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Melting Point Enhancement of a Self-Assembled Monolayer Induced by a van der Waals Bound Capping Layer

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Using in situ surface X-ray diffraction, the thermal stability of a self-assembled monolayer (SAM) of decanethiol, sandwiched between a Au(111) substrate and a van der Waals bound capping layer of PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride), is measured. While the bare SAM on Au(111) undergoes a melting transition at 100 °C, this transition temperature is raised to 115 °C if the SAM is capped by PTCDA. Possible mechanisms and implications of this capping-layer-mediated melting point enhancement are discussed.

I. Introduction

Phase transitions in reduced geometry have received considerable attention over the past several years. The experiments and their theoretical interpretation have reached a high level of detail, particularly for several semi-infinite systems, for which the corresponding bulk reference has been thoroughly investigated.¹ For two-dimensional systems, several different scenarios have been reported,² and even the seemingly simple case of hard disks in two dimensions continues to be matter of discussion.³ An interesting situation arises if a thin film is subject to interactions on both the bottom and the top interface.⁴ The cases of, for example, alkalis intercalated in graphite⁵ and Lennard-Jones fluids between “hard” walls⁶ have been thoroughly studied as model systems. A rich variety of scenarios have been found, and the phase transition point as well as the nature of the transition can be changed considerably depending on the type of interactions with the confining media. Also, besides the importance of phase transitions from a fundamental perspective, issues related to thermal stability have an obvious relevance for thin-film device applications and are thus of significant practical interest.

Phase transitions in complex low-dimensional organic materials are generally less well understood. An important characteristic of organic materials is the specific internal

degrees of freedom of the molecules which can give rise to a very rich phase behavior, as seen, for example, in Langmuir films (on liquid surfaces).⁷ Among the well-defined, crystalline two-dimensional organic thin films chemisorbed on a solid substrate, self-assembled monolayers (SAMs) are probably the best-characterized system, and the phase behavior of the archetypal SAM system, alkanethiols on Au(111), as a function of coverage and temperature has been thoroughly studied.^{8–12}

In this paper, we present the case of rather soft boundary conditions for an organic monolayer, namely, a SAM of decanethiol on Au(111)^{8–12} capped by a van der Waals bound crystalline multilayer of PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride), a model compound for organic molecular beam deposition (OMBD).^{13–18} A schematic of this sandwich structure is shown in Figure 1.

X-ray scattering allows for high-resolution access to structural information, both in the surface plane as well as along the surface normal. Moreover, X-ray scattering can also detect buried layers such as a SAM underneath a PTCDA film and is applicable in situ and also at elevated temperatures. This has enabled us to gather evidence for an enhanced melting temperature of the SAM induced by the capping layer using grazing-incidence diffraction (GID).¹

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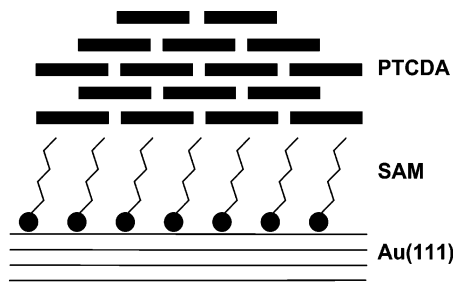


Figure 1. Schematic of the layered structure of the sample (Au(111) substrate/SAM/PTCDA).

Besides their use in the present study, perylene-based organic heterostructures are also attractive due to their, by virtue of synthetic modification, potentially tunable optical, optoelectronic, and electronic properties. Several applications, such as organic light-emitting devices, solar cells, sensors, and so forth, have already been demonstrated.¹³ Thin films of these materials can be deposited in ultrahigh vacuum (UHV), which offers the chance to combine a clean environment and control of the growth on the submonolayer level with in situ analysis.

II. Experimental Section

The experiments were performed at beamline X10B of the National Synchrotron Light Source (NSLS) at Brookhaven using a wavelength of $\lambda = 1.13$ Å. A small UHV chamber containing the single-crystal Au(111) substrate was mounted on a four-circle diffractometer. The chamber is equipped with a Be window, a sputter gun for in situ cleaning, a leak valve for dosing the decanethiol vapor, and a resistively heated home-built Knudsen cell for the evaporation of PTCDA. The Knudsen cell can be separated from the main chamber by a gate valve, and the dosing can be controlled by a flag located in front of the Knudsen cell. The Au(111) surface was prepared by repeated Ar sputter and anneal cycles until the $22 \times \sqrt{3}$ reconstruction characteristic of the clean Au(111) surface was seen.¹⁹ During growth, the substrate was kept at ambient temperature.

