Wetting Transition in Solid Films: Reflection-High-Energy-Electron-Diffraction Study of Multilayers of CF_4 Adsorbed on Graphite

J. Suzanne, J. L. Seguin, M. Bienfait, and E. Lerner[(a)]
Département de Physique, Faculté des Sciences de Luminy, F-13288 Marseille Cédex 9, France

(Received 12 October 1983)

The stability of multilayer formation versus clustering of CF_4 films adsorbed on graphite has been studied by reflection high-energy electron diffraction. It is found that an incomplete-to-complete wetting transition occurs at $T_w = 37$ K, a temperature far below the bulk triple point (89.5 K). The presence of a hysteresis indicates that the transition is first order.

PACS numbers: 68.10.Cr, 61.14.Hg, 68.40.+e, 68.55.+b

The nature of wetting transitions has recently been the subject of intensive theoretical work.[1-10] These transitions occur when a substance that incompletely wets a surface at low temperature and exhibits a finite angle of contact changes its wetting behavior at higher temperature in such a way that its contact angle becomes zero. The temperature of the transition between these states is called the wetting temperature.

The majority of the calculations deal with models simulating adsorbed multilayers on a fluid or a solid surface. A few experimental studies have been performed in order to determine the growth habits of atomic or molecular layers on uniform substrates.[11-14] Only a few systems have shown complete wetting at low temperature.[14] The others do not wet but should undergo a wetting transition at some high enough temperature. This has been predicted theoretically[15] and shown experimentally.[11,12,16,17] The experimental wetting temperature has always been found close to the bulk triple point or above.

The nature of the wetting transition has not been resolved experimentally. Most theoretical papers have been concerned with the order of the transition.[1-10] Mean-field theory and the renormalization-group approach agree that with short-range forces, the transition can be either first order or continuous; with long-range forces, such a transition can only be first order.

We report here what we believe to be the first experimental evidence of a first-order wetting transition in a solid film. This transition occurs at a temperature well below the bulk triple point, that is, at a solid-solid interface.

The experiment has been performed on solid CF_4 multilayers adsorbed at low temperature ($10 < T < 60$ K) on the (0001) face of a graphite single crystal. The multilayer stability is measured by reflection high-energy electron diffraction (RHEED), a technique well adapted to the determination of the mode of growth of surface films.[14,18] The experimental setup has been described elsewhere.[14,19] Let us recall that the angle of incidence is very low (3°–4°). The electron beam energy was 32.74 keV in the present experiments. Besides the RHEED setup, our ultrahigh-vacuum system includes a high-resolution low-energy-electron-diffraction (LEED) capability to observe the structures of the substrate and first adsorbed layer, a mass spectrometer to monitor the gas purity, and an ion gauge to record the vapor pressure surrounding the crystal. The cleanliness and the long-range order of the graphite single-crystal surface are checked by observation of the otherwise known LEED diffraction patterns of the CF_4 monolayer.[20] The temperature measurements are made by means of a silicon diode thermometer placed into the copper sample block. The graphite crystal is cemented on the copper block with silver paste. The temperature of the crystal was regulated to better than 0.1 K. The absolute uncertainty is estimated to be 1 K.

The thickness of the film was measured as follows. Beginning with the bare substrate at constant temperature and a background pressure less than 1×10^{-10} Torr, the pressure was raised abruptly by the introduction of CF_4 gas through a leak valve to a constant value p. The time required to condense a monolayer was determined by observation of the evolution of the LEED pattern. We first observe, around 40 K, an almost commensurate solid corresponding to the so-called "triple-peaked" phase.[21,22] Then a rotated incommensurate solid[20-22] appears at monolayer completion. It manifests itself in the LEED pattern by the appearance of doublets in a position close to the 2×2 structure. The time $\Delta\tau$ needed to observe the doublets gives the exposure $p\Delta\tau$ required to condense a complete layer. This exposure is used to estimate the pressures and times necessary to deposit any desired quantity, with the assumption that the sticking coefficient is constant over the entire range.

Two kinds of experiments were carried out. In the first set, we observe the growth mode of the film under a constant flux of CF_4 vapor (in the 10^{-7}-Torr range) by monitoring continuously the RHEED pattern. In the second set of experiments, we condense a given thickness of CF_4, stop the gas introduction, and observe the RHEED pattern at different temperatures.

