Subsurface condensation of potassium for K/graphite

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Photoemission from quantum well states show that K films can be grown nearly layer by atomic layer on a cooled graphite substrate. The data also indicate that this growth is preceded by the formation of one intercalated monolayer of K metal. The successive steps of intercalation and adsorption means that the properties are more intricate than suggested by previous results, which have established K/graphite as a prototype metal/semimetal adsorption system.

Characteristic of the K/graphite surface system at low K coverage is a uniform adatom distribution and a significant redistribution of alkali valence charge, which involves the substrate.[1–3] Such a dispersed phase is typical of alkali metals on metals over a wide range of submonolayer coverages.[4] On the graphite substrate by contrast a K metal condensate forms already at a relatively low threshold coverage above which the two phases coexist.[1] The early onset of aggregation is explained by the semimetal character of graphite; the low density of electron states near above the Fermi energy means that only few electrons can be transferred to the graphite before the cost in energy becomes high making K solidification preferred.[5]

The early results have stimulated a number of experimental studies[6–10] and the simple 2×2 order of the condensed phase observed by low energy electron diffraction (LEED) has made the system attractive to theoretical modeling for a prototype metal on semimetal system.[11–13] The picture, which has emerged from the experiments and served as a starting point for the theoretical work, is that the condensate consists of adsorbed K metal islands.[1–3] The purpose of this Report is to show photoemission data which indicate that the first condensed phase actually is an intercalated 2×2 K monolayer. On this modified graphite substrate an adsorbed monolayer, or thicker films can be grown nearly layer by atomic layer. The new information comes mainly from the observation of atomic layer resolved quantum well states (QWS) formed by valence electrons confined to the adsorbed films. Photoemission is an excellent method to probe such states down to monolayer thickness.[14] Furthermore another observed state is assigned to an intercalated K monolayer. Also this state may be described as a QWS. Helpful for the interpretation are our recent photoemission results for Na/graphite.[15] For that system all valence states induced by Na deposition are well explained in terms of quantum well states for adsorbed Na films.

As in the previous studies the substrate is a sample of highly oriented pyrolytic graphite (HOPG), which is kept at 90 K or 40 K during the experiments. HOPG consists of microcrystals, which have a nearly common orientation of the *c*-axes but are azimuthally disordered. The alkali metal is evaporated from a glass ampoule broken *in situ* and held at constant temperature during an experimental run. The deposition rate has been varied between 1 and 9 min per atomic layer. The photoemission spectra are recorded in the MAX-

laboratory, Lund University, at BL52, which provides synchrotron light in the photon energy range 3.6–35 eV. All spectra shown below are recorded along the surface normal with *p*-polarized light incident at an angle of 50°. In some of the experiments we used as light source also a 1 mW He–Cd laser (3.82 eV photon energy). The rapid data collection obtained with this source is convenient for observing the emergence of new emission lines as the K deposit is increased in small doses.

The spectra shown in Fig. 1 are measured after different evaporation times with the sample held at 90 K. A peak, labeled A in Fig. 1, appears as the evaporation is continued beyond a threshold coverage. Photoemission at low photon energy is possible due to a rapid initial decrease of the work function, by 2.0 eV, upon K deposition. Peak A appears
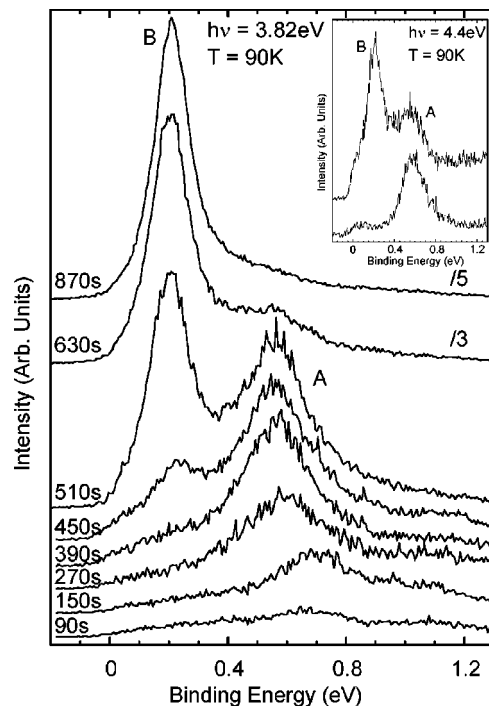

