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Search for evidence of commensurate argon-on-graphite films near monolayer completion

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The structural properties of argon films adsorbed on graphite at 85 K were investigated as a function of coverage using neutron diffraction. This study was prompted by the recent high-resolution heat-capacity measurements of Day *et al.* which uncovered a series of anomalies near monolayer melting. These features were attributed to the formation of a registered, $\sqrt{3}\times\sqrt{3}\ R30°$ phase. The diffraction study presented here shows that this commensurate phase does not exist in the portion of the phase diagram suggested by the thermodynamic study. On the contrary, a compressed solid phase with a lattice constant close to that of the close-packed plane of the bulk solid forms. Evidence of second-layer population in the diffraction study suggests that these heat-capacity anomalies might be direct evidence of layer promotion. [S0163-1829(97)03635-7]

INTRODUCTION

The study of adsorbed films has proven to be a fruitful field of research for over a century.[1] For example, a wide variety of two-dimensional (2D) phases and associated transitions have been revealed including: 2D solid, liquid, and vapor phases; solid films that are both registered with and structurally incommensurate with the underlying lattice; and molecular films that are orientationally (dis)ordered. More recently, work has centered on multilayer films in an attempt to elucidate the principles which govern the development of three-dimensional or bulk material properties from nominally 2D matter. Here such phenomena as layer-by-layer melting, commensurability transitions between layers, and reentrant layering transitions have been observed.[2] The phenomena mentioned above can be understood by considering the relative magnitudes of the adatom-adatom and adatom-substrate interactions and their variations both parallel and normal to the surface.

Volumetric adsorption isotherms and heat-capacity methods have traditionally been used to study adsorbed films. These measurements are valuable because they provide a rapid means for investigating large portions of a phase diagram and because they can subsequently be used to calculate physically important quantities such as the heats of adsorption, surface area, and spreading pressure. It is important to note that in order to derive a microscopic description of the processes responsible for the observed thermodynamic behavior, studies which employ techniques such as elastic diffraction, inelastic scattering, ellipsometry, and scanning probe microscopy must also be performed. In fact, it has been a combination of macroscopic and microscopic techniques along with computer simulations that has led to a clearer understanding of the structure and dynamics of these films.

Studies involving films of rare gases and small molecules adsorbed on exfoliated graphite have been used to explore the wide range of phases and phase transitions listed above. Rare-gas films have been widely used as prototype systems because the simplicity of their electronic structure has led to the development of accurate interatomic potentials. Knowledge of these interaction potentials makes it possible to perform detailed calculations and computer simulations which are necessary to develop a microscopic picture of layering and melting behavior. As we noted earlier, it is the strength of the adatom-adatom interaction relative to the adatom-substrate forces that plays a primary role in determining the physical properties of the adsorbed film. In many cases a rather complete picture has emerged of how these atoms order on the graphite substrate. For example, at submonolayer coverages and low temperatures, Kr forms a solid phase which is in registry with the graphite basal plane.[3] This $\sqrt{3}\times\sqrt{3}\ R30$ phase forms because the close-packed plane of the bulk Kr has a near-neighbor spacing which is only a few percent smaller than the corresponding spacing of the graphite surface. Hence, in the low-coverage regime the strength of the Kr interaction with the substrate dominates. However, as the coverage is increased toward monolayer completion, the Kr-Kr attraction becomes the dominant interaction leading to the formation of a close-packed triangular solid phase which is no longer in registry with the graphite substrate. Arguments based on steric considerations can be made which would suggest that other rare-gas atoms (e.g., Ar and Xe) are either ‘‘too small’’ or ‘‘too large’’ to adopt a commensurate structure on graphite. However reports of Xe registry on graphite[4] bring such ‘‘common wisdom’’ arguments into question. Recently, precision heat-capacity measurements by Day *et al.*[5] of the Ar-on-graphite system found a series of heat-capacity anomalies just prior to the melting of the monolayer. It was suggested that these anomalies might

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represent a commensurability transition between the adsorbed film and graphite substrate. In order to investigate the possibility that Ar is commensurate with the graphite substrate at higher temperatures near monolayer completion we performed an extensive set of elastic neutron-diffraction measurements starting from submonolayer to above monolayer completion (i.e., the region in which the Ar-on-graphite anomalies were observed). While we found no evidence to support the formation of a solid commensurate ($\sqrt{3}\times\sqrt{3}$) Ar film structure we were able to use a combination of the thermodynamic and diffraction measurements and existing computer simulations in order to suggest what these anomalies might be the result of.