We first report on the experiments under constant flux. At $T<37$ K (typically 30–36 K), we observe parallel streaks distinct from the graphite as soon as one or two statistical layers are deposited. Upon further condensation, the streaks become modulated and after deposition of a few more layers, sharp spots are superimposed on the streaks within the experimental uncertainty in the parameter measurement (~2%). Moreover a few extra sharp spots appear outside the streaks. When a thick film is condensed (~20–100 layers), the streaks disappear totally and the RHEED pattern is only made of sharp spots [Fig. 1(a)]. The same pattern is observed down to 15 K. The succession of the different RHEED patterns corresponds first to condensation of a few ordered solid layers, second to the deposition of bulk crystallites coexisting with the two-dimensional adsorbed structure, and finally to the covering of the whole surface by bulk crystals. In each case, the angular separations between streaks and the positions of the sharp spots are consistent with the lattice parameter of the LEED-determined structures and with the α-CF_4 bulk structure, respectively.[19] These results clearly indicate that below 37 K thick films of CF_4 incompletely wet the graphite surface and that the mode of growth is of type 2.

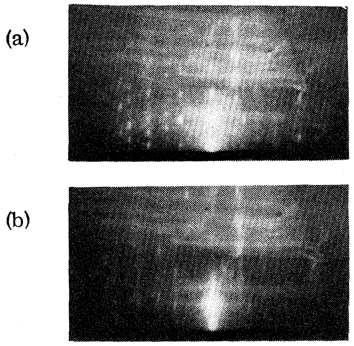

FIG. 1. Typical RHEED pattern of a thick film (20–100 layers) of CF_4 molecules adsorbed on graphite; electron energy 32.7 keV, aximuth $[\bar{1}3.0]$. The central modulated streak is the superposition of the (0001) graphite and CF_4 diffracted beams. (a) Only sharp spots are visible, characteristic of bulk clusters of CF_4 molecules. Their structure is compatible with that of α-CF_4. Thus, at 35 K, CF_4 films incompletely wet the graphite surface. (b) The sharp spots of (a) have disappeared and only modulated streaks are visible, characteristic of the layerlike nature of the film. Thus, at $T=40$ K, CF_4 films completely wet the graphite surface. The wetting transition occurs at $T_w=37$ K. Note that (a) and (b) are not reproduced at exactly the same scale.

At $T>37$ K (37–50 K temperature range), the type of growth is quite different. We still observe streaks at the beginning of the condensation; then the streaks become modulated. There is no other change upon further exposure. The modulation of the streaks is a well-known effect and results from the finite penetration of the grazing-incidence beam.[14] A typical example of the RHEED pattern obtained for thick films at 40 K is given in Fig. 1(b). These results show unambiguously a layer-by-layer growth above 37 K at all thicknesses studied. Hence, the mode of growth becomes type 1 above the wetting temperature (37 K) of the CF_4 surface film.

In order to check whether this complete-to-incomplete wetting transition at 37 K is an artifact due to kinetics effects which are well known in crystal growth, we examined the RHEED patterns under a fixed quantity of gas in the chamber. This is our second set of experiments. After condensing a thick multilayer (from 20 to 100 layers), we stop the introduction of the CF_4 vapor. Within the temperature range studied (30–40 K), the extrapolated CF_4 pressure at coexistence falls in the 10^{-15}–10^{-13}-Torr range.[23] This pressure is too small for significant transport through the gas phase. Still, our observations indicate that local equilibrium is achieved very rapidly by surface mobility. In the type-2 configuration, the sharp spots weaken and broaden gradually over a period of a few minutes. However, the sharp spots can be restored by sweeping the electron beam over the surface. We believe that the beam carries enough energy to produce a slight local heating of the film, causing the distillation of bulk crystallites from the probed region to adjacent areas of the film. Such an effect is not observed when the film is under constant flux of CF_4 vapor as described previously. This is probably due to the rate of condensation being larger than the rate of distillation.

During these experiments, we crossed the wetting transition back and forth, changing the temperature between 40 and 30 K by steps of 0.5 K. In order to prevent an apparent thermal hysteresis due to the position of the thermometer with respect to the graphite crystal, we waited about 5 min for each step. We know from other experiments[20] that a steady state at constant temperature is reached on the surface in less than 1 min. It takes about 10 sec to go from one step to the next. First, we condense a thick film at about 40 K. We obtain nice parallel streaks. After closing the calibrated leak valve, we cool the surface down to 35 K, step by step. At 36 K, we still observe the streaks even after 10 min. At 35 K, the streaks are replaced by sharp spots after 1 to 2 min. If we change the temperature from 36 to 33 K in 30 sec (no step), the sharp spots appear a few seconds after the lowest temperature (33 K) is reached. On the reverse temperature scan, if the film is warmed up to 40 K, step by step, the previous parallel streaks are restored at 37 K. We repeated the experiment several times for different thicknesses. We always found upon rewarming that the spots disappeared at 37 ± 0.1 K.

Hence, when the temperature is lowered, the complete-to-incomplete wetting transition always occurs at about 2 K below $T_w = 37$ K. This hysteresis phenomenon is an indication that the wetting transition is first order.

