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Exchange processes in the contact formation of Pb electrodes

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ABSTRACT

Motivated by recent experiments on electrochemically controlled Pb atomic-scale switches we have studied the self-diffusion of Pb on flat and stepped surfaces since diffusion processes play an important role in the growth of metal substrates. Kinetic modelling based on Monte-Carlo simulations using a model potential suggests that exchange processes play an important role in the contact formation at the nanoscale. Periodic density functional theory indeed find that the barriers for exchange diffusion across the steps are significantly lower than for hopping diffusion. The consequences for the contact formation in electrochemically controlled switches are discussed.

1. Introduction

Recently, an electrochemically controlled atomic-scale quantum conductance switch has been realized, where the position and dynamics of a single (or few) atom(s) decides about the current flow and current switching [1–4]. External control over this degree of freedom is maintained in the experiments by the electrochemical electrode potential. However, the details of the basic atomic switching processes are still not fully understood.

As a possible mechanism, a switching mechanism has been suggested that is based on the collective deposition of metal atoms from the electrolyte onto the switch [1,2,5]. Still, the exact nature of the collective process was not clarified. Here we report the results of a joint theoretical effort in order to elucidate elementary steps in the collective switching mechanism on an atomic scale and to develop concepts to describe the corresponding processes.

The fundamental elementary process occuring in the switch is the deposition of metal atoms from the electrolyte onto the metallic electrodes and the formation of a contact. The specific metal structure growing on the electrode upon metal deposition is controlled by diffusion processes [6–10]. Hence a crucial part in the modeling of the atomic-scale switch is the determination of metal self-diffusion paths and the corresponding diffusion barriers [11].

As the first step, we performed Monte Carlo simulations [12] of the breaking of contacts in a two-dimensional geometry based on simple model potentials. These simulations provide insights into the statistical nature of the motion of the electrode atoms. In particular, they show how the elementary processes - atoms moving over diffusion barriers - transform into collective many-body processes when the junction is (slowly) closed. These simulations also suggest that exchange processes play an important role in the contact formation at the nanoscale.

In order to check whether exchange processes indeed occur at realistic electrode surfaces, we have then determined metal diffusion paths using total-energy calculations based on density functional theory (DFT). As the specific metal, we have considered lead which has also been used as an electrode material in the quantum conductance switch [13]. To the best of our knowledge, diffusion processes on stepped Pb surfaces have not been addressed yet by DFT calculations, but by a computational study [14] based on embedded atom potentials.

Note that the controlled formation of nanostructures at metal surfaces is of critical importance not only for the realization of the electrochemical quantum conductance switch, but also for several further applications at surfaces and interfaces, including heterogeneous [15–20] and electro-catalysis [21–23], quantum [24–27] and magnetic data storage [28,29]. However, in spite of the fact that such important diffusion processes have been studied in detail

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[30–32], it is fair to say that the atomic level understanding of these processes, in particular at complex, structured surfaces, is still limited. It is also important to note that the formation of the contact in the switch occurs at the electrochemical solid/liquid interface which adds further complexity to the system [33–35].

2. Theoretical Methods

First-principles total energy calculations were performed using a periodic DFT program, the Vienna ab initio simulation package (VASP) [36,37], employing the generalized gradient approximation (GGA) to describe the exchange-correlation effects, using the Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional [38]. The ionic cores are represented by projector augmented wave (PAW) potentials [39] as constructed by Kresse and Joubert [40]. The electronic one-particle wave functions are expanded in a plane-wave basis set up to a cutoff energy of 400 eV.

The specific choice of the functional requires special attention due to the fact that lead is a heavy metal where exchange-correlation and relativistic [41] effects may play an important role. However, while for semiconducting lead compounds the inclusion of exact exchange and spin-orbit coupling is necessary in order to reproduce the correct electronic band structure [42,43], bulk and surface properties of Pb metal are satisfactorily described using semi-local exchange-correlation functionals [44–46].

Within the supercell approach, the Pb electrodes were modeled by slabs of finite thickness separated by a vacuum region of 2 nm, which is sufficient to neglect the interactions between the periodic slabs. Five layers have been used to describe the Pb(100) and Pb(111) surfaces. For the stepped surfaces, 10 layers for Pb(311),15 layers for Pb(211) / Pb(511) and 20 layers for Pb(711) surfaces have been used. The optimized positions were relaxed until the residual forces were smaller than 0.1 eV/nm using a 3×3 supercell for Pb(111)/ Pb(100) and 1×3 supercell for stepped surfaces. We optimized the uppermost two layers for the flat (111) and (100) surfaces. For the stepped surfaces, the corresponding number of layers were relaxed as far as the terraces are concerned, which amounts to the uppermost four layers for the (311) surface, five layers for the (211) and (511) surfaces and eight layers for the (711) surface. A k-point sampling of $5 \times 5 \times 1$ k-points was used to perform the integration over the first Brillouin zone. The convergence of the results with respect to these parameters has been carefully checked. To determine the diffusion paths in the exchange mechanism, the nudged elastic band method (NEB) was employed [47], which is an automatic search routine for finding the energy minimum path between specified initial and final state.