EXPERIMENT

The powder-diffraction data were recorded in a transmission geometry at the H5 beamline of Brookhaven National Laboratory's high flux beam reactor (HFBR) using TAMPA, a medium-resolution, multidetector array. The incident neutrons, with a wavelength of 2.44 Å, were selected by an in-pile, pyrolytic graphite monochromator using the (002) reflection. The horizontal divergence of the neutron beam was determined by using 20′ Soller collimators before the monochromator, between the monochromator and the sample and in between the sample and ^{3}He-filled detectors. This results in an instrumental resolution of about 0.02 at a Q of 1.90 Å^{-1}. The H5 beamline and detector package is controlled by a program developed using commercial LabVIEW® software available from National Instruments.

As in our previous experiments, the substrate was an exfoliated form of graphite known as graphite foam obtained from union carbide (UOP). Before being placed in an aluminum sample can the graphite foam was heat treated at 1000 °C in vacuum for at least 12 h. This substrate was chosen for its large, homogeneous surfaces and the lack of any preferential ordering (i.e., it is a "perfect" powder). The adsorptive capacity of the graphite was determined to be 80 STP cm^3 using a 77.4 K N_2 isotherm. Our coverage units are such that $X=1.0$ represents the number of atoms needed to complete the commensurate $\sqrt{3}\times\sqrt{3}$ solid phase. Stability of the substrate was monitored by performing adsorption measurements before and after the diffraction measurements. No change in the adsorption isotherm was observed. The sample cell was cooled using a helium closed cycle refrigerator, whose temperature was regulated to within 2 mK using a model LTC-10 temperature controller from Conductus, Inc.

Diffraction measurements from adsorbed films involve two steps: measurement of the diffraction profile from the bare substrate; and measurement of the total diffraction profile from the substrate with the adsorbed film in place. The diffraction profile from just the adsorbed film is then obtained by taking the difference of these measurements. This difference technique is necessary due to the low intensity of the diffracted signal from the film (which is scaled approximately by the ratio of adsorbed molecules to the number of molecules in the substrate).

Diffraction profiles from the graphite substrate, held at 85 K, were measured first and represented a counting time of about 10 min/point in steps of 0.05°. The diffracted intensities were such that approximately 6×10^5 neutrons were counted at the peak of the graphite (002) reflection. Ar gas was introduced to the system and used to grow films ranging in thickness from $X=0.7$ to 2.2 in ≈ 0.1 steps. Note that these coverage figures include corrections for the gas which occupies the empty space within the sample cell. Isotopically enriched ^{36}Ar gas was chosen due to its large coherent neutron-scattering cross section. Counting times with the adsorbed film in place were comparable to those used to acquire the graphite backgrounds.

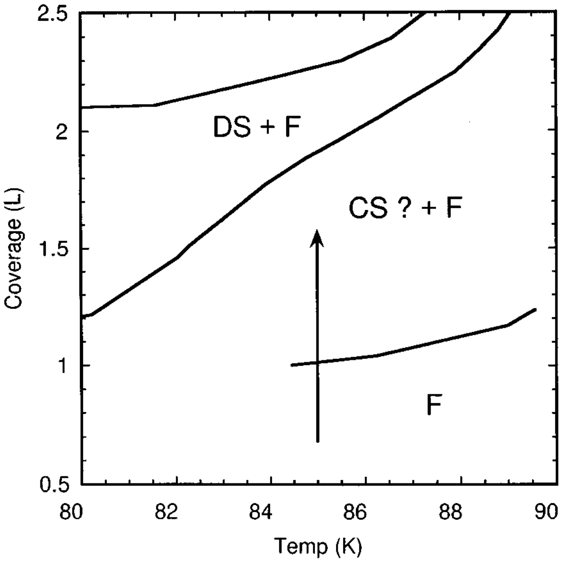

FIG. 1. An expanded section of the near-monolayer Ar-on-graphite phase diagram proposed by Day *et al.* Coverage units, X, are expressed, as in the test, using $\sqrt{3}\times\sqrt{3}$ layers. The isothermal path (at 85 K) followed in our diffraction measurements is shown with an arrow. The various regions in the diagram have been labeled following the convention of Day *et al.*, where "F" represents a fluid phase, "CS?" the commensurate solid phase, and "DS" a disorderedsolid phase.

