MOLECULAR SIMULATIONS OF THE FORMATION OF GOLD-MOLECULE-GOLD JUNCTIONS IN MOLETRONICS DEVICE

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Summary We perform classical molecular simulations by combining grand canonical Monte Carlo (GCMC) sampling with molecular dynamics (MD) simulation to explore the dynamic gold nanojunctions in a benzenedithiol (BDT) solvent. With the aid of a simple driving-spring model, which can reasonably represent the long-range elasticity of the gold electrode, the spring forces are obtained during the dynamic stretching procedure. A specific multi-time-scale double reversible reference system propagator (double-RESPA) algorithm has been designed for the metal-organic complex in MD simulations to identify the detailed metal-molecule bonding geometry at metal-molecule-metal interface. We investigate the variations of bonding sites of BDT molecules on gold nanojunctions at Au (111) surface at a constant chemical potential. Simulation results show that an Au-BDT-Au interface is formed on Au nanojunctions, bond-breaking intersection is at 1-1 bond of the monatomic chain of the cross-section, instead of at the Au-S bond. Breaking force is around 1.5 nN. These are consistent with the experimental measurements.

INTRODUCTION

The combined Au-BDT-Au electrode system has been intensively investigated both experimentally and theoretically[1][2][3]. Because of its importance towards building of single molecules based functional devices[3]. The understanding of metal-molecule-metal junctions effects on electron transport through molecular junctions requires the exploration of the current-voltage (I-V) characteristics, which are particularly determined by the bonding geometry at metal-molecule interface. Our molecular simulation combining grand canonical Monte Carlo (GCMC)sampling with molecular dynamics (MD) will focus on the metal-molecule geometries and their mechanical properties, in order to provide accurate inputs to quantum calculations of the conductance properties for Au-BDT-Au electrode system.

SIMULATION METHODS

Simulation Systems

A model system (Fig. 1 (a)) has been built according to the experimental setup[1]. The system involves the long-range elasticity of the gold electrodes in BDT solvent. The total number of gold atoms in the system is 832. The two layers at the far ends of the gold tips are kept rigid, and the atoms between them are dynamic. The upper gold tip is connected to a driving support through a spring and follows a driven dynamics motion due to the pulling of the driving support.

Combining Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD) Simulations

In order to reflect the experimental environment[2], in our simulation we propose a method of combining GCMC and MD techniques alternatively to keep the BDT density at a bulk value during the pulling process. Temperature is controlled at 298K. During the elongation process, we assume that the binding sites of BDT molecules on an Au nanowire are unchanged. The equilibrium absorption configuration obtained from GCMC run then is taken as the input for the MD simulations. After the 3Å retraction MD simulation run is finished, MD is switched back to GCMC for a new equilibrium adsorption run based on the configuration of the system from MD. These two procedures proceed alternatively until the breakage of gold single atomic contact begins to form. According to the experiment[2], we remove all the nonbonded BDT molecules and stretching without the insertion and deletion of new BDT molecules. We observe the formation mechanism of single Au-BDT-Au junction.

Force Fields and double-RESPA in Molecular Simulations

The potential model for BDT molecules employed are based on the universal forcefield (UFF) plus Mulliken partial charges derived from recent *ab initio* calculations. The non-bonded interactions between gold atoms and BDT molecules are modeled by Lennard-Jones pair potentials from UFF. The Au-Au interaction is simulated by Tight-binding second moment of approximation potential (TB-SMA). The chemical bonding between the sulfur atom in BDT and Au atoms are modeled by Morse potential. The 3-D Ewald summation technique (EW3DC) is used to compute the electrostatic energies. A general double-RESPA scheme for the systems with short-long-range force separations and disparate mass problems has been considered, a much smaller time step is needed for the fast variation with large magnitude of intramolecular forces, within the intramolecular forces, the H atoms have much higher vibration frequencies than others.We extended the double-RESPA scheme in order to fit our Au-BDT interaction system.[3]