Building upon the experience from previous detailed studies of the growth of decanethiol SAMs on Au(111) from the vapor phase,^{11,12,20} it could easily be verified that a full-coverage (complete) SAM had been grown by checking the time-evolution of the corresponding SAM diffraction signal. After completion of the SAM, PTCDA (typically about 20 monolayers) was evaporated from the Knudsen cell, similarly as in a recent study of PTCDA on the bare Au(111) surface.¹⁵

The sample stage was heated by a tantalum filament. The temperature was measured by two thermocouples located in close vicinity of the Au(111) crystal. We estimate the absolute accuracy of the sample surface temperature to be better than 5 °C and the relative accuracy and reproducibility to be better than 2 °C.

III. Results and Discussion

The full-coverage structure of alkanethiol SAMs has been thoroughly studied before. It is characterized by a $c(4 \times 2)$ superlattice of a hexagonal ($\sqrt{3} \times \sqrt{3}$)R30° structure (see Figure 2) and a tilt of the hydrocarbon chains away from the surface normal by about 30°. ^{10,11,21–24} PTCDA forms a well-defined capping layer on the SAM with its bulk-cleavage plane (102) (in the notation of the

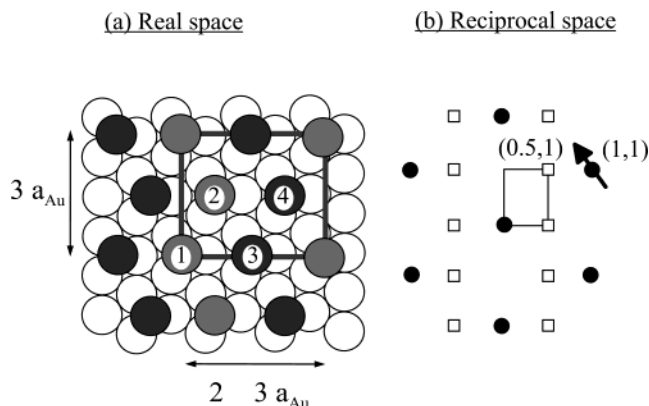


Figure 2. (a) Schematic of the in-plane structure (real space) of the SAM with its hexagonal ($\sqrt{3} \times \sqrt{3}$)R30° base lattice and rectangular $c(4 \times 2)$ superstructure containing four molecules. (b) Schematic of the corresponding reciprocal space structure. The hexagonal lattice points are shown as circles, whereas the rectangular $c(4 \times 2)$ superstructure is indicated by squares.

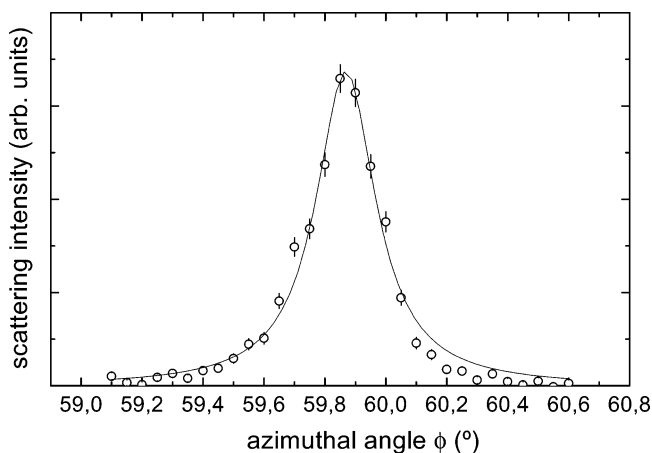


Figure 3. Azimuthal scan through the first-order hexagonal in-plane diffraction peak at room temperature (scan direction corresponding to the arrow in Figure 2).

bulk α -phase^{18,25}) exposed to the surface.¹⁷ The (102) direction is also the stacking direction of flat-lying molecules with a periodicity of 3.2 Å.

Since it was shown in a previous study¹⁷ that the PTCDA/SAM/Au sandwich structure exhibits well-defined interfaces and in particular that the structure of the SAM does not change upon deposition of PTCDA, neither in terms of its in-plane unit cell nor in terms of the out-of-plane structure including the tilt angle, we can address the temperature dependence and melting transition of the SAM and the changes induced by the capping layer. From previous studies carried out on uncapped monolayers, it is known that the SAM exhibits the lowest melting point (100 °C) of the three materials involved (PTCDA remains solid up to well above 200 °C).^{8,10–13,18} It is therefore expected that in a certain temperature interval the capped SAM forms a liquid layer between two crystalline substances but that the interaction with the capping layer has an impact on the melting transition of the SAM.

