Multiscale simulation of thermal disruption in resistance switching process in amorphous carbon

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Abstract. The switching of material atomic structure and electric conductivity is used in novel technologies of making memory on the base of phase change. The possibility of making memory on the base of amorphous carbon is shown in experiment [1]. Present work is directed to simulation of experimentally observed effects. Ab initio quantum calculations were used for simulation of atomic structure changes in amorphous carbon [2]. These simulations showed that the resistance change is connected with thermally induced effects. The temperature was supposed to be the function of time. In present paper we propose a new multiscale, self-consistent model which combines three levels of simulation scales and takes into account the space and time dependencies of the temperature. On the first level of quantum molecular dynamic we provide the calculations of phase change in atomic structure with space and time dependence of the temperature. Nose–Hover thermostats are used for MD simulations to reproduce space dependency of the temperature. It is shown that atomic structure is localized near graphitic layers in conducting dot. Structure parameter is used then on the next levels of the modeling. Modified Ehrenfest Molecular Dynamics is used on the second level. Switching evolution of electronic subsystem is obtained. In macroscopic scale level the heat conductivity equation for continuous media is used for calculation space-time dependence of the temperature. Joule heat source depends on structure parameter and electric conductivity profiles obtained on previous levels of modeling. Iterative procedure is self-consistently repeated combining three levels of simulation. Space localization of Joule heat source leads to the thermal disruption. Obtained results allow us to explain S-form of the Volt-Ampere characteristic observed in experiment. Simulations were performed on IBM Blue Gene/P supercomputer at Moscow State University.

1. Introduction
The switching of material atomic structure and electric conductivity are used in novel technologies of making memory on the base of phase change. The possibility of making memory on the base of amorphous carbon is shown in experiment [1]. Present work is directed to simulation of experimentally observed effects. Ab initio quantum calculations were used for simulation of atomic structure changes in amorphous carbon [2]. These simulations showed that the resistance change is connected with thermally induced effects. Each MD simulation was done with constant in space temperature. Also periodic boundary conditions were supposed. Temperature was maintained using Nose–Hoover thermostat. In this paper we propose a new multiscale, self-consistent model which combines three levels of simulation scales. The space and time dependencies of temperature are calculated at the macroscopic level. Transport coefficients
are obtained in the molecular dynamics simulations. We show that atomic structure is localized near graphitic layers inside high temperature conducting dot with low temperature boundaries. Histogram technique for analyzing ions density is used for formulating the structure parameter and free energy profile. Structure parameter is used then in the next levels of the modeling. The heat conductivity equation for continuous media is used to calculate space-time dependence of the temperature. Joule heat source that depends on structure parameter and electric conductivity is proportional to the temperature. The space profiles of transport coefficients are calculated on previous levels of the modeling. Three dimensional heat conductivity equation is solved on the finite difference grid, using implicit finite difference scheme. Iterative procedure is self-consistently repeated combining three levels of simulation. Distributed temperature is maintained in MD calculations using Nose–Hoover thermostats for different groups of atoms. We show that the increasing of the space localization of the Joule heat source leads to the thermal disruption if perpendicular heat conductivity is small. Obtained results allow us to explain S-form of the Volt-Ampere characteristic observed in experiment. Simulations were performed on IBM Blue Gene/P supercomputer at Moscow State University.

2. Ab initio quantum simulation of atomic structure changes in amorphous carbon

We use CPMD ab initio code [3] which is based on density functional theory (DFT) and Car–Parrinello (CP) method. Within DFT and the Born–Oppenheimer approximation the movement of massive nuclei is described with a classical approximation. Forces acting on nuclei due to the interactions with the electrons are calculated solving the Kohn–Sham equations for ground state. Norm-conserving pseudopotentials are used, and Kohn–Sham orbitals are expanded in plane waves basis set up to a kinetic energy cutoff of 70 Ry. A fictitious electronic mass of 500 a.u., and a time step of 0.125 fs are used. We consider initial configuration of $sp^2$ sites within the $sp^3$ matrix. The density of system is $n = 2.34 \text{ g cm}^{-3}$ in the cell.

In [2] MD calculations are conducted with different temperatures. We found two different final types of atomic configurations in different MD runs. First type configurations exists at temperatures below $T = 2000$ K and has complicated amorphous structure which includes mixture of $sp^2$ atoms and $sp^3$ atoms. In all these cases the number of $sp^2$ atoms is increasing and the number of $sp^3$ is decreasing in comparison with initial state. In the work [2] MD calculations are conducted with different temperatures, but the temperature was supposed to be uniformly distributed in space. It was shown that with the temperature of order $T = 3000$ K effect of graphitic structure forming is obtained. Atomic configuration evolution at $T = 3000$ K is shown in fig. 1 obtained (a) at the beginning of heating process and (b) at the end of process. Note that all volume of unit cell is graphitic up to the boundaries.

In this paper, we suggest to define parameters, which characterize the appearance of structure from amorphous atomic state. We analyzed density of ions space distribution. Let us look at density of atoms evolution in the MD process and define $x$-direction as perpendicular direction to graphitic surfaces, and $(y,z)$ directions are parallel to graphitic surfaces. Atomic density distributions are approximated by using histogram technique. Atomic densities profiles for atomic configuration at $T = 3000$ K obtained at the end of heating process are shown in fig. 2. Density distribution is shown in perpendicular direction. Distributions are approximated by Gaussians with the height $H$ and semi-width $S(t)$. So, we introduce space structure parameter $S(t)$, which is characterized by semi-width of ions density distribution. The structure is localized during the evolution in the neighborhood of graphitic layers and $S(t)$ become smaller. Time evolution of structure parameter $S(t)$ is shown in fig. 3 during the time period of MD process. Time evolution in this period we call structural phase change or phase change of the second kind.
Figure 1. Atomic configuration evolution at $T = 3000$ K, obtained (a) at the beginning of heating process and (b) at the end of the process.

