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Nanoscale mechanical tailoring of interfaces using self-assembled monolayers

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ABSTRACT

Functional groups in self-assembled monolayers (SAMs) provide a way to tailor the structural, thermal and electrical properties of interfaces, as the interaction between SAMs and target surfaces can range from weakly bonded to strong bonding. The present study focuses on evaluating the interfacial mechanical properties of SAMs with different affinities to a gold film. We use molecular dynamics (MD) with the ReaxFF potential to evaluate the spallation response of the SAM-gold interface characteristics for two SAMs, namely dodecyltriethoxysilane (DTES) and 11-mercapto-undecyltrimethoxysilane (MUTMS), which respectively have weak and strong bonding with gold. MD simulations predict the MUTMS-gold interface to be four times stronger than the DTES-gold interface. Laser spallation experiments performed to evaluate the cohesive strength of the two SAMs show a similar ratio of cohesive strength; however MD results are about 50 times higher than experimental observations. AFM surface analyses of interacting interfaces demonstrate that surface roughness values are of the same order as atomistic interactions. The role played by surface roughness is then incorporated in a simple continuum model.

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1. Introduction

Self-assembled Monolayers (SAMs) are assemblages of short hydrocarbon chains capped by functional head and tail groups. These chains uniquely arrange themselves lengthwise to form highly ordered and stable structural assemblies at the nanoscale. The capability to tailor the head and tail groups of SAMs makes them excellent for applications associated with molecular ordering, growth, wetting, adhesion, lubrication and corrosion (Ulman, 1996). Applications of SAMs can be grouped into two broad categories: surface modification and interfacial tailoring. The present research is relevant to applications of the second category, wherein SAMs are used as tailoring agents for modification of interfacial properties. Most notable is the capability to produce bio-compatible interfaces (Schaeferling et al., 2002; Mrksich et al., 1996) where selectively chosen terminal groups can be used to produce the desired tailoring (Chen et al., 2003). These technologies are able to produce synthetic surfaces with possible extensions and spreading of biological cells in different directions based on chosen functional groups on SAMs (Ostuni et al., 1999). Along the same line of interface tailoring are applications in the electronics industry where SAMs offer a range of electrical and thermal transport and chemical stability to different substrates through functional groups (Losego et al., 2012; Aswal et al., 2006; Campbell et al., 1997). SAMs have also been studied in nanotribological applications in MEMS and NEMS, where the influence of terminal groups offers significant possibilities in reducing mechanical wear and tear at submicron regimes (Liu and Bhushan, 2002).

In the present work, we examine the interfacial mechanical properties between a layer of gold and SAMs of different functional groups. We use molecular dynamics (MD) owing to the small size and structured nature of SAMs. Most of the atomistic-level analyses available in literature have focused on evaluating the overall structural properties of SAMs and tilt angles. Examples include the prediction of the structure of SAMs of alkanethiols on gold (Gerdy and Goddard, 1996) and other metallic substrates (Alexiadis et al., 2007). A few studies have focused on using MD techniques to probe the constitutive response of SAMs. For example, in Tupper et al. (1994) and Tupper and Brenner (1994b), MD was used to

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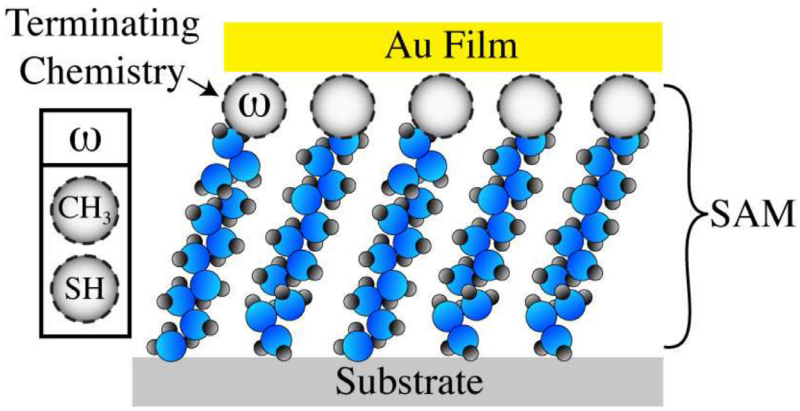

Fig. 1. Schematic of Au film on SAM-functionalized substrate. Two terminating chemistries of the SAMs are investigated: methyl ($-CH_3$) for DTES, and thiol (–SH) for MUTMS. This figure is reproduced with permission from Grady et al. (2014b), copyright 2014 American Chemical Society.

investigate the effect of the substrate roughness on the compressive response of hexadecanethiol on gold and the friction between SAMs. Siepman and McDonald (1993) studied the mechanical relaxation of an alkanethiol SAM on gold subjected to compression. Henda et al. (1998) used a static energy calculation approach to investigate the same alkanethiol/Au SAM system under compression. Tupper and Brenner (1994a) simulated the structural transition of n-hexadecanethiol SAMs on Au during compression. More recently, Fang et al. (2010) utilized a combination of united-atom and all-atom force fields in their MD simulations of nanoindentation on alkanethiol SAMs adsorbed on gold substrate.

