Multilayer Growth and Wetting Behavior of Nitrogen Physisorbed on Graphite

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The multilayer growth of N_2 on graphite has been studied by ellipsometry and stray-light measurements. Above the α-β transition temperature of bulk N_2, there is incomplete wetting with a sequence of layering transitions which could be followed from the fifth to the tenth layer. At lower temperatures, the adsorption isotherms show only two stable monolayer steps; however, optically smooth layers of α solid can be grown on top of the double layer.

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From a macroscopic point of view, wetting of a substrate by an adsorbate is discriminated from incomplete wetting depending on whether the contact angle of the bulk condensate is zero or finite.[1] A more microscopic insight is obtained from adsorption isotherms.[1] Here wetting systems, e.g., Xe on graphite,[2] show multilayer isotherms which suggest that the number of monolayer steps increases to infinity for the pressure above the adsorbate approaching the saturated vapor pressure p_0. For incomplete wetting, e.g., CO_2 on graphite,[3] the number of successive monolayer steps stays finite for $p \rightarrow p_0$ and excessive material forms bulk droplets or crystallites at p_0. Many substances, e.g., C_2H_4 or C_2H_6 on graphite,[4] are known to show a crossover from incomplete to complete, i.e., a wetting transition[1,5] at a characteristic temperature T_w. As far as we know the wetting transitions of all sufficiently well documented examples are induced by phase transitions of the bulk system, the most prominent one being the solid-liquid transition at the triple point T_t. For wetting to occur in the solid state, matching of the crystal structures of the adsorbed layers and of the bulk is necessary.[6]

In the specific example of N_2 adsorbed on graphite, there is no doubt that, below about 20 K, the number of monolayers is limited to two before the growth of solid α-N_2 crystallites (cubic $Pa3$, orientationally ordered) sets in.[7] At 46.2 K, which is in the T range where bulk N_2 crystallizes in the orientationally disordered hcp β phase, the adsorption isotherms show about eight discrete steps.[8] Based on adsorption isotherms for CO and on the isomorphism of CO and N_2 in the monolayer as well as in the bulk state, it has been suggested[9,10] that N_2 on graphite undergoes a wetting transition induced by the α-β structural phase transition at $T_{\alpha\beta}=35.6$ K.

We report ellipsometric adsorption isotherms below and above $T_{\alpha\beta}$. We will show that the wetting is incomplete throughout the T range studied ($10\text{ K} < T < 53$ K) and that there is a sequence of layering transitions of the fifth to the tenth monolayer. The film growth is anomalous insofar as the bulk condensate on top of the finite number of monolayers is optically smooth below $T_{\alpha\beta}$ and rough above, as illustrated schematically in Fig. 1.

Our ellipsometer[11] measured the phase delay Δ between the perpendicular and the parallel components of the electric-field vector of the light after reflection from the sample. Upon adsorption, Δ changes by $\delta\Delta$. $\delta\Delta$ is for all practical purposes proportional to the product of the coverage and a combination of the principal values of the polarizability tensor of the admolecules, which depends on their orientation with respect to the substrate.[8] $\delta\Delta$ is determined by means of a self-nulling technique. Because of the high sensitivity of this technique, the signal is lost for optically inhomogeneous ("rough") adlayers. The stray light from such films is detected by a photomultiplier which is at a position perpendicular above the substrate. $\delta\Delta$, the stray light intensity I_s, and the pressure p in the vacuum chamber are recorded as a function of time t, while the gas inlet is open (adsorption) or while the gas is pumped off (desorption).

Ellipsometric adsorption isotherms are obtained as $\delta\Delta$ vs p plots by eliminating t. The chamber fills from the initial pressure of usually 10^{-9} Torr to p_0 in usually 5000 sec. Filling rates up to a factor of 5 higher have been tested occasionally. The substrate is a piece of monochromator-grade pyrolytic graphite with a c-axis mosaic width of 0.4°.

Two different types of film growth of N_2 on graphite have been observed, depending on whether T is smaller or larger than a crossover temperature T_c, $T_c=34.5$

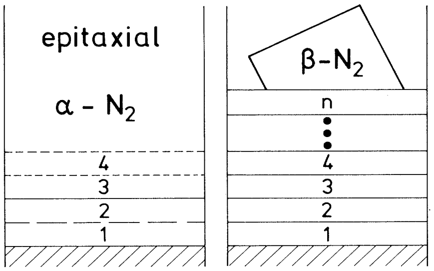

FIG. 1. Schematic view of N_2 films on graphite above and below $T_{\alpha\beta}$.

±0.5 K, which we identify with $T_{\alpha\beta}$. The nominal value of $T_{\alpha\beta}$ is actually about 1 K higher,[12] but the specific-heat results of Zhang, Kim, and Chan[13] have shown that $T_{\alpha\beta}$ shifts to 34 K for smaller bulk aggregates.

