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Indium on a copper phthalocyanine thin film: Not a reactive system

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The chemical and electronic structure of indium-on-copper phthalocyanine (CuPc) contacts is addressed. Both core levels and valence-band evolutions were inspected during the incremental formation of the indium-CuPc interface. In contrast to the previous study [V. Y. Aristov *et al.*, Phys. Rev. B **72**, 165318 (2005)], our results suggest that the In-CuPc system is not a reactive one. This is corroborated by the absence of reactive components in the C 1*s* and N 1*s* regions. A component shifted toward high binding energy in the In 4*d* spectrum and gap states—the latter emerging between the highest-occupied molecular orbital and the Fermi level, which were regarded as an evidence of a reaction between In and CuPc—are consistently interpreted in terms of the final-state effect of finite indium nanoclusters exposed at the CuPc surface.

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I. INTRODUCTION

Metal-organic interfaces are becoming integral parts of nowadays electronic devices. This applies both for the conventional electronics in virtue of ongoing applications of polymers in the role of low-dielectric-constant alternatives to inorganic insulating films and for organic electronics. The latter roots in applications of electronically active organic films, yet these have to be provided by metallic contacts. Among other techniques, photoemission spectroscopy offers unique possibilities to investigate both chemical and electronic structures at the onset of the contact formation: An analysis of core levels of concerned elements permits to discriminate reacted ones via their chemically shifted components and an inspection of the valence band reveals relative positions of electronic energy levels at interfaces, namely, barriers for charge carriers. Since the overall properties of thin films may be dramatically affected by their contacts, numerous studies have addressed properties of corresponding interfaces.[1–22] Basically, there are two types of contacts employed in organic electronic devices: the bottom contact and the top one, i.e., the organic-on-metal and the metal-on-organic contacts, respectively. The bottom contact has been prevailingly investigated compared to the top contact since well-defined metallic surfaces are convenient substrates for organic film growth studies. Importantly, the bottom and top contacts represent technologically distinct problems; while the morphology of a metallic substrate is usually negligibly affected by the organic film growth and a planar contact is established, the metal growth on organic films may occur in distinct fashions depending on the nature of both the metal and the organic film: The metal may react with the film[1,2,4–6,8,13,15–18,21,22] or remain chemically inert,[1,11,19,20] diffuse into its interior,[1–4,7,9,14–16,21] or form clusters[8,10,12,23] on the organic film surface.

Diffusion of metal atoms into an organic film would result in gradual and ill-defined interfaces, which impair breakdown voltage, deteriorate long-term stability of devices, and may induce quenching of the photoluminescence.[3,8,24] Chemical reactions between metal atoms and organic film determine the interfacial band alignment and may heavily affect the structure of involved molecules. In principle, the reaction of a particular metal with an organic film may be estimated according to the reactivity between the metal atom and the basic building block of the organic film. However, the behavior of particular metal atoms on polymer and oligomer surfaces may differ due to their distinct structures; polymers are amorphous and exhibit a relatively high void volume, while oligomer films are usually polycrystalline and more densely packed. Concerning the former systems, the reader is referred to Ref. 25, and references therein.

Understanding the fundamental processes occurring at interfaces is of great importance for the controlled formation of contacts. Some contradicting conclusions illustrate the complexity of the problem: For example, Hirose *et al.*[1] reported that inert metals form abrupt interfaces while the reactive ones diffuse into the organic film. In contrast, Probst *et al.*[2] observed that weakly interacting metals diffuse into the interior of the organic film while the reactive ones remain on the surface forming stable reacted interface. The entanglement may be caused due to both the specificity of each metal-organic system and also the interpretation of observations. The principal consideration of this study is the photoemission examination of a top metal contact on an oligomer—represented by indium evaporated onto a copper phthalocyanine (CuPc) thin film—at early stages of its formation. We show that clustering of indium on the CuPc surface is an important factor, which, if neglected, may considerably affect an interpretation of photoemission spectra.

II. EXPERIMENTAL

The entire sample preparation and its characterization by photoelectron spectroscopy were performed *in situ* at room temperature at the Russian-German Beamline at BESSY (Ref. 26) using the MUSTANG experimental end station equipped with a PHOIBOS 150 electron-energy analyzer (SPECS GmbH).

