Lithium adsorption on the graphite (0001) surface

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Initial exposure of single-crystal graphite samples to lithium vapor from a molecular beam source results in no long-range order in the lithium overlayer as observed by low-energy electron diffraction over the temperature range 80–500 K and coverage range 0.01–5 monolayers. A hexagonal close-packed incommensurate structure is observed only after annealing the surface to $\sim$ 500 K. Auger electron spectroscopy measurements of the lithium KVV transition for a multilayer coating prior to annealing reveal an Auger electron energy of 51 eV (that of metallic lithium), whereas after annealing the Auger energy shifts to 42 eV. This energy shift is due to diffusion of lithium into the bulk graphite and formation of a lithium-graphite submonolayer structure with resultant change of the lithium electronic configuration from that of metallic lithium to a configuration similar to that in lithium compounds such as LiB_2, LiN_3, and LiF. The hcp incommensurate two-dimensional structure is a lithium structure on the surface with no indication of lithium residing within the top surface layers. This phase shows no phase transitions over the temperature range 80–500 K.

I. INTRODUCTION

Graphite has been widely used as a substrate for studying two-dimensional (2D) behavior in adsorbed and absorbed layers. A number of studies have been reported on physical adsorption, chemical adsorption, and intercalation[1-10] of various atomic and molecular species with graphite, with alkali-metal/graphite interaction being an important subset of those studies. Previously, the investigations of potassium adsorbed on a graphite (0001) surface and intercalated into graphite have been undertaken through by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) studies.[9,10] The present work is a continuation of that research effort focused on lithium adsorption on a low-step-density graphite surface. The adsorption process and the phases of lithium adsorbed on the graphite surface are investigated by LEED and AES techniques.

II. EXPERIMENT

The experiments were undertaken in a UHV (ultrahigh vacuum) chamber containing a four-grid LEED-AES apparatus, a universal manipulator for controlling the sample position precisely, and a quadrupole mass spectrometer. The sample on the manipulator could be heated to 1000 K and cooled to liquid-nitrogen temperature.

A natural graphite crystal was cleaved by a high-pressure dry nitrogen stream and attached to the sample holder by a tantalum O ring to expose the (0001) face of graphite. A pure lithium molecular-beam source shielded from the graphite by a shutter was installed in the vacuum chamber approximately 7 cm from the sample. Because of the lithium's chemical reactivity (it strongly reacts with quartz at temperatures higher than 270 °C) the lithium was loaded into a small stainless-steel cup encapsulated by an evacuated quartz tube. The quartz tube was broken off by a shutter in the UHV chamber and subsequently heated by supplying a current to a nickel tape wound around the tube. Temperatures as high as 700 °C could be reached by the lithium

source. The degree and extent of adsorption of lithium were changed by controlling the temperature of the lithium source and the time of evaporation. The rate of lithium evaporation at a source temperature of 570 °C was determined by AES measurements on a silicon substrate to be about 1×10^{14} atoms/$(cm^2 min)$.

The cleaved graphite crystal was cleaned by heating the sample at 5×10^{-10} Torr to 700 °C for 4 h. The surface contamination was checked by AES and showed only an oxygen impurity at a level of less than 3% of a monolayer. After exposure to lithium the graphite sample could be recleaned by the above procedure.

A low step density on the graphite surface was defined by LEED through the observation of a threefold symmetric diffraction pattern. Such regions of area $\sim$ 1 mm^2 and step density of better than 0.05% were readily found on the surface. The graphite sample surface was aligned normal to the incident electron beam by the criterion that the intensities of symmetric beams, i.e., (10), ($0\bar{1}$), ($\bar{1},1$), were identical to each other to within a few percent.

The diffraction-beam intensities were measured via the spot photometer-fluorescent screen method. The measured LEED I-V curves were compared with those obtained from dynamical calculations which have been described previously.[8,10] In the full dynamical LEED calculation, both the reverse scattering perturbation (RSP) method and renormalized forward scatter (RFS) method were used.[11]

