Interfacial Adhesion at the Molecular Level

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INTRODUCTION

Interfacial adhesion is of extraordinary technological importance and has long been of intense scientific interest. However, the study of the adhesive bond and its failure is made difficult by the complexity of the interfacial interaction and the problems involved with establishing carefully characterized and controlled interfacial surfaces and that of quantitatively evaluating the bonding after its formation. In the present work, we outline the results of studies using Interfacial Force Microscopy (IFM) to study the adhesive bond formation and failure between (1) differing end-group combinations on self-assembling monolayer (SAM) films covering Au surfaces and (2) between clean surfaces of a W probe and a Au single-crystal sample. The IFM is a scanning probe technique distinguished by its use of a mechanically stable, zero-compliance force sensor. This sensor permits the study of the interfacial force as a function of separation without the mechanical instability giving rise to the “jump-to-contact” seen in all presently used displacement-based sensors, such as the surface forces apparatus and the atomic force microscope [1]. Thus, information can be obtained concerning the details of the adhesive bond formation and failure over the entire range of the interfacial interaction. We demonstrate that such measurements yield valuable quantitative information concerning the individual bond strengths between chemically distinct SAM end groups and show that the clean metal-surface interaction is dominated by surface roughness and plastic deformation.

RESULTS

Figure 1 shows the force profiles for end-group combinations consisting of methyl-methyl (-CH₂--H,C-), amine-amine (-NH₂----H,N-), carboxyl-carboxyl (-CHOH----HOHC-) and carboxyl-amine (-HCOH--H,N-). These combinations cover the range from pure van der Waals through hydrogen bonding to a full acid-base interaction. Note that beyond the weak van der Waals case, the strength of the bonding interaction increases qualitatively as the product the of acid/base characters, i.e., the amine group is a strong base and weak acid while the carboxyl group is a strong acid and reasonable base. This means that the amine-amine bond should be weak, the carboxyl-carboxyl intermediate and the amine-carboxyl strong—as we observe. We have used the peak bonding force, along with a commonly applied adhesion model (the DMT model [2]), and the known molecular coverage, to quantitatively evaluate the end-group bond strengths [3]. These values are shown in Table I compared with values obtained from more traditional methods.

We show in Fig. 2 a typical result for a clean 1000 Å W probe interacting with a Au(111) surface which has been sputter cleaned but not annealed. After an initial jump-to-contact, the interaction force can be seen to be attractive over the entire range covered (the turn-around force was selected to be zero). Upon withdrawal, the force reaches a maximum value of about 4 μN, after which it decreases until the contact fractures at about 1 μN. The position of the maximum force would be the point at which jump-from-contact would occur if we were using a force sensor with large compliance, corresponding to the so called “pull-off force”. The total range of the contact interaction is approximately 120 Å and the jump-in, jump-out hysteresis is only about 10 Å.

DISCUSSION AND CONCLUSIONS

Aside from the encouraging agreement between our quantitative results and those from other experiments, several other features of the force profiles in Fig. 1 should be emphasized. First, the force appears to begin increasing suddenly at a relative separation of about 50 Å from the zero-crossing point. Secondly, the approach and withdrawal curves show a considerable level of adhesive hysteresis, especially for the more strongly bonding interactions. The hysteresis is undoubtedly due to the time
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dependent nature of the bonding and reflects the molecules adjusting their steric configurations to maximize the interaction. The range of the interaction and the slow rise near threshold involves the ability of the thiol molecules (which are normally leaning at about 30°) to suddenly stand up to meet each other as the two surfaces approach. However, the force at this point would be greatly reduced since the average molecular density would be decreased (the van der Waals force is proportional to the sixth power of the density). As the approach continues, the molecules return to their normal position and the force gradually increases until the point at which repulsion begins. The calculations for the bonding energies in the thiol experiments involved the use of an approximate adhesion model which is often applied for such purposes (the DMT model [2]) but which, from the above discussion, is not necessarily appropriate for the present case. We believe that the model works here because all experimental condition are held constant except for the chemical nature of the end-groups. Thus, we are making relative bonding-energy measurements, which should be largely independent of the model.

To the authors knowledge, the data of Fig. 2 represents the first time that the behavior of strongly bonding systems have been observed in the absence of the sensor jump-to-contact. The advantage of the zero-compliance sensor is clearly illustrated in this data, i.e., the details of the initial bond-formation and the contact-failure regions are observable. Due to the materials jump-to-contact and their compliance under the contact force, the range of the interaction from initial contact to the zero applied force point is expected, under ideal conditions, to be about 30 Å. The 120 Å range observed in Fig. 2 is a result of the fact that the Au surface is plastic under the contact interaction. In addition, the fact that the jump-to-contact results in a force smaller than the maximum indicates that the contact involves a rough surface, which would be expected for our non-annealed samples [4]. The plastic compaction of the rough interface continues after contact until repulsion dominates and the response is essentially linear, i.e., a response similar to that for a cylindrical punch. Using the Au elastic modulus, we estimate the contact radius in this region to be ~250 Å, which corresponds to a spherical punch deformation of ~65 Å. This latter value closely matches the distance from “snap in” to the beginning of the linear region in Fig. 3, and corresponds to the depth of the plastic deformation of the roughness region. Upon withdrawal, little hysteresis is observed (again, indicating an elastic response) until the Au again starts to plastically flow, necking down until it eventually fractures to break the contact [5]. The energy necessary to create the new surfaces in separating a 250 Å radius contact is about one fiftieth the energy expended in withdrawing the probe in Fig. 3, which clearly illustrates the critical role that mechanical behavior plays in determining the overall strength of an adhesive bond.

We have demonstrated that contact measurements with the IFM’s zero-compliance sensor can yield invaluable information concerning the details of the contact mechanics and quantitative values for the interfacial bonding energies. Both of these areas are critically in evaluating the adhesive bonding of materials and their failure under loading.

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REFERENCES

Figure 1. Force profiles for various combinations of thiol end groups. The end groups and the tip radii are noted on the figure.

Figure 2. A typical force profile for the interaction of a clean 1000 Å W probe with a sputter cleaned but unannealed Au(111) single-crystal sample.

Table I. The bonding-strength values calculated from the maximum adhesive forces from Fig. 1 compared with the values obtained from other methods. SFA refers to the surface forces apparatus and HC indicates hydrocarbons. $W_{ij}$ is twice the surface energy in mJ/m$^2$. 