Figure 3 shows an azimuthal GID scan through the hexagonal (1,1) Bragg reflection (scan direction indicated by the arrow in Figure 2). With the radial resolution relaxed to collect the full intensity, the area under the

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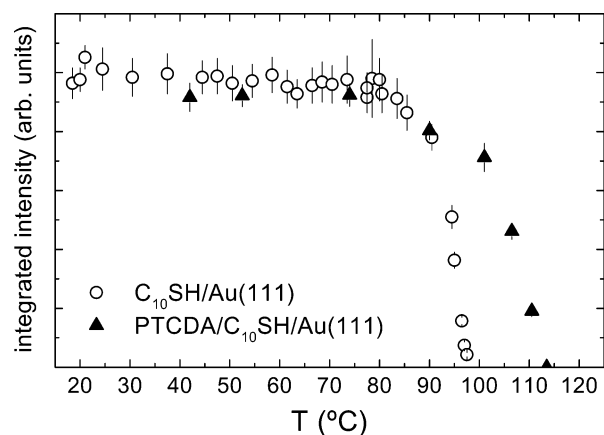


Figure 4. Melting curve as determined from the temperature dependence of the Bragg intensity (integral of the hexagonal in-plane peak as shown in Figure 3) of the SAM with and without the PTCDA capping layer. For the capped SAM, the melting temperature is enhanced by ≈ 15 K.

azimuthal scan as a function of temperature gives the melting curve of the SAM (Figure 4). Compared to the uncapped SAM, the melting temperature of the PTCDA-capped SAM is clearly enhanced by about 15°C , while the character of the transition appears largely unaltered. We note that for both the uncapped^{8,10–12} and the capped SAM, the melting includes the chains as well as the sulfur headgroups (i.e., the chains *and* the headgroups are disordered above the melting temperature), as seen from the complete vanishing of the diffraction intensity.

At first glance, the situation might seem to be conceptually similar to a pressure-induced melting point change (as described by the Clausius–Clapeyron equation for the case of bulk systems). In this comparison, the pressure would have its analogue in the pressure exerted by the PTCDA layer. However, the PTCDA layer is only coupled to the SAM itself, so it cannot directly exert a significant pressure on the SAM, since the interaction of PTCDA with the Au(111) substrate over a distance of about 16 \AA is weak.²⁶ Therefore, we believe that the mechanism for the melting point enhancement observed here is different from the pressure-induced scenario.

We note that the system studied here does not correspond to a confined-melting phenomenon in the con-

ventional sense of a hard confinement,⁶ since the capping layer is connected only to the SAM itself and thus is not at a fixed height above the substrate. In fact, one way for the SAM to gain space and thus reduce its density during the phase transition is to reduce the tilt angle of the chains and thereby increase the effective chain–chain distance in the plane. The exact need for this extra volume is not known, but it is clear that the capping layer would not impose serious restrictions on this change of effective height of the SAM, again due to the weak interaction of the capping layer with the substrate over this distance. Nevertheless, one should expect that the PTCDA layer at least tends to reduce the fluctuations along the surface normal, which may well have an impact on the phase transition.

In addition, the capping layer can have an effect on the lateral interactions within the SAM in that it tends to “clamp” the chain termini to certain positions in the corrugated potential of the flat-lying PTCDA molecules and, thereby, effectively stabilizes a certain chain–chain distance. In this context, it is important to note that PTCDA grows with a well-defined epitaxial relationship,¹⁷ implying that the lateral variation of the PTCDA–SAM interaction potential does not average out. While it is difficult to quantify these interactions, the impact of the capping layer on the fluctuations both along the normal and on the (indirect) in-plane interaction appear to be plausible mechanisms for the melting point enhancement.

In conclusion, we have observed an enhancement of the melting temperature of a monolayer due to a van der Waals bound capping layer. Melting of organic monolayers is a complex area, and the observations in the present system require further work to be fully understood. In addition to their importance for the fundamental question of phase transitions, the present results also suggest that capping can be a way to achieve enhanced thermal stability of thin films, which is an important issue in technical applications.

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(26) Thermal desorption experiments of PTCDA on *bare* Au(111) show that only the first monolayer (about 3 \AA above the Au(111) surface) and, to a small degree, the second monolayer (distance about 6 \AA) experience a significant interaction with the substrate (ref 15). This suggests that for the present case with a SAM spacer layer, for which the first PTCDA layer is at a distance of around 16 \AA away from the substrate, the interaction with the Au substrate is indeed weak.