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Complete and incomplete wetting of krypton and oxygen on graphite: Reentrant type-2 growth on a scale of substrate strength

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Reflection high-energy electron-diffraction (RHEED) studies of krypton and oxygen films on basal-plane graphite show that the low-temperature mode of growth of Kr is type 1 (complete wetting) whereas that of O_2 is type 2 (incomplete wetting). The present results extend earlier RHEED measurements on other gases, and indicate the existence of two distinct regimes of incomplete wetting growth separated by a narrow region of complete-wetting growth. These results, together with published work on other films, are analyzed on an improved scale of relative interaction parameters. Arguments are presented to suggest that the mechanisms for incomplete wetting are different in the weak and strong substrate regimes. The present study also shows certain distinct structural relationships between crystallites and layered film in the incomplete wetting growth regime.

INTRODUCTION

Recent experimental and theoretical studies have stimulated interest in the growth habits of simple molecular gases on uniform substrates. The various modes of growth exhibited by physically adsorbed films, as well as other film systems, have been given various names. Layer formation, which continues up to coexistence with bulk is known as Franck—van der Merwe growth,[1] type 1 growth, or complete wetting. Formation of a limited number of layers up to bulk coexistence is known as Stranski-Krastanov growth,[1] type 2,[2,3] or incomplete wetting.[4] An extreme form of type 2 growth, in which virtually no adsorption takes place before bulk is formed is called type 3 (Refs. 2, 3, and 5) or nonwetting.[4]

A recent publication[6] from this laboratory reports on the nature of multilayer Ne, Ar, N_2, and Xe films adsorbed on graphite at low temperature. It was observed that the crossover between complete and incomplete wetting contradicts the predictions of theory,[4,7] in that the systems with stronger relative substrate interaction strength undergo incomplete wetting while weaker substrate systems are completely wet at low T. The new Kr results are consistent with the previous reflection high-energy electron diffraction (RHEED) study, in that its relative interaction parameters are comparable to Xe and Ar, which also show complete wetting growth at low T. The O_2 film, however, is incompletely wet at low T, while its relative parameter is appreciably smaller than those of other type 2 films examined by the RHEED method. These results indicate that incomplete wetting is reentrant. Published reports on other films support this conclusion. A recent lattice-gas calculation[8] shows similar nonmonotonic wetting growth behavior.

The RHEED technique is well suited to the observation of the various modes of growth of molecular layers on uniform substrates.[9] It can clearly distinguish between successive layer formation and bulk-crystal growth. For a flat, layered film, the diffraction pattern consists of parallel, slightly modulated streaks normal to the substrate plane [see Fig. 1(a)], whereas small bulk crystallites produce sharp spots. If a few molecular layers coexist with crystallites (type 2) the diffraction pattern exhibits streaks together with sharp spots [see Fig. 1(c)]. Our apparatus includes, in addition to the RHEED diffractometer, a low-energy electron diffraction (LEED) system, a mass spectrometer, and an ion gauge to measure vapor pressure. The complete system permits observation of the structure and perfection of the bare substrate and the adsorbed layers, the gas purity, and the vapor pressure. The substrate was a cleaved crystal of natural graphite. It was mounted on a stage which could be cooled to temperatures down to 8 K. The temperature was regulated to better than 0.1 K. The thickness of the film was estimated from the impinging flux: The deposition rate was calibrated by observing the attenuation of the graphite LEED pattern. The incident RHEED beam energy was 28 kV, and the graphite-crystal azimuthal orientation with respect to the beam was in the 13.0 direction. Further details are given in our earlier publication[6] and in a forthcoming paper.[10]

EXPERIMENTAL RESULTS

Krypton

To prepare the krypton films we deposited successive quantities of one statistical layer at temperatures between 15 and 50 K, observing the RHEED pattern after each deposition, up to a thickness of about ten layers. As thickness increased, the streaks became more intense and more strongly modulated [Fig. 1(a)]. The sharpness and positions of the streaks were not observed to undergo any major changes with coverage. This behavior was similar to the earlier results on Xe and Ar films.[6] The experiment was repeated by condensing directly about ten layers and observing the RHEED pattern immediately after deposition. Intense and modulated streaks were seen. The incident pressure was varied from 10^{-8} to 10^{-6} Torr, and the surface temperature was regulated between 15 and 50 K. The structure of the multilayers, as observed by LEED, was always hexagonal, in agreement with previous studies.[11] These results clearly show type 1 growth at the experimental temperatures.