Indium was stepwise deposited on freshly prepared about 5-nm-thick CuPc films (supported by silicon substrates) at a

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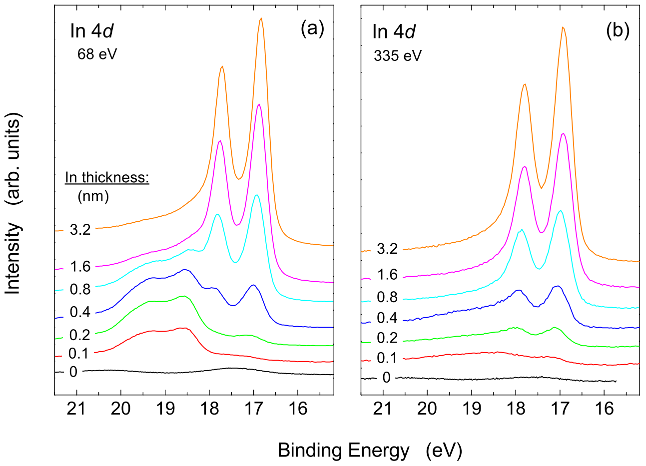

FIG. 1. (Color online) Evolution of the In $4d$ core level photoemission spectrum recorded at photon energy of (a) 68 eV and (b) 335 eV upon incrementally increased indium deposited on a CuPc layer. The nominal indium thicknesses are indicated next to the spectra.

rate of 0.02 nm/min. All thicknesses given in the study are nominal thicknesses provided by a quartz microbalance. During the indium growth the pressure was better than 3×10^{-9} mbar. The preparation and photoemission characterization of CuPc films were described elsewhere.[27] The core levels and the valence band were probed after each deposition step and the molecular orientation was measured by means of near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. The typical instrumental resolution—as measured via the Fermi edge width (in the intensity range from 15% to 85%) of a platinum foil at room temperature—was 150 meV. Work-function measurements were accomplished using the secondary electron emission cutoff measured in normal emission with the sample biased at -10 V. After the preparation and complete photoemission characterization, the samples were probed *ex situ* by scanning electron microscope (SEM, model LEO 1560).

III. RESULTS

A. Photoemission characterization

1. Core levels

Figure 1(a) presents the evolution of the In $4d$ core-level photoemission spectra upon indium incremental deposition onto the CuPc film recorded with photon energy of 68 eV. The nominal indium thickness was doubled in each deposition step. The spectra were normalized to the intensity of the incidence photon beam. A broad doublet located at about 18.5 eV appears at the lowest indium thickness and remains most pronounced one for the next two doubled nominal coverages. A further doublet emerging at about 17 eV is negligible at low indium coverages, however, it dominates the spectrum beyond the nominal indium thickness of 0.8 nm. Its binding energy (BE) converges to 16.8 eV with increasing thickness, the binding energy of metallic indium.[28,29] The doublet will be referred to as the *metallic* component in this study.

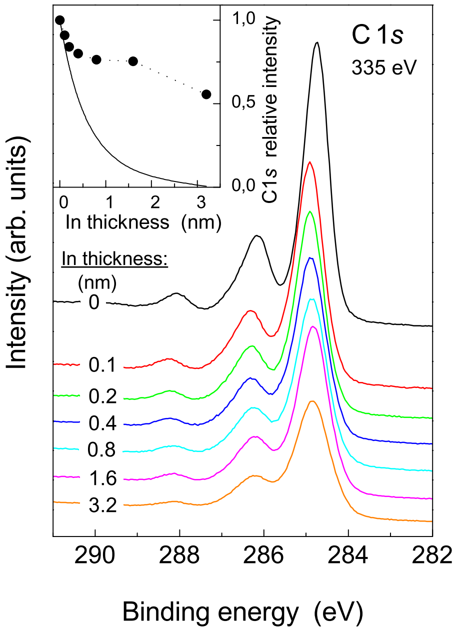

FIG. 2. (Color online) Evolution of the C $1s$ core-level photoemission spectrum of the CuPc layer upon incremental indium deposition taken at photon energy of 335 eV. The nominal indium thicknesses are indicated next to the spectra. The inset shows the evolution of the integral intensity of the C $1s$ core level upon indium deposition normalized to the C $1s$ of the pristine CuPc film (filled circles) and calculated attenuation supposing laminar indium growth and electron mean free path of 6 Å (solid line).