It is important to point out that this wetting transition occurs far below the bulk triple point (89.5 K).[11] This result is different from experimental observations performed up to now.[11,12,16,17] The beautiful experiments by Moldover and Cahn,[16] or more recently by Schmidt and Moldover,[17] are the only ones, to our knowledge, indicating a first-order wetting transition. However, they concern a fluid-fluid interface. Specific-heat measurements of O_2 on polycrystalline graphite suggest the existence of a prewetting phase boundary below the bulk triple point.[12] More experiments are needed to confirm this interpretation.

One can wonder whether the observed wetting transition is related to any solid-solid transition in the monolayer or in the bulk crystal. To the best of our knowledge of experimental data, this is not the case. This makes the CF_4/graphite system particularly interesting for undergoing model calculations in order to compare theory and experiments.

We are grateful to J. G. Dash for his permanent interest in this work and for his critical comments. We also thank J. A. Venables and M. Schick for numerous suggestions and comments. The Département de Physique, Faculté des Sciences de Luminy, is an Equipe de Recherche associée au Centre National de la Recherche Scientifique (ERA No. 070899).

---

[a] Permanent address: Instituto de Fisica, Universidad Federal do Rio de Janeiro, 21941 Rio de Janeiro, Brazil.

[1] J. W. Cahn, J. Chem, Phys. 66, 3667 (1977).

[2] C. Ebner and W. F. Saam, Phys. Rev. Lett. 38, 1486 (1977).

[3] C. Ebner, Phys. Rev. A 22, 2776 (1980).

[4] D. E. Sullivan, J. Chem. Phys. 74, 2604 (1981).

[5] R. Pandit and M. Wortis, Phys. Rev. B 25, 3226 (1982).

[6] R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B 26, 5112 (1982).

[7] W. F. Saam, Surf. Sci. 125, 253 (1983).

[8] G. F. Teletzke, L. E. Scriven, and H. T. Davis, J. Chem. Phys. 77, 5794 (1982), and 78, 1431 (1983).

[9] E. H. Hauge and M. Schick, Phys. Rev. B 27, 4288 (1983).

[10] M. P. Nightingale, W. F. Saam, and M. Schick, Phys. Rev. Lett. 51, 1275 (1983).

[11] J. Menaucourt, A. Thomy, and X. Duval, J. Phys. (Paris), Colloq. 38, C4-195 (1977).

[12] M. Sutton, S. G. J. Mochrie, and R. J. Borgeneau, Phys. Rev. Lett. 51, 407 (1983).

[13] D. D. Awschalom, G. N. Lewis, and S. Gregory, Phys. Rev. Lett. 51, 586 (1983).

[14] J. L. Seguin, J. Suzanne, M. Bienfait, J. G. Dash, and J. A. Venables, Phys. Rev. Lett. 51, 122 (1983).

[15] See for instance the very complete paper of Ref. 6.

[16] M. R. Moldover and J. W. Cahn, Science 207, 1073 (1980).

[17] J. W. Schmidt and M. R. Moldover, J. Chem. Phys. 79, 379 (1983).

[18] M. Bienfait, J. L. Seguin, J. Suzanne, E. Lerner, J. Krim, and J. G. Dash, Phys. Rev. B 29, 983 (1984).

[19] J. A. Venables, J. L. Seguin, J. Suzanne, and M. Bienfait, to be published.

[20] S. Calisti, thesis, Marseille, 1981 (unpublished); S. Calisti and J. Suzanne, to be published.

[21] B. Croset, C. Marti, P. Thorel, and H. Lauter, J. Phys. (Paris) 43, 1659 (1982).

[22] K. Kjaer, M. Nielsen, J. Bohr, H. J. Lauter, and J. P. McTague, Phys. Rev. B 26, 5168 (1982).

[23] P. Dolle, M. Matecki, and A. Thomy, Surf. Sci. 91, 271 (1980).

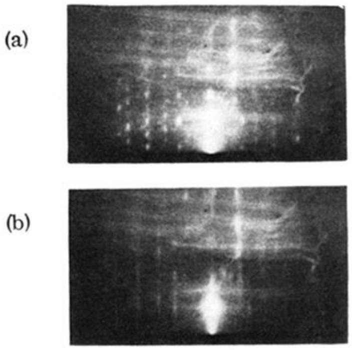

FIG. 1. Typical RHEED pattern of a thick film (20–100 layers) of CF_4 molecules adsorbed on graphite; electron energy 32.7 keV, aximuth $[\bar{1}3.0]$. The central modulated streak is the superposition of the (0001) graphite and CF_4 diffracted beams. (a) Only sharp spots are visible, characteristic of bulk clusters of CF_4 molecules. Their structure is compatible with that of α-CF_4. Thus, at 35 K, CF_4 films incompletely wet the graphite surface. (b) The sharp spots of (a) have disappeared and only modulated streaks are visible, characteristic of the layerlike nature of the film. Thus, at $T = 40$ K, CF_4 films completely wet the graphite surface. The wetting transition occurs at $T_w = 37$ K. Note that (a) and (b) are not reproduced at exactly the same scale.