Reentrant First-Order Layering Transitions in Multilayer Argon Films on Graphite

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(Received 24 August 1989)

We report ellipsometric coverage–vapor-pressure isotherm measurements for argon on graphite over the temperature range 65 to 84 K, which resolve up to eight layers. We confirm previous observations that the first-order layering transitions broaden near 67 K. However, in the fourth and higher layers, condensation again becomes sharp and apparently first order in the range between about 73 K and a new series of layer critical points near 77 K. Thus the surface-roughening transition is above 77 K and the behavior near 67 K represents disordering of only the top layer of the film.

PACS numbers: 68.55.Jk, 64.70.Dv, 68.45.Gd

A face of a crystal is said to exhibit surface melting[1] if a mobile "quasiliquid" layer exists on the equilibrium surface at a temperature below the bulk melting point T_m, and its thickness increases with temperature, diverging as T approaches T_m. Surface roughening[2,3] is the unlocking of the crystal surface from a particular lattice plane through the proliferation of steps, resulting in the loss of faceting in thermal equilibrium.[3] This transition is preceded on the low-temperature side by the appearance and proliferation of vacancies in and adatoms on the initially smooth surface plane. As the temperature increases towards the roughening temperature T_R, the characteristic size of clusters of adatoms and vacancies diverges, and the clusters gain their own (divergent) adatom and vacancy clusters. Roughening is thus an essentially many-layer phenomenon, but it must be preceded by short-range disordering of the surface layer. Simulations show a strong correlation between disordering of the top layer and onset of a large surface mobility.[4] Therefore, while surface roughening and surface melting are quite distinct many-layer phenomena, their precursors in the top layer may be coupled.

The properties of the surfaces of bulk crystals should be reflected in the properties of the surfaces of multilayer wetting films of the same solid on a foreign substrate.[5-7] Disordering of the (partially filled) top layer of a film is a transition of the 2D Ising class. A succession of Ising critical temperatures $T_{c,n}$ is expected for films of different coverages near $n-\frac{1}{2}$ layers, but always the transition is in the top layer. Using different models, Huse[8] and Nightingale, Saam, and Schick[9] have shown that the sequence $T_{c,n}$ should converge to the roughening temperature, with $T_R - T_{c,n} \sim (\ln n)^{-2}$.

Zhu and Dash[7] (ZD) have reported evidence for both surface melting and surface roughening in heat-capacity studies of two-layer to about twenty-layer films of both neon and argon on graphite. The evidence for surface roughening is small heat-capacity peaks near $0.8T_m$, attributed to disordering of the partially filled top layer. Previous volumetric isotherm measurements for argon on graphite by Gilquin[10] found broadening of the second- and third-layer condensation steps above $T_{c,2}=70$ K and $T_{c,3}=68$ K, respectively, in good agreement with ZD.

In this Letter we report ellipsometric adsorption isotherm measurements for argon on highly oriented pyrolytic graphite (HOPG) from 64 K to slightly above the melting point, $T_m=83.8$ K. The technique by which we measure the amount of adsorbate on a small area of graphite surface has been described elsewhere.[11] In this work we used a polarization-modulation ellipsometer in a slightly different configuration, but its characteristics are almost the same. The ellipsometer output I_1 at the modulation frequency is proportional to the adsorbate coverage. We find first of all that solid argon does not completely wet graphite. Apart from a small bump near 69 K, the solid-film growth stops on a plateau at coverage equivalent to 11 ± 1 layers, at which point there is evidence from weak attenuation of the specularly reflected light intensity of coexistence of a small, variable quantity of three-dimensional crystallites.[11] On the other hand, just above the melting point liquid films grow to the equivalent of at least 23 layers. An electron-diffraction experiment[12] found a lower limit of 10 layers at lower temperatures, while ZD (Ref. 7) reported no indication of bulk argon on exfoliated graphite to greater coverages. A limiting thickness of 11 layers would result if defects or strain in the film produced a marginal excess energy per adsorbed atom of 0.2 K. A strain of about 1% is required. Dash[13] has proposed that substrate defects may control the scale of polycrystallinity in the film, hence the completeness of wetting.