In order to understand the qualitative phenomena related to the closure of a junction, it is both sufficient and most efficient to employ Metropolis Monte-Carlo simulations in canonical ensembles [12], using semi-empirical interaction potentials; hence, we simulated the junction dynamics with a tight-binding second-moment approximation model (TBSMA) also known as the Gupta-potentials [48]. These potentials are of the form

$$V(\{r_{ij}\}) = \sum_{i}^{N} \left[\sum_{j \neq i}^{N} A e^{-p\bar{r}_{ij}} - \sqrt{\sum_{j \neq i} \xi^2 e^{-2q\bar{r}_{ij}}} \right]. \tag{1}$$

Here, i and j are atom labels, $\bar{r}_{ij} = r_{ij}/r_0 - 1$, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the modulus of the distance between two atoms at positions $\mathbf{r}_i$ and $\mathbf{r}_j$. The parameters have been determined by fitting the experimental bulk lattice parameters and elastic moduli [48] as $A = 0.098$ eV, $\xi = 0.914$ eV, $p = 9.576$, and $q = 3.648$ for Pb. Distances are measured in units of the bulk first neighbor distance $r_0 = 0.35$ nm.

Gupta potentials were chosen basically for two reasons. First, they are rather popular [48] for studying metal atom dynamics as they incorporate enough many-body physics in order to reproduce metal lattice constants, cohesive energies, and elastic constants quantitatively while at the same time they allow for good computational efficiency. Second, our Monte-Carlo simulations are intended to demonstrate atom dynamics on a qualitative level. The exchange processes that we observe are expected to exist for broad classes of inter-atomic potentials. Therefore, going beyond the Gupta-level will not create any additional qualitative insights. In the same spirit, we concentrate on mono-atomic layers in our simulations. The collective phenomena we are after are not specific to three spatial dimensions. They appear already in film geometries, as we will see.

For numerical efficiency we used a potential truncation scheme using a mixed Verlet list automatically updated by a Cell list [12]. A large cutoff (~7× nearest neighbor distance) was used to avoid any possible truncation errors. The TBSMA used in our simulations is a true many-body potential which for an N-atom system in principle requires N^2 loops for evaluation of energy. Since we define a unit of Monte Carlo time as 10× N computational steps, our simulations roughly have an approximate computational cost of N^3 for a fixed MC time. Our implementation of the truncation scheme along with a look up table for energy calculations brings down the computational time by a factor of 10, effectively, without introducing visible artifacts. A typical simulation usually involves 10^4 to 10^5 MC steps for equilibration followed by 10^6 MC steps for collection of statistics.

3. Results and discussion

3.1. Monte Carlo simulations

The contact formation dynamics is simulated, starting from initial configurations which are then relaxed/equilibrated for 10000 steps per atom, to avoid any artifacts before collection of statistics begins. To observe the time evolution of contact closure an initial situation will be chosen, where the contact layer consists of a single atom only. One may think about it as an atom that has been quenched when the electrodes have approached each other in the experimental control cycle. The numerical protocol foresees an adiabatically slowly process, so that at every distance for most of the observation time the contact is (nearly) equilibrated.

Fig. 1 shows three snapshots showing how a contact forms after the electrodes have quenched a single atom, see initial state Fig. 1A. The contact atom is surrounded by vacancies to the left and to the right. In Fig. 1A a single vacancy on each side is shown; for broader junctions it can be many more. These vacancies cannot be filled easily by surface diffusion of the adsorbate atoms (blue), since the associated barrier height for the process is high. It is true, that also a given exchange process is associated by a large barrier height. However, due to the large number of possible exchange paths, these processes can become compatible and in fact dominate in the situation shown in Fig. 1. This is evident from Figs. 1B and C that indicate the typical exchange processes which have been responsible for filling the junction in our MC-simulations.

Such two-particle exchange can in fact be viewed as the simplest representative of a class of processes involving N particles and M vacancies (or holes); in the example we have N=2, M=1. The time evolution of these processes is such that all M vacancies are filled with particles thereby creating M new vacancies at other sites. In a lose way of speaking, one could say that M particles (vacancies) have been moved from old positions into new positions. (Processes with M=0 are *ring exchange* processes, i.e. cyclic permutations. Due to the fact that atoms are not distinguishable one from another, these processes are not accompanied with density fluctuations. Therefore, they can be ignored for thermodynamic considerations.)