FIG. 1. Photoelectron energy spectra recorded along the surface normal at 3.82 eV photon energy at different K evaporation times. Note the change of vertical scales for the two uppermost spectra. The inset show spectra measured at 4.4 eV after evaporation times that give peak A (lower curve) and peak B (upper curve) maximum intensity.
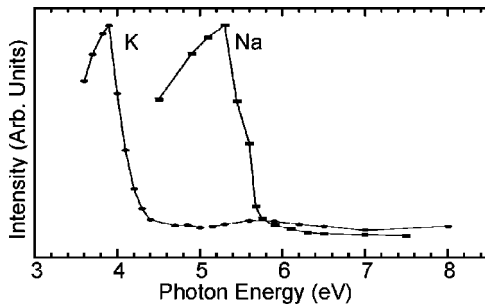
FIG. 2. The intensity of peak B at different photon energies and the intensity of a corresponding peak for 1 ML Na on graphite. The intensity scale is arbitrary and different for the two cases.

shortly after the work function has reached saturation. The work function decrease is explained by the dipoles created by the presence of dispersed K adatoms, which have transferred electronic charge to the substrate. As noted in previous work saturation of the work function change marks the threshold coverage for K metal condensation[3] and, as also noted previously,[9] peak A is characteristic of the first condensed phase. The LEED pattern at this point shows diffraction rings characteristic of 2×2 order. We observe rings rather than spots due to the azimuthal disorder of HOPG. Peak A is first observed after around 20% of the deposition time required to give the peak maximum intensity. As it emerges the peak falls at a binding energy of 0.75 eV but with increasing coverage it shifts to 0.57 eV (Fig. 1).

The new observations of main interest are made upon further K evaporation when a state at 0.20 eV binding energy appears (peak B in Fig. 1). The intensity of B reaches a maximum at around twice the evaporation time required to get maximum intensity for peak A and at $h\nu = 3.82$ eV the intensity is then approximately ten times higher than the maximum intensity of A. The 2×2 order is maintained. Due to the high intensity of peak B the emission line at 0.57 eV binding energy is obscured at 3.82 eV photon energy. The state at 0.20 eV binding energy has a cross section, which drops rapidly with photon energy. At 4.4 eV photon energy one finds that the intensity of A is reduced by 30%–40% upon adding the K dose required to maximize peak B (Fig. 1, inset). In Fig. 2 the cross section of peak B is shown together with a corresponding peak observed at 0.17 eV binding energy for 1 ML Na on graphite.[15] Upon Na adsorption there is a similar rapid work function decrease and the 0.17 eV peak appears as the work function change saturates. For both A and B the lateral dispersion obtained by varying the polar detection angle is near free electron like. Due to the disorder of HOPG this measurement gives merely an average of the dispersion in different azimuthal directions.

If the sample is instead kept at 40 K the results are qualitatively the same. The initial work function drop is somewhat bigger, 2.4 eV rather than 2.0 eV. Peak B appears somewhat sooner and obtains a higher maximum intensity relative to peak A. The likely reason for the higher intensity ratio is that the K layer producing A is not as complete at the lower temperature. An indication of this is that, if the evaporation is continued beyond the time at which peak A has reached maximum intensity so that both A and B are present, then a
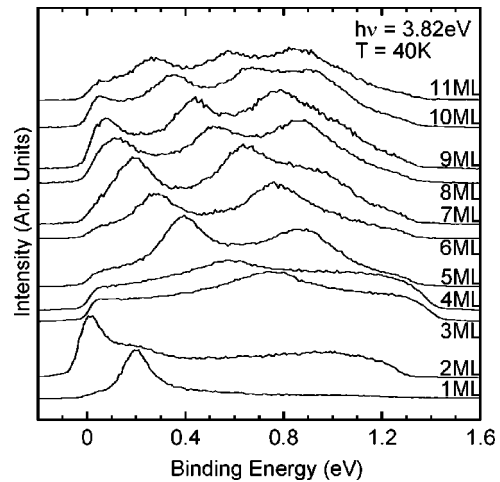

FIG. 3. Quantum well state emission peaks for K films having different thickness, given in units of atomic layers.

short anneal at around 90 K gives A higher and B a lower intensity. Peak A is less sensitive to a temperature increase than B and remains if the temperature is increased to around 200 K. Peak B on the other hand loses intensity if the temperature is raised above around 100 K. This explains why peak A but not B was observed in a previous experiment, which was made with the sample at 160 K.[9] With repeated cycles of evaporations at 40 K in monolayer doses followed by short anneals at 90 K near layer by layer growth for K films is obtained in the thickness range tried, 1–11 ML. The evidence for this is the layer resolved QWS observed in photoemission spectra (Fig. 3).

