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Evidence for metallic states in potassium-intercalated picene film on graphite

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We report the results of photoemission spectroscopy on the potassium concentration (x) dependence of K_x picene films on graphite. The results show a systematic shift of a whole valence band and the appearance of a clear Fermi edge for a certain value of x, with additional structures at higher binding energies. Observed spectral evolutions are reminiscent to those of doped C_{60}, implying that the K_x picene film has multiple phases depending on the K concentration. Appearance of a clear Fermi edge, in contrast to multilayer K_x picene films on Au, SiO_2, and Ag(111) substrates, where no clear Fermi edges are observed, suggests that the emergence of the metallic states for K_x picene films depends on the specific molecular orientations in the films on different substrates.

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I. INTRODUCTION

Organic conductors exhibit a rich variety of physical properties, charge/spin density waves, Mott transitions, magnetism, exotic superconductivity, and so on, originating from the interplay of electron-phonon and electron-electron interactions, and therefore constitute an important research field in the condensed matter physics.[1] Aromatic hydrocarbon superconductors that contain benzene rings form a new family of organic conductors, which was first discovered in potassium-doped picene (K_x picene, $K_xC_{22}H_{14}$) with superconducting critical temperatures of 7 and 18 K.[2] The potassium concentration x of superconducting phase is estimated to be 3. Recent studies have reported selective synthesis methods for the 7 and 18 K phases as well as zero resistance that makes further confirmation of superconductivity.[3,4] Importantly, the family of aromatic hydrocarbons is made up of a large number of molecules, having the potential of new superconductors with higher transition temperatures. Indeed, several aromatic hydrocarbon superconductors, with the highest transition temperature reaching 33 K, have already been reported.[5–7]

Theoretical studies have been performed to understand the possible crystal structure as well as the fundamental interactions that provide a major influence on the low energy electronic states.[8–18] While band structure calculations using structure optimization have provided insight into the crystal structure for K_3 picene and its metallic electronic structure,[11,15] those for K_3 picene also reported the importance of electron correlation that can induce magnetic instability because of the comparable energy scale between the bandwidth W and Coulomb energy U.[9,10] These suggest a possible interplay of these interactions for the physical properties of doped picene. For the mechanism of the superconductivity, the importance of intramolecular phonon, intermolecular phonon, intercalant phonon, and electron correlations have been proposed.[12–14,16–18]

In contrast to the observation of superconductivity, however, other bulk physical properties of aromatic hydrocarbon superconductors have hardly been able to be explored experimentally, due to the unstableness of doped samples under atmospheric condition and the low superconducting shielding fraction of the bulk samples. Neither the exact superconducting composition nor the crystal structure have yet been determined.

Regarding spectroscopic studies, *in situ* measurements using films grown under ultrahigh vacuum, which have the benefit of avoiding the deterioration of the doped samples under atmospheric condition and the availability of systematic study of x dependence, can investigate the physical properties from an electronic-structure point of view. However, photoemission spectroscopy (PES) using multilayer films on different substrates has provided growing evidence for absence of states near the Fermi level (E_F),[19–21] which contradict the observation of superconductivity. Our previous PES study has reported appearance of new states that cross E_F in the K-doped picene ($x \sim 1$) film on Au.[22] However, a similar result observed in a K-doped picene ($x \sim 0.8$) film on oxidized Si was attributed to a lack of thermodynamic equilibrium originating from the weak intermolecular van der Waals coupling.[21,23] Recent PES studies on doped picene films have reported an absence of states near E_F, which signifies the insulating nature of K_x pience ($x \sim 3$) films on Au, SiO_2, and Ag(111) substrates.[19–21] Considering that the physical properties of aromatic hydrocarbon molecule films synthesized on substrates have been known to be markedly dependent on the specific conditions of the substrate,[24] searching for metallic films on different substrates is one of the research directions toward understanding superconductivity in doped picene.

In this paper, we report potassium concentration x dependent PES measurements of K-doped picene films on highly oriented pyrolytic graphite (HOPG) using He I and Xe I resonance lines, which exhibits a clear Fermi edge indicative of metallic character. The appearance of a clear Fermi edge is in contrast with the absence of clear Fermi edges in multilayer films on Au, SiO_2, and Ag(111) substrates.[19–21] This discrepancy proposes that the emergence of the metallic states for K_x picene films depends on the aspect of the molecular orientations in the films on different substrates, which may shed light on the metallicity leading to superconductivity in doped picene.

