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Effects of interface roughness on cohesive strength of self-assembled monolayers

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ABSTRACT

Self-assembled monolayers (SAMs) are aggregates of small molecular chains that have the property to form highly ordered assemblies. The choice of terminal groups on the chains makes them excellent contenders of molecular-level tailoring. Molecular dynamics (MD) simulations and experimental observations of spallation of two SAM-enhanced gold-film/silicon-substrate interfaces have shown that the cohesive strength of SAM-enriched transfer-printed interfaces is strongly dependent on the choice of terminal groups. Though the MD results of perfectly ordered atomistic surfaces show the same qualitative trend as the experiments, they over-predict the interfacial cohesive strengths by a factor of about 50. Results from AFM studies have revealed that the roughness of these interfaces is of the same order (~1 nm) as the range of atomistic interactions. Hence, surface roughness is a key contributor in significantly reducing interfacial cohesive strength in these systems. In this manuscript, a continuum-level study is performed to investigate the influence of surface roughness on the cohesive strength of the interface between a Si/SAM substrate and a transfer-printed gold film. We approximate the film as a deformable continuum interacting with a rough substrate of SAMs represented by a harmonic function. Using a cohesive law derived from MD, spallation is simulated to evaluate the effective traction-separation characteristics for the rough SAM–gold interface. Our analysis shows that incorporating roughness may reduce the interfacial cohesive strength by an order of magnitude depending on the film properties and the surface roughness. Additionally, we observe that the gold film adopts unique separation attributes based on roughness parameters and material properties.

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1. Introduction

Self-assembled monolayers (SAMs) are aggregates of small molecular chains formed spontaneously by chemical adsorption of an active surfactant in an organic solvent on a solid substrate. The monolayers are usually closely packed and have a highly ordered structure. SAMs consist of three building blocks: a head functional group that has strong affinity to the substrate, a tail function group that establishes the outer layer of the film and a short nanometer-range hydrocarbon chain that connects the head and tail groups. Examples of this formation include the widely used alkanethiol chains on gold surfaces [1,2]. A large number of attractive features can be achieved by using SAMs with different functional groups, especially for applications associated with molecular ordering, growth, wetting, adhesion, lubrication and corrosion [3].

The interfacial properties of SAM-enhanced systems have stimulated extensive research in the recent past. Chemical abilities of SAM terminal groups were studied and examined to produce biocompatible interfaces [4,5]. In these studies, synthetic interfaces with possible extensions and spreading of biological cells in different directions based on chosen SAM functional groups were produced and examined. Losego et al. [6] looked at the effects of chemical bonding on heat transport across SAM interfaces. They found that the nature of bonding between SAMs and adjacent solid layers has a major effect on the heat conductance of SAM system. In a later study, Tian et al. [7] examined the SAM-enhanced solid–liquid interface and showed that a stronger bonding in the SAM-system causes an improved thermal transport across the solid–liquid interface. Researchers have also studied SAMs for interfacial electrical transport to substrate through different functional groups [8,9].

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The focus of this manuscript is to evaluate the mechanical properties of SAM-enhanced film/substrate interfaces. Related studies include the work of Bush et al. [10], who measured the elastic modulus, work of adhesion and interfacial shear strength of methyl-terminated alkylsilane SAMs through scanning probe normal and lateral force measurements. Houston and coworkers [11–13] measured differences in frictional behavior of alkanethiol monolayers due to different end group chemistries and chain lengths. Liechti et al. [14] developed a high-vacuum facility to study the interfacial toughness between silicon surfaces and carboxyl/diamine terminated SAMs, and compared their different behavior under vacuum and ambient conditions. Li et al. [15] examined the adhesion, friction and water contact angle of SAM-modified titanium substrate. Owing to the small size and structured feature of SAMs, molecular dynamics (MD) simulations have also been used to study the interfacial mechanical properties of SAM-modified interfaces. Gerdy and Goddard predicted the structure and tilt angles of SAMs of alkanethiols on gold [16]. Zhang et al. [17] performed *ab initio* quantum chemical calculations of alkanethiols on Au(111) and used the force field to perform MD simulations to study the superlattice structures of alkanethiol SAMs on Au(111) for various chain lengths over a range of temperatures. Wu et al. [18] examined the sliding friction behavior of SAM under non-flat contact. Fang et al. [19] modeled nanoindentation of SAM-enhanced gold film and observed the deformation and energy transform in the process. Jia et al. [20] studied the stability of gold/SAM/epoxy resin interfaces with different monolayer chain lengths. In more recent studies, Fang and coworkers utilized a combination of united-atom and all-atom force fields in their MD simulations of nano-indentation on alkanethiol SAMs absorbed on gold substrate [21]. Lane et al. [22] modeled the interaction between water molecules and SAMs and measured the degree of water penetration depending on different initial damage to the SAMs.

