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Nanotribology of self-assembled monolayer with a probe tip investigated using molecular dynamics simulations

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ABSTRACT

The nanotribology of an alkanethiol self-assembled monolayer (SAM) under tilt contact with a scanning probe tip is studied using molecular dynamics (MD) simulations. The tilt contact is described in terms of the tilt angle and the magnitude of the specimen–tip separation. The effects of tilt angle and magnitude of the specimen–tip separation on the normal force, friction force, friction coefficient, shear strength of the tip–SAM junction, and self-recovery characteristics are evaluated during the scanning probe tip process at a temperature of 300 K. The simulation results clearly show that the magnitudes and periods of the normal force and friction force increase with decreasing magnitude of the specimen–tip separation due to a large change of the tilt angle of the SAM chains during the deformation and recovery stages. For scanning and indentation processes, the effect of the tilt angle of the probe tip on the normal force is more significant than that on the friction force for the SAM. The behaviors of interfacial contact forces, friction coefficient, and shear strength strongly depend on the number of interacting atoms and the contact area, which increases with decreasing magnitude of the specimen–tip separation and increasing tilt angle of the probe tip. The self-recovery of SAM is significantly affected by the magnitude of the specimen–tip separation; the recovery ability of SAM is worse for magnitude of the specimen–tip separation below −0.9 nm with a large tilt angle of the probe tip.

1. Introduction

Self-assembled monolayers (SAMs) have been applied in biological (Mrksich, 2009; Matsunaga et al., 2007; Chang et al., 2008), physical (Henry et al., 2006), optical (Long et al., 2009; Li, 2009), and chemical (Bowen et al., 2008) sensors. SAMs have proven to be effective nano-lubricants in nano/microelectromechanical systems (N/MEMS) and in nanoimprinting lithography (NIL) (Guo, 2004; Kohno et al., 2010) helping to avoid failure during the operation of these devices (Maboudian et al., 2000; Tambe and Bhushan, 2005). Among the useful characteristics exhibited by SAMs are low friction (Wu et al., 2008), low adhesion, hydrophobicity, and strong bonding to a substrate (Ashurst et al., 2001).

A SAM consists of three building groups: a head group that binds strongly to a substrate, a tail group that constitutes the outer surface of the film, and a spacer chain (backbone chain) that connects the head and tail groups. The surface properties of SAM can be controlled by their tail groups. The monolayer thickness (on the order of a few nanometers) is a function of the backbone chain. SAMs can be deposited via either a liquid-phase process or a vapor-phase process. For liquid-phase deposition, the head group of a SAM film is formed by the spontaneous adsorption of molecules from a solution onto gold film (Azzam et al., 2006; Noh et al., 2006; Birss et al., 2003) under ambient conditions because gold exhibits strong interaction with thiol. Bhushan and Liu (Bhushan and Liu, 2001) used an atomic force microscope (AFM) to measure the frictional and adhesion forces of SAMs with various end groups and found that hexadecanethiol exhibited the lowest adhesion force and was insensitive to changes in relative humidity. Zhuang et al. (Zhuang et al., 2006) investigated the thermal stability of SAMs and found that fluorocarbon coatings are far more stable than hydrocarbon coatings.

In general, the reported experimental data includes noise and turbulence on the nanometer scale. Molecular dynamics (MD) simulation is an effective tool for studying material behavior at the nanometer scale; it provides detailed deformation information at the atomic level. Atomic-scale simulation effectively avoids experimental noise problems and can be used to analyze and understand the molecular trajectories and dynamic properties of SAMs.

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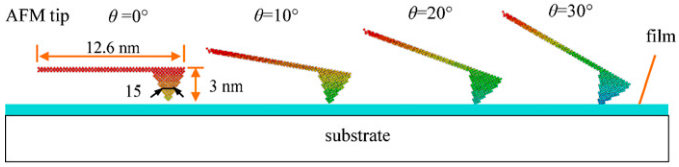

Fig. 1. Schematic illustration of an unstable dynamic AFM tip scanning over a film. The unstable tip is described by θ values of 0°, 10°, 20°, and 30°.

Hautman and Klein (Hautman and Klein, 1989) proposed a SAM model and simulated the alkylthiol interactions under compression at various temperatures (Hautman and Klein, 1990). To better model the deformation and distortion of bonds caused by compression, Tupper and Brenner (Tupper and Brenner, 1994) modified the harmonic bond stretching terms to account for possible shortening of the bonds. Previous a few MD results showed that studied nanotribology of SAMs using the tip in contact with SAMs (Chandross et al., 2008; Knippenberg et al., 2008) pointed out that the ubiquitous JKR and DMT models do not accurately describe the contact mechanics of these SAM systems. Chandross et al. (Chandross et al., 2008) studied nanotribology of alkylsilane SAMs on a SiO_2 substrate and found that the chain length has minimal effects on the friction force and coefficient. Knippenberg et al. (Knippenberg et al., 2008) studied atomic contact forces between a spherical tip in sliding contact with a SAM on a diamond substrate and found that that different regions around the tip contribute in unanticipated ways to the total friction. Mikulski et al. (Mikulski et al., 2005a,b) examined the differences in friction between tightly and loosely packed hydrocarbon chains on diamond and found that under high loads, the tightly packed monolayer exhibits significantly lower friction than the loosely packed monolayer. Jia et al. (Jia et al., 2009) investigated the interface structures and interaction energies between alkanethiol and epoxy. Aydogmus and Ford (Aydogmus and Ford, 2008) conducted a molecular simulation of SAMs with alkyl functionality on the surfaces of a mesoporous inorganic substrate. We recently reported the frictional behavior in various sliding directions for a SAM (Wu et al., 2007) and found that the frictional period varies with the tilt angle of SAM. Coating SAMs on a surface can avoid interface effects such as friction and adhesion (Wu et al., 2008).