$T > T_{\alpha\beta}$.—This T regime has been investigated up to 53 K. The isotherms $\delta\Delta(p)$ show the typical shape of stepwise multilayer growth (Fig. 2) known, e.g., from the heavier noble gases on graphite.[2,11] Comparing adsorption and desorption, a small hysteresis is observed in some of the steps. The number of monolayer steps which can be resolved in the isotherms depends on temperature. At 35 K there are five resolved steps. Above this coverage, the ellipsometer ceases to produce reliable nulls, the stray light intensity I_s increases abruptly above the background level (see Fig. 3), and the pressure in the chamber stabilizes at a constant value. This increase of I_s is a very sensitive indicator that the saturation pressure p_0 is reached where the excess of gas condenses into a rough overlayer of crystallites (on top of a finite number of discrete monolayers). This is what is expected in the case of incomplete wetting. The heavier noble gases, which are believed to wet graphite, behave differently for larger film thicknesses. Here we could follow the film growth even beyond the point where discrete steps can be no longer resolved in the $\delta\Delta$ vs p plot, until the experiment was eventually stopped at the equivalent of fifty or so layers without any dramatic increase of I_s. For N_2, the number of monolayers which can be adsorbed before bulk condensation occurs at p_0 is limited. The number is five at 35 K, the sixth layer forms above 38 K, the seventh at 40 K, the eighth at 44 K, the ninth at 46.2 K, and the tenth at 50 K. All these layering transition[1] temperatures T_i are uncertain to ±0.5 K. Within this error, the T_i's are equally spaced. In the critical regime of a second-order wetting transition, one expects a divergence of the coverage,[1,14] that is, a sequence of the T_i's which converges at T_w. We have no experimental evidence for such a behavior. We can only speculate that eventually N_2 will wet graphite at the triple point, $T_t = 63$ K. Our layering sequence extrapolates to 14 monolayers at T_t.

20 K $< T < T_{\alpha\beta}$.—In this T regime, some aspects of the adsorption and desorption behavior are reproducible, others are not. In slow adsorption runs, either two,

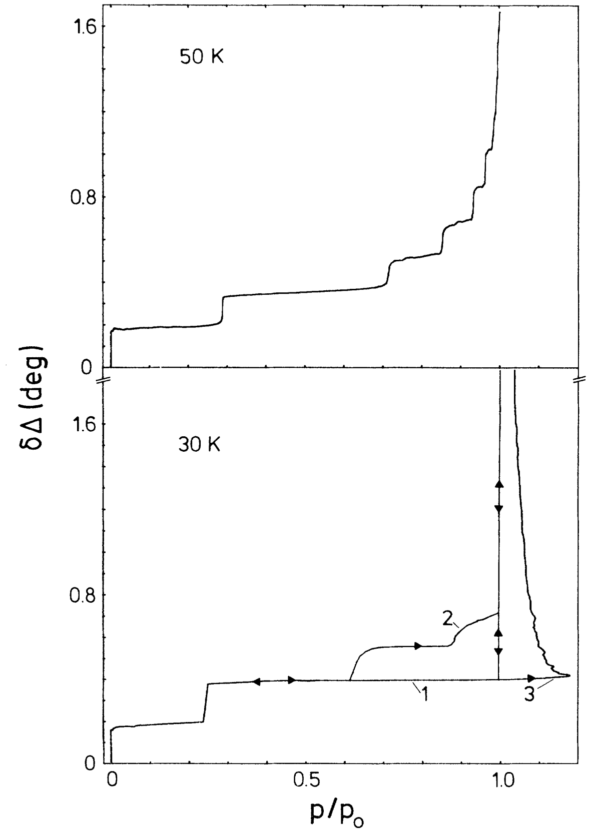

FIG. 2. Ellipsometric adsorption isotherms $\delta\Delta(p)$. Curves 1 and 2 represent slow adsorption runs. For curve 3 the adsorption rate was faster by a factor of 3. All desorption data coincide with curve 1.

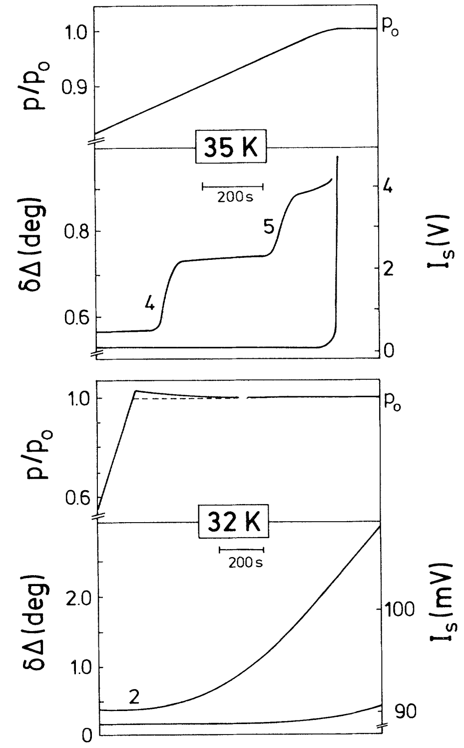

FIG. 3. Ellipsometric thickness $\delta\Delta$, stray light intensity I_s, and the pressure as a function of time in slow adsorption runs. For $T = 35$ K, the ellipsometer signal is lost and I_s increases abruptly at p_0, at a thickness of five monolayer equivalents. For $T = 32$ K, $\delta\Delta$ grows steadily beyond two monolayer equivalents at $p = p_0$ without any significant increase of I_s. Note that the scales for I_s are different.