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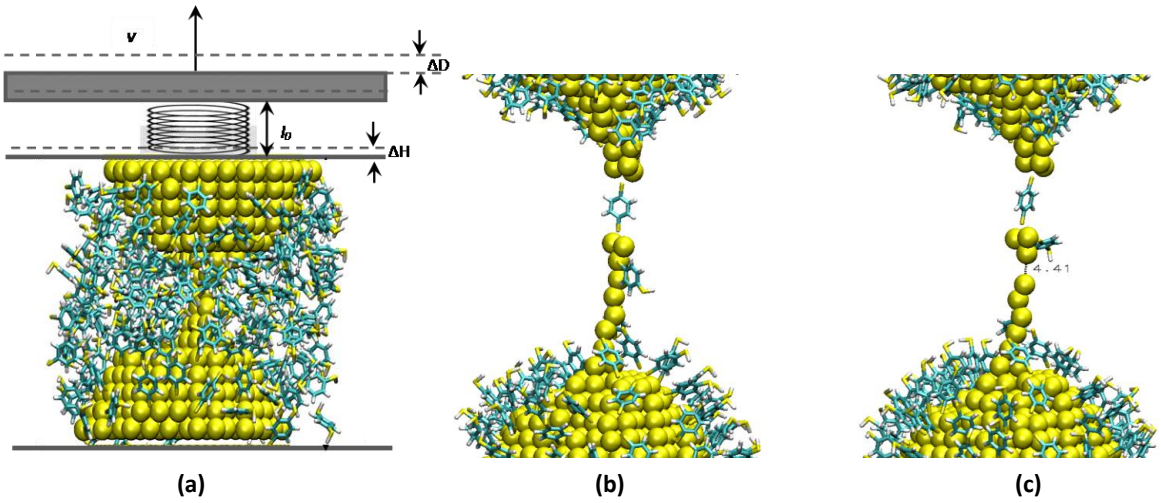

Figure 1. Dynamic spring simulation system and snapshots of break-junction configurations. (a)The schematic of the simulation system. The upper gold tip is pulled by a driving support through the spring. A driving distance (ΔD) leads to the elastic elongation of the spring (Δl) and the elastic deformation of the gold nanojunction (ΔH);(b)The snapshot of the Au-BDT-Au junction and monatomic chain after the evaporation of nonbonded BDT solvent at room temperature;(c)The snapshots after the break-junction configuration.

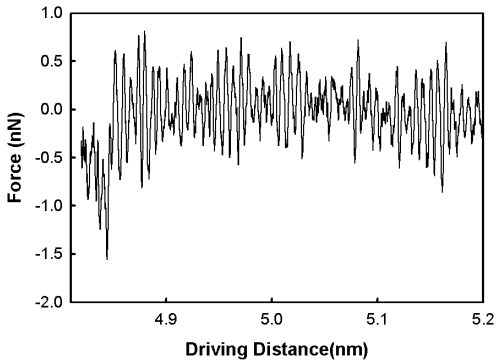

Figure 2. Spring force as a function of the driving distance, starting at the breaking of the monatomic chain.

RESULTS AND CONCLUSIONS

We repeat the GCMC-(multiple-time-scale with driving spring model)MD pattern for each 3 Å stretching of driving block to explore the behaviour of gold nanojunction in BDT solvent and the details of binding geometry at the Au-BDT-Au interface. In GCMC simulations BDT molecules form chemical bonds with Au atoms on the surface, some BDT molecules with their S atoms at both ends bonded with Au atoms. A single BDT molecule bonding in between of the Au nano electrodes is formed during the stretching of the nanojunction. We further study the mechanisms of the break-junction procedure including the breaking force, and the binding energy with bonded molecules only. We find that the structure of the atomic contact interface just before the break-junction step is a Au-BDT-Au contact sequenced by a 5-atom gold monatomic chain. Figure.1(c) shows the monatomic chain breaks at 1-1 bond closest to the top electrode, while the breaking force is around 1.5 nN at 4.85nm (Figure.2). This result is consistent with those obtained from experiments[2].

References

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