Research Article

Conventional Nanoindentation in Self-Assembled Monolayers Deposited on Gold and Silver Substrates

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Self-assembled monolayers (SAMs) are promising materials for micromechanical applications. However, characterization of mechanical properties of monolayers is challenging for standard nanoindentation, and new efficient analysis techniques are needed. Hereby, a conventional nanoindentation method has been combined in a unique way with efficient data analysis based on consumed energy calculation and load-displacement data. The procedure has been applied on SAMs of 4,4′-biphenyldithiol (BPDT) on Au, 1-tetradecanethiol (TDT), and 1-hexadecanethiol (HDT) on Au and Ag substrates being the first study where SAMs of the same thiols on different substrates are analyzed by nanoindentation providing a new insight into the substrate effects. Unlike TDT and HDT SAMs, which are found to strongly enhance the homogeneity and stiffness of the underlying substrate, the BPDT covered Au substrate appears softer in mechanical response. In the case of TDT and HDT SAMs on Ag the structures are softer showing also faster relaxation than the corresponding structures on Au substrate. The proposed procedure enables a fast and efficient way of assessing the complex behaviour of SAM modified substrates. As a consequence, the results are relevant to practical issues dependent on layer activity and toughness.

1. Introduction

Self-assembled monolayers (SAMs) have already found applications in chemistry, biology and physics [1, 2]. For example, a hydrophobic monolayer of 1-hexadecanethiol (HDT) has a low friction coefficient [1] and therefore may be used as a solid lubricant in a MEMS device [3]. However, it is necessary to take into account that the volume of modern MEMS devices is very small. Therefore, distances between the surfaces of components achieve their absolute limits, making physical contacts between materials more likely [3].

From applications point of view, it is crucial to know the mechanical properties of SAMs [1, 2, 4–12]. Furthermore, statistical evaluation of the experimental data is increasingly needed in mechanical testing as size effects and statistical variation of data are getting more prominent with decreasing dimensions [13]. For instance, the plastic behaviour of

metals can be predicted from the statistical averages of separated defect nucleation and migration events [14]. Therefore standardized experimental procedures and analysis methods describing the statistical properties of the reference materials in nanoscale are needed for quantitative analysis of more complicated systems, such as SAMs. In the literature, mechanical properties of alkanethiol/biphenyl thiol SAMs on Au substrate have been determined experimentally by employing a sharp or spherical indenter (radius 20–200 nm) which has been pressed onto the sample surface using relatively high loads (in the μN range). Consequently, the indentation depths have varied between 10 and 190 nm [4, 7, 8, 11]. Also a few molecular dynamics simulation studies have been performed for systems consisting of alkanethiol SAMs on Au. In these cases, the indentation depths have been very shallow being only of 0.5–1.5 nm [5, 6, 12].

We have previously studied mechanical responses of 1-dodecanethiol and 11-mercaptoundecanoic acid SAMs, which are of same height but different hydrophobicity, using ultralow load contact probing with a relatively large spherical diamond tip [15]. Here we go well beyond these initial results and present the indentation response of HDT and 1-tetradecanethiol (TDT) SAMs which both have a –CH_3 terminal group but height difference of two –CH_2– units, and for 4,4′-biphenyldithiol (BPDT) which forms a less ordered SAM than alkanethiols and has potential stronger interaction with the indenter tip through free –SH groups. The aim for using a relatively large spherical tip (radius of ~2 μm) is to probe a greater area of the monolayer in order to avoid the effect of local structural variations within the SAM layer. Indeed, the local variations of the van der Waals bonds between the molecules would not affect drastically the nanoindentation results, buckling of the molecules at the surface asperities is minimized, and the better statistics is obtained for larger indenter-layer contact area.

The similar idea (usage of virtually flat punch indenter to increase the contact area) was already advocated for MD-simulations of indentation in crystalline clusters to display average response of a crystal [13, 16]. However, it proved for the first time of practical importance through our previous [15] and present publications.

SAM layers thickness ranges usually from 2 to 4 nm and depends on the actual length of the molecules and their orientation on the substrate [5]. The size of the molecules studied in the present study are about 1.60 nm (TDT), 1.70 nm (HDT), and 1.25 nm (BPDT) [17–19], which require ultra shallow indentation depth (beyond all the limits recognized for the indentation technique). Hence, our demonstration that different monolayers are showing dissimilar response already at 2 nm indentation depth range is of great importance to application of this particular method. We have to confess that the consistent, repeatable results we obtained employing the hitherto conventional indentation method to requiring single-molecular SAM films appeared to us as a pleasant surprise that surpasses all expectations. Indeed we confirmed that nanoindentation in its conventional form can provide sound information on the mechanical behaviour of SAMs on various metallic substrates and to properly resolve the substrate effect.

