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Multilayer adsorption isotherm study of Ar films on boron nitride

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We have measured multilayer isotherms for Ar films adsorbed on BN between 65 and 80 K. We have found reentrant layering for the third and fourth layers of the films. We have also found individual-layer melting transitions for the second and third layers. We constructed a phase diagram for the system in the region studied.

In spite of the fact that multilayer physisorbed films have been studied for over 20 years,[1] unexpected phenomena have recently been discovered in these systems. In an ellipsometric adsorption isotherm study of Ar films on graphite, Youn and Hess[2,3] found a series of reentrant layering transitions: Isotherm steps corresponding to the fourth, fifth, and sixth layers are sharp at low temperatures; they are then observed to broaden considerably between 68 and 72 K (as occurs for isotherms taken above the critical layering temperature); subsequently, the steps become sharp again between 72 and 80 K; at even higher temperature they broaden, and remain broad.[2,3] The resharpening of the layering steps is called reentrant layering. Reentrant layering was not observed for the three layers closest to the substrate.[2,3]

A satisfactory theoretical understanding of reentrant layering is presently lacking.[2,3] It has been suggested that the reentrant layering behavior exhibited by multilayer Ar films on graphite might be linked to a possible preroughening transition taking place in this system.[4]

Presented here are the results of an adsorption isotherm study of multilayer Ar films physisorbed on BN. Details on the substrate preparation and quality, as well as results on the monolayer melting of Ar films on BN, have been provided elsewhere.[5]

The adsorption isotherms were measured at 14 temperatures between 65 and 80 K. They typically start at coverages just above monolayer completion and extend up to at least the fifth layer. The film's isothermal compressibility K_T was obtained from the isotherm data using the expression

$$K_T = \frac{1}{n^2 v}\frac{dn}{dP}\,, \tag{1}$$

where n is the two-dimensional (2D) density, P is the pressure of the 3D vapor coexisting with the film, and v is the volume per atom in the 3D vapor phase.

Figure 1 shows isotherm traces taken at 67, 71, and 80 K. Reentrant layering behavior can be seen by following the evolution of the third and fourth layers at these three temperatures. Both the third- and fourth-layer steps are sharp at 67 K; they both become very broad, barely resolvable, at 71 K; and both steps resharpen for the 80-K isotherm. The isotherms in Fig. 1 are representative of the behavior of this system: broad third-layer steps are observed between 71 and 77 K and sharp third-layer steps are present above and below this temperature range; broad fourth-layer steps occur between 70 and 72 K and sharp fourth-layer steps are present above and below this range. The results displayed in Fig. 1 for Ar on BN have one important difference with those reported in the ellipsometric study for Ar on graphite:[2,3] the third-layer of the Ar films on BN exhibits reentrant layering while Ar films on graphite exhibit this behavior only on the fourth and higher layers.[2] This difference in the behavior of Ar films on graphite and BN is surprising because the two are very similar substrates: both have a hexagonal array of sites, with the lattice parameters of BN 2% larger than graphite and the monolayer melting behavior of Ar on both substrates is very similar.[5] It is not clear at this time whether this difference in the third-layer behavior of Ar on these two substrates is a true characteristic of these systems or whether it is a reflection of differences in the

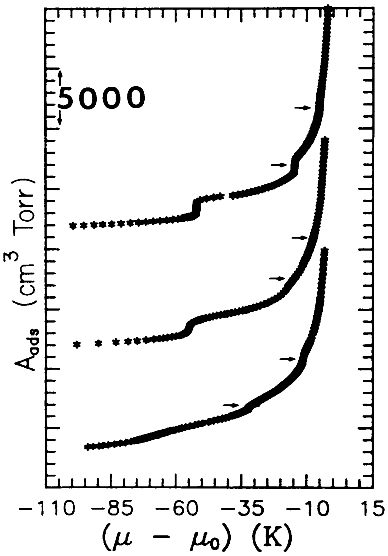

FIG. 1. Multilayer adsorption isotherms of Ar on BN. From top to bottom: 67, 71, and 80 K. Arrows mark the locations of the third and fourth layers; these two steps are broader at 71 K than at either 67 or 80 K, indicating reentrant layering. The coverage is in cm^3 Torr and the chemical potential is measured relative to bulk solid.

resolution of the two sets of measurements.