All too often, the SAM-modified interfaces are not perfectly flat, and rough SAM surfaces are frequently encountered in real devices [23]. Due to the different nature of the substrate, polishing techniques, and film growth conditions, SAMs exhibit a roughness in RMS ranging from a few to tens of nanometers [24,25], surpassing the chain length of SAM molecules. This roughness profile can significantly affect the formation of SAMs, reduce the real contact area of SAM-modified interface and detriment their desired interfacial properties [26–28]. Duan et al. [29] varied SAM-substrate surface roughness via different etching time and studied its effect on water contact angles. Kulinich et al. [30] calculated the wetting characteristics of various SAM groups and found that surface roughness can lead to considerably increased hydrophobicity of surface. Ulman et al. [31] used surface force apparatus (SFA) to measure the deformation and contact forces of smooth mica and SAMs absorbed to rough gold. Their study found that the pull-off force to separate the two surfaces was dependent on measured roughness of the interface. Xu et al. [24] investigated the adhesion force of Octadecyltriethoxysilane (OTE) SAMs on surface of crystalline Si(100) and silica nano-particle films with atomic force microscopy (AFM). Their experiment indicates that adhesion measured on OTE-modified Si(100) surfaces was approximately 15 times greater than that on the silica particle surfaces, where the latter exhibit rougher profiles in terms of RMS of the height distribution.

This paper is motivated by the recent work of Awasthi et al. [32], where MD simulations were performed on perfectly flat interfaces consisting of a thin gold film and various functionalized SAMs. MD simulations consistently predicted interfacial strengths of Au–SAM interfaces about 50 times higher than those measured by spallation experiments. When probed by atomic force microscopy (AFM), surface roughness measurements of interacting surfaces were found to be about 1 nm, the same order of magnitude as the range of atomistic interactions. Using a continuum model of the interface between a rigid film and substrate, it was shown that nano-scale surface roughness significantly mitigates interfacial interactions and hence that the influence of surface roughness must be correctly incorporated to predict nano-scale interfacial strength. In this work, we study the characteristics of deformation of a thin film on a SAM-modified substrate using a deformable continuum model of the film. Special treatment is given to simulating the spallation process, evaluating the energy exchange and assessing the effective cohesive characteristics of the SAM-enhanced interface.

The article is organized as follows: In Section 2, a brief overview of the MD simulations and experimental observations is provided for completeness. In Section 3, we discuss the deformation of the thin film and its initial profile after it is transfer-printed onto the SAM-enhanced substrate. In Section 4, we focus on the spallation process and evaluate the effective cohesive properties of the film/substrate interface.

2. MD modeling and experimental observations

We begin by summarizing the key results of the MD simulations and the AFM observations which motivate the present work. Fig. 1(a) depicts a schematic of the system composed of a silicon substrate which tethers a layer of SAM about 1 nm in thickness. A thin transfer-printed film of gold rests on the SAM surface directly interacting with the functionalized end of the SAM. As shown in Fig. 1(a), SAMs can be functionalized differently by replacing the head groups. MD simulations were set up for two SAMs with head groups, –CH3 and –SH as shown in Fig. 1(a). These SAMs are respectively called dodecyltriethoxysilane (DTES) and mercapto-undecyltrimethoxysilane (MUTMS). The force-displacement responses of the SAM-Au interfaces of these two cases are shown in Fig. 1(b) and (c), respectively, for different velocities of separation. Note the typical shape of the force-displacement profile first increases with separation, reaches a maximum and then reduces to zero for large interfacial separations. Since MUTMS bonds much stronger with Au than DTES, its interfacial strength is calculated to be about 3 GPa while that of the DTES interface is about 0.9 GPa. Spallation experiments [32,33] for the same interfaces have determined these strengths to be about 80 MPa and 20 MPa, respectively. Though MD simulations yield very similar strength ratio, between MUTMS and DETS, the magnitude of strength is about 50 times higher than those observed experimentally. AFM measurements were performed to probe surface roughness of the top surface of SAM and underside of Au layer (Fig. 1(d)). It was found that the nanoscale surface roughness is about the same order of magnitude as the range of atomistic interactions, i.e., about 1 nm. Spallation test performed on interface with different roughness have determined the interface stress of Au film on the MUTMS-functionalized silicon substrate to be 250% greater than on MUTMS-functionalized fused silica substrates, where the former have a significantly reduced surface roughness (Fig. 1(d)). This might explain the high strength values predicted by MD simulations, which pertain to a perfect interface as shown in insets of Fig. 1(b) and (c). For more details, please refer to references [32,33].

Motivated by experiments and MD simulation results, we investigate the role played by the surface roughness on the spallation strength of SAM-enhanced interfaces. Our model is based on a two-step approach: In the first step (Section 3), the initial equilibrium profile of the deformable gold film transfer-printed on the rough substrate is analyzed, with the interface interaction captured using the cohesive law derived from aforementioned MD simulations. In the second step (Section 4), we use the initial profile obtained in the first step to assess the effective cohesive response associated with a rapid spallation of the gold film.

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