III. RESULTS AND DISCUSSION

Lithium evaporation onto graphite at liquid-nitrogen temperature resulted in two modes of behavior as monitored by AES. When the amount of lithium evaporated onto the graphite was less than one monolayer the KVV lithium Auger line was at 42 eV [Fig. 1(b)]. When the amount of lithium on the surface was increased to several layers [Fig. 1(a)], the Auger signal shifted to 51 eV. This difference in Auger electron energy for lithium has its basis in the chemical interaction of lithium with the graphite substrate. Previ-
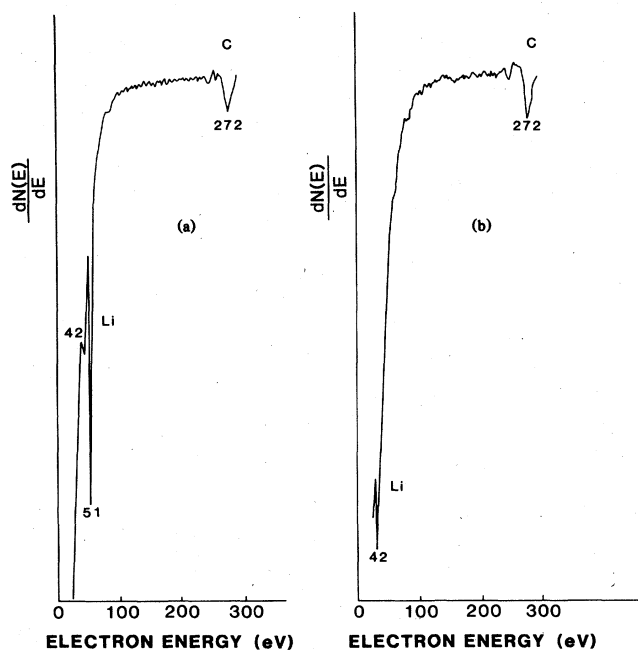
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FIG. 1. Auger electron spectra of lithium on graphite: (a) multilayer coverage of graphite; (b) submonolayer coverage of graphite.

ous studies[12] have shown that the Auger energy for lithium in lithium compounds such as Li_2C_2, LiB_2, Li_3N, and LiF is ~ 43 eV, whereas the Auger energy for lithium in its metallic state is ~ 52 eV. In the submonlayer region of lithium on graphite, therefore, there is significant enough charge transfer to the graphite to generate a lithium-electronic configuration similar to Li_2C_2 [although Li_2C_2 is only stable above 750 K (Ref. 4)]. For the multilayer case, after several hours at liquid-nitrogen temperature and much shorter times at higher temperature (but below room temperature) the lithium Auger signal shifted back to 42 eV and remained there for all temperatures below 200 °C. As the lithium vapor pressure below room temperature is less than 10^{-12} Torr, lithium did not desorb from the surface during this time, but instead diffused into the graphite bulk to leave only a submonolayer coverage on the surface. The exact coverage of lithium on the graphite surface was not readily measurable as electron beam effects (possibly electron-stimulated desorption, ESD) were very severe and prevented the obtainment of repeatable AES data. However, distinctions could be made in the AES data as to submonolayer or multilayer coverage.

For lithium evaporated onto graphite at liquid-nitrogen temperature no ordered or superstructure phases were observed in LEED for all coverages (~ 0.1–5 monolayers) studied. Graphite has an hcp lattice structure with honeycomb layers in an ABAB . . . stacking. This results in a threefold LEED pattern for clean cleaved crystals with low step densities, i.e., with principally a single surface termination (A and B).[8] Upon lithium exposure, the graphite/lithium LEED pattern remained threefold with no changes in relative beam intensities but with decreased absolute intensity and very weak diffuse spots and high background intensity at the highest exposures.

Upon heating the graphite/lithium crystal to ~ 200 °C

and cooling to liquid-nitrogen temperature (for all lithium exposures greater than $\sim 1 \times 10^{14}$ atom/cm^2) a ring structure appeared in the diffraction pattern (Fig. 2). The appearance of this structure was accompanied by a shift of the Auger electron energy to 42 eV.

The ring was quite sharp and visible in the primary electron enery range of 66–170 eV. The ring half-width was equal to that of the substrate graphite spots and indicated structure ordered to at least the transfer width of the LEED instrument. Second- and third-order diffraction rings could also be observed. The ratio of the diameter of the first-order ring to the distance between two opposite graphite diffraction spots was constant at 0.74. This incommensurate lithium structure indicates clustering of the lithium into small islands (~ 100-Å-diam lower bound) of random orientation with respect to the graphite surface and in a close-packed structure with interatomic spacing of 3.3 Å at 80 K. In comparison with metallic lithium, the lithium atomic radius for the above structure is 1.65 Å, about 6% larger than that for metallic lithium (1.55 Å for fcc lithium).