II. EXPERIMENT

PES measurements were performed at Okayama University, Japan, using a GMMADATA-SCIENTA R4000 electron-energy analyzer. The spectra were measured at room temperature with He I (21.2 eV) and Xe Iα (8.44 eV) resonance lines, and the total energy resolutions were set to 20 and 5 meV, respectively. The base pressure was 2.0×10^{-8} Pa. Picene powder was synthesized by photosensitization of 1,2-di(1-naphthl)ethane with 9-fluorenone in chloroform. The details of the procedure are described elsewhere.[25] Picene thin films (24 nm thick) were prepared by deposition on HOPG substrates with a heated quartz crucible under a pressure lower than 1×10^{-7} Pa. The deposition rate was 2.4 nm/min. These thickness and deposition rates were estimated by a thickness monitor with a quartz microbalance which computes the thickness with the density of picene bulk (1.232 g/cm^3). We assumed that the sticking probability of a picene molecule on an HOPG surface is the same with that on a picene film surface. The films were doped with potassium in several steps by *in situ* evaporation from commercial SAES (SAES GETTERS S.p.A., Italy) dispensers at a pressure lower than 1×10^{-7} Pa keeping the substrates at room temperature.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the evolution of the valence band spectra of a picene film on a HOPG substrate after K doping as measured with the He I resonance line. The bottom spectrum for a pristine picene film (0 s) has eight peaks *a*–*h* between E_F and 10 eV binding energy. The peaks *a* and *b* are assigned to be the HOMO-1 and the HOMO-2 derived bands, respectively, from the angle-resolved PES measurement.[26] The intensity of the peak *a* is higher than that of the peak *b*, and the peaks *d* and *e* are clearly visible. These features are consistent with the previously reported valence band spectra for pristine picene films on Au substrates measured with He I.[19,27] This supports the fact that the long axis of most of the picene molecules in the film is parallel to the HOPG surface, and this molecular orientation coincides with that of pentacene molecules in a film grown on HOPG.[28] The maxima of peaks *a*–*h* are at 2.14, 2.82, 3.46, 4.90, 5.74, 6.72, 8.44, and 9.24 eV, respectively. These values are smaller by 0.4–0.8 eV than the ones for picene films on metal substrates [Au[19,27] and Ag(111)[20]] and an *n*-type Si substrate covered with a native oxide layer on top,[27] although the spectrum for the film on another natively oxidized Si substrate (the doping type is not mentioned) has almost the same values as our data.[21] If the Si substrate used in Ref. 21 is *p* type, the tendency of the energy-level alignment between molecules and various substrates will be quite similar with the one reported for C_{60} films.[29] C_{60} molecules on various metal surfaces strongly interact with the substrates and, as a result, the binding energies of the valence bands of C_{60} films have relatively large and almost the same values for various metal substrates owing to a redistribution of charges at the interface. If the interaction between the molecules and the surface is weak, like a case of C_{60} molecules on a *p*-type GaAs surface, the binding energies of the valence bands of the C_{60} film become small. The smallest binding energies of the peaks for the picene film on HOPG means that the interaction of picene bands with HOPG valence states is very weak and there is almost no redistribution of charges at the interface due to the mixing of the states there.

After a K deposition of 20 s, the spectrum of the pristine picene film shifts toward higher binding energy by 1.6 eV and becomes slightly broader. This shift means that the E_F level moves to the LUMO-derived band edge, and may correspond

