# SLIDING DYNAMICS IN ZnO PIEZOELECTRIC NANOGENERATOR

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*Summary* A molecular dynamics model has been developed to study the interfacial sliding dynamics in piezoelectric nanogenerator in conductive atomic force microscope experiment. The molecular system includes a vertical semiconductor ZnO (0001) nanowire supported by a substrate and a Pt (111) metal tip. Simulation results show that the dynamic process of the Pt (111) tip sliding over the (0001) top surface of the ZnO nanowire, from the tensile side to the compressive side of the nanowire due to its lateral bending, involves the shear off of one monolayer of Pt atoms and the subsequent relaxation of the Pt (111) surface. However, no atomic inter-penetration or material transfer between the metal tip and the semiconductor material was observed. The calculated piezoelectric potential distribution due to the polarization of nanowire under bending is similar to the result derived from the continuum theory approach.

## INTRODUCTION

Search for renewable and green energy resources is one of the most urgent challenges under the threat of global warming and energy crises. In 2006, Zhonglin Wang's research group at Georgia Institute of Technology developed an innovative approach for converting mechanical energy into electrical energy, through sliding a conductive atomic force microscope (AFM) metal tip over piezoelectric zinc oxide nanowire arrays [1]. The so called "piezoelectric nanogenerator" [1] provides one of the most effective and promising approaches for scavenging energy and developing independent, sustainable, and continuous-operation nanodevices and nanosystems in sensing, medical science, defence technology and even personal electronics [2]. Due to its unique semiconducting and piezoelectric dual properties, as well as the biocompatible and environmental friendly features [2], the wurtzite-structured ZnO crystal becomes one of the most important semiconductors adopted in the design and fabrication of nanogenerators. As the research focusing on the fabrication of high-power output nanogenerators has made significant progress [3], there is a compelling need to understand the atomic structure and dynamic properties at the noble metal-ZnO interface, which ultimately determine the electronic transport properties at the interface. The current state-of-the-art in the area is quite lacking.

For a fairly large vertical ZnO nanowire under lateral bending, the first-order perturbation calculations for the piezoelectric potential compared remarkably well with the results from the finite element analysis [4]. These calculations, however, are largely suitable for the field prediction away from the metal-semiconductor contact interface, where the Schottky barrier [5] is a key component for the realization of electric power generation [1]. Therefore, fundamental understanding of the structure and dynamics at metal-ZnO interface is critical to the rational development of nanogenerators. The effects of contact configuration, the interfacial structural evolution under dynamic loading, and interfacial chemical and physical properties, on the piezoelectric potential and electron transport at the metal-ZnO interface must be thoroughly studied. Molecular simulations, from both quantum mechanical and large-scale classical levels, thus have the privileges to provide the atomic-level insights into the nanogenerator process. While several versions of nanogenerators have been developed recently [1, 3], our present work focuses on a molecular dynamics (MD) study on the lateral sliding of a Pt (111) metal tip over a ZnO (0001) nanowire.

## SIMULATION METHOD AND RESULTS

### Simulation model

A realistic molecular model is developed to mimic the sliding dynamics in nanogenerator experiment. Figure 1A shows an ideal presentation in the experiment [1], Figure 1B shows a real Pt (111) AFM tip scanning a vertical ZnO nanowire. The metal tip is dragged by a dynamic spring that moves right with constant speed. The Pt tip follows a driven dynamics motion which is controlled by the normal (not shown here) and lateral springs in AFM [6]. The wurtzite ZnO nanowire is built on a ZnO substrate (Fig. 2B). The nanowire is 120 Å long, has a hexagonal cross-section area with a side length of 30 Å. The spherical Pt (111) tip has a radius of 35 Å. The Buckingham potential with charge interactions for ZnO [7] and the EAM potential for Pt [8] are used in the simulation. The long-range Coulomb interaction is calculated with the Wolf method [7]. The interaction between ZnO and Pt is described based on a universal force field [9].

### Sliding friction at ZnO-Pt contact interface

Figure 2 shows at room temperature (T=298K) the four snapshots of the ZnO-Pt contact when the Pt tip is dragged by the spring to slide over the ZnO nanowire. In the MD regime, the lateral driving velocity is 15 m/s. It is seen that during this dynamic sliding process ZnO nanowire undergoes significant bending deformation (Fig. 2B), while at the same time the Pt tip maintains an intimate contact with the ZnO (0001) surface, from the tensile side to the compressive side. It is on the compressive side that the Pt-ZnO Schottky contact is positively biased, allowing electrons to flow from ZnO to metal tip [1]. Interestingly, it is seen that one monolayer of Pt atoms at the outmost contact is sheared off (a nanoscale

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wear), leaving a more blunted metal tip with subsequent fast atomic relaxations. However, no atomic inter-penetration (material transfer) occurs between the metal tip and the semiconductor material. The ZnO nanowire remains almost intact during sliding.