RESULTS

As mentioned above our main purpose here is to investigate the portion of the Ar/Gr phase diagram where heat-capacity signals suggest that a commensurate solid phase might form. Figure 1 shows an expanded view of the Ar/Gr diagram (derived from Fig. 7 in Ref. 5) and the path followed in the measurements presented here. Figure 2 shows a subset of the neutron-diffraction scans recorded along the 85-K isothermal path between $X=0.7$ isothermal path between $X=0.7$ and 2.2. As the argon coverage is increased the diffraction profiles evolve from a broad humped (fluidlike) spectrum with a peak position near 1.8 Å^{-1} at low coverage to a composite spectrum made up of a sharp peak (located near 1.9 Å^{-1} as expected upon film compression/solidification) riding on a broad background (i.e., solid plus fluid coexistence) at higher coverages. A dashed vertical line has been inserted in Fig. 2 to identify the position in Q where

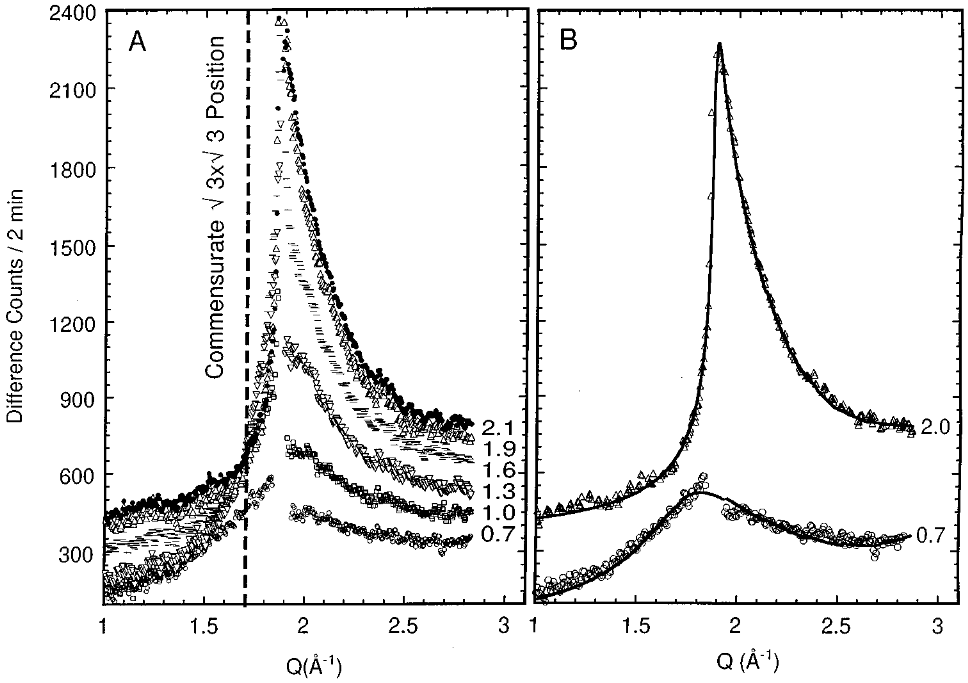

FIG. 2. (a) A subset of the neutron-diffraction measurements. Ar coverages are listed on the right-hand side in terms of $\sqrt{3}\times\sqrt{3}$ layers. Note that the position where a $\sqrt{3}\times\sqrt{3}$ commensurate solid would be expected to appear is indicated by a dashed line. As the coverage is increased the diffraction peak shifts steadily towards higher Q, as would be expected upon film compression. Recall that the solid would have to expand with increasing coverage if the registered $\sqrt{3}\times\sqrt{3}$ solid phase were to form. Gaps in the data appear where the strong (002) Bragg peak from the graphite substrate appears. (b) Representative linefits to neutron difference data at low ($X=0.7$) and high ($X=2.0$) coverages. As discussed in the text the data in the lower diffraction trace ($X=0.7$) are representative of a fluid phase as indicated by the broad peak. The solid line fit assumes a spatial correlation range of 30 Å and a near-neighbor distance of 4.20 Å. The upper trace illustrates the formation of a 2D solid phase at higher coverages as indicated by the sharp diffraction peak and its asymmetric tail at high Q. The solid line is a composite line shape which has both a sharp (2D solid) and broad (fluid) component. The range of spatial correlations in the solid and liquid components of the film (obtained from the inverse of the peak widths) differ by at least an order of magnitude in the $X=2.0$ trace. The near-neighbor spacing in the solid phase is found to be 3.82 Å, which is about 10% smaller than the 4.26-Å spacing expected for the $\sqrt{3}\times\sqrt{3}$ commensuate phase.

