Heat capacity measurements of two-dimensional self-assembled hexadecanethiol monolayers on polycrystalline gold

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The melting characteristics of hexadecanethiol two-dimensional self-assembled monolayers (SAMs) grown on polycrystalline Au surfaces are obtained via heat capacity measurements using nanocalorimetry at scanning rates of \(~30000^\circ\text{C/s}.\) The analyzed amount of alkanethiol in the form of SAMs is typically in the \(10^{-11}\) mol range. Melting occurs over a broad (full width on the half height \(~100^\circ\text{C}\)) temperature range with a melting temperature of about \(70^\circ\text{C},\) if the alkanethiol is partially desorbed from the Au surface during thermal treatment. SAMs in their as-deposited state without desorption have melting temperatures above \(100^\circ\text{C}\). The heat of fusion is about \(20\ kJ/mol.\) Partial desorption of the alkanethiol is directly observed. The melting characteristics of three-dimensional SAMs on Au nanoparticles are comparable to earlier studies using conventional calorimetry. © 2004 American Institute of Physics. [DOI: 10.1063/1.1764938]

In recent years, self-assembled monolayers (SAMs) have generated great interest both in the fundamental issues of two-dimensional (2D) melting and in applications for molecular electronics, diffusion barriers in microelectronic device fabrication, corrosion control, and lubrication. The \(n\)-alkanethiol SAMs on Au surface serve as the model SAMs system. The thermodynamic and structure characteristics of SAMs, in particular the order–disorder (melting) phase transitions, are essential for developing technological applications. This transition has been studied using a variety of experimental techniques.

Calorimetry is the standard method for phase transition studies. It provides unique characteristics of the transition such as enthalpy and entropy as well as the specific heat of the phases. Although conventional differential scanning calorimetry (DSC) is routinely used for thin film calorimetry measurements using nanocalorimetry at scanning rates of \(~30000^\circ\text{C/s}.\) The analyzed amount of alkanethiol in the form of SAMs is typically in the \(10^{-11}\) mol range. Melting occurs over a broad (full width on the half height \(~100^\circ\text{C}\)) temperature range with a melting temperature of about \(70^\circ\text{C},\) if the alkanethiol is partially desorbed from the Au surface during thermal treatment. SAMs in their as-deposited state without desorption have melting temperatures above \(100^\circ\text{C}\). The heat of fusion is about \(20\ kJ/mol.\) Partial desorption of the alkanethiol is directly observed. The melting characteristics of three-dimensional SAMs on Au nanoparticles are comparable to earlier studies using conventional calorimetry. © 2004 American Institute of Physics. [DOI: 10.1063/1.1764938]

In this letter, we report \(C_p(T)\) measurements of 2D SAMs on planar polycrystalline Au samples. We also measure 3D SAMs synthesized from solution in order to compare with previous studies using conventional DSC.\(^{14,15}\) We obtain the peak melting temperature \(T_p,\) heat of fusion \(H_m,\) and desorption information from the \(C_p(T)\) data. Hexadecanethiol (\(\text{CH}_3(\text{CH}_2)_{15}\text{SH}\)) SAMs (abbreviated as \(C_{16}\) SAMs) were chosen in this study because the long chain alkanethiols \((>C_{14})\) easily form well-ordered monolayers.\(^{8,9}\)

The nanocalorimetry method is reported in detail elsewhere.\(^{17,18,21}\) The MEMS-based sensor is microfabricated on a Si wafer as shown in the inset of Fig. 1. In this work, Al is selected for the metallization layer, because alkanethiolate SAMs are not expected to grow on the native Al oxide layer,\(^{22}\) which forms spontaneously on exposure to air.\(^{23}\) Sensors made with Pt metallization show similar but less reproducible results. Transmission electron microscopy (TEM)
JEOL 2010F is used to image the Au nanoparticles (3D SAMs) and ellipsometry (Focus Ellipsometer FE-III, Rudolph Technologies, Inc.) is used to measure the average thickness of the 2D SAMs.

Sample preparation for 2D SAMs proceeds as follows: first, a 4 nm Cr (adhesion layer) and a 75 nm Au layer are sequentially thermally deposited onto the SiN_4 side of the sensors using a shadow mask. Then the baseline TDSC and ellipsometry measurements are obtained. Finally, the sample sensor is immersed into a 1 mM hexadecanethiol in ethanol solution for 48 h at room temperature, after which it is extracted from the solution and thoroughly rinsed with ethanol. The colloid dispersion of 3D SAMs on Au nanoparticles is synthesized following the standard method and then deposited directly onto the sensor using a pipette. Commercial hexadecanethiol (Aldrich, >95% purity) is used without further purification.

All TDSC measurements are performed in a vacuum chamber (1×10^{-8} Torr). Both the sample and reference sensors are mounted on a copper stage, which is cooled by liquid nitrogen (LN2). TDSC measurements are obtained using ultrafast scanning rates (heating: ~30 000°C/s and cooling: ~5 000°C/s) from LN2 temperature. Multiple scans were taken at 2 s intervals.

The amount of alkanethiol in the 2D SAMs was determined using three different methods: (1) C_p measurements, (2) ellipsometry, and (3) the surface coverage on the Au surface area. Using C_p measurements of the liquid and solid states of the SAMs, we estimate the amounts of alkanethiol assuming bulk values of specific heat of hexadecane. In addition, the alkanethiol amount is also estimated using thickness values from ellipsometry and the density of bulk hexadecanethiol. We also estimate the amount of alkanethiol by assuming that the 2D SAM completely covers (100%) the measured sample area with a uniform molecular area density of the alkanethiol (0.214 nm^2/molecule). The average amount of the alkanethiol estimated by all these methods is 1.42±0.16×10^{-11} mol.

