surface in the KMC simulations was 20×20 (i.e. 400 ions), with periodic boundary conditions applied. A typical simulation included 4×10^6 events. Firstly, the resulting isotropic two-dimensional diffusion coefficients can be extracted from these simulations using the standard result $\langle r^2 \rangle = 4Dt$ where D is the diffusion coefficient and are shown in figure 3(a).

Secondly, we can calculate the mean formation time of islands on the surface, starting from a random distribution of molecules. Molecules attract each other to form larger clusters. Figure 3(b) shows the characteristic time necessary for most of the molecules to form one or more islands (defined here as five or more molecules clustered together). The starting point

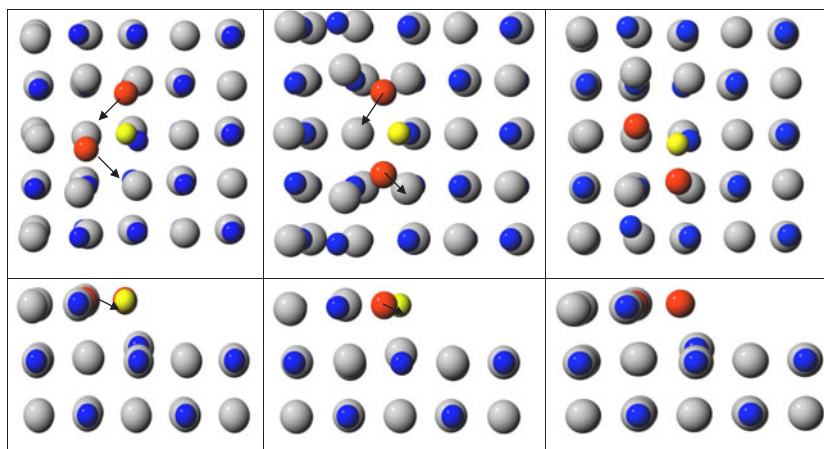


Figure 2. Exchange mechanism at a step (top and side views). Colours are as follows: BaO crystal, Ba in red, O in grey; BaO molecule, Ba in blue, O in green; the yellow ion is the Ba ion displaced during the exchange mechanism.

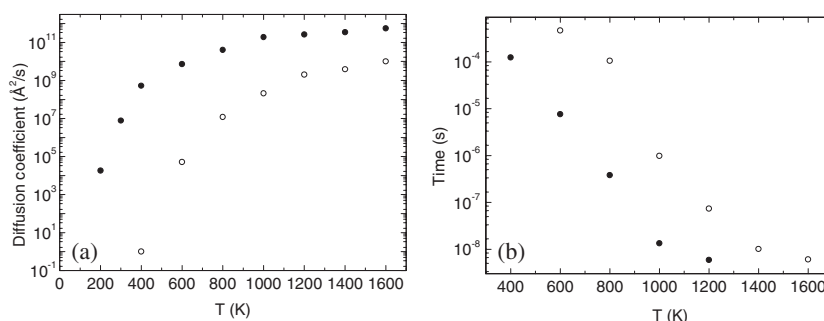


Figure 3. (a) Diffusion coefficient for BaO molecule on the (100) surface of BaO using TAD and including exchange (solid circles) and using a simple surface molecular mechanism (empty circles). (b) Time for the random BaO molecules to condense into an island on the BaO surface as a function of temperature using TAD and including exchange (solid circles) and using a simple surface molecular mechanism (empty circles).

was a random distribution of 40 Ba and O pairs on the 20×20 BaO surface consistent with an overall coverage of 20%. As the KMC simulation proceeds, randomly moving pairs meet and create initial clusters, which cannot move in our model; the proto-steps so produced attract molecules in turn, resulting in the spontaneous creation of islands. Usually a few thousand such elementary events are enough to reach a stable final configuration. For relatively small coverages, the final configuration consists of many small islands; with increasing coverage, the average size of an island increases and the total number of islands decreases. Just as in figure 3(a), results are presented with and without the exchange mechanism taken into account. Including the exchange mechanism drastically accelerates island formation, typically by two or three orders of magnitude. The evolution of the islands is shown in figure 4.

Well defined layers of crystalline oxides, grown by molecular beam epitaxy, on semiconductors are candidate materials for gate dielectrics in solid state electronics [10]. More generally, molecular beam epitaxy is being used to create layered structures of ferroelectric, ferromagnetic and dielectric oxides [11]. The question of whether the exchange mechanism is

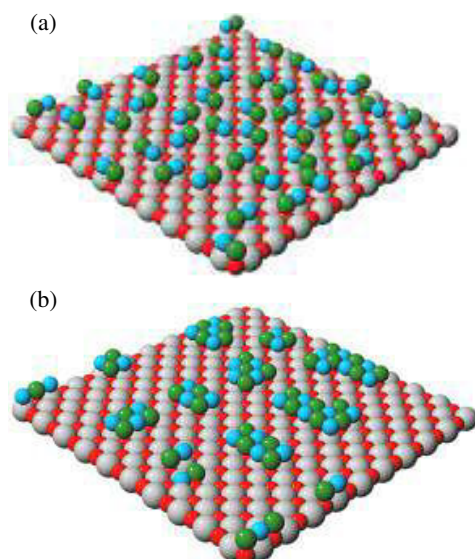


Figure 4. Evolution of BaO islands on the (100) surface of BaO. (a) Starting configuration; (b) after 380 ns simulation at 1000 K.

still active when a molecule of one oxide diffuses on a different oxide substrate is of fundamental importance for creating sharp interfaces in such structures. We have considered the simple BaO/SrO interface. Calculations using a BaO molecule on the (100) SrO surface and SrO on the (100) BaO surface were performed. The large size of the barium ion, relative to the strontium ion, prevents embedding of the Ba ion into the SrO surface. In contrast the Sr ion readily exchanges with a surface layer barium ion. In this case the activation energy is about 0.6 eV. The existence of this low-energy mechanism suggests that, in some cases at least, ionic materials cannot be grown on a substrate with a similar structure without significant intermixing. Further investigations of this effect for the perovskite structures are in progress.

We have shown the importance of exchange mechanisms in a variety of surface diffusion processes in simple oxides. The possibility of this kind of mechanism has been neglected in the past, although there has been one recent observation [12]. The mixing effect inherent in such a process means that the possibility of these mechanisms must be considered when attempting to build oxide nanostructures and multilayers.

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