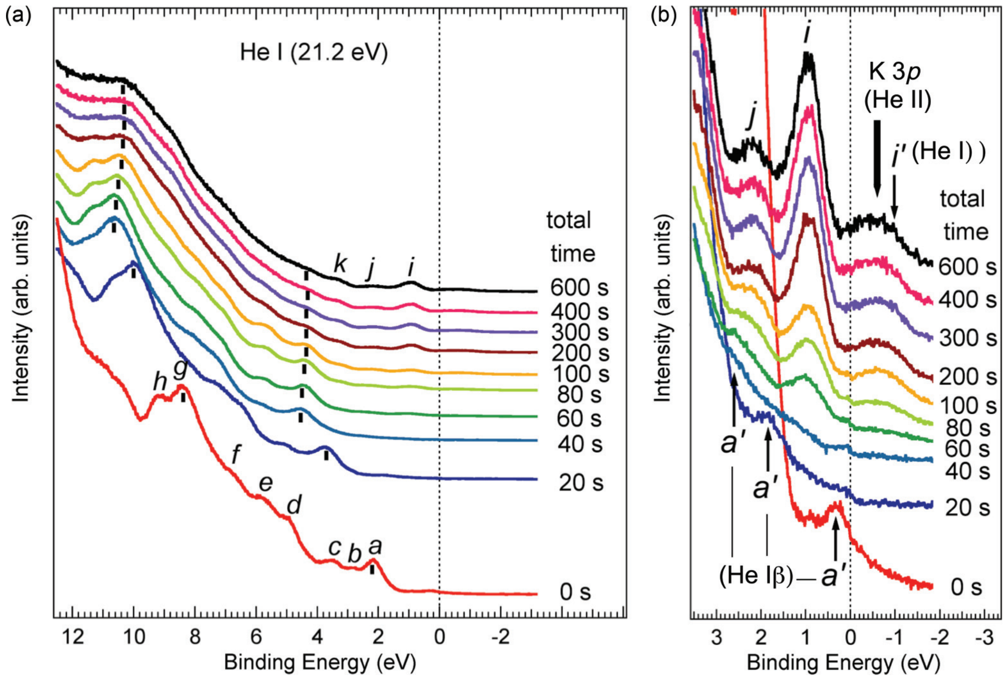

FIG. 1. (Color online) (a) Evolution of the valence band photoemission spectra of a picene film on a HOPG substrate upon K doping measured with He I. (b) The magnified spectra around E_F in (a).

to the formation of the solid solution state observed for K_xC_{60} at the initial doping stage.[30,31] K deposition for an additional 20 s (total of 40 s) leads to further 0.6–0.8 eV shifts of each peak towards the same direction. The total shifts are 2.2–2.4 eV, which are the largest reported for K-doped picene films and correspond to the lowest peak positions of our pristine picene spectrum. This shift of the spectrum is not a sudden single shift observed for a K_xC_{60} film on W(100) in the initial stage of the K deposition,[31] and is consistent with the large and gradual shifts reported in the C 1s spectra for K_x picene and Na_x picene films on Au substrates,[19] and in the valence band spectra for Cs-doped biphenyl on Pd(110).[32] In our previous study,[22] we observed a small shift (0.5 eV) at $x \sim 1$ for a K_x picene film on a gold substrate. The interaction between organic molecules and a metal substrate is strong in general, and the observed binding energies of the valence bands are in fact larger than ones observed for picene films on HOPG. The large values of the binding energies of the valence bands mean that the energy difference between LUMO bands and E_F is small. Then, the energy shift under K doping must be small. Furthermore, the estimated x value in Ref. 22 is relatively small ($x \sim 1$), and it should result in a relatively small shift. We consider therefore that the observed small shift in Ref. 22 originates from those two reasons: the large interaction between the molecules and the gold substrate at the interface and the relatively small value of x.

After K depositions of more than 60 s, the spectra in Fig. 1(a) show only slight shifts (the shifted positions of peaks a and g are shown by the black bars), and three new peaks i–k appear between the shifted peak a and E_F [see Fig. 1(b), where the spectra around E_F in Fig. 1(a) are magnified]. After a K deposition of 200 s, the three new peaks grow and the spectrum, in the binding energy region higher than that of the shifted peak a, becomes broader and less structured. K depositions of more than 300 s merely produce subtle changes to the spectra. The energy positions of the three new peaks after a K deposition of 600 s are 0.92, 2.20, and 3.32 eV, respectively, and they are almost the same as the ones reported previously.[19] The peak i is attributed to a filling of the LUMO and LUMO + 1 derived bands.[20,21] For the origin of the peak j, two candidates are proposed: the plasmon excitation[20] and the oxidation of surface K atoms.[21] The latter is not consistent with the absence of the strong peak at ~5.5 eV in Fig. 1(a), which is observed for the oxidized surface K atoms on the K_xC_{60}.[33] The peak k is assigned to the relaxed HOMO, induced by the structural distortion experienced by the doped picene molecules.[21]

Despite the correspondence of the new peaks, there is a distinct difference between our data and the previous results on K-concentration dependence of valence band spectra of K_x picene films[19–21]: we observe small but clear Fermi edges as seen in Fig. 1(b). The Fermi edge emerges after a K deposition of 20 s, and becomes indistinguishable after a K deposition of 200 s. These spectra, however, contain the signals excited by He Iβ line (23.1 eV), as indicated by thin arrows. The peak a excited by the β line (labeled by a') emerges just under E_F in the pristine spectrum. After K depositions, the shifted peak a' overlaps with the signals around the peak j. The K 3p signal excited by He II line (40.8 eV) emerges at about −0.6 eV as indicated by the thick arrow, which may be overlapped with the peak i excited by the β line (labeled by i'). These signals introduce some ambiguity into the discussion regarding the precise features in the vicinity of E_F of the spectra especially for the pristine spectrum and the spectra measured after the K deposition of more than 100 s. The simple subtraction correction, in which intensities of He satellite signals are subtracted from a raw spectrum, does not work very well in the present study, since the spectral shape near E_F of the corrected spectrum depends on the assumption of the spectral shape of the K 3p signals excited by He II.