2. Experimental

2.1. Materials and Sample Preparation. For the preparation of the SAMs, a well-established and generally approved preparation procedure was used (for details refer to [20]). The Au and Ag substrates were prepared by thermal evaporation of ~150 nm of Au and Ag on Si(100). The Au specimens were primed with a ~5 nm thick Ti layer for better adhesion. The (111) orientation of the evaporated Au and Ag films on Si wafers was confirmed with X-ray diffraction analysis. Self-assembled monolayers of TDT (CH_3−$(CH_2)_{13}$−SH) and HDT (CH_3−$(CH_2)_{15}$−SH), terminated with hydrophobic–CH_3 tail, as well as BPDT (HS−C_6H_4−C_6H_4−SH), terminated with hydrophilic–SH tail, were formed by immersing freshly evaporated gold and silver substrates in 1 mM EtOH

(absolute) solution of the respective molecules for 24 h at room temperature. After removal from the solutions, the samples were rinsed with EtOH and dried in a nitrogen stream. All thiols were purchased from Aldrich and used as received.

2.2. Nanoindentation. The nanoindentation experiments as well as the surface topography evaluation were conducted using the commercially available nanoindentation equipment (Hysitron Triboindenter-, Hysitron Inc., Minneapolis, MN) enabling us probe the mechanical response of the investigated layers as well as to image the surface features in low-load contact mode. The stated transducer noise floor levels of loading and depth scale were as low as ±50 nN and ±0.1 nm, respectively. The effect of the instrumental drift was found negligible as it is compensated for in the indentation procedure. The total time of the indentation cycle is kept short compared to nominal drift rate (shorter than 0.02 nm/s). The same spherical diamond indenter with the nominal tip radius R of 2 μm was used for surface imaging and profiling as well as loading.

The indented samples were in a dry state and they were subjected to nanoindentation cycles consisting of 5 seconds loading and unloading with 2 seconds dwell time at the peak load of 10 μN, which resulted in average loading/unloading rate of 2 μN/s. The indentations were performed along the *a priori* programmed pattern that consisted of 5 to 25 points with 5 μm lateral and horizontal separation between indentation marks. A total of 25 to 125 indentation tests were performed on each of the specimens that to our experience secured reliability of the obtained results.

Furthermore, having in mind the critical experimental limitations that apply to requiring SAM samples, the special experimental precautions have been applied to secure high accuracy of the indentation probing. They include: rigorous stabilization of temperature inside the indenter chamber (variation less than 0.05 deg), humidity kept at a constant level, and placement of specimens in a chamber several hours before the test to allow the stabilization of the environment.

In closing, one may recognize the scale of our experiment using a simple evaluation. Since the approximate contact area of a tip (at the indentation depth of 1 nm) equalled 12 500 nm^2, and the cross-section of SAM molecule is close to 2.1 nm^2 [21], our probing involved over 5000 molecules with an average load per molecule of 2 nN (at peak-load). The above rough estimation gives a reader quite instructive picture of the probing we carried out.

3. Results and Discussion

Nanoindentation experiments were performed for five different SAM/substrate systems (TDT/Au, HDT/Au, BPDT/Au, TDT/Ag and HDT/Ag) and for pristine Au and Ag substrates. For data analysis, we measured the average maximum indentation depth before the dwell time together with the standard deviation at 9.5 μN and calculated the consumed energy over the loading–unloading cycle for each sample [15]. The obtained data is summarised in Table 1.

TABLE 1: Statistical data obtained for pristine Au and Ag substrates and SAM/substrate systems.