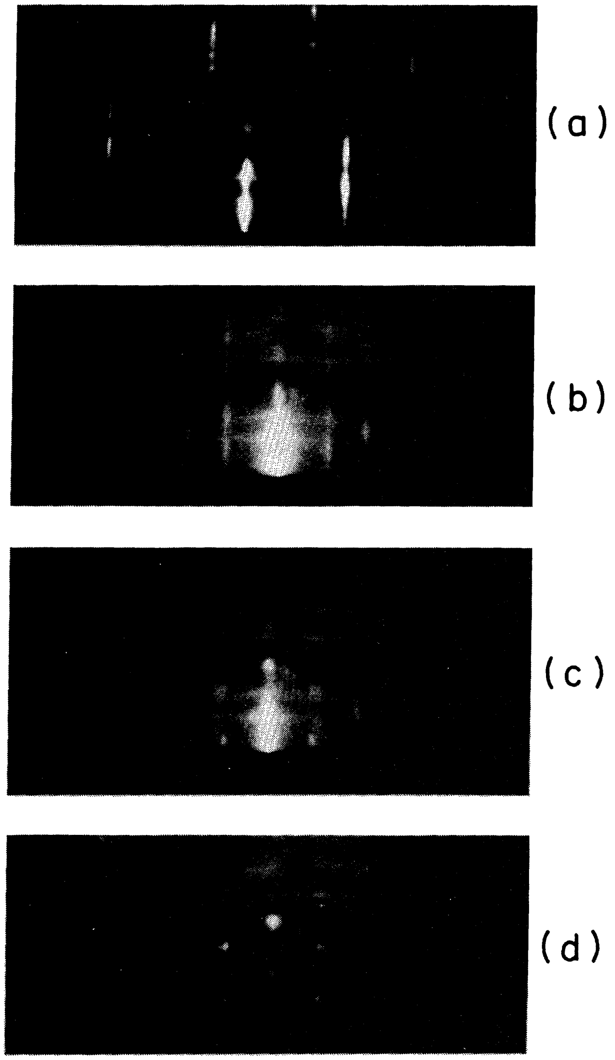

FIG. 1. RHEED diffraction patterns of Kr and O_2 showing that Kr grows as a type 1 (complete wetting growth) film on graphite at low temperature, whereas O_2 grows as a type 2 (incompletely wet) film. Pattern (a) of approximately 10 Kr statistical layers at 15 K consists of parallel modulated streaks, indicating a flat, layered film. The central streak is the superposition of the 00.1 graphite and Kr diffracted beams. Left-hand and right-hand streaks are the 13.l and -1 -2.1 Kr beams. The other modulated streaks are Kr higher-index beams. Oxygen exhibits different RHEED patterns as a function of exposure to gas flux. At 28 K, after an exposure at 2×10^{-7} Torr for 8 min, the pattern consists of modulated streaks (b). After 14 min at the same pressure the pattern shows streaks and sharp spots (c), and after an additional 16 min, only sharp spots (d). The central streak, corresponding to the diffraction from the graphite and the film, is not present in (d), being replaced by an intense sharp O_2 spot. The sequence of oxygen photographs shows that a few layers are first deposited, then solid crystallites are formed in coexistence with the layered film, and finally the entire surface becomes covered by bulk crystallites.

Oxygen

The procedure for the oxygen films was somewhat different. We observed that the sticking coefficient for the first adsorbed layer was smaller than unity and dependent on coverage, and hence it was impossible to use the value of incident flux to calibrate thickness. We therefore carried out the RHEED observations under constant ambient pressure. The temperature range was limited to values between 20 and 32 K: At lower T the equilibrium time for the structural reorganization of the film (indicated by LEED, consistent with earlier LEED work[12]) was too long, and at higher T the vapor pressure at saturation would have been hazardous for the electron-gun filaments. Under the conditions of the experiment we were able to follow the evolution of the film growth by continuously monitoring the RHEED pattern.

At 28 K and 2×10^{-7} Torr we observed several streaks whose intensities increased with time [Fig. 1(b)]. The streaks gradually became modulated, and sharp spots appeared at azimuths symmetric about the central graphite peak; one spot was superimposed on the central peak, but others were distinct from the overlayer streaks [Fig. 1(c)]. In the previous study[6] we also observed Ne and N_2 spots that were not superimposed on the overlayer streaks. The intensity of the spots continued to rise while the intensity of the streaks decreased, until after about 30 min, when the streaks disappeared [Fig. 1(d)]. It can be concluded that the growth mode is type 2. The attenuation and disappearance of the streaks indicate continued growth of bulk crystallites, finally shielding the underlying layers.