An effective way to avoid such a severe overlap of signals near E_F which are excited by the Iα, Iβ, and II lines from a discharge lamp, without a grating, is to use the appropriate combination of a photon source and a filter, for example, a Xe discharge lamp and a CaF_2 filter. The spectra measured with this combination of a lamp and a filter reveal no evident signals excited by the higher photon energy lines as shown in Fig. 2. It should be noted here that the escape depth of a photoelectron excited by Xe Iα (8.44 eV) is more than three times longer than that of He Iα, which means that the results obtained with Xe Iα are more bulk-sensitive ones.[34] Figure 2 shows the evolution of the valence band spectra of a picene film on a HOPG substrate after K deposition as measured with Xe Iα. The procedures of the sample preparation are the same with those for Fig. 1. After a K deposition of 20 s, the valence bands shift to higher binding energy and the Fermi edge is apparently observed again as seen in the five-times magnified spectrum for the 20 s K deposition. The intensity at E_F grows

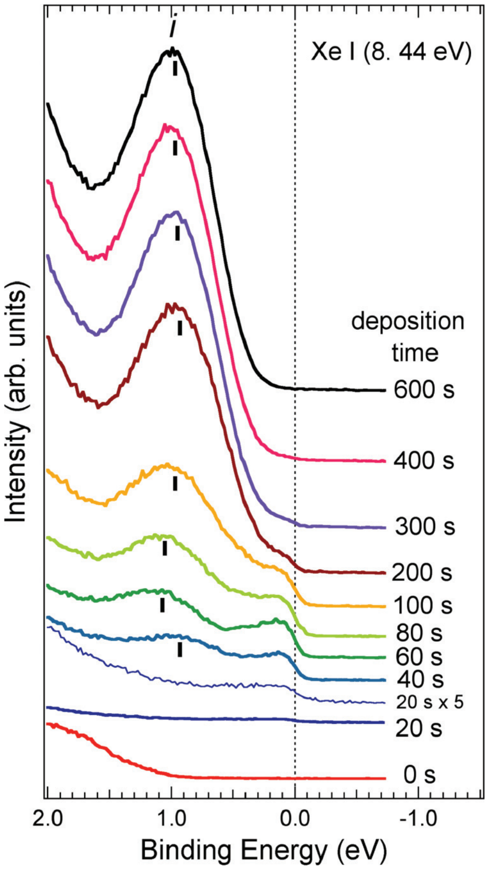

FIG. 2. (Color online) Evolution of the valence band spectra of a picene film on a HOPG substrate upon K doping measured with Xe Iα.

until a K deposition of 80 s and then decreases and disappears completely in the experimental error after K deposition for 600 s.

Here we consider possible extrinsic effects for the observation of the appearance and disappearance of the metallic edge. Formation of a metallic K layer on the film surface and its late oxidation could be one possible scenario. However, we did not observe O $2p$ signals from oxidized K atoms,[35] which means that almost no excess K layer on the surface exists within our total K-deposition time. A potassium intercalation to the graphite interface can induce a metallic edge. Evaporation of K atoms onto graphite at room temperature indeed exhibits a metallic edge due to the filling of the graphite band by electrons donated by the K atoms.[36] However, we do not observe disappearance of the metallic edge for K deposition on a bare HOPG substrate (not shown). One could imagine an alternative scenario in which the appearance and disappearance of the Fermi edge with dosing time could be due to a morphological change of the film during the K deposition, where a K doping to the graphite interface at an early stage produces the Fermi edge and a stronger damping of the photoemission signal at high K dosing associated with the morphological change removes it. We cannot fully exclude this scenario as we do not have AFM and XRR data. Different K-doping behaviors of the intensity at E_F between the surface and the bulk sensitive measurements which will be discussed later is, however, not consistent with this scenario.