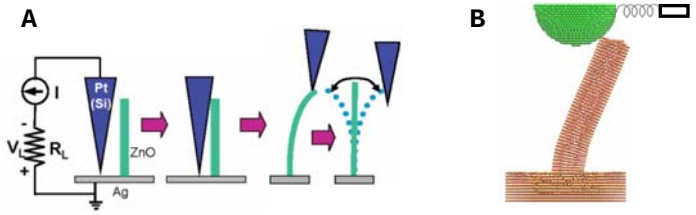


**Figure 1** Sliding friction of a Pt (111) metal tip over ZnO (0001) nanowire: A. Experimental cartoon; B. MD simulation result.

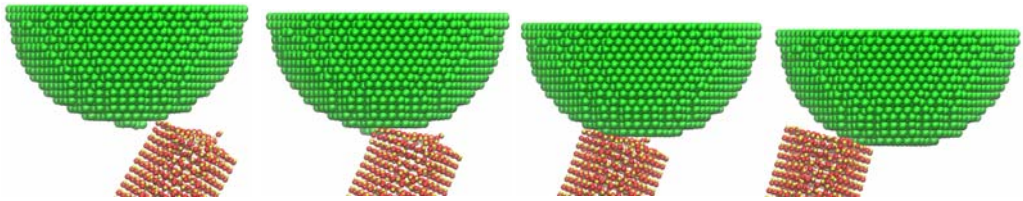

**Figure 2** Snapshots of the contact between the Pt (111) metal tip and the ZnO nanowire during sliding friction.

## Piezoelectric potential in the bent ZnO nanowire

Figure 3 shows the detailed piezoelectric potential distribution in the bent ZnO nanowire, corresponding to the fourth snapshot configuration in Fig. 2. At the atomic scale, the polarization distribution in ZnO nanowire is calculated based on each ZnO unit cell, viz $\boldsymbol{p} = (1/V)\sum q_i \boldsymbol{d}_i$, where $q_i$ and $\boldsymbol{d}_i$ are the atomic charge and coordinate of the $i$th atom, respectively, in the unit cell with a volume $V$. For a two-dimensional spatial grid in the $x$-$z$ plane, the piezoelectric potential at node $\boldsymbol{R}$, induced by the $j$th unit cell at distance $\boldsymbol{r}$, is given by $\boldsymbol{U}_j = \sum \boldsymbol{p}(\boldsymbol{R}-\boldsymbol{r})/|\boldsymbol{R}-\boldsymbol{r}|^3$. The potential associated with each node $\boldsymbol{U}(\boldsymbol{R})$ is the summation of $\boldsymbol{U}_j$ over all unit cells (in fact what is obtained is the potential density, or the potential normalized by the volume of unit cell). This piezoelectric potential distribution is obtained by averaging over atomic configurations in 200 ps MD equilibrium run. It is seen that the tensile strain at the left side results in a positive potential, while the compressive strain at the right side results in a negative potential. These results are similar to those from continuum theory calculations [4], but show more detailed potential variation at the contact interface.

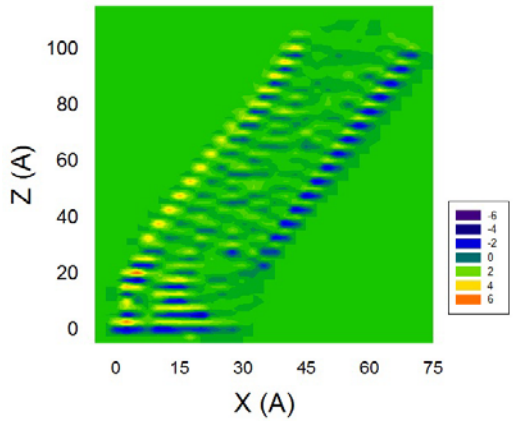


**Figure 3** Piezoelectric potential density distribution $\boldsymbol{U}[(e/Å)\times(4\pi\varepsilon_0 V)^{-1}]$ in ZnO nanowire.

## CONCLUSIONS

Molecular dynamics simulation provides atomic insights into the interfacial structure and dynamics in nanogenerator. This information is critical to the rational design of the novel nanosystem. Future work will focus on high-level quantum mechanical structure and transport calculations, based on the classical-level inputs, such as MD simulation results.

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