three, or four monolayers could be traced in the $\delta\Delta(p)$ isotherms (see curves 1 and 2 in Fig. 2). Maintaining the gas flow into the chamber, the pressure in the chamber eventually stabilizes, suggesting that p_0 has been reached, while $\delta\Delta$ continues to increase. $\delta\Delta$ has been followed up to values equivalent to forty monolayers without any significant increase of the stray light (Fig. 3). On desorption, the $\delta\Delta$ readings continuously decrease. At the point at which a reduction of the pressure in the chamber is finally noticed, $\delta\Delta$ has reached the value of the second plateau of the adsorption run. Thus the number of $\delta\Delta(p)$ steps varies between two and four in adsorption, but is always two in desorption. Optically smooth films of higher thickness can be grown at p_0. From the experiment we cannot tell whether these thick layers are stable or metastable since the control parameter p is no longer operative. There is, however, a clear contrast to the behavior of thicker films in the high-T regime which are apparently optically rough.

In adsorption runs with somewhat faster rates of pressure increase, the formation of the third and fourth monolayers was always suppressed. The $\delta\Delta$ vs p trace of such a run is shown as curve 3 in Fig. 2. Here the chamber can be slightly overpressurized beyond p_0, the $\delta\Delta$ value saturating at two monolayer equivalents. As soon as bulk condensate is formed, $\delta\Delta$ increases beyond this value and the pressure relaxes back to p_0.

As mentioned above the behavior above $T_{\alpha\beta}$ is classified as partial wetting, presumably heading for a first-order wetting transition at the triple point. There is no such clear-cut classification for $T < T_{\alpha\beta}$: The limited number of steps in the adsorption isotherm suggests incomplete wetting. On the other hand, a thick, smooth, presumably epitaxial film can be grown on top of a bilayer. From a macroscopic point of view we call this situation wet, i.e., with the contact angle being zero. Perhaps the term thin-film–infinitely-thick-film transition is appropriate for the growth below $T_{\alpha\beta}$. A schematic picture of thick films above and below $T_{\alpha\beta}$ is shown in Fig. 1.

Several questions evolve from the present study. A more specific one is to the stability of the third and fourth layers below $T_{\alpha\beta}$. On exfoliated-graphite substrates, the existence of a third layer (respectively, a trilayer) has been established by specific-heat measurements[13] and somewhat more indirectly by neutron diffraction,[15] though the conclusions on the structure of this layer and the interpretation of a specific-heat anomaly at 23.8 K as layering or a melting transition are in conflict. Our measurements suggest that the third and fourth layers—the fourth layer has not been observed in the measurements cited—are metastable with respect to the formation of the first layers of an epitaxial α solid. On exfoliated graphite, the third layer is presumably stabilized by a large number of structural defects in the substrate and by capillary condensation.

In both solid phases of N_2, the center-of-mass lattice is a stack of triangular net planes, though with different stacking sequences, $AB\ldots$ in the β phase and $ABC\ldots$ in the α phase.[12] Adsorbed monolayers and bilayers have triangular center-of-mass structures[15,16] too. Since, furthermore, the next-neighbor distances in the layers[15,16] and in the bulk[12] differ by hardly more than 1%, there is no obvious structural reason why N_2 should behave in a way different from the heavier noble gases. One could, of course, argue that one of the stacking sequences of the bulk cannot be matched to the stacking of the adsorbed layers. A recent study of Ar multilayers[17] shows, however, that—at least for this system—this problem does not interfere with a multilayer-type growth eventually leading to wetting. The apparently different behavior of N_2 and the noble gases may be due to the orientational degrees of freedom. But again, there is evidence that the orientational arrangement of the monolayer and bilayer and of the bulk system are closely related. In the ordered state, a pinwheel-type orientational arrangement has been favored for the bilayer.[15,18] Such a structure is, however, not much different from two adjacent (111) layers of the α phase. The only reason we can see for the limitation of the layer growth below $T_{\alpha\beta}$ to just two layers is the recent observation that the bilayer is slightly distorted from hexagonal symmetry.[15] Thus there is a breaking of symmetry between the bilayer and the (111) planes of the α phase which necessarily leads to a discontinuity in the growth. From this reasoning it is, however, difficult to understand why an epitaxial α solid can form on the bilayer. Clearly intermediate layers are needed to match the bilayer to the α structure. Such layers had to be distorted or even disordered. In fact, the diffraction result suggests that the third layer is amorphous.[15]

We have no structural argument why the wetting is incomplete in the T range of the β phase, since here the symmetry breaking should no longer exist because of orientational disorder. The fact that the bulk overlayer is rough rather than smooth may, of course, be related to a more macroscopic aspect, namely, the anisotropy of the surface tension. Note that an easy growth direction different from [001] would lead to a faceted bulk overlayer. A theoretical description of wetting will eventually have to face such effects on the borderline of multilayer growth and crystal growth.

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