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Nonwetting growth and cluster formation of CF_4 on graphite

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An ac heat-capacity study of CF_4 on graphite in the multilayer region is reported. The results indicate that CF_4 does not wet graphite between 18 and 80 K. Below 72 K, the thickness of the adsorbed film is limited to two layers. A bilayer-to-trilayer layering transition is observed near 72 K. The heat-capacity signal shows unusual behavior near $T_{\alpha\beta}$ which may be related to the surface transition in the CF_4 bulk clusters due to the presence of the graphite substrate.

I. INTRODUCTION

There are two distinctly different growth modes, namely wetting and nonwetting (or incomplete wetting), for an adsorbed film on an attractive substrate when the bulk coexistence line is approached.[1] Under the variation of temperature, a crossover from one kind of growth mode to the other can occur in an adsorption system. This is the wetting transition.

Nonwetting growth and the wetting transition have been experimentally observed in a large number of adasorption systems.[2-6] However, up to now, most of the wetting transitions observed in the physisorption systems are at the bulk melting point.[4-6] In such systems, the solid phase does not wet the substrate, but the liquid does. These experimental observations seem to be consistent with the theoretical prediction that the structure of the bulk adsorbate solid phase is important in determining the growth behavior of an adsorption system.[7,8] It has been suggested that, due to the structural misfit between the bulk and the adsorbed film, complete wetting of the solid adsorbate is unlikely and no wetting transition can occur along the gas-solid or liquid-solid phase boundaries.[7,8] Recently, a reflection high-energy electron diffraction (RHEED) study of CF_4 on graphite seems to show a "true" first-order wetting transition near 37 K.[9] This is far below the bulk melting point at 89.5 K and the solid-solid α-β transition (another triple point) at 76.5 K ($T_{\alpha\beta}$).

In this paper, we shall report a detailed heat-capacity study of multilayer CF_4 on graphite. Contrary to the RHEED result, we do not observe any wetting transition or growth behavior change at temperatures near 37 K. The experimental evidence clearly shows that below 70 K, a maximum of two layers can form on the graphite substrate. A bilayer-to-trilayer layering transition is found near 72. K. Furthermore, unusual heat-capacity behavior is observed near the bulk α-β transition. This unusual behavior is interpreted as a surface transition of the nonwetting bulk clusters under the influence of the substrate coupling field.

The heat-capacity results reported in this paper range in temperatures from 18 to 80 K, and in coverages from monolayer completion up to an equivalent of more than 20 layers. The procedures and apparatus of the experiment have been described previously.[3,10] Due to the large heat-capacity and weak thermal conductivity of the Graphite Foam substrate used in this experiment, it is not easy to determine precisely the absolute value of the heat capacity of the adsorbed system with the ac heat-capacity technique.[11] However, this technique has been shown to be very sensitive in detecting changes in the heat capacity due to phase transitions.[3,10] In a multilayer experiment the equilibrium vapor pressure in the cell is very close to the saturated value of the bulk. In dosing the adsorbate gas into the sample cell, a small temperature gradient between the (colder) sample cell wall and the (warmer) calorimeter will cause preferential condensation of the adsorbate as bulk on the cell wall. Despite the extreme care in cooling down the sample cell, the real coverage on the substrate (denoted as n_e, the effective coverage) is often less than the initial coverage for $n \geq 5$. In this experiment the three-dimensional vapor pressure is very low (< 0.08 torr); the possible effect of the vapor pressure on the thermal equilibrium time of the calorimeter can be neglected. Since heat-capacity anomalies serve as the basis of our discussion, the vapor pressure effect will not affect any conclusions presented in this paper. In the following discussion $n=1$ is defined as the coverage for completing a (2×2) commensurate layer, which for our calorimeter corresponds to 9.9×10^{18} molecules. In order to compare the heat-capacity behavior near $T_{\alpha\beta}$ for CF_4, with and without the graphite substrate, CF_4 gas was introduced into a thin-wall (0.005 cm) brass cell containing no graphite substrate, and the heat capacity as a function of temperature was measured near $T_{\alpha\beta}$.