Possibly the most comprehensive study to date aimed at relating MD-modeling results to a continuum description of the nonlinear response of SAMs can be found in Wang et al. (2006), where the authors combined an MD tool to investigate the compressive response of a repeating (periodic) cell of octadecyltrichlorosilane (OTS) on Si/SiO_2 substrate, with a cohesive, axisymmetric finite element model of the interaction between a tungsten tip and the $OTS/SiO_2/Si$ multilayered system to simulate nanoindentation experiments performed with an interfacial force microscope. The outcome of the MD simulations was put in the form of a nonlinear hypoelastic model of the OTS and the resulting continuum model of the SAM was shown to capture very well the observed force-displacement curve.

The literature however lacks MD investigations of interfacial characteristics of substrates with SAMs having different functional groups. In particular, there are no atomistic studies focused on the use of SAMs on tailoring interfacial separation for a film/substrate system. In the present work, we use MD to evaluate cohesive properties of SAM interfaces with a layer of gold. The effect of two functional groups, namely methyl, ($-CH_3$) and thiol, (–SH) is studied. We employ the ReaxFF potential (van Duin et al., 2001), capable of bond breaking and formation, to model the interactions between constituent atoms. MD simulation results are compared to laser spallation experiments performed at the microscale to evaluate the cohesive strength of interfaces, while AFM scans are used to probe surface morphologies at the interface. The MD predictions are qualitatively similar to laser spallation observations but the magnitudes of interfacial strengths evaluated by MD are significantly higher than experiments. AFM scans reveal surface irregularities to be of the same range as atomistic interactions and a simple continuum model demonstrates that surface roughness effects can significantly reduce the strength of an otherwise perfect interface.

The manuscript is organized as follows: Section 2 contains the problem description and the details of modeling the SAM–gold interface using MD. Section 3 discusses the MD results, which are compared with experimental spallation observations in Section 4. The influence of surface roughness is investigated in Section 5 with the aid of AFM experiments, which lead to a continuum analysis aimed at obtaining homogenized interfacial cohesive properties of a SAM-enhanced Au/SiO_2 interface.

2. Problem description and MD modeling

The main objective of the present work is to evaluate the mechanical response of interface between SAMs and a layer of gold. The SAM is envisioned to serve as a tailoring layer between silica and gold, providing tunable interfacial stiffness through modification of SAM functional groups. We investigate the interfacial strength and adhesion energy characteristics between SAM and gold through separation tests on MD models containing two functional groups namely methyl and thiol (Fig. 1), focusing on the different chemical affinities of interacting species. In the MD model, the interfaces are assumed to be perfect, in the absence of any defect or surface roughness.

2.1. Atomistic model of SAM for molecular dynamics

To study the interfacial behavior at the SAM/gold interface, we prepare a model that enables dynamic relative separation between the two atomistic structures. Since we aim to study SAMs with different affinities to gold, the MD model needs to address the different types of chemical bonding possible at the interface. We start with a setup consisting of 3D periodic atomistic model consisting of silica (SiO_2). By eliminating its periodicity along the z direction, cleaved surfaces are created at the top and bottom containing unsatisfied valencies of Si atoms. Each Si atom at the top cleaved surface is attached to a SAM hydrocarbon chain as shown in Fig. 2(a) such that the functional group of each chain is situated at the opposite side of the silica layer. Similarly, chemical valencies of Si atoms at the bottom surface of silica layer are satisfied with H atoms. Each hydrocarbon chain composing the DTES SAMs contains 12 carbon atoms while the MUTMS model is prepared by replacing the terminal methyl ($-CH_3$) linkages of DTES by thiol groups (–SH). Next, the [1 1 1] plane of a gold layer is placed on top of the free surface of SAM as shown in Fig. 2(a). The 2D periodic parameters of gold and the underlying SAM layer are different due to the periodicity of silica. To contain both layers in the same MD domain, the gold layer is shrunk by 10% to adjust with the SAM periodicity. This adjustment shrinks the gold layer laterally, yet the variation of stiffness parameters evaluated in the vertical direction is assumed to be marginal, due to the smaller number of SAM chains than interfacial gold atoms (Fig. 2). The gold layer is made