a diffraction peak from a $\sqrt{3}\times\sqrt{3}$ commensurate phase would appear (i.e., $Q=1.703$ Å^{-1}, near-neighbor spacing of 4.26 Å). Line-shape analysis indicates that a solid, triangular phase with a near-neighbor spacing of 3.82 Å forms (this spacing is close to the near-neighbor spacing in bulk Ar). The analysis was performed by assuming that the fluid component of the composite line shape remains relatively constant (near-neighbor spacing of about 4.2 Å) and that only the relative fraction of this component increases with increasing coverage (as signaled by the growth of the steady rise in the intensity in the Q range between 1.0–1.5 Å^{-1}). At the highest coverages, i.e., $X\approx2.2$, inclusion of a small solid bilayer component in the linefits has been found to slightly improve the ‘‘quality’’ of the fit. A small but definite change in the functional form of the ‘‘fluidlike’’ component takes places in the neighborhood of $X=1.4$. This change is difficult to characterize quantitatively but is very likely a result of an increase in the number of second-layer atoms. It is important to note, however, that regardless of the details of the fitting process no adjustment of the fit parameters could be made which would indicate the presence of either a fluid or solid phase which is commensurate with the graphite substrate.

SUMMARY

The diffraction measurements presented here do not find evidence of a commensurate-incommensurate transition in the near-monolayer completion region of the phase diagram as suggested in the thermodynamic studies. On the other hand, it is important to note that the measurements by Day *et al.* do indicate that there is some change in entropy occurring in the film just prior to the monolayer melting. Hence based on a combination of both experimental studies as well as related computer simulations, we would like to suggest the following explanation. As the Ar film melts, atoms are promoted from the first layer into the second. While the vacancies created in the first layer allow the near substrate solid film to expand somewhat, the atoms which populate the second layer must still experience a large enough attractive force with the graphite substrate to stabilize the solid film beneath it thereby raising the melting temperature. This suggestion is consistent with the behavior observed in the heat-capacity scans in which the monolayer melting temperature is seen to increase with increasing film coverage above it. Our results provide further confirmation of this by noting that as the diffraction profiles indicate the presence of a disordered second-layer population (above about $X=1.4$), the diffraction from the first-layer becomes much sharper (i.e., it has become ‘‘solid’’). We note that earlier studies have shown that layer promotion is the vacancy creation mechanism primarily responsible for the onset of melting in multilayer and high-density monolayer rare-gas films.[6–8] Thus, we believe that the heat-capacity anomalies recorded are direct evidence of the promotion of argon atoms into the second layer. Future work will focus on the behavior of analogous methane films.

ACKNOWLEDGMENTS

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[1] See, e.g., A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, 1990).

[2] See, e.g., *Phase Transitions in Surface Films 2*, edited by H. Taub *et al.* (Plenum, New York, 1991), and references therein.

[3] M. H. W. Chan, *Phase Transitions in Surface Films 2* (Ref. 2), pp. 1–10.

[4] See P. A. Heiney *et al.*, Phys. Rev. B **28**, 6416 (1983), and references therein.

[5] P. Day *et al.*, Phys. Rev. B **47**, 10 716 (1993).

[6] J. Z. Larese, Acc. Chem. Res. **26**, 353 (1993), and references therein.

[7] J. M. Phillips, Q. M. Zhang, and J. Z. Larese, Phys. Rev. Lett. **71**, 2971 (1993).

[8] J. M. Phillips, Phys. Rev. B **51**, 7186 (1995).