In order to understand the heat-capacity scans to be discussed, it is beneficial to describe some general features of the heat-capacity signal associated with a wetting transition. The experimental system for our heat-capacity measurement consists of a fixed amount of adsorbate N_{tot} on the substrate. In a nonwetting system, if $N_{\text{tot}} > N_f$, where N_f is the amount of adsorbate in the layered film on the substrate, $N_{\text{tot}} - N_f$ will exist as bulk clusters. Whenever there is a wetting or a layering transition, a heat-capacity anomaly C_{tr} should be observed. This heat-capacity signal depends on the entropy difference Δs between the adsorbate in the film phase and in the bulk phase. The signal also depends on the adsorbate exchange rate dN/dT between these two coexisting phases. Therefore, a first-order wetting transition will exhibit a δ-function-like heat-capacity peak. In the nonwetting system, a finite Δs should exist; however, as the layered film thickness approaches infinity, Δs approaches zero. Hence, the size of this first-order wetting peak does not increase linearly with

N_{tot}. For a continuous transition, the amount of layered adsorbate will change with temperature like $N_f \sim (T_w - T)^{-\theta}$, where $\theta > 0$ and T_w is the wetting temperature.[6,12] The anomalous heat-capacity signal related to the transition should behave like $C_{\text{tr}} \sim (T_w - T)^{\theta'}$ with $\theta' > 0$.[11,13] However, in the fixed coverage scan, N_f is limited by N_{tot}; therefore, C_{tr} will drop to zero at a temperature T_0 ($< T_w$) where $N_f = N_{\text{tot}}$.

II. GROWTH PROCESS BELOW 65 K

Between 18 and 55 K, a total of 14 heat-capacity scans of different coverage, from monolayer to 20 effective layers, were made. No heat-capacity anomaly was observed in any one of these scans. Because of the RHEED result,[9] we have been very careful in carrying out the measurements. We made heat-capacity scans both during warming and cooling with small temperature steps (~0.2 K). As we have discussed in the preceding section, a heat-capacity anomaly should show up in either a first-order or continuous wetting transition. (In the heat-capacity study of ethylene on graphite, such an anomaly is clearly seen at the layering and wetting temperatures.[4]) The heat-capacity curves in this temperature region show smooth evolution with temperature for all 14 coverages. Therefore, our results appear to rule out the possibility of a first-order wetting transition between 18 and 55 K. For coverages above bilayer completion and in temperatures between 37 and 45 K, the heat-capacity signal at a constant temperature shows an unusual amount of fluctuations with time. The fluctuation is about ten times larger than that outside this temperature-coverage region. However, when the heat-capacity signal is averaged over a long time interval (> 10 min), no heat-capacity anomaly is observed. The observed fluctuation may be related to some kinetic processes among the bulk clusters. It is possible that it is such kinetic processes that led to the incorrect (in our view) wetting transition interpretation of the RHEED result.[9]

A double heat-capacity peak structure is seen around 59 K (see Fig. 1). The peaks are located at 57.6 and 61 K, respectively. The peaks appear at a coverage near $n_e = 1.5$ and grow with coverage until approximately $n_e = 2.5$. Although this structure is present for all scans with higher surface coverages, the size, location, and shape of the anomaly do not show change with coverage above $n_e = 2.5$. Near monolayer completion, the 2D CF_4 solid is in a dense hexagonal incommensurate phase. In this phase no heat-capacity anomaly was observed in this temperature range.[11] The appearance of this double-peak structure at $n_e = 1.5$ is probably a signature of the formation of a bilayer solid, and the observed peaks are related to the phase transitions in the second layer or bilayer solid. The most simple and reasonable explanation for the saturation of this double-peak structure beyond $n_e = 2.5$ is that no more layers form on top of bilayer film in this temperature range. The fact that no heat-capacity anomaly was observed around 37 K, and the saturation of this double-peak anomaly at the bilayer completion coverage suggest that CF_4 does not wet graphite below 60 K. This conclusion is supported by a recent ellipsometric isotherm study.[14]