Valuable information about how the substrate is affected by the K deposition is given by the shift in energy of a prominent emission line from graphite due to a state 7.6 eV above E_F and populated by secondary electrons (Fig. 4, inset).[16] This type of information is conventionally obtained by monitoring energy shifts of core and valence electron binding energies. In the present case this secondary emission line turns out to provide more detail than the broad π-band emission line which is the alternative within the photon energy range of the experiment. As shown in Fig. 4 the shifts of the line reflect well three initial stages characterized by (a) the rapid work function drop, (b) the appearance of peak A and (c) the appearance of B. Initially upon K deposition (0–80 s in Fig. 4) the line splits into two components, one of which shifts in energy as the work function decreases. We ascribe this to a bulk-surface splitting of the energy with the bulk component stationary. The probing depth is uncertain and as discussed below the shifted component may be representative of two rather than one atomic layer. The energy shift is proportional to the work function change, with $\Delta E = 0.32\Delta\Phi$. The initial condensation marked by the appearance of peak A is reflected by a stepwise additional energy shift (0.3 eV) and a significant line narrowing. This line and peak A reaches maximum intensity at the same K dose and upon further deposition the intensity decays, by approximately a factor of 3, as the dose approaches that giving maximum intensity to peak B.

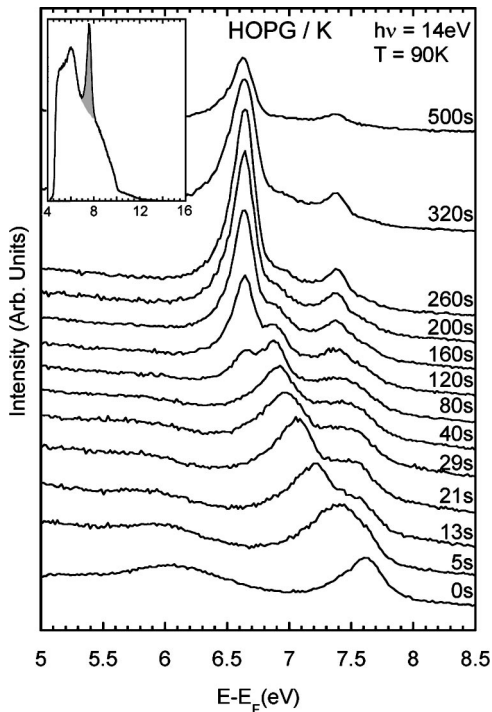We note that previous $C 1s$ core level binding energy

FIG. 4. Splitting and shift upon K deposition of an emission peak, which for graphite lies 7.6 eV above the Fermi level (inset). By the spectra is given the K evaporation time. The evaporation rate is 70% higher than used to obtain the spectra in Fig. 1.

measurements made with high resolution at $h\nu = 350$ eV on samples annealed at 90 K (Ref. 10) surprisingly did not distinguish the different phases as well as the secondary line in Fig. 4. A single $1s$ line was observed for clean graphite (HOPG) as well as for the dispersed and the 2×2 ordered K phase. For the two latter the $1s$ level was in both cases downshifted by 0.4 eV. Since at 350 eV photon energy around 20% of the $1s$ intensity for clean graphite is due to layers beneath the surface layer[17] one could expect K deposition to give a shifted surface component and a largely unshifted bulk component in the manner observed for the secondary peak. A reason why this is not the case may be that intercalation occurs already at low surface coverage to such an extent that the C $1s$ binding energy is almost equally effected in the two topmost carbon layers, which are the only ones effectively probed at $h\nu = 350$ eV. The difference between the two sets of data is then explained if the shifted component of the secondary peak is representative of the two outermost atomic layers in graphite. Support for this interpretation is given by the results of Hock and Palmer,[2] who found the low coverage phase to be unstable with respect to intercalation over a 30 min period even at 50 K.