As this ring pattern indicates an incommensurate structure at the surface, it is readily possible to extract out from LEED calculation the exact atomic structural parameters of the surface. The ring may imply lithium atomic clusters *on* the graphite surface, lithium clusters *in* the graphite surface, or some Li-C compound *on* or *in* the surface (the narrow width of the ring and the observation of second- and third-order rings rule out the existance of a lithium-liquid-like layer). For the latter case, other than the intercalation compounds, the Li-C compound (Li_2C_2) forms only above 750 K and is, therefore, not a good candidate for the ring structure. In addition, the close match of interatomic spacing to that of metallic lithium for an assumed simple structure of a single lithium basis atom at each hexagonal 2D lattice site gives credance to the 2D close-packed lithium atom cluster model although close packing is not observed for the high-temperature metallic lithium phase (bcc above 78 K). These lithium clusters, however, may still be either *on* or *in* (intercalated in) the graphite surface. If the lithium was *in* the surface it would be expected, as measured by x-ray diffraction[13] that the graphite layers would be expanded to about 3.71 Å (vs 3.35 Å for pure graphite), that the graphite stacking would be AAA, and that the LEED pattern would be sixfold and not threefold. Such changes would result in significant changes in the graphite LEED spectra. Figures 3 and 4 show the measured and calculated spectra of the (10) and (01) graphite beams for clean graphite and for the lithium/graphite ring-structure system. Note that
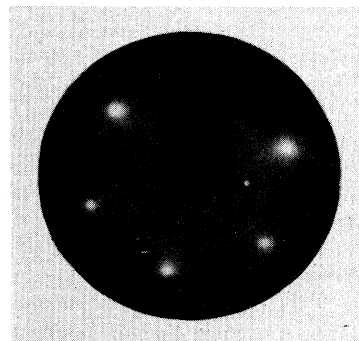

FIG. 2. LEED pattern of ring structure at 125 eV and 80 K obtained after annealing lithium/graphite to 500 K.
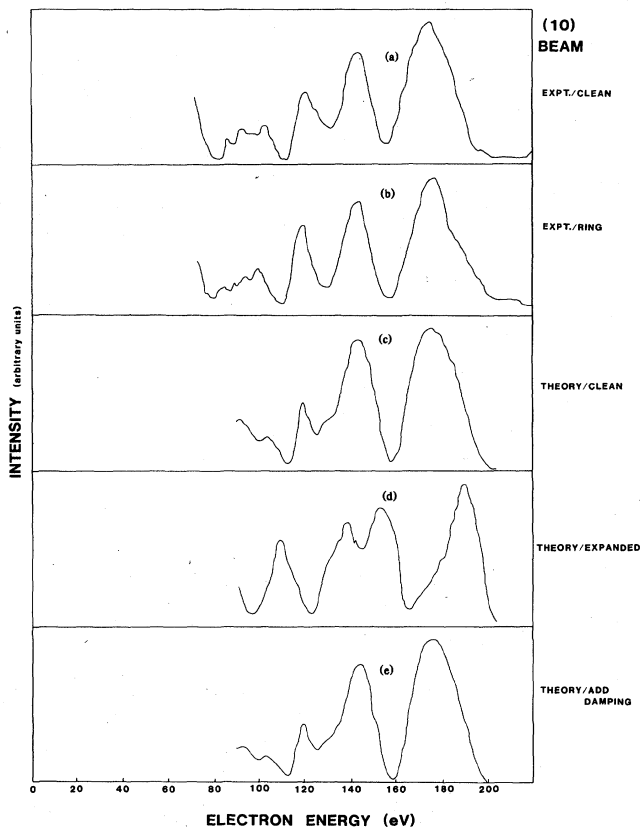
FIG. 3. (10) beam LEED spectra measured and calculated for different conditions: (a) clean experiment; (b) ring-structure experiment; (c) clean theory, $ABAB$ . . . stacking; (d) top-layer expanded theory, $ABAB$ . . . stacking; (e) damping added to the top surface to extend 4.0 Å above the center of the top-most graphite plane theory.

