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Report:

A number of fundamental studies on alkane thiols have addressed the relationship between molecular structures and the resulting film structure and properties with the goal being to develop a rational design of thiol self assembled monolayers (SAMs). Among a number of factors which contribute to the energetics of thiol SAMs such as intralayer interactions and interactions of the SAM with the environment, the SAM-substrate interface is of particular importance since substrate-sulfur bonding (126 kJ/mol for Au-S), adsorption site, and bonding geometry are mutually dependent parameters which enter into the energy balance in a crucial way. Even though the details of the S-Au interface are still far from being understood, some essential points have been unravelled. One is the crucial role of the C-S-Au bending potential as pinpointed in a recent experimental study of a homologue series of ω -(4'-methyl-biphenyl-4-yl)-alkanethiols ($\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-(\text{CH}_2)_n-\text{SH}$, BP_n , $n=1-6$). The orientation of the aromatic units is crucially influenced by the number of methylene units in the alkane spacer, which results from a pronounced directional force originating from the S-Au interface due to an sp^3 -like bonding geometry of the sulfur. Consequently, the film structure, e.g., the intermolecular distance d , alternates between odd and even numbers of CH_2 units. For $n=\text{even}$ a dense molecular packing, i.e., maximization of intermolecular interactions, and an optimum C-S-Au bond angle cannot be simultaneously realized. For this reason, insertion of one methylene unit or, more general, an odd number of them between the aromatic unit and the sulfur appears preferable to optimize quality and stability of the monolayers. This picture was fully confirmed by studies which demonstrated the odd-even variation in the properties of BP_n SAMs. Compared to BP_n SAMs with $n=\text{even}$, the ones with $n=\text{odd}$ were found to be electrochemically more stable and more resistant to exchange by other thiols [1]. While the outlined design concept holds for BP_n SAMs prepared at room temperature, the even-numbered BP_n SAMs exhibit a very unexpected behavior if prepared or annealed at elevated temperatures. In contrast to odd-numbered BP_n SAMs which just show the well-known annealing effects of domain growth and Ostwald ripening of vacancy islands but no structural changes, the even-numbered BP_n SAMs undergo a pronounced temperature-induced change in structure [1]. The initial structure observed for preparation

temperatures below 343 K is described by a unit cell containing eight molecules. In this so-called α -phase, which is described by a rectangular unit cell, the intermolecular spacing of more than 6 Å is significantly larger than the 5 Å of the ($\sqrt{3} \times \sqrt{3}$) gold matching lattice. If the samples are annealed at higher temperatures, fundamental changes occur. After annealing at 373 K, large-scale STM images show extended areas which differ in contrast and correspond to a new phase. This β -phase differs substantially from the α -phase. The shape of the unit cell with again eight molecules is changed to oblique and has substantially increased in size by 20%. Further increase of the temperature to 423 K yields the pure β -phase.

The aim of this experiment was to use surface x-ray scattering to probe the structure at the SAM-Au interface in the systems described above. A systematic set of experiments were performed on 3 samples. Each sample had been prepared and characterized by STM at the University of St Andrews prior to transportation to the ESRF. The α -phase of BP4, a ($5\sqrt{3} \times \sqrt{3}$) structure, was present on the Au(111) surface in each case. The samples were mounted in a N₂ atmosphere and a detailed x-ray diffraction study was performed. This consisted of 2 parts; (i) a search for in-plane x-ray diffraction from the ($5\sqrt{3} \times \sqrt{3}$) structure and (ii) a detailed measurement of the crystal truncation rods (CTR's) from the Au(111) surface.

(i) The results from the in-plane studies were rather disappointing in that no scattering from the ($5\sqrt{3} \times \sqrt{3}$) structure could be detected despite an exhaustive search of reciprocal space. It is interesting to note that in LEED studies of the same system a diffraction pattern from the SAM was not obtained. This (and the x-ray results) suggest that the long-range order observed in the STM studies is not present on the atomic scale that is probed by the diffraction techniques, i.e. there may be disorder within the SAM structure that leads to a lack of coherence in the electron density distribution, hence the inability to observe diffraction from the layer. After annealing of the samples to switch the SAM structure from the α to the β phase (see below) a repeated search for superlattice reflections from the SAM was performed but, again, no peaks due to an ordered structure were detected.

(ii) 11 CTR's were measured from each sample, including 3 CTR's that were symmetry-equivalent (these allow estimates of both the statistical and systematic error on the data to be obtained). The samples were then annealed at a fixed temperature in an inert atmosphere for ~12 hours. This procedure is known to transform the α -phase to the β -phase (this was subsequently confirmed by STM after the experiment had finished). The CTR's were again measured for the β -phase as STM measurements imply that the phase transition in the SAM is accompanied by a significant change in the structure at the SAM/Au interface. Changes in the termination of the Au lattice at the interface can be understood by modeling of the changes in the CTR profiles. The figure below shows the results for one of the CTR's that was measured, the example shown is the specular CTR which is sensitive only to changes in the electron density perpendicular to the surface. The top panel shows the CTR's measured before and after the phase transition from the α to the β phase of the SAM and the lower panel shows the ratio of the two data sets. From the ratio data it can clearly be seen that there is a systematic change in the measured intensity, particularly at the 'anti-Bragg' positions, (0, 0, 1.5) and (0, 0, 4.5) which are sensitive to the surface Au atomic layers. Similar systematic changes were observed for all of the measured CTR data and the results were confirmed by repeated measurements on the other two samples. The data is currently being fitted to a structural model in order to quantify the changes in the Au(111) surface structure. It is apparent, however, that the phase transition from the α to β phase in the SAM is accompanied by a significant change in the underlying Au(111) substrate. The role of substrate restructuring in the self-assembly process has yet to be understood and the results obtained in this experiment will give valuable insight into the phenomenon.