No oxygen was detected during the preparation of the In/CuPc structure with the O $1s$ probed using a photon energy of 585 eV, in order to ensure equal surface sensitivity. Needless to say that the same applies for the choice of the photon energies employed for probing both the C $1s$ and N $1s$ core levels as well as the valence band introduced below. Owing to the absence of oxygen, the presence of the (former) high-BE shifted doublet would suggest a reaction of indium with CuPc indicated by the chemical shift of about 1.5 eV. In fact, such model was recently proposed.[16] The model would also be corroborated by the vanishing of the reactive component with increasing indium coverage suggesting that the reacted indium is buried beneath the metallic indium. However, the notion of the buried reacted components is invalidated by probing the system using higher photon energy of 335 eV, as seen in Fig. 1(b). The higher photon energy results in higher electron kinetic energy and therewith in higher probing depth. For indium thicknesses up to 0.8 nm, it is obvious that the relative intensity of the “reactive” component with respect to the metallic one is markedly lower at a photon energy of 335 eV [Fig. 1(b)] compared to the ratio revealed in the surface-sensitive spectra taken at 68 eV [Fig. 1(a)]. This suggests that the reactive component is rather associated with the surface of the probed system, not with the buried reacted indium at the indium/CuPc interface. An alternative model explaining the described behavior will be provided in Sec. IV.

Figures 2 and 3 present evolutions of the C $1s$ and N $1s$ core levels of the CuPc ($C_{32}CuH_{18}N_8$) film upon the indium

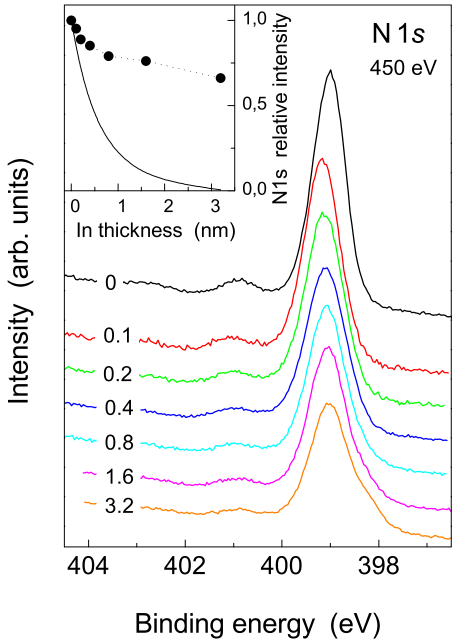

FIG. 3. (Color online) As in Fig. 2, for the N 1s core level recorded at photon energy of 450 eV.

deposition. The spectra of pristine CuPc films resemble those reported previously.[16,30,31] Upon the first indium deposition, the C 1s and the N 1s core level shift by 0.18 eV toward higher BE, while the further indium evaporation produces a tiny gradual shift back toward lower BE. The behavior can be qualitatively rationalized being induced by a varying work function[32] (Fig. 4). Except the N 1s spectrum for the highest indium coverage, the line shapes of both core levels reveal virtually no changes suggesting the absence of any reaction with indium. Both core levels exhibit a gradually increased full width at half maximum (FWHM) with the increased indium thickness. In the insets, the circles represent the dependence of integral intensities of the corresponding core levels on the nominal indium thicknesses. The solid lines show the calculated attenuation of core-level intensities supposing laminar growth of the indium overlayer and employing a photoelectron mean free path of 6 Å. It is obvious that the intensity attenuation of both core levels being weaker than the calculated one excludes laminar growth of indium and rather suggests that the island growth prevails.