The experiment was repeated at several temperatures between 20 and 32 K and always gave the same results. We also tested the influence of the high-energy electron beam on the film. When the pressure was in the low, 10^{-8}-Torr range the sharp spots slowly broadened and eventually disappeared if the beam was focused on any given location of the crystal, but the sharp spot pattern could be restored by sweeping the beam over the surface. We interpret this observation as being due to local desorption and distillation to colder parts of the film. It also indicates relatively rapid equilibrium of the film, whether by mobility along the surface or by transport through the gas phase.

Our conclusion of type 2 growth of O_2 on graphite at low temperature is not new. It was deduced from calorimetric[13] and magnetic[14] studies that a maximum of two layers can form at temperatures between 10 and 25 K. These conclusions have been confirmed recently by x-ray scattering studies.[15] Our technique made it difficult to determine the thickness of the O_2 layered film, although estimates based on the streak intensities are consistent with two layers. The particular advantage to the RHEED technique is its avoidance of capillarity condensation, which interferes with the examination of growth behavior in high-area adsorbents near saturated vapor pressure (see, e.g., Ref. 16).

DISCUSSION

Comparison of the results with theoretical predictions can be made on the basis of the ratios of molecule-substrate to molecule-molecule interaction strengths, denoted as u/v in the work of Pandit *et al.*[4] In this work as well as Sullivan's[7] it is predicted that systems with stronger relative substrate interaction, i.e., larger u/v ratio, are more likely to display type 1 growth, while those with smaller u/v should be type 2 or type 3 systems. In our earlier study of Ne, Ar, N_2, and Xe on graphite we found an inverted order of wetting growth behavior: The "strong substrate" systems (Ne and N_2) undergo type 2 growth, while those with relatively weaker substrate interactions (Ar and Xe) are type 1 films. The ratio u/v was gauged in two ways: by the ratio of the exponent α of the thickness dependence of vapor pressure to the energy parameter ϵ_0 of the pair potential, and by the parameter ϵ_0 alone. All of the experimental systems were ordered consistently by the two scales. We now wish to combine the present results with the previous measurements as well as with other gases whose low-temperature growth habits have been determined by other methods.

We first propose a somewhat improved gauge of u/v that may give a closer correspondence to relevant physical parameters. Although the van der Waals α is directly accessible from vapor-pressure measurements, it does not reflect the substrate interaction alone, since the films at low temperature have appreciable self-energies. A much better gauge of u is the isosteric heat of adsorption at low coverages. In particular, if the film is a low-density, mobile two-dimensional gas and the surface normal vibrations are harmonic, with classical vibrational energy, the isosteric heat is nearly equal to the single-particle ground-state energy u_1.[17] For certain systems suitable isosteric heat measurements are not available, but theoretical estimates, detailed analysis of other thermodynamic properties, or molecular scattering data can be used. In place of the molecule-molecule pair interaction we choose the molecular ground-state energy h_0 of the bulk crystal at $T=0$. Experimental values for most gases of interest are generally available in published literature. Although h_0 does not bear the same relation to v as u_1 does to the theoretical u, h_0 should be better than ϵ_0 as a gauge of the physically important quantity in determining wetting growth. This is because the question of wetting growth involves the relationship between the free energies of adsorbed and bulk phases. We recognize that other properties must also enter, e.g., the structures and densities of the competing phases, but they cannot be included in a simple ratio scale. However, we comment below on the possible relationship between the ratio scale and the structures of film and bulk phases.

Table I lists the ratios of molecule-graphite binding energy u_1 to the 0 K cohesive energy h_0 of the bulk phase for those gases whose films were examined by the RHEED technique. Also included are several films whose low-temperature wetting growth behavior has been ob-

TABLE I. Molecule-graphite binding energy u_1, bulk-phase ground-state energy h_0, and correlation of u_1/h_0 with wetting growth behavior at low temperature.