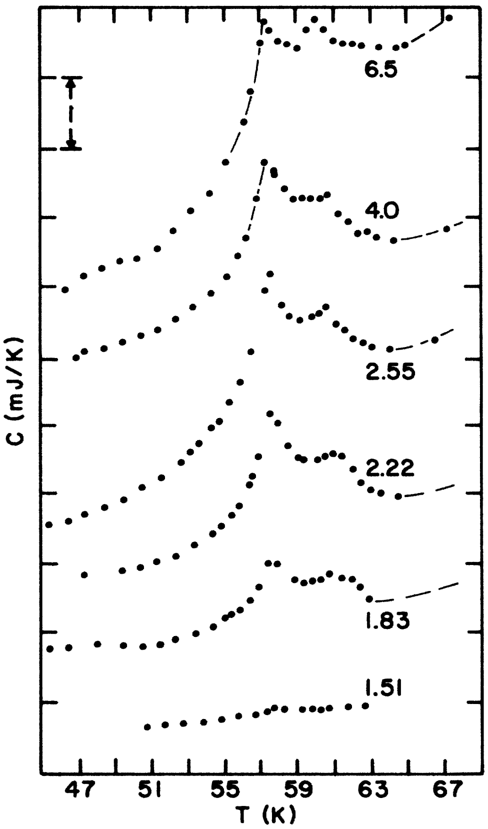

FIG. 1. Heat-capacity traces of multilayer CF_4 on graphite at temperature near 59 K. The double-peak structure is related to transitions in the bilayer system. The label on each scan is the effective coverage n_e. The heat-capacity values at 45 K for each scan (from bottom to top) are, respectively, 1.8, 2, 2.45, 3.3, 4.3, and 8.2 mJ/K. These values correspond to approximately $8.5k_B$ per adsorbate molecule; this is somewhat larger than the expected "regular" contribution of an adsorbed film. It is possible that the transitions near 59 K extend to 45 K.

Without other experimental evidence, we cannot determine the nature of the transitions related to the double-peak anomaly. One possibility is that the peak at 57.6 K is a signature of a single-layer to bilayer layering transition. This was suggested by a vapor pressure isotherm study.[15] It is also possible that both peaks are from the bilayer film. This interpretation would suggest that the bilayer film can form on the substrate down to at least 18 K.

III. LAYERING TRANSITION AND SURFACE TRANSITION NEAR $T_{\alpha\beta}$

In Fig. 2, heat-capacity traces near the α-β transition temperature are shown. For comparison, the heat-capacity signal of bulk CF_4 near the α-β transition measured in a cell with no graphite is also shown. The bulk α-β transition temperature determined in our study at 76.5 K is in reasonable agreement with the earlier reported value of 76.2 K.[16]

In scans of coverages of $n_e = 2.2$ and below, no anomaly is seen between 61 and 80 K. At $n_e = 2.55$, just above the