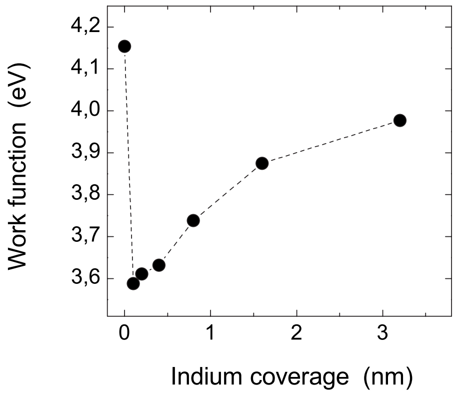

FIG. 4. The work-function evolution of the CuPc film upon nominal indium coverage.

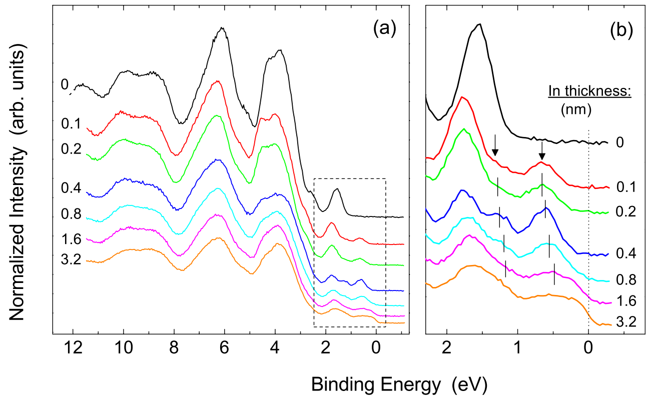

FIG. 5. (Color online) (a) Evolution of the valence-band photoemission spectrum of the CuPc layer recorded at a photon energy of 55 eV upon stepwise increased indium coverage. The nominal indium thicknesses are given next to the spectra. (b) Blow up of the region near the Fermi level marked by a rectangular in the left panel. The arrows indicate new orbitals.

The C 1s spectrum (Fig. 2) consists of three peaks associated (going toward higher BEs) with benzene and pyrrole rings, and the shake-up of pyrrole rings, respectively, while the shake-up of the benzene rings is obscured by the pyrrole-associated feature located at about 286 eV.[31,33] The shake-ups reflect inelastic energy-loss processes caused by π-π^* intramolecular transitions. As the shake-ups should vanish if a reaction between a metal and a molecular film occurs,[17,18,22,30,31,34] in the present case, the persistence of shake-up features upon indium deposition suggests preserved pristine molecular structure in accordance with other studies of nonreactive systems such as Au/CuPc (Ref. 14) and Ag/CuPc (Ref. 20).

The N 1s spectrum consists of two peaks, namely, the N 1s core level and the shake-up shifted by about 2 eV toward higher BE. Similarly to the C 1s, the N 1s shake-up is also retained upon indium deposition. The overall shape of the N 1s spectrum is conserved as well except the two highest coverages; a hump on the low-binding energy side suggests an additional component.

2. Valence band

Figure 5(a) shows the valence-band (VB) spectra of the CuPc film upon indium deposition. The pristine CuPc (the top spectrum) resembles the previously reported spectra.[16,27,30,31] Already the first indium deposition yields new orbitals below the Fermi level. This is seen in greater detail in Fig. 5(b), where the region below the Fermi level is blown up. The new orbitals are located at about 0.6 and 1.3 eV in accordance with a recent finding.[16] Such emissions are commonly referred to as "gap states," as they are located between the Fermi level and the highest-occupied molecular orbital (HOMO), i.e., in the gap of the organic semiconductor. With increasing indium coverage, the intensity of the gap states increases and their centroid shifts toward the Fermi level. For the highest coverages (1.6 and 3.2 nm), the emissions tend to merge and the Fermi edge becomes obvious. The presence of the Fermi edge indicates the presence of metallic indium.