Molecule	u_1/k_B (K)	h_0/k_B (K)	u_1/h_0	Growth mode Type	T (K)
^3He	136[a]	2.52[b]	54	2[c]	0.5–1.5
^4He	143[a]	7.22[b]	20	2[d]	1.3–2.5
Ne	350[e]	226[f]	1.55	2[g]	7–8
N_2	1170[h,i]	900[k]	1.30	2[g]	10–20
O_2	1065[j]	1040[k]	1.02	2[l]	20–32
Ar	1180[i]	930[f]	1.28	1[g]	10–20
Xe	2260[m]	1908[f]	1.18	1[g]	10–60
Kr	1560[m]	1353[f]	1.15	1[n]	15–50
CH_4	1660[m]	1160[m,o]	1.43	1[p]	64–105
C_2H_4	847–1609[q]	2309[q]	0.37–0.70	2[r]	10–91
CO_2	1430[s]	3230[s]	0.44	2[t]	<193
H_2O	1870[u]	5720[v]	0.33	2[w]	240

[a] Reference 18.
[b] Reference 19.
[c] Reference 20.
[d] References 2, 21, and 22.
[e] References 23 and 24.
[f] Reference 25.
[g] Reference 6.
[h] References 26 and 27.
[i] Reference 28.
[j] Reference 29.
[k] Reference 30.
[l] This work and Refs. 13–15.
[m] Reference 31.
[n] This work.
[o] Reference 10.
[p] Reference 32.
[q] Reference 33.
[r] References 16 and 33–35.
[s] Reference 36.
[t] References 36 and 37.
[u] Reference 38.
[v] Reference 39.
[w] Reference 40.

served by other methods. The ratios for the various gases are displayed on a linear scale in Fig. 2. We point out that three distinct regimes of growth are exhibited. In addition to the type 1 and type 2 regimes of "intermediate" and "strong" substrate systems, there is a type 2 or type 3 regime for "weak" substrate systems. Although many of the molecules are more complicated than the structureless atoms of the theoretical models, it is noteworthy that all of the gases, with the exception of CH_4, are consistently ordered on the scale. This discrepancy may be due to the fact that CH_4 growth has not been studied at sufficiently low temperature: According to the scale it should exhibit a crossover to type 2 growth below 64 K, the lowest temperature of multilayer experiments reported to date.[32] However, the consistency in the wetting growth scale is probably fortuitous since the simple ratio of interactions cannot account for orientational effects in films of nonspherical molecules. In O_2, for example, there are several phases in the first monolayer at low temperature which exhibit orientational ordering.[12] As an example of the influence of orientation on the wetting parameter, we list two values for C_2H_4 corresponding to the extreme values of binding energy for different orientations on the substrate. Thus the growth characteristics of the various molecules, as shown in Fig. 2, can only be taken as portraying overall reentrant wetting behavior as a function of relative substrate strength. It is noteworthy that the only films exhibiting complete wetting are the rare-gas molecules Ar, Kr, and Xe. Their wetting growth parameters fall within a narrow range, $1.15 \leq u_1/h_0 \leq 1.28$. The ratio for N_2 is marginally higher, a difference which is well within the uncertainty of the interaction parameter measurements and the possible effects of orientation. The next lighter rare gas, Ne, falls appreciably higher on the scale at 1.55. It is quite possible that quantum effects play a significant role in Ne, as they certainly do for He. Therefore, the narrow width of the type 1 region may be simply due to the similarity of the ratios of the heavier rare gases together with the perturbation due to orientational and quantum effects in all other films. This important question can be answered by experiments with other substrates.

The weak to intermediate wetting sequence is in accord with theoretical prediction that complete wetting growth is promoted on stronger substrates. Moreover, the magnitude of u_1/h_0 at the weak-intermediate substrate crossover is in close agreement with a theoretical estimate. Schick[41] has applied the mean-field theory of Pandit *et al.*[4] to a Lennard-Jones 6-12—potential gas on a smooth substrate. His calculation predicts that crossover depends on the relative strengths and molecular diameters of the molecule-substrate and molecule-molecule interactions. For diameters ranging from those corresponding to Ne/graphite to Xe/graphite the crossover is predicted to lie in the interval $0.6 \lesssim u_1/h_0 \lesssim 1.1$, virtually identical with the experimental range.

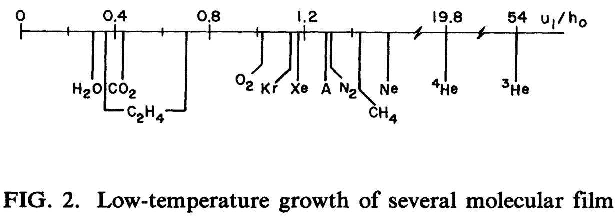

FIG. 2. Low-temperature growth of several molecular films on graphite. The scale corresponds to the ratio of single molecule-graphite ground-state energy to the 0 K sublimation energy of the bulk phase. The overall sequence shows that type-2 growth is reentrant.