FIG. 4. (01) beam with descriptions as in Fig. 3.

the experimental $I\text{-}V$ curves for the clean and lithium adsorbed graphite [Figs. 3(a), 3(b) and (4a), 4(b)] are essentially identical. Figures 3(c), 3(d) and (4c), 4(d), however, show significant changes expected in the $I\text{-}V$ spectra on increasing the top graphite layer spacing from 3.35 to 3.71 Å. As this is not observed in the experimental data, the lithium clusters responsible for the ring pattern are not within the graphite surface, but are on top of the graphite surface.

The lithium clusters on the graphite surface could, however, also affect to some degree the measured electron diffraction data since they introduced additional damping to the incident electrons to a level of 4.0 Å above the top graphite layer. This possibility was included in the calculations shown in Figs. 3(e) and 4(e) where it is noted that in comparison to the clean graphite calculation [Figs. 3(c) and 4(c)] little effect is observed due to the additional damping. It is well also to note that although we observed lithium diffusion into the graphite as a function of time and sample temperature, there is no indication for lithium residing in between the top two to three layers of the graphite crystal. It diffuses deeper into the bulk in sharp contrast to the layer-by-layer intercalation of a graphite crystal observed for potassium.[14] Also, in comparison, potassium formed commensurate structures on graphite [($\sqrt{3} \times \sqrt{3}$)$R30°$ and
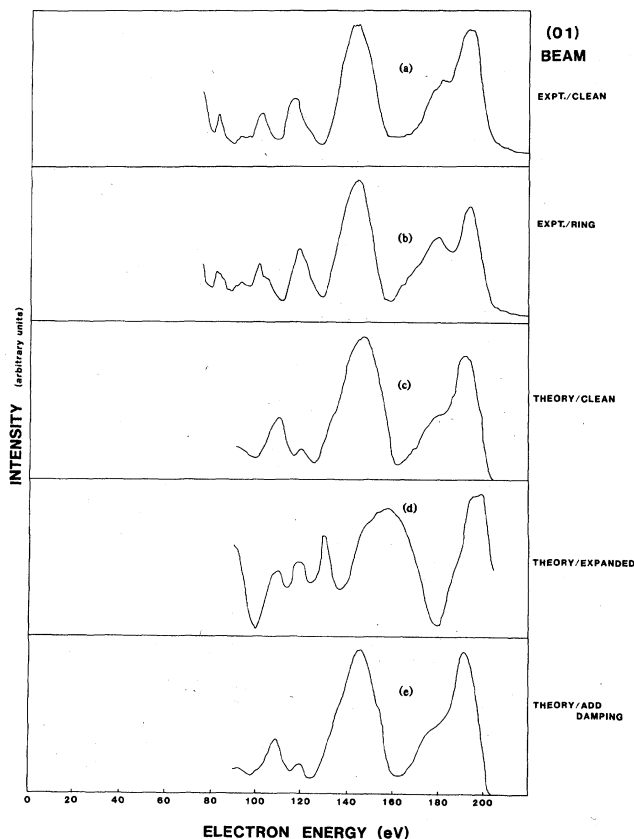
(2×2)],[9] whereas lithium forms only an incommensurate close-packed structure.

A final note to make is that the diffraction ring is observed up to temperatures $\sim 200\,°C$. Upon heating from 80 K, the intensity of the ring decreases in accordance with Debye-Waller behavior and no additional changes in ring intensity or width are observed until extinction of the ring in the high thermal diffuse background intensity at about 500 K. There are, therefore, no phase transitions observed for the close-packed lithium clusters over this range of temperature.

IV. CONCLUSION

Lithium evaporated onto a low-step-density graphite basal plane surface condenses in a disordered phase. The disordered phase transforms to an ordered one after heating to 500 K and then cooling to liquid-nitrogen temperature. The latter phase is a close-packed structure of lithium on, and incommensurate with the graphite surface. This phase shows no phase transitions and is stable over the temperature range of liquid-nitrogen temperature to 500 K.

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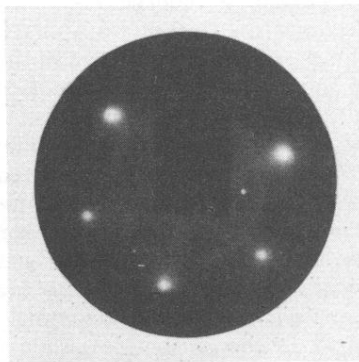[14]N. J. Wu and A. Ignatiev, Solid State Commun. **46**, 59 (1983).

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