The average orientation of CuPc molecules of the pristine film, as determined by means of NEXAFS, was about 85° with respect to the substrate surface, so the molecules were oriented nearly upright. We note that the molecular orientation is distinct to that of CuPc films employed by Aristov *et al.*[16] in the role of substrates for their indium growth studies, where near-lying down molecules were claimed. In our recent communication,[27] the valence band of the CuPc was analyzed in detail and we determined the energy levels of particular molecular orbitals and character of the molecular orbitals in terms of their association with constituent atoms of CuPc. We also showed that the line shape of the VB—particularly, the band located at about 4 eV—reflects the molecular orientation; note that apart from the new orbitals in the band gap, the line shape of the remaining portion of the valence band (Fig. 5) shows virtually no changes. In other words, none of molecular orbitals was affected by the indium deposition. Thus, the retained VB line shape upon indium deposition—except the emerging gap states, which will be rationalized in the discussion chapter—would imply that both the electronic and the geometric structure of the CuPc are preserved upon indium deposition.

3. Work function

Figure 4 shows the dependence of the work function of the In/CuPc system on indium coverage. The work function of the pristine CuPc dropped abruptly upon the first indium deposition and it gradually increases with the indium coverage up to about 4 eV, a value near to the indium work function being 4.12 eV.[35]

B. Scanning electron microscopy

Figures 6(a) and 6(b) show the SEM maps of CuPc films with nominally 0.5- and 3.2-nm-thick indium films deposited on top. It is obvious that the film is not continuous even for the highest coverage investigated in the study; the surface is rather populated by nanoclusters with lateral dimensions up to about 10–20 nm. The sample with the lower coverage reveals only traces of few possible clusters. This can either be due to the cluster size below the detection limit of the technique and/or due to the low contrast between the presumably charged clusters and the supporting CuPc film. Both the in diffusion and the continuous film formation can be excluded as photoemission characterization suggests that indium accumulates at the surface (Fig. 1) and shows only marginal attenuation of C 1*s* and N 1*s* core levels (Figs. 2 and 3). Even though only two samples with distinct indium nominal thicknesses were probed by SEM, it is reasonable to presume that the cluster size increases with indium coverage.

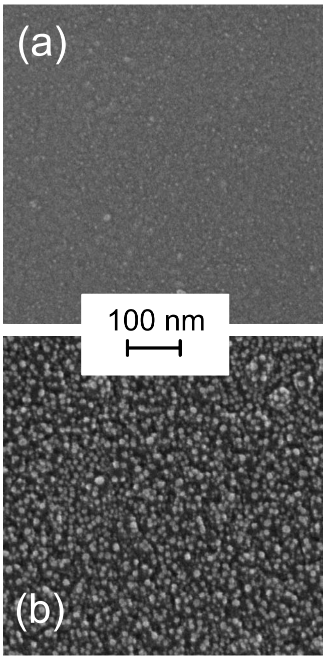

FIG. 6. Nominally about (a) 0.5-nm-thick and (b) 3.2-nm-thick indium films on the CuPc film probed by SEM.

IV. DISCUSSION

A. Core levels

The appearance and the evolution of the In 4*d* spectra with indium coverage [Fig. 1(a)] are in substantial agreement with the data reported in Ref. 16, yet, our interpretation differs as shown below. The measurements at different photon energies suggest that the reactive component is associated with the surface of the In/CuPc system, not with a buried interface. If a reaction between indium and CuPc exists, basically two models may apply: (a) the reaction is confined to early stages of indium deposition and it leads to a reacted interface buried beneath the unreacted metallic indium overlayer; (b) after a reacted layer is formed, the following nonreactive indium atoms diffuse through the surface reacted layer. The in-diffused indium atoms should, however, react with the CuPc, too, therewith increasing the reacted layer thickness, albeit from the side of the CuPc. The latter scenario would explain the location of the reacted component at the surface. It does not, however, explain neither the vanishing of the reacted component with indium thickness nor the presence of the unreacted metallic component. Thus, the dependence of the In 4*d* on the photon energies [Figs. 1(a) and 1(b)] contradicts both models.