Up to 67 K we observe sharp layer condensation steps, indicative of first-order layering transitions, while at slightly higher temperatures the steps for layers $2 \le n \le 6$ are found to broaden, suggesting passage through two-dimensional critical points. If we assume (but see below) the compressibility exponent appropriate to the 2D Ising model, we obtain critical temperatures $T_{c,2}=69.4\pm0.2$ K and $T_{c,3}=67.6\pm0.2$ K, in agreement with Gilquin;[10] in addition, we find $T_{c,4}=67.0\pm0.2$ K and $T_{c,5}=67.4\pm0.4$ K. The remarkable new feature we find[14] is that at higher temperatures there is a reappear-

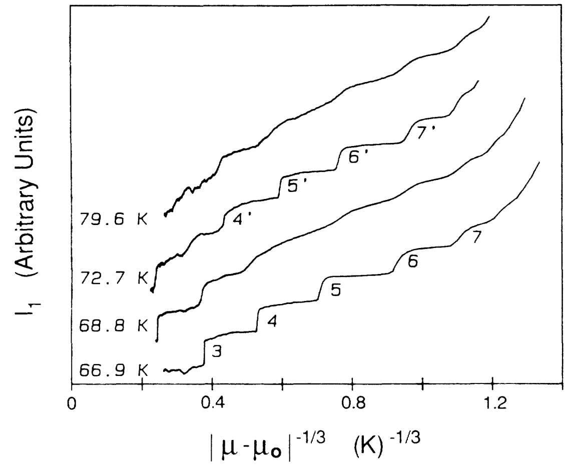

FIG. 1. Ellipsometric coverage isotherms at four temperatures. The abscissa is a function of the reduced pressure, given by Eq. (1). With the particular functional form used, the simple Frankel-Halsey-Hill model predicts a uniform staircase.

ance of sharp steps, characteristic of first-order transitions, but at shifted values of reduced pressure. These persist through the range $73 < T < 77$ K and then begin to broaden again near 77 K. This progression is illustrated by four selected isotherms in Fig. 1. Figure 2 shows the measured widths in chemical potential, $\Delta\mu = T\Delta p/p$, of the fourth, fifth, and sixth steps, as functions of temperature. The pressure width Δp is obtained by dividing a nominal step height ΔI_1 by the slope (dI_1/dp) at the inflection point. The steps attain a minimum background width $\Delta\mu \simeq 0.2$ K just below 67 K. In the temperature range of approximately 73 to 77 K, the step widths shown in Fig. 2 are again close to the minimum, whereas the second- and third-layer steps remain extremely broad. Thus there is a sequence of "bubble" coexistence regions in the coverage-temperature plane, starting with the fourth layer, with critical points near 77 K and lower end points near 71 to 73 K. Some of the heat-capacity peaks observed by ZD (Ref. 7) appear to be associated with crossing these bubble boundaries. Figure 3 shows the chemical potential at layer condensation steps (or at inflection points, where the steps are not sharp), relative to the chemical potential μ_0 of saturated bulk solid at the same temperature:

$$\mu_n - \mu_0 = T\ln(p_n/p_0)\,. \qquad (1)$$

(We set $k_B = 1$.) The layering transition lines in the low-temperature region ($T < 67$ K) in Fig. 3 are horizontal within experimental error. This implies that the partial entropy during layer condensation, given by the Maxwell relation

$$(\partial S/\partial N)_T = -(\partial\mu/\partial T)_N\,, \qquad (2)$$

is essentially equal to the entropy of bulk solid. We take this as justification to attempt to apply a Frankel-Halsey-Hill (FHH) model,[15] in which the film is regarded as a slab with bulk solid properties, in the presence of the extra attractive potential of the graphite substrate. Thus the chemical potential during condensation of the nth layer is

$$\mu_n = \mu_\infty + V(nd_1)\,, \qquad (3)$$

where μ_∞ is the chemical potential of a semi-infinite slab of adsorbate coexisting with vapor and d_1 is the thickness of an adsorbate monolayer. The potential of the substrate (relative to the continuation of the adsorbate crystal which it replaces) can be represented by[16]

$$V(z) = -3C_3 d_0 \sum_{m=0}^{\infty} (z + md_0)^{-4}\,, \qquad (4)$$

where $d_0 = 3.348$ Å is the layer spacing of graphite and C_3 is an effective van der Waals coefficient. This model gives an excellent fit to the layer chemical potentials from the third layer on, with $C_3/d_0^3 = 256$ K and $\mu_\infty - \mu_0 = 0.25$ K, where μ_0 is our experimental estimate of the chemical potential at saturation.