A plausible argument can be made[6] that in order for preroughening to occur, a facet of the solid undergoing the preroughening transition needs to be present. For the (111) facet of a fcc crystal, the case considered for Ar on graphite, and also presumably the case for Ar on BN, this would require the presence of at least three nonparticipating layers in the film before preroughening occurs. Thus, the reentrant layering behavior in the third layer makes less likely the interpretation of this phenomenon in terms of a preroughening transition.[6]

Aside from the difference in the third layer, many details of the behavior of Ar films on BN and on graphite are the same. The second layer of Ar on BN does not exhibit reentrant layering; the same behavior is observed for the second layer on graphite.[2,3] The sharp, high-temperature reentrant, layering steps appear at a lower chemical potential relative to that of bulk solid than the sharp, low-temperature layer steps (see Fig. 4 below); this also agrees with what is observed for Ar on graphite.[2,3]

What is the nature of the phase present in the intermediate region of broad isotherm steps? This question remains unanswered. It has been suggested that it is a disordered layer or a quasiliquid layer.[2,6] From the thermodynamic evidence available, it must be concluded that the broad isotherm steps correspond to single-phase regions. However, it is difficult to imagine a condensed phase which exists as a single-phase region throughout the full extent of one layer without coexisting at any point with a vapor phase in the same layer. Structural studies in the region of the broad isotherm steps should prove to be helpful in elucidating the nature of the phase(s) present.

In addition to the layering steps present in the isotherms, which can be easily identified as such because they involve large coverage changes, a series of small isotherm substeps or isotherm kinks (involving much smaller coverage differences) are found in some of the isotherms that we measured. These kinks or small substeps are observed between the second and third layers and between the third and fourth layers. We identify them as individual layer-melting transitions.

The existence of a sequence of melting transitions in adsorption isotherm data between the fourth, fifth, and sixth layers had been inferred in the ellipsometric study of the basis of entropy continuity considerations.[2,3] However, the corresponding features were not detected due to the relative insensitivity of the ellipsometric technique to the small density difference involved in melting.[2] Evidence for layer-by-layer melting of multilayer Ar films has been found in a heat-capacity study by Zhu and Dash.[7] Heat-capacity peaks corresponding to the melting of the second and third layers were observed. (These results were substantially free from the effects of capillary condensation, which were certainly present for the thicker films surveyed in the same study.) Neutron-scattering studies[8] performed for bilayer and trilayer films by Larese and Zhang have shown directly that the number of solid layers present decreases in layer-by-layer fashion as the temperature increases. At the same time, the liquid portion of the film is observed to increase, also in layer-by-layer fashion.[8] These two sets of experimental results are in good agreement with two computer simulation studies conducted by Phillips[9] and by Cheng and Steele.[10] Both sets of simulations observe layer-by-layer melting behavior.

Figure 2 displays the portion of isotherms taken at 71 and 74 K in the bilayer melting region. In Fig. 3 the corresponding isothermal compressibilities are shown. The isothermal compressibility data are qualitatively similar to the bilayer melting-heat-capacity data (see Fig. 12 of Ref. 7). The heat capacity rises sharply to a cusp as melting is approached; the rise is followed by a gradual drop at higher temperatures.[7] In the isothermal compressibility there is first a gradual rise to a peak, followed by a sharp drop. (The order of appearance of corresponding features is reversed because in the heat-capacity measurements the system goes from solid to fluid by increasing temperature, while in the isotherms it goes from fluid to solid by increasing pressures.)

Both the heat-capacity and the isothermal compressibility data appear to suggest a sequence of two closely spaced steps involved in the melting of the second layer of the Ar film. Such a two-step process is present at the monolayer melting of Ar on both BN (Ref. 5) and graphite.[11,12] There are some differences with the monolayer case: the separation in chemical potential between compressibility features for the bilayer is small, so that it is difficult to resolve them as separate peaks (they are clearly separate features in the monolayer); more importantly, the sharp feature seen in the bilayer compressibility is just a sharp drop, not a sharp peak as is the case for the monolayer.[5,12] The existence of two features at melting appears to be more common for the bilayer than it is for monolayer melting [Ar (Refs. 5, 11, and 12) is the only monolayer example]. Other systems which have two-step bilayer melting include Ne on graphite[13] CF_4 on graphite,[14] and O_2 on graphite.[15]

The bilayer isothermal-compressibility data could suggest that the melting of the second layer of Ar on BN is

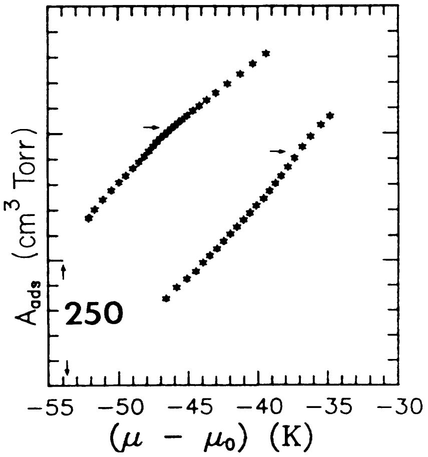

FIG. 2. Second-layer melting at 71 K (left) and at 74 K (right). The interval between data points in the 71-K isotherm is less than 1% of a layer near the transition region.