The new peak *i* becomes visible at 0.93 eV after a K deposition of 40 s and shifts to 1.07 eV after a K deposition of 60 s. After K depositions of more than 80 s, the peak *i* shows slight and nonmonotonic shifts (∼0.2 eV); first, it approaches to E_F for a K-deposition period of 200 s and then begins to shift away from E_F. These nonmonotonic shifts seem to synchronize the appearance and the disappearance of the Fermi edge. Quite similar behavior in the valence band evolution after K deposition was observed for C_{60} films and is interpreted as the sequential emergence of different phases of K_xC_{60} with increasing x values involving structural transitions.[30] Our observations, therefore, illustrate that the K_x picene film on HOPG has multiple phases depending on the K concentration. The emergence of the Fermi edge exhibits the formation of the metallic states at the early stage of the K deposition and the disappearance after a K deposition of 600 s means that the film becomes an insulator at this K concentration, implying that x has reached 4.[15] This behavior as a function of the K-deposition time is in good agreement with the x dependence of the magnetic properties in normal states of K_x picene bulks: Pauli-like for $x < 4$ and Curie-like for $x \geqslant 4$ (the superconductivity was observed for $2.6 \leqslant x \leqslant 3.3$).[2]

If we assume a linear relation between the doping level x and the deposition time, a deposition time of 200 s correlates with a doping level of about $x = 1.3$. A better estimation obviously needs identification and isolation of each phase of K_x picene. Recently, Roth *et al.* succeeded in obtaining three K-doped phases with compositions $x = 1,2$ and 3 for K_x dibenzopentacene.[37] K_1 dibenzopentacene is stable at room temperature, while K_2 dibenzopentacene is unstable and the potassium atoms diffuse out of the film at room temperature. These two phases are obtained by K deposition keeping the pristine film at room temperature. The last one, K_3 dibenzopentacene, is obtained only with annealing procedure and stable at room temperature. From an electron-energy-loss spectroscopy measurement, they conclude that K_1 dibenzopentacene is an insulator and K_x dibenzopentacene ($x = 2,3$) may be metallic. These findings shed light on the importance of the substrate temperature on diffusion of K atoms in the film, while the properties of the metallic phases for K_x dibenzopentacene show a sharp contrast with ones for K_x picene on HOPG (this study) and K_xC_{60},[30] for which the metallic phases emerge at the initial stage of K doping and are stable at room temperature.

For the surface of K_x picene film, there is a possibility that the electronic state is different from that of bulk as observed for K_xC_{60} films.[38,39] To address this problem, it is useful to compare the spectra measured with He I and Xe I resonance lines because the emitted photoelectrons excited by using these lights have different escape depths as mentioned above. Figure 3(a) provides a comparison of the spectra with the same K-deposition times (20, 40, 60, and 80 s) in Figs. 1 and 2. The spectra measured with He I (dotted lines) in the first three pairs include almost unnoticeable or very small signals excited by the He Iβ and II lines around peak *i* and E_F because of the small intensities of the new peaks during the early stages of the K deposition, and finite intensities at E_F are observed without ambiguity for a K-deposition period of 60 s. For a K deposition of 80 s, the spectrum measured with He I has a relatively large contribution of K $3p$ excited by He II as shown by the background gradient indicated by the gray bars. Although the x values of the spectral pairs are not exactly equal to each other, this comparison exhibits clear and common differences between them. At first sight, the intensity at E_F decreases and the intensity of the peak *i* grows for the data measured with He I, while the intensity at E_F grows together with the intensity of the peak *i* for the data measured