Figure 1 shows a calorimetric curve of 3D SAMs. (7×10^{-11} mol of alkanethiol). Typical 3D SAMs exhibit a somewhat broad [full-width-on-the-half-height (FWHH) ~35°C] endothermic peak with peak temperature T_{p,3D} ~25±3°C and a heat of fusion H_m,3D ~16±5 kJ/mol. The calorimetric scans up to 100°C are reproducible over 100 scans and the effects of desorption are not apparent. These results are consistent with previous works (T_{p} ~30°C, H_m,3D=14 kJ/mol) and (T_{p}=41°C, H_m,3D =13.8±0.8 kJ/mol) for 3D SAMs dry powder samples (~2×10^{-5} mol of alkanethiol) using conventional DSC at ~0.1°C/s scan rate. Our sample is ~10^6 smaller than used for conventional DSC work.

The broadness of the transition peak cannot be explained by the instrumentation broadening for the extremely small sample. The inset to Fig. 1, demonstrates the resolution of the TDSC technique for small samples, a C_p measurement of a single crystal polyethylene sample which has ~100 times smaller amount of material than the samples used for our 2D SAMs measurements. The narrow (FWHH ~5°C) melting peak ensures that the instrumentation broadening is negligible. The broadness of the peak may be partially due to the variation in particle size coupled with the size-dependent melting temperature of 3D SAMs.

One complication in analyzing calorimetry measurements of 3D SAMs is the effect of interdigitation between neighboring clusters during calorimetry. Interdigitation makes it difficult to separate the melting properties due to cluster–cluster overlap from the intrinsic melting properties of the SAMs on individual separated nanoparticles. Previous work suggests that most of the transition enthalpy in 3D SAMs is due to the interdigitation. Investigation of 2D SAMs, made possible by TDSC technique, allows one to decouple SAMs melting from the interdigitation effect.

Typical C_p(T) curves for 2D SAMs are shown in Fig. 2 of the first and second scans to 200°C. The broad endothermic peak with FWHH ~100°C of the calorimetric curves starting at ~100°C and persisting up to about 150°C corresponds to the endothermic peak on the 3D SAM C_p(T) data (Fig. 1). The sharp endothermic signal at the end of the scans starting at ~170°C is attributed to the desorption process of alkanethiol. While T_p for the first scan is about 120°C, the T_p for the second scan is substantially lower by about 50°C. The transition temperature for 2D SAMs is consistent with the value of 80°C, found for full coverage 2D SAMs.

Desorption during the first scan is considered to be the reason for the large shift of the melting peak to a lower temperature in the second scans. We estimate that 5% of the alkanethiol desorbs due to the first scan. This estimate is made using the change in C_p for the solid film between the first and second scans. The large effect of desorption on the melting characteristics of SAMs also has been observed previously in C10 2D SAMs. It has been shown for C_{10} 2D SAMs, that the highest value of T_p occurs at coverage close to 100%. Furthermore, a few percent decrease in the coverage causes a substantial drop in T_p (e.g. ΔT_p=50°C decrease in T_p occurs by changing the coverage from 100 to 95%). If coverage decreases even further, T_p stabilizes. In our case the
difference between $T_p$ of the first and second scans is also about 50°C. This parallelism to $C_{10}$ SAMs results also implies that the coverage probed by the first scan is close to 100%. The desorption process also occurs during the second and subsequent scans (see Fig. 3), but to a lesser degree and does not cause a noticeable peak shift, which is also consistent with the work on $C_{10}$ 2D SAMs, if we suppose the same plateau on the $T_p$ versus coverage dependence. The large difference between 2D and 3D SAMs has also been shown by simulations in the C12 system: $T_{p \text{3D}} = 21°C (FWHH \sim 35°C)$ and $T_{p \text{2D}} = 130°C (FWHH \sim 100°C)$.

The measured value of heat of fusion $H_m^{2D} (20 \pm 4 \text{ kJ/mol})$ is nearly equal to $H_m^{3D} (16 \pm 5 \text{ kJ/mol})$. However, both $H_m^{2D}$ and $H_m^{3D}$ are considerably lower than the bulk value for pure hexadecane (53 kJ/mol). This observation is also supported by molecular dynamics simulations where $H_m^{3D}$ for $C_{12}$ SAMs on Au(110) and Au(200) clusters are found to be $\sim 20 \text{ kJ/mol}$, which is significantly smaller than the bulk value for dodecane, $H_m^{\text{bulk}} (40 \text{ kJ/mol})$. One explanation for why $H_m^{2D} < H_m^{\text{bulk}}$ is that only part of the film (e.g., a portion of the chain) is involved in the melting process. Using the estimation that the heat of fusion is $3 - 4 \text{ kJ per mole of CH}_2$ groups, the effective number of CH$_2$ segments involved in the melting is only four to six per chain. On the microscopic level $H_m^{2D}$ will be associated with the population and energetics of the generation of gauche defects over the broad temperature range (formation energy of a gauche defect is about 2 kJ/mol-defect for a free alkane). Another explanation is that melting process of SAMs should also be compared to the gel-to-liquid crystalline transition.

In summary, TDSC shows that the temperature of the transition for 2D SAMs is much higher and broader than 3D SAMs and the heat of fusion for 2D and 3D SAMs are comparable but much lower than for bulk alkanethiol. Melting characteristics of the 3D SAMs are comparable with earlier studies using conventional DSC.

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