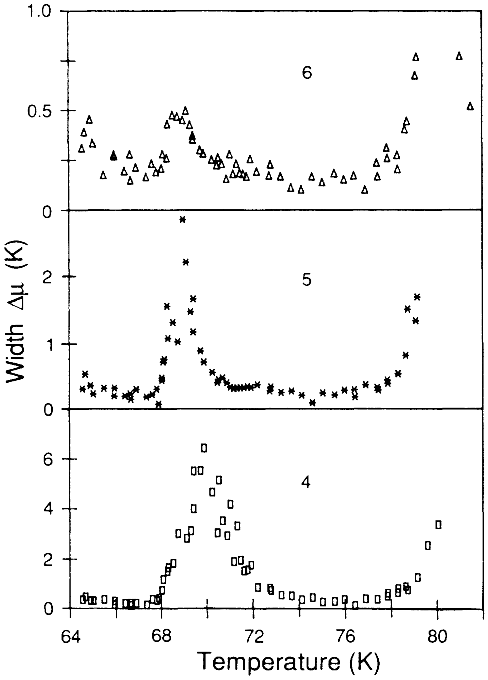

FIG. 2. Widths (in chemical potential) of layer condensation steps as functions of temperature for layers 4, 5, and 6. Note the differences in vertical scale.

The layer condensation chemical potentials in the bubble region, labeled by primed numbers in Fig. 3, again have nearly zero-temperature dependence. This, together with the step heights, implies that the coexisting phases differ by one layer of ordered solid. For the fourth layer, the two segments of first-order condensation are offset from one another in chemical potential by about 5.7 K. The slope $(\partial\mu/\partial T)_N$ is about -2 in the in-

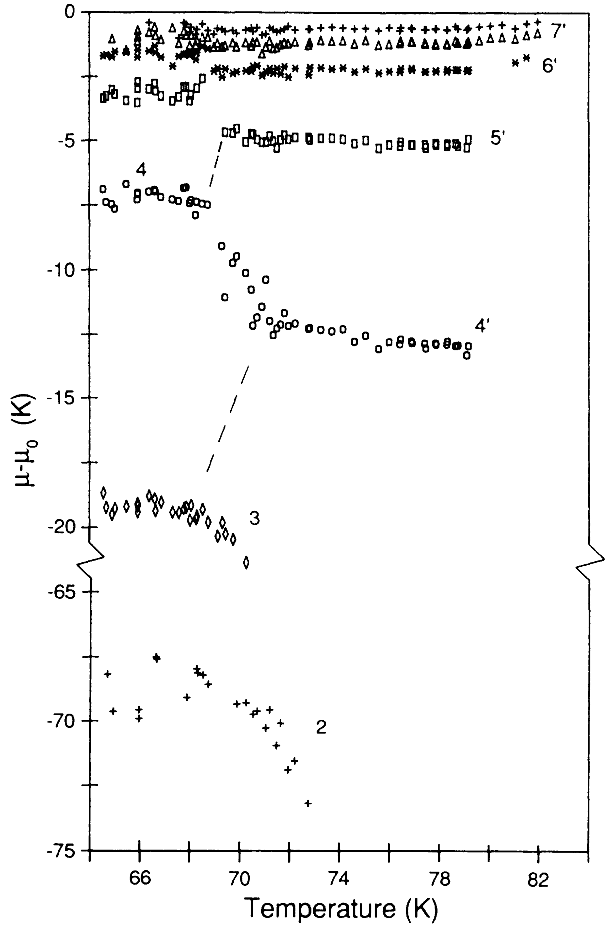

FIG. 3. Chemical potential (relative to bulk solid) at condensation of layers 2 through 8 as functions of temperature. The dashed lines indicate conjectured regions of top layer melting.

tervening region for coverages at the center of the 4′ step, so that the partial entropy given by Eq. (2) is comparable to the entropy of melting of bulk argon, $1.71k_B$. This means that the adsorbate added in this region has disorder comparable to a liquid. The higher layering lines have progressively smaller offset in chemical potential, but this offset occurs over a correspondingly smaller temperature range, so that the partial entropy in the crossover region may be similar to that for the fourth layer.