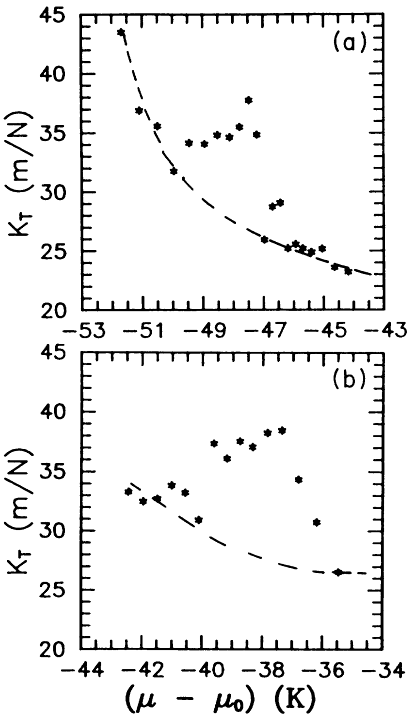

FIG. 3. Isothermal compressibility corresponding to the bilayer melting data for the (a) 71 K and (b) 74 K isotherms. The dashed line is a guide to the eye showing a smooth isothermal compressibility background.

continuous; however, great caution should be exercised with such an identification. The computer simulation studies of Phillips,[9] as well as those of Cheng and Steele,[10] have both found considerable layer promotion taking place prior to melting. Cheng and Steele[10] have pointed out that under these conditions the melting process cannot proceed at constant spreading pressure and, hence, melting signatures would not appear sharp even if the process were first order.

The melting transitions for the third layer lack any sharp features in the isothermal compressibility within the resolution of our measurements. This corresponds very well with the heat-capacity data of Zhu and Dash in the appropriate regime.[7] For trilayer films, layer promotion is more important than in the bilayer[9,10] and, hence, the cautionary comment made above[10] applies here as well.

The chemical-potential vs temperature-phase diagram for Ar on BN is presented in Fig. 4; it summarizes our results. While the slopes of the chemical potential lines relative to bulk solid for layering in both the low-temperature and the reentrant regions are small, they are not zero. This complicates phase identification in the film by simple reference to the bulk. With the exception of the existence of reentrant layering in the third layer,

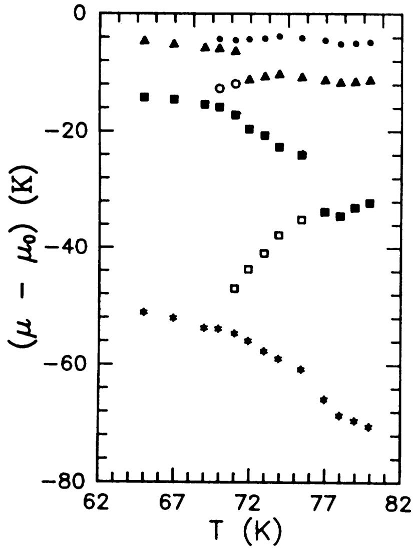

FIG. 4. Chemical-potential vs temperature phase diagram for Ar on BN. Asterisks denote second layer; open squares denote second-layer melting; filled squares denote third layer; open circles denote third-layer melting; filled triangles denote fourth layer; and filled circles denote fifth layer. Broad layering steps occur in regions of large negative slope, while sharp steps are present in regions of near-zero slope.

Fig. 4 is quite similar to the phase diagram of Ar on graphite.[2,3] We note that this phase diagram also agrees qualitatively very well with the second- and third-layer portions of the corresponding diagram for Kr on graphite,[16] even though the phases and transitions have been differently identified for that case.[16,17]

In summary, we have conducted a multilayer vapor-pressure isotherm study of Ar films adsorbed on BN. We found evidence for reentrant layering in the third and fourth layers. Such evidence for the third layer makes an explanation of reentrant layering in terms of preroughening unlikely. We have also found evidence for individual melting transitions for the second and third layers. Our melting results agree qualitatively very well with data obtained using other techniques for Ar on graphite, further emphasizing the similarities between the Ar on graphite and Ar on BN systems.

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