The mechanisms for incomplete wetting growth in the weak and strong regimes are evidently different. In the weak regime the mechanism is probably that which is given by theory, i.e., the relatively strong surface free energy of the bulk phase. However, in the strong substrate regime the bulk surface energy is much less important. In this domain it appears that incomplete wetting is caused by a mismatch between the film and bulk-crystal structures, which prevents continued epitaxial growth of higher layers. Direct evidence is obtained from the RHEED patterns, which show supplementary sharp spots inside the layer streak positions. The occurrence of reentrant type 2 behavior on strong substrates contradicts the predictions of Pandit *et al.*[4] and Sullivan.[7] But a recent calculation by Ebner, Rottman, and Wortis[8] does agree with the observed reentrant behavior. These authors investigated the behavior of a lattice gas on attractive substrates, for particles with nearest-neighbor repulsions and next-nearest-neighbor attractions. In the intermediate regime the film and bulk structure at $T=0$ consists of alternate cell occupation, and the growth is of type 1. Strong enough substrate attraction produces high-density, compressed layers, quenches epitaxy, and causes type 2 growth. Reentrant behavior is also indicated in current calculations of the stability of rare-gas films.[42] In the earlier lattice-gas calculation of Pandit *et al.*[4] and in the liquid-layer model of Sullivan[7] there is no provision for possible density or structural differences in the layers near the substrate, hence the question of epitaxy did not arise. The measurements and the more recent theories both suggest that type 1 growth is much more delicate than either type 2 regime, requiring similar lattices, densities, and molecular orientations in the film and bulk phases. However, the question of lattice structure is clearly inapplicable to helium films since the top surface of the incompletely wet films as well as the coexisting bulk phases are liquid.[43] It is reasonable to expect that quantum effects play a significant role in the wetting behavior of these systems.

Concerning the extra sharp spots in the type 2 films, they indicate an important feature of the film configuration. For a given adsorbate, the spots were always found at the same position on the screen in all of our numerous observations. This means that the crystallites of N_2, O_2, and Ne have a preferential orientation with respect to the graphite surface. This fact should be taken into account in more complete theories of film growth. Further experiments will be undertaken to explore the structural relationships of type 2 films in greater detail.

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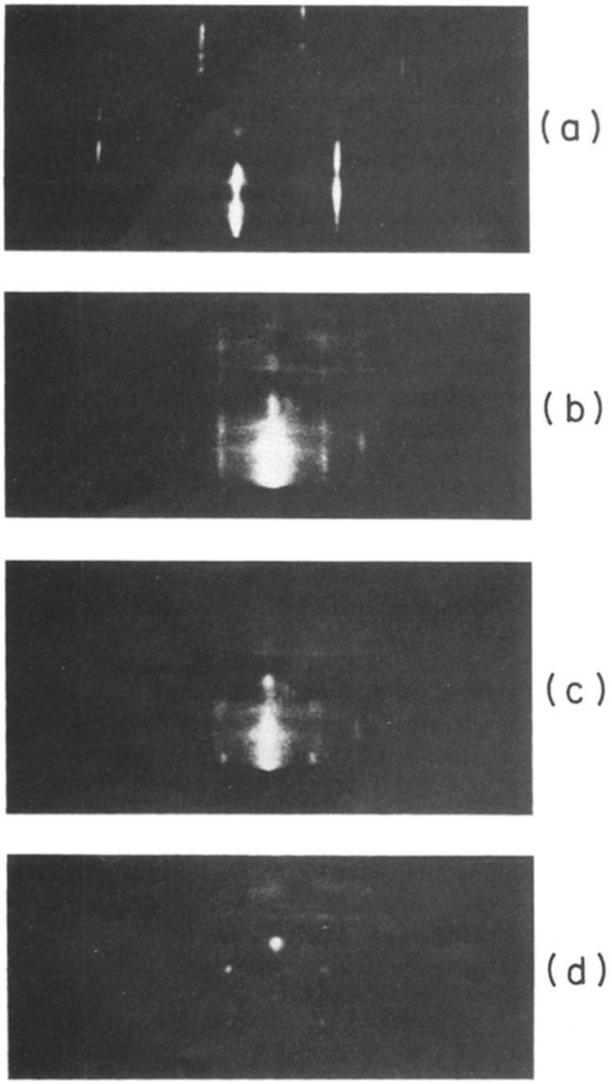

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