Our interpretation of the results is that peak A is due to an intercalated 2×2 K monolayer while B and the other K deposition induced QWS are characteristic of adsorbed K films, 1 ML and thicker. One reason for assigning peak A to an intercalated K monolayer is that it remains also when another atomic layer is added (Fig. 1, inset). This means that the two layers are not in contact since otherwise new states characteristic of a duolayer would have appeared. This argu-

ment has the weakness of relying on emission intensities. Peak A could remain due to the existence of big holes in the layer giving peak B although we would regard this unlikely considering the near equal deposition times required for the two layers. A likely explanation for the intensity decrease is that the electrons propagate through the added K layer. At the low energy of the final state (3.8 eV above E_F at $h\nu = 4.4$ eV) the mean free path is long and the intensity reduction therefore is modest (30%–40%). The mean free path decreases strongly with the energy and the corresponding intensity reduction for the secondary line, at 6.5 eV above E_F, is therefore much bigger ($\sim 70\%$).

A second indication that peak B rather than A is representative of one adsorbed monolayer is given by its binding energy. If the first condensed layer is excluded the energies measured for the QWS are quite consistent with those measured for Na/graphite[15] and for alkali metal films on Cu(111). For the present purpose it is sufficient to consider the case of one adsorbed atomic layer. If 1 ML of either Li, Na, or Cs is adsorbed on a Cu(111) substrate the QWS with one node in the film have binding energies that are close: 0.14 eV for Li,[18] 0.10 eV for Na,[19] and 0.04 eV for Cs.[20] The near equal energies can be understood in simple terms. A QWS has a perpendicular wave vector, k, given by the phase rule $2Ndk + \Phi = 2\pi m$, where N is the number of atomic layers, d is the thickness of a layer, Φ the sum of the phase shifts at the boundaries, and m is the number of nodes in the well.[14] For $N = m = 1$ this gives $k = \pi/d(1 - \Phi/2\pi)$. If Φ is small and positive this gives a wave vector reaching close to the π/d Brillouin zone boundary. For a monovalent metal also the Fermi wave vector comes near the zone boundary and therefore the energy is near the Fermi level. Since for Na/graphite the $N = m = 1$ state has a binding energy of 0.17 eV a binding energy near this value is expected for one adsorbed monolayer of K on graphite. The comparison between the two alkali metals is however complicated by the fact that the adsorbed K monolayer resides on top of a substrate with an intercalated K layer. The two substrates are thus different and this will modify the QWS energy. We suggest that this energy change will be modest. The QWS energies fall near the middle of a wide substrate band gap, which means that the states have short tails in the substrate and thus are sensitive mainly to the uppermost atomic layer. In this layer the states are down shifted as indicated by the energy shift of the secondary peak (Fig. 4). Here one notes that there is only a small change of the shift as the K metal condenses to form the intercalated monolayer. If the graphite bands are assumed to shift rigidly the difference between the QWS energy with and without an intercalated layer will be a small fraction of the band shift.

A third reason for identifying peak B with an adsorbed monolayer is that the cross section is similar to that observed for 1 ML Na on graphite (Fig. 2). For a free electronlike metal the surface photoelectric effect is enhanced near below the plasma frequency due to strong spatial field variations near the surface[21] and a monolayer of metal is sufficient to observe a significant enhancement.[22] Recent measurements of the photoyield for Na/Al(111) and K/Al(111) at near 1 ML coverage[23] show that the photoyields have maxima at $h\nu$

=5.3 eV for Na and 3.6 eV for K and then fall off rapidly above these photon energies. As shown in Fig. 2 this fits well with the present observations.

In summary, our results indicate that the first condensed K metal phase for K/graphite is an intercalated monolayer rather than an adsorbed one as hitherto believed. While K/graphite can then no longer serve as a prototype of metal/semimetal adsorption the so far neglected Na/graphite system seems to be a good candidate for this. That Na and K behave differently is not surprising since Na is well known to intercalate less readily than K.[24] Rather unexpected is that a subsurface K monolayer is the preferred alternative to continued diffusion into the bulk. Finally we should point out

that our results give circumstantial evidence and that a firm conclusion regarding the position of the K atoms must await a structure determination. A full structure determination may not be required. Intercalation is accompanied by a substantial increase of the distance between the adjacent carbon planes and a measurement sensitive to this distance would be conclusive.

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