In order to identify particular components in the In 4*d* spectra, their deconvolutions were attempted. The metallic component was fitted using a doublet with the branching ratio of 1.5, a high-BE asymmetry of 0.11, and a spin-orbit splitting of 0.85 eV and 0.88 eV for low and high coverages, respectively. The spin-orbit splitting of 0.88 eV is in agreement with that reported for metallic indium[28,29] while the lower value for the lower coverages may reflect the spin-orbit splitting dependence on cluster size[36,37] (see below). The FWHM decreased to about 0.4 eV when going to higher indium coverages. Concerning the reactive component, the fitting suggests that it should consist of at least four doublets for thinnest indium films, while at least three doublets are required for the thickest indium film. Their FWHMs employed in the fitting ranged from 0.7 to 0.9 eV. Figures 7(a)

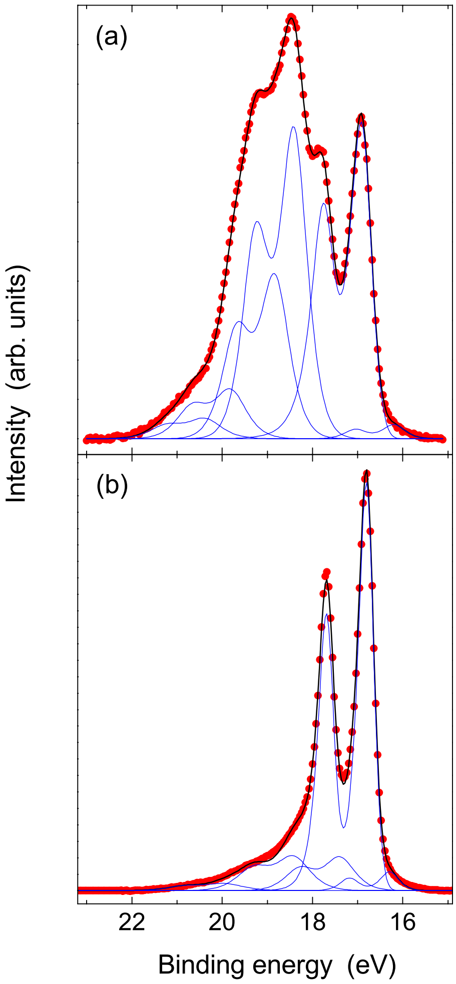

FIG. 7. (Color online) Deconvolution of the In 4*d* core-level spectra (dots) exemplified for indium coverages of (a) 0.4 nm and (b) 3.2 nm. Particular components being a product of the fitting procedure (see the text) are indicated by blue thin solid lines, summation of all components are drawn by the black thick solid lines.

and 7(b) illustrate the result for the 0.4 nm and 3.2 nm indium coverages, respectively. Importantly, the fitting of the former spectrum reveals components shifted from ~1.5 to ~3.5 eV with respect to the metallic component. The reactive component at higher indium coverages appears as a featureless high-BE tail of the In 4*d* spectra suggesting—if indium reacts with the CuPc—many reaction pathways. Admittedly, the reactive component cannot be fitted certainly for chemical shifts of potential reaction pathways related to the involved elements appear out of the reported range; in particular, indium strongly chemisorbs oxygen and accordingly the largest chemical shift is expected for a component corresponding to oxidized indium being about 1 eV.[38,39] Yet, no oxygen was detected in the O 1*s* region. Even though the shifts and relative intensities of the particular features forming the reactive component may not be reliably determined here, their markedly higher shifts compared to tabulated values infirm their chemical origin. We mention in passing that Hirose *et al.*[1] also observed components of Al 2*p* and In 4*d* with their shift significantly larger than chemical shifts of corresponding oxides; they associated the shifts with oxidized Al and In, although the O 1*s* region was not probed in their study.

In this context, we also discuss the low-BE component in the N 1*s* spectrum observed for the two highest indium coverages. Virtually the same evolution of the N 1*s* spectrum with the indium deposition was reported in Ref. 16, although spectra at the lowest coverages were not shown. The presence of the component was suggested to manifest the reaction between indium and the CuPc, so being complementary to the presence of the reactive component in the In 4*d* spectrum. Yet, we consider such arguments contradictory, for there is a lack of correlation between the appearance of the reactive component in the In 4*d* and that in the N 1*s* spectra; the former dominates at the lowest indium coverages while the later becomes obvious for the highest indium coverages only. Thus, the appearance of the low-binding energy component in the N 1*s* spectrum is not related with the onset of the In-CuPc interface formation. We admit that its origin is unclear at this point. We also note that the overall shift of the N 1*s* peak upon the indium deposition reported in Ref. 16 may manifest rather varying surface electronic properties instead of the chemical shift; the former would occur due to indium-induced changes of the work function.[32] Yet, the work function had not been probed in Ref. 16.