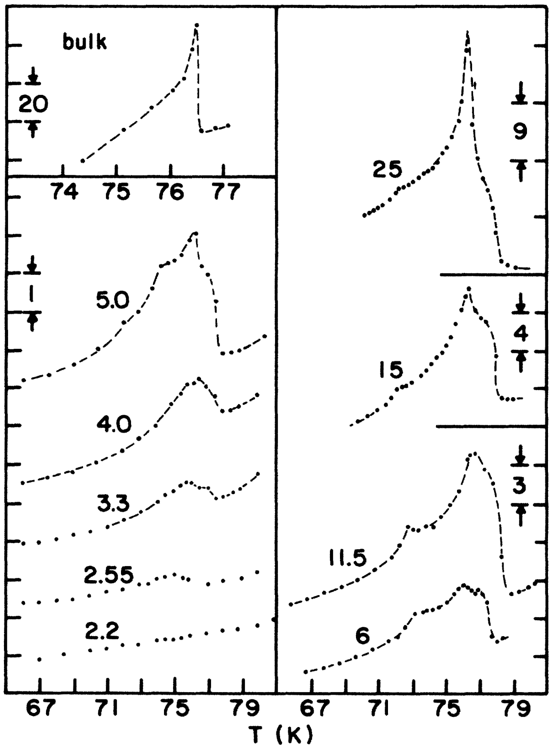

FIG. 2. Heat-capacity traces of multilayer CF_4 on graphite at temperature near the α-β transition. The bulk α-β transition signal is also shown. The amount of CF_4 in the bulk run is comparable to that in the $n_e=25$ scan. The temperature scale for the bulk signal is expanded to show the sharp falling edge on the high-temperature side. The effective coverage is shown for each scan. The heat-capacity values at 80 K for each scan (from low to high coverage) are, respectively, 4, 5.3, 6.3, 6.8, 8.5, 12.2, 21.4, 35, and 53 mJ/K. These values probably include contributions due to desorption. This value was not determined for the bulk CF_4 scan. The dashed lines are drawn to guide the eyes.

bilayer completion coverage, a peak shows up near 75 K. In the subsequent three scans of $n_e=3$, 3.3, and 4, this peak grows in size and stays at 75.6 ± 0.1 K. Beyond $n_e=4$ the size of this peak does not increase with coverage, but the transition temperature gradually decreases to 72 K. Therefore, this signal is not from the bulk CF_4 clusters. Since only a maximum of two layers can form on graphite at temperatures near and below 60 K, and the coverage range between $n_e=2.5$ and 4 corresponds approximately to that for a third layer, we interpret this heat-capacity anomaly as a signature of layering transition from a (bilayer+bulk) to a (trilayer+bulk) system. This interpretation is consistent with the early vapor pressure isotherm and the recent ellipsometric isotherm results.[14,15] A layering transitions should occur at the bulk coexistence boundary, and should not show variation in transition temperature. We do not understand why this layering transition temperature decreases for $n_e>4$. A shift in the layering transition temperature is also observed in the ethylene on graphite system.[4] This shift may be an effect related to the finite size of the bulk clusters.

Figure 2 also shows that in the thick-film limit, the heat-capacity scans of CF_4 on graphite near $T_{\alpha\beta}$ do not resemble that due to bulk CF_4. A sawtooth anomaly with a sharp falling edge on the high-temperature side is observed at 76.5 K for the bulk system. In the adsorbed CF_4 system, for scans of $n_e=11.5$ and 15, the heat-capacity curve has a rounded peak at 76.5 K and a sharp falling edge near 77.8 K. In the scan of $n_e=25$, the peak at 76.5 K sharpens up, but the high-temperature side peak near 78 K also shows growth with coverage. The most straightforward interpretation is that in the adsorbed CF_4 system (that is, under the influence of the graphite substrate), there are two transitions, one near 76.5 K and the other near 78 K. The transition at 76.5 K is associated with α-β transition, and the 78 K peak not present in the bulk system reflects the effect of the graphite substrate on the adsorbed system.