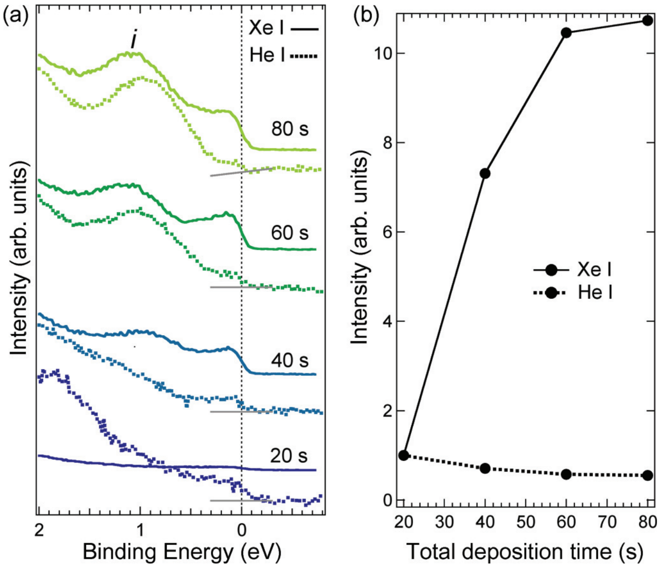

FIG. 3. (Color online) (a) Comparisons of the spectra with the same K-deposition times (20, 40, 60, and 80 s) in Figs. 1 and 2. The gray bars around E_F are the assumed base lines for the data measured with He I for the intensity estimation at E_F in (b). The bar for a K-deposition time of 80 s is slightly inclined because of the overlap of the K $3p$ signals excited by He IIα. (b) Intensity variations at E_F in (a).

with Xe I. To see the difference more precisely focusing on the intensities at E_F, in Fig. 3(b), we show the intensity variations at E_F in the spectra of Fig. 3(a). The intensities are normalized to the ones for a K deposition of 20 s. The variation tendency is clearly opposed to each other. It should be noted here that this difference is difficult to be simply explained by a K doping to the graphite interface because, if it is the case, both intensities should change in the same manner. The observed differences in Figs. 3(a) and 3(b) strongly suggest that the surface and bulk of K_x picene films have different electronic structures and evolution processes from each other, due to the differences in the stoichiometry, the structure, and/or the electron correlation strength. For a K deposition of 80 s, the bulk is metallic and the surface may be an insulator as reported for K_3C_{60}.[38]

For the multilayer K_x picene film on a Ag(111) surface, on the contrary, no evident difference between the surface and bulk electronic structures near E_F was observed and both show no clear Fermi edges.[20] The presence of the Fermi edge in the present study is different from no clear Fermi edges observed in multilayer K_x picene films on Au, SiO_2, and Ag(111) substrates.[19–21] A monolayer film on a Ag(111) surface is the only exception which shows a clear Fermi edge on K deposition besides our picene-HOPG system.[20] One feasible origin for the above discrepancies among the K_x picene films on different substrates is the possible existence of some differences in the precise molecular orientations in the films grown on different substrates. For pentacene films, it was found that the molecular orientations in the unit cell vary among different substrates while the unit cell dimensions are identical for the pentacene polymorphs with the same layer periodicity of 15.4 Å.[40] Furthermore, the conductivity of pentacene films on a SiO_2 and an H-terminated Si surfaces exhibits different behaviors on K deposition; the former shows temperature dependence of an insulator and the latter a metallic one.[24] (The AFM observation revealed that the latter film has larger pentacene islands than the former.) Although there has not been a comparative study of the precise molecular orientations in picene films on different substrates so far, the above findings suggest that the appearance of the clear Fermi edge for a K_x picene film strongly depends on the molecular orientations in the films grown on different substrates (this is not the case for a C_{60} film because of the remarkably high symmetry of the molecular structure). Such different molecular orientations may result in different equilibrium positions of K atoms in the films and cause the different lattice constants as reported for the newly synthesized sample of K_x picene bulk.[3] Further studies using the metallic film obtained in this study can give insight into the metallic and hopefully superconducting properties of doped picene.

IV. CONCLUSIONS

We have performed high-resolution PES measurements of K-doped picene films on HOPG, which reveal the appearance of states near E_F with a clear Fermi edge. The intensity at E_F grows until a K deposition of 80 s and then decreases and disappears completely after a K deposition of 600 s, indicating that a transition from a metallic state to an insulating state occurs. The valence band spectrum for a pristine film reveals that the long axis of most of the picene molecules in the film is parallel to the HOPG surface. At the initial stage of a K deposition, the valence band spectra show relatively large shifts, which implies that the interaction of picene bands with HOPG valence states is very weak. The shift behaviors of the spectra for the longer K-deposition time are quite similar to those observed for C_{60} films indicating that the K_x picene film on HOPG has multiple phases, depending on the K concentration. The comparison of the spectra measured with He I and Xe I resonance lines reveals that the surface and bulk of K_x picene films have different electronic structures and evolution processes from each other. The discrepancy with the multilayer K_x picene films on Au, SiO_2, and Ag(111) substrates, which show no clear Fermi edges,[19–21] suggests that the emergence of the metallic states for K_x picene films depends on the specific molecular orientations in the film grown on different substrates. These findings will serve as a guideline for the future study on the superconducting properties of the metal-intercalated aromatic hydrocarbons.

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