Figure 2. Atomic densities profiles at $T = 3000$ K at the end of process represented as histograms. Histograms are approximated by Gaussians.

Figure 3. Time evolution of structure parameter $S(t)$ during phase change transition.

3. Electronic density evolution during atomic structure changes. Ehrenfest model
The thermal induced changes in atomic structure of a-C in the presence of an external electric field is analyzed through the usage of a multiscale model of conductivity switching.

As we can calculate electronic Kohn–Sham orbitals and we can build a reduced model on the base of Ehrenfest molecular dynamics and time dependent DFT [3]. The goal is to obtain the electronic density perturbation due to the external electric potential. We showed the appearance of total current and estimate the electric conductivity.

We expand the electronic wave functions using the full set of Kohn–Sham orbitals to get the solution of time-dependent Schroedinger equation.

$$\Psi(r, R, t) = \sum_m c_m(t) \psi_m(r, R), \quad \hat{H} \psi_m(r, R) = E_m \psi_m(r, R)$$  (1)
Figure 4. Temperature profiles in $x$-direction during time.

Figure 5. Structure of atoms corresponding to the localized spatial dependence, calculated in macroscopic scale.

where $\mathbf{r}$ and $\mathbf{R}$ are electronic and ionic positions. According to Ehrenfest molecular dynamics, the time dependence of the coefficients $c_m(t)$ represents the evolution of the system in time.

The main suggested approach for the computation using reduced Ehrenfest model is based on separation of scales. Long time scale CPMD calculations are used for formation of quasi-equilibrium structure of ionic positions at the given temperature. For each final equilibrium state we calculate HOMO and LUMO. Then, using excited orbitals and Ehrenfest electronic equations at the fast time scale, we determine switching to the next graphitic structure. For these positions of ions (structure parameter) we determine HOMO orbitals and excited orbitals. Process of switching is determined by overlapping integrals for HOMO and other excited orbitals.

Switching of HOMO and LUMO orbitals at fast time scale occurs around ground state — state of phase transition. This electronic switching can be define as the transition path through excited states to new graphitic atomic configuration. We introduce fictitious particle (structure parameter $S(t)$) that corresponds to ions positions at the given temperature. Approximated motion equations for ions can be formulated as

$$
\mu \frac{d^2 \mathbf{S}}{dt^2} = -\frac{\partial U_F}{\partial \mathbf{S}} - \sum_m |c_m(t)|^2 \frac{\partial E_m}{\partial \mathbf{S}} - \sum_m \sum_{k \neq m} c_m(t) c_k(t) (E_m - E_k) \mathbf{d}_{mk}(\mathbf{S})
$$

The equations for electrons motion will include ions motion through structural parameter $\mathbf{S}(t)$:

$$
i \frac{dc_m(t)}{dt} = c_m(t) E_m(\mathbf{S}) - i \sum_k c_k(t) \left( \frac{d\mathbf{S}}{dt} \cdot \mathbf{d}_{mk}(\mathbf{S}) \right) + \sum_k V_{mk}^{\text{ext}} c_k(t).
$$

Connection between electrons and ions equations exists owing to overlapping integrals of orbitals $d_{mk}$. Oscillators connections are determined by overlapping integral $V_{mk}$ corresponding to an external potential.

$$
\mathbf{d}_{m \neq k}(\mathbf{R}(t)) = \int \psi_m \frac{d}{d\mathbf{S}} \psi_k d\mathbf{S},
V_{mk}^{\text{ext}}(s) = \langle \psi_m | V^{\text{ext}} | \psi_k \rangle.
$$

Existence of the term corresponding to ions movement $S(t)$ makes the full system nonlinear.
We calculate the density of electric current due to switching process of atomic orbitals which are forced by external electric field. This was important for estimation of electric conductivity switching. Obtained data give us a possibility to calculate spatial model of joule source of heating, which we use on the next, macroscopic level of simulation.

4. Macroscopic transport equation
We determine spatial and time dependencies of the temperature using heat conductivity equation with the source as the Joule heat generated by $j$.

$$\rho C \frac{\partial T}{\partial t} = \nabla_\perp (K_\perp \nabla_\perp T) + \nabla_\parallel (K_\parallel \nabla_\parallel T) + q_0 \cdot (j \cdot E)$$ (5)

where current density is determined by

$$j = \sigma(E, T, S(t))E$$ (6)

Transport coefficients $\rho, C, K_\perp, K_\parallel$ correspond to graphite-like structure. Temperature profiles in $x$-direction (perpendicular to current filament) during time are shown in fig. 4. Equation includes electric conductivity which is proportional to the temperature $T(x, y, z, t)$ and structure factor $S(t)$. Changes in the structure are taken from atomistic configuration and depend on temperature.

Heat conductivity equation is solved on the finite difference grid by implicit scheme. Founded temperature profiles are used again in MD calculations. Then, molecular dynamics of the system was recalculated with new temperature localized profile. New structure of ions is shown in fig. 5. Note that figure presents the periodic extension of unit cell. It is seen that for new distribution of temperature the boundaries are corresponded to the diamond-like sides but the central part of conducting dot are graphitized. Critical diameter of conducting dot and threshold voltage for excitation of thermal instability can be estimated analytically. These critical parameters are found close to experimental data.

5. Conclusions
Multiscale model of phase change on the base of amorphous carbon is suggested. Taking into account the spatial change dependence of temperature is fundamentally important for explanation of experiment. It is shown that localization of spatial dependence of electric conductivity leads to thermal instability, which supports the structure.

References
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