Figure 3 shows the size of the heat-capacity anomalies due to the α-β related transition and the transition near 78 K as a function of effective coverage. We made the assumption that the shape of the heat-capacity anomaly due to the α-β related transition for the adsorbed system is similar to that of the bulk α-β transition, resembling a sawtooth with a sharp drop at 76.5 K. This assumption allows us to separate the observed anomaly into contributions from the α-β related transition ($T<76.5$ K) and from the 78 K transition ($T>76.5$ K). Due to the significant difference in the peak sizes between the 76.5 and the 78 K transitions, the uncertainty associated with this simple assumption does not seriously affect the observation we are going to make, namely, that both anomalies grow with coverage. By subtracting the heat-capacity scan of a specific coverage from that of a neighboring higher coverage, the increase of this 78-K side peak with coverage is also confirmed. It is striking that this increase extends to the highest coverage studied in this experiment at $n_e=25$. The linear increase of the 78-K side peak with coverage for

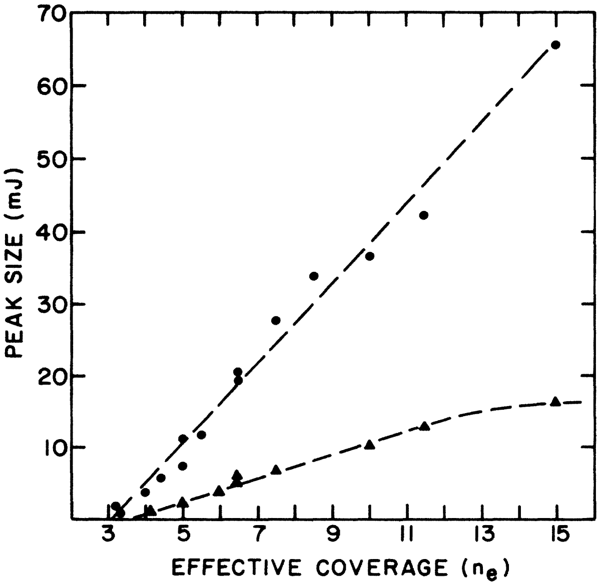

FIG. 3. The size of the α-β related transition (closed circles) and the size of the high-temperature side peak near 78 K (triangles) as a function of effective coverage. The dashed lines are drawn to guide the eyes.

$n_3 < 10$ may be fortuitous: Figure 3 should only be interpreted to show a monotonic increase in the peak size with coverage.

Since CF_4 on graphite is in the nonwetting growth mode below $T_{\alpha\beta}$, it is tempting to interpret the observed heat-capacity feature near $T_{\alpha\beta}$ here as a sign of a wetting transition induced by the bulk α-β transition.[11,17] However, results from the ellipsometric isotherm study on this system indicated that the thickness of the layered film is limited to four layers below 80 K.[14] This appears to rule out the wetting transition interpretation. The coverage dependence of the 78 K peak, as shown in Fig. 3, indicates that this transition does not have its origin in the layered film of three or four layers. Instead, we propose this transition is related to the presence of the nonwetting bulk clusters which are coexisting with the layered film. In the thermodynamic limit the bulk α phase is unstable at temperatures above $T_{\alpha\beta}$. However, it is possible that the effective couplings between the CF_4 molecules in the surface region near the graphite substrate are different from those of the bulk. This effect may keep the interface region in the ordered state above the bulk transition temperature. The order-disorder transition of the surface layers, therefore, is higher than the bulk. The existence of such a surface transition has been suggested theoretically.[18] Heat-capacity measurement of the bulk system (without graphite) was made with an amount of CF_4 comparable to that in the $n_e = 25$ scan. In this scan, as shown in Fig. 2, a sharp heat-capacity peak without side peak is observed. This would suggest that the surface transition does not take place in the "free" surfaces of the CF_4 bulk clusters. We are left with the interpretation that the 78-K side peak has its origin in the interface region between the graphite substrate and the nonwetting bulk clusters. The increase of the 78-K peak with coverage, as shown in Fig. 3, suggests that this interface region also increases with coverage. Therefore in this system, the bulk clusters that are coexisting with the adsorbed layers sit on the substrate with a nonzero contact angle. This specific observation on the configuration of the nonwetting system and our interpretation of a substrate-induced transition in the interface region of the bulk clusters above the α-β transition clearly deserve further careful and high-resolution scattering studies.

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