	Average maximum depth at 9.5 μN (nm)	Standard deviation at 9.5 μN (nm)	Energy consumed (fJ = 10^{-15} J)
Au	1.25	0.15	2.4
TDT/Au	0.82	0.22	0.5
HDT/Au	0.89	0.17	1.3
BPDT/Au	1.40	0.30	2.8
Ag	1.20	0.25	3.0
TDT/Ag	1.40	0.29	4.0
HDT/Ag	1.20	0.21	2.8

Load-displacement (P-h) curves of samples on Au substrate are presented in Figure 1. Nanoindentation of the TDT/Au and HDT/Au samples (maximum depths of 0.82 and 0.89 nm, resp.) show a stiffening response of about 30% in comparison to bare Au (maximum depth of 1.25 nm), whereas no noticeable change, within the noise floor of the apparatus, in the maximum indentation depth is observed for the BPDT/Au (maximum depth of 1.40 nm). On the other hand, the P-h curve for BPDT/Au shows clearly more hysteresis between loading and unloading than the data of bare Au, whereas the hysteresis decreases by ~80% and ~46% in the presence of TDT and HDT SAMs, respectively (see the calculated consumed energy values of Table 1). It is well known that BPDT molecules form less ordered SAMs than alkanethiols and exhibit a higher density of gauche defects [22, 23], which allow a deeper penetration towards the Au substrate. On the other hand, while BPDT SAMs are chemically reactive, alkanethiols that are terminated by the inert CH_3 group produce a lower surface energy, and due to their high hydrophobicity, they usually exhibit lower adhesion and friction [24]. Therefore, the pronounced hysteresis (higher consumed energy) in the P-h curve of the BPDT SAM on Au is mainly attributed to the lower degree of order and stronger interaction between the SAM molecules and the indenter tip than in the case of the hydrophobic CH_3-terminated alkanethiols and bare Au surface. Additionally, there may be some variations in the surface coverage of the molecules and in the tilt angle which depends on the chain length of the SAM molecule [25]. The angular degrees of freedom for a self-assembled monolayer of alkanethiol can be described by the tilt angle θ and the tilt direction χ, as schematically represented in Figure 2. Based on a molecular dynamics study, Vemparala et al. [26] have reported that at room temperature the effect of chain length on the tilt angle is most pronounced. There is a jump of 3 and 6 degrees in both vertical and rotational alignments, respectively, as chain length increases from 14 to 16 [24, 25]. The resulting variation in the rotational alignment χ of the HDT molecules induces more molecular disorder explicating the observed higher hysteresis of the longer HDT molecules compared with the shorter TDT molecules (Figure 1).

To further study the features of the P-h curves, we performed nanoindentation experiments on TDT and HDT SAM covered Ag surfaces. In Figure 3 the mechanical responses of bare Ag and TDT and HDT coated Ag substrates are plotted. The TDT covered Ag sample exhibits a slightly
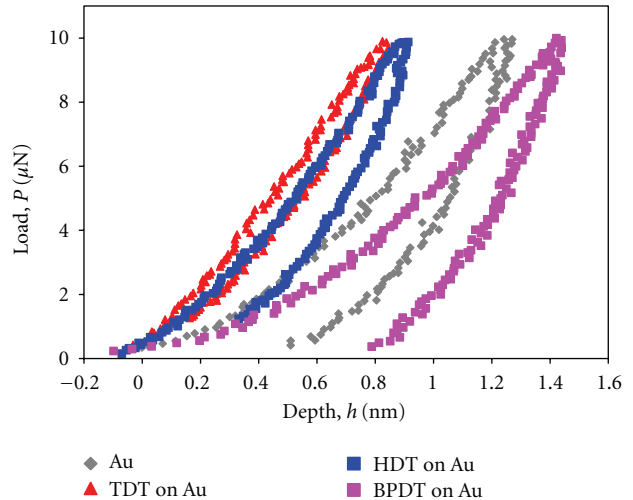

FIGURE 1: Averaged data obtained from nanoindentation of bare Au and TDT, HDT and BPDT SAMs on Au substrate.

deeper penetration depth (1.40 nm) and higher hysteresis (consumed energy ~4 fJ) compared to bare Ag and the HDT covered Ag substrates (both have a penetration depth of 1.20 nm and consumed energies of 3.0 and 2.8 fJ, resp.). Both TDT/Ag, and HDT/Ag samples exhibit higher hysteresis, greater maximum indentation depths and larger creeping during the dwell time than the samples with the same SAMs on Au (Figure 1).

Monolayers grown on Au have tilted contact angles in the range of 20–40° [24–29], while the ones on Ag tend to grow more perpendicular to the substrate surface with a tilt angle of approximately 6-7° [16, 26]. In the case of Ag surfaces, the nearly perpendicular orientation of the molecules may initiate higher disorder already at the beginning of the indentation because there is no local preferential bending. Therefore, the noted large variations in the adhesive and elastic responses are in accordance with the expectations. When comparing the indentation curves obtained for bare Au and Ag, they show similar indentation depths and hysteresis, Ag though exhibiting larger creeping during the dwell time than Au.

