MECHANISTIC STUDY OF PARTICLE BOMBARDMENT OF AN ALKANETHIOLATE/AU SYSTEM

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1. Introduction

Interest in alkanethiolate/Au self-assembled monolayers stems from their ease of preparation and a wide range of technological applications [1]. This system has been well characterized [2-4]. Among the techniques used, SIMS has been particularly important in probing the surface chemistry of the thiolate overlayers [5]. The consistent detection of Au dialkanethiolate molecules in the SIMS spectra suggests information regarding the chemical composition and surface order. These are particularly important for assemblies with binary monolayers [6]. One structural feature, namely whether the binary monolayers are phase segregated or randomly mixed, might be addressed with SIMS. It has been suggested that these Au dialkanethiolate molecules in the SIMS spectra may be used as a monitor for determining the local chemical environment [7-8]. One would like to assume that the two thiolate molecules were nearest neighbours on the surface. The mechanism of their formation, however, is not understood. In this study, we report the use of molecular dynamics (MD) to simulate Ar particle bombardment process on an assembly of alkanethiolate chains adsorbed on a Au (111) surface. Au dialkanethiolate molecules are observed together with a variety of other Au clusters in the simulation.

2. Method

The model used in this study will be detailed elsewhere [9]. It consists of 68 alkanethiolates adsorbed on threefold sites of a Au(111) surface. The size of the substrate is chosen to be 9 layers with 288 atoms per layer. Both the gold substrate and adsorbate are quenched to a minimum energy configuration prior to impact. An Ar atom of 700 eV is directed at an angle parallel to the direction of the tilt angle of the chain. The impact zone encompassing the aiming points of the Ar impact is chosen to be a parallelogram. Each trajectory is allowed to run for 2 ps and a total of 300 trajectories have been obtained. A Molière potential [10] is used for interactions with the Ar atom. The S-S and S-C interactions are described by Morse potentials [11] and the S-H, Au-C and Au-H by Lennard-Jones potentials [12]. The MD/MC-CEM [13-14] is used for the Au-Au interactions and the Brenner's potential [15-16]

for the hydrocarbons. A modified Morse potential is used for the Au-S interactions which allows the energy parameter, D_e, to change with respect to the heights of Au and S atoms above the surface. Details on the modification scheme and the parameters used will be given in the forthcoming publication [9].

3. Results

The simulations do predict the presence of clusters of Au atoms and thiolate molecules. Of particular interest in this study is the formation of AuM_2 species where M denotes the thiolate molecule.* Cluster species are sensitive to their chemical environment as a result of the formation process. The question is whether these species are created from the ejection process where neighbouring molecules eject as a unit, or whether significant mixing occurs. The latter case is not impossible although timing and geometric considerations may well limit the lateral displacement of surface molecules that form clusters.

There are 32 Au alkanethiolate molecules and 18 Au dialkanethiolate molecules recorded in the 300 trajectories. Among these two types of species, a majority of them (over 80%) arise from close neighbours between Au and thiolate molecules. While some of the Au atoms involved originate from one of the threefold sites adjacent to the thiolate molecules, many of these Au atoms are found to be close neighbours to the thiolate molecules with distances less than 6.0 Å The remaining 10-20% of the Au atoms are more than 6.0 Å away from the thiolates. In the case of the Au dialkanethiolate molecules, most of the dimers arise from thiolates of nearest neighbours with only two of them formed from next nearest molecules.

The formation of AuM_2 is related to the relative positions of its constituent species. We have chosen a trajectory which clearly illustrates this behaviour. The Au atom involved (shaded atom on the surface) is close to both thiolate molecules and does not belong to any of the adjacent three-fold sites, Fig. 1(a). The two thiolates are nearest neighbours with a separation of ~5 Å to one another. As the Ar atom (coming in the direction parallel to the tilted chain) imparts its energy to the substrate, the sub-surface Au atoms collide with the surface Au atoms. The momentum is directed such that it is moving upward and towards the two thiolates. The surface Au atoms then push the thiolates from below causing them to move up also, Fig. 1(b). As a result of the concerted motions of both of these species which is facilitated by their intimate contact, the three entities bind together and eject as a single unit, Fig. 1(c). Of note is that the adjacent chains are still bound to the surface. In most cases, the surface Au atom attains its momentum which is moving away, and not directly into the thiolate. The thiolate is then ejected from, or *rolled off of*, the surface intact. This is similar to the observation reported by Talyor on the C_2H_3/Pt [17] system.

* The tradition in SIMS nomenclature is to use M to designate the molecules on the surface. In this case, the surface species is a thiolate yet the preparation procedure uses thiol molecules. Some experimentalists use M to designate the thiol, a species not present on the surface.

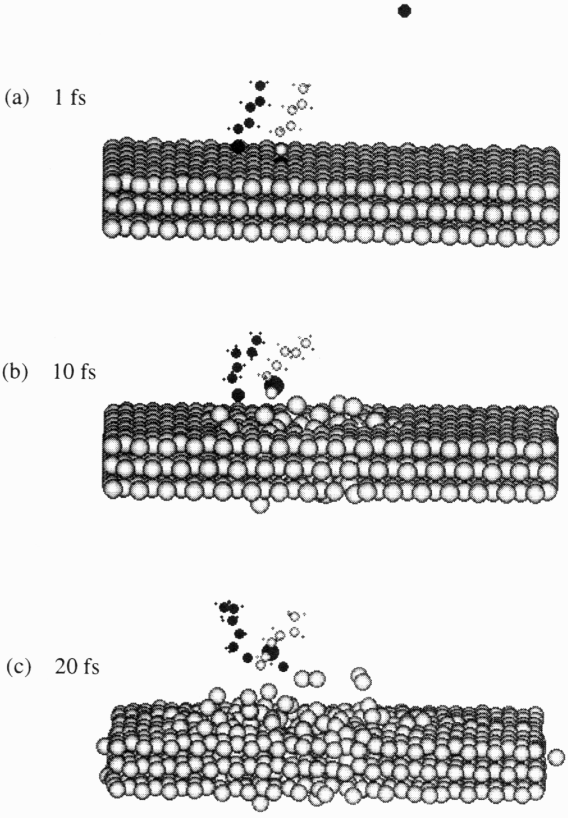

Fig. 1 Events showing the formation of a AuM_2 molecule. The unit of time is fs = 10^{-15} s. The atoms arranged in layers are the Au atoms. The Au atom of the AuM_2 is shaded. The isolated atom well above the surface in (a) is the Ar atom. The thiolate molecules are represented as dark grey and light grey chains. See text for detail.

4. Conclusions

Au dialkanethiolate molecules have been identified in the simulation study. Almost all of the thiolates in these molecules are nearest neighbours to one another on the surface. A majority of Au atoms were also found to be in close proximity with the thiolates. It is these geometric contact and concerted motions that enable the cluster to form and eject as a single unit.

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