In AFM experiments, films often exhibit tilted contact respect to the probe tip due to surface roughness, nonuniform coatings, wear of the tip, or mechanical vibration. In the present study, MD simulation is used to investigate the nanotribology of SAM under tilt contact. The effects of the magnitude of the specimen–tip separation and tilt angle of the probe tip on the normal force, friction force, friction coefficient, shear strength, and self-recovery characteristics are evaluated. A magnitude of the specimen–tip separation of 0.0 nm is defined as a height at which the normal force exerted by the probe tip on SAM averages 0 nN.

2. Methodology

2.1. MD model

Fig. 1 shows a schematic MD model of an AFM tip with tilt angles (θ) of 0°, 10°, 20°, and 30° used to study the scanning of a film. The simulation consists of a Si (silicon) tip and a SAM on an Au substrate with a face-centered cubic (FCC) lattice. The dimensions of the Au substrate are 12.2 (length) × 13.7 (width) × 2.3 (height) nm. Four layers of atoms fixed at the substrate bottom support the entire system. A Cartesian coordinate system is used in the system. The origin is set at the center of the lower-left atom of the fixed layers. Eight layers of isothermal atoms with a temperature of 300 K are set above the fixed layers to depict surface atoms influenced by sulfur atoms during thermo vibration. A periodic boundary condition is imposed on surface plane *Y*. The probe tip consists of 798 silicon atoms and arranged as a pyramid tip with an included angle of 15°. The dimensions of the probe tip are 12.6 (length) × 1.7 (width) × 3.0 (height) nm and assumed to be ideally rigid (including the cantilever beam) in order to focus on the scanning friction behavior with a SAM. The film is scanned by the probe tip along the *X*-axis, and the time step is 1 fs.

The SAM consists of alkanethiol chain $S(CH_2)_{15}CH_3$ and is chemisorbed on the Au substrate. The SAM arrays are set to 28 × 28. The CH_2 and CH_3 groups are treated as a single spherical molecule, simplified as 17 united molecules per chain. Initially, the molecules are all-trans and arranged with a spacing of 0.5 nm to the nearest neighbor distance of the triangular lattice formed by the sulfur head groups on the Au substrate. The system is equilibrated to its minimum energy configuration at 300 K before the MD simulation; the average thickness of the SAM film is about 2.0 nm. The tip scans over the SAM at a constant speed of 30 m/s. This scanning speed is much higher than the μm/s speeds that are used in AFM experiments. However, the speed is typical for MD simulations of this scale due to computational limitations (Knippenberg et al., 2008; Mikulski et al., 2005a,b).

2.2. Potential energy models

The alkylthiol chain description proposed by Hautman and Klein (Hautman and Klein, 1989) is used in this study. Because the bonds undergo distortion and the chain length decreases under high compression, the Hautman and Klein model is modified to correct the potential functions to allow for bond stretching and the 12-3 chain-surface (Tupper and Brenner, 1994). The bond-bending terms are modeled using a harmonic potential. The torsional terms are assumed to have a Rychaert–Bellmans dihedral potential form, which is a power series expansion of the dihedral angle (Hautman and Klein, 1989). The intermolecular interaction and intramolecular non-bonding interaction for atoms separated by more than three bonds along a chain are represented by the Lennard-Jones potential. The Lennard-Jones potential function (Sung and Kim, 2005) is also employed to describe the physisorption interaction with a cut-off radius of 1 nm between the Si tip, SAM, and Au atoms. The Morse potential (Sung and Kim, 2005), $U_{\text{Morse}}(r_{ij})$, is used as the binding potential energy of the sulfur head group on the gold substrate. The second moment approximation for tight-binding (TB-SMA) many-body potential (Fang et al., 2008), $U_{\text{TB-SMA}}(r_{ij})$, has been proven to be capable of reproducing a variety of experimental observations (Gomez and Diep, 1995; Miguel and Miranda, 2002) for the interaction of Au atoms.

3. Results and discussion

3.1. Effect of the magnitude of the specimen–tip separation

Fig. 2(a)–(d) shows the probe tip moving above SAM at a magnitude of the specimen–tip separation of −0.9 nm for θ values of 0°, 10°, 20°, and 30°, respectively. During the scanning process, some molecules are pushed and dragged by the probe tip rather than being removed directly from the substrate. This can be attributed to the strong van der Waals (VDW) interaction between the SAM and the chemical interaction between S and Au atoms. The averaged VDW energies for a single chain, that between two chains, and that between chain atoms and the metal surface are 26.47 kJ/mol, 41.60 kJ/mol, and 1.71 kJ/mol, respectively. These energies are significantly different from the evaluations of Sung and Kim (Sung and Kim, 2005) due to the simple model (only two chain molecules with vertical arrangement) used in their study. Note that mainly