To account for the nanoindentation results, the P-h curve features are shown to be associated with several factors. The molecule chain length: the longer molecules show higher hysteresis compared with that of the shorter molecules. The terminal group of the molecule: a reactive group results
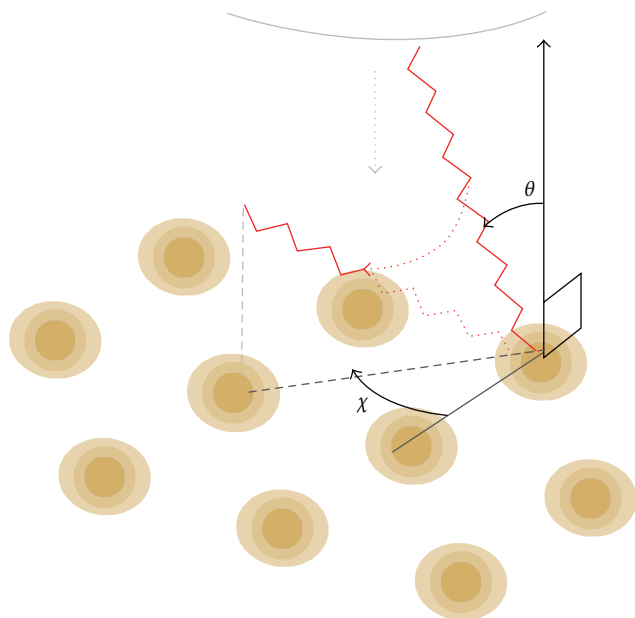
FIGURE 2: Schematics of the angular degrees of freedom of alkanethiol SAMs. The brown areas represent S atoms of the molecules on the surface. Angle θ refers to the tilt of molecular axis with respect to substrate surface normal and χ defines the tilt direction, that is, it is derived from projection of molecule in the substrate plane.
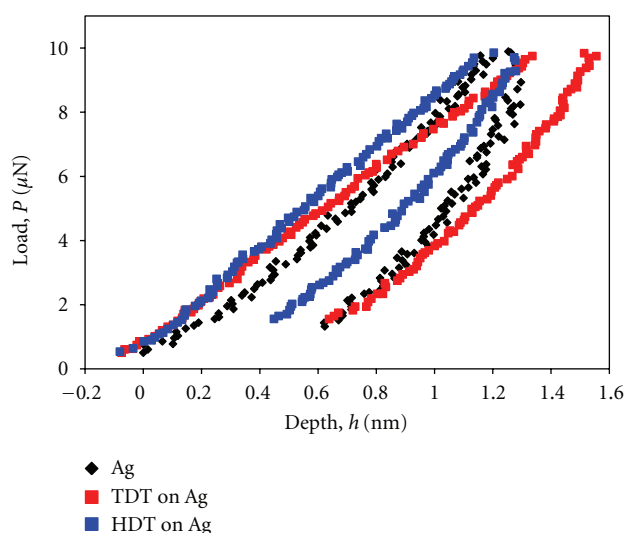

FIGURE 3: Averaged data obtained from nanoindentation of bare Ag, TDT and HDT SAMs on Ag substrate.

in pronounced hysteresis. The less ordered SAMs show deeper penetration depths. The substrate (Au versus Ag) effect is expressed through the molecule tilt angle which it affects, substrate topography and through the varying surface coverage.

4. Conclusions

Mechanical responses of different thiolate monolayers (BPDT, TDT and HDT) on gold and silver substrates were studied experimentally with classical nanoindentation complemented with appropriate statistical analysis. A conical diamond tip with a 2μm tip radius was used in order to sample a larger number of SAM molecules and mitigating the impact of local effects. As indicated by the tip displacements in the P–h curves, the BPDT covered Au substrate was softer in mechanical response compared with the TDT and HDT SAMs, due to the lower degree of order of the BPDT molecules and stronger interaction between the SAM molecules and the indenter tip. On the other hand, more gauche defects and extended dislocations arise upon indentation into SAM coated Ag surfaces as a consequence of the SAM orientation. The herein proposed procedure enables a fast and efficient way of finding the essential mechanical response of monolayer structures needed for many practical applications.
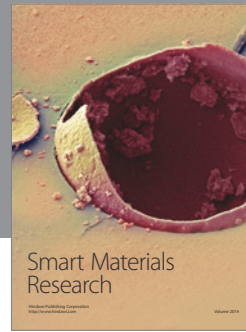
Acknowledgments

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