Entropy continuity considerations suggest that the bends in isosteres coinciding with the layer lines must be points of intersection with other lines of entropy increase, i.e., lines of layer melting or disordering, located approximately on the dashed lines in Fig. 3. These transitions could be first order or continuous; simulations favor the latter.[4] We see no experimental signature at these lines, but we would not expect to detect a melting transition unless it were sharp and involved significant density change. Disordering (and, we suppose, melting) of the top layer of the film then occurs on a zigzag band in the μ-T plane. In heat-capacity scans, films close to integer coverage may cross pure melting line segments.

In the region $72 \lesssim T \lesssim 77$ K the top layer is presumably disordered, with a substantial concentration of vacancies and adatoms.[4] One might suppose that a film with this degree of surface disorder could grow continuously, but the growth mode we observe is an addition of an ordered layer in a first-order transition, displacing the disordered surface outward by one layer. Evidently there is some mechanism which locks the surface profile to a particular distribution of partial occupancy.[17] In this region, we expect the potential $V(z)$ to be the same as at low temperatures and an important contribution to lowering of the chemical potential to be the fact that the coexisting phases differ in the occupancy of about three layers instead of just one, so that the effective n in Eq. (3) is noninteger. The convexity of $V(z)$ then lowers the average potential at fixed coverage. More important, there is a coverage offset of about -0.3 layer, which means that the disordered layer has more vacancies than adatoms. The effective layer number n which must be inserted into Eq. (3) to give the experimental $\mu_{n'}$ is $n' - (0.63 \pm 0.06)$ for $n' = 4$ to 8. Profiles which will account for this, together with coverage 0.3 layer below nominal, require about 45% vacancies in the nominal top layer, hence 15% of a layer of adatoms.

Finally, we note some features of isotherms in the range $78 < T < 82$ K, above the new series of layer critical points. These critical points might be attributed to disordering of the second-to-top layer of the film, after which growth is indeed continuous. The fourth-layer step remains discernible although it becomes very broad across this range. The fifth step is completely lost. The sixth-, seventh-, and eighth-layer steps can be tracked continuously across the range, but shift upwards in coverage by one full layer relative to the fourth, while remaining at constant chemical potential relative to bulk. At 81.5 K the nominal sixth-layer step appears to become somewhat narrower (Fig. 1); beyond this temperature the isotherms rapidly lose all structure.

The phase diagram in Fig. 3 is reminiscent of that given by An and Schick[18] for a model system exhibiting both layering and surface melting: Lines of layering transitions are offset in chemical potential where they are crossed by layer melting lines. An important difference here is that layer melting is apparently continuous and the first-order character of the layering transitions is lost where they overlap the melting transition. The points at which the low-temperature first-order lines terminate near 67 K evidently do not approach a roughening transition as previously supposed,[7] but relate to disordering of only the top layer. The roughening transition may be at the limit of layer critical points near 77 K or it could be higher. The actual nature of the 67-K end points depends on unresolved details of how melting relates to each layering transition; one possibility is that continuous melting closely precedes a critical point. In a variational treatment of roughening in solid films, Weeks[19] found first-order transitions near half-integer coverages at temperatures in the range $T_{c,n} < T < T_R$. We do not know whether this result might relate to the phenomena we observe. We have made preliminary studies of krypton and xenon films on graphite[20] and find that these systems also exhibit the main features reported here for argon.

We wish to acknowledge helpful conversations with M. Schick, J. M. Phillips, and J. G. Dash. This work was supported by National Science Foundation Grant No. DMR8617760.

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