The appearance of shifted components in core-level spectra is commonly taken to imply the chemical reaction (hence the term chemical shift) but this is not necessarily the case. Previous photoemission studies of metal nanoclusters[36,37,40–43] showed that photoemission spectra of a particular metallic element are affected by the size of clusters; the smaller the cluster size, the higher was the BE shift of core levels observed. Likewise, the density of states below the Fermi level of small metal clusters was shifted with its line shape distorted and with the Fermi edge absent. If small metal clusters are probed by photoemission, the screening of the photohole may be insufficient due to the limited size of the cluster and that becomes positively charged with its photoemission spectra shifted toward higher binding energy. With increased cluster size, the photoemission spectra converge toward "metallic" ones including the forming of the Fermi edge. The nature of an element and its interaction with the supporting substrate play a major role;[40,41] the shifts are higher for metal clusters on weakly interacting substrates. Notably, photoemission spectra of such clusters need not to shift rigidly, i.e., the particular shifts of core levels and the valence band may differ.[42] As an illustration, a critical cluster size necessary to observe the metallic behavior for gold on a carbon substrate was found to be about 150 atoms.[37]

Given the data communicated above, we believe—in contrast to the aforementioned study[16]—that the reactive component in the In 4*d* spectrum does not indicate the chemical reaction between indium and CuPc (no reaction was unveiled neither in the corresponding carbon and nitrogen core levels nor in the valence band except the gap states) but it is rather due to the positively charged nonmetallic indium nanoclusters. We remind that the presence of nanoclusters on the CuPc surface was proven by means of SEM even for the sample with the highest nominal indium thickness [Fig. 6(b)]. We note that our recent study on the identical system by Raman spectroscopy also suggested a nonreactive behavior of indium on CuPc.[44] The evolution of the In 4*d* spectrum may thus be rationalized by means of the varying size distribution of indium nanoclusters; "nonmetallic" nanoclusters prevail at low indium coverages, whereas the increasing indium deposition leads to the increase in the cluster size—and therewith the gradually vanishing effect of the final state—up to the indium thicknesses, where nanoclusters with their size sufficient to exhibit metallic behavior dominate the surface. Given the photoemission detection limit about 1%, it is conceivable that a fractional in diffusion cannot be excluded; still, our data justify to infer that the determining effect is the clustering and not the in diffusion.

As already mentioned above, both the core levels and the VB spectra display a small amount of broadening upon indium deposition. We suppose that the effect is induced by the locally scattered work function varying due to the presence of indium clusters; since the varying work function results in a corresponding rigid shift of photoemission spectra,[32] the photoemission spectrum of an inhomogeneous—in terms of its work function—surface sums up contributions from areas with varying work functions[45] leading to the broadening of photoemission features.

B. Valence band

If the emissions between the HOMO and the Fermi level were due to gap states, the high concentration of the gap states—their intensity is comparable to the HOMO intensity—would indicate a massive reaction between indium and CuPc. This should result in the charge redistribution over the molecules and affect the Fermi-level position in the gap of the organic semiconductor. In contrast, none of such effects is detected, as suggested by the retained line shape of the valence band (which suggests the retained molecular orientation as well[27]) and fixed position of the Fermi level with respect to the HOMO. The supposed gap states emerging below the Fermi level can be rationalized by the formation of inert metal clusters as well; the gap states come from 5*p*-derived states (otherwise determining the Fermi edge) of the isolated indium clusters. With increasing nominal indium thickness, the final-state effect vanishes correspondingly and the features merge and move toward the Fermi level eventually forming the Fermi edge.

Thereby, we advocate the view that the emissions between the Fermi level and the HOMO do not indicate any reaction between indium atoms and CuPc; they are not a product of defect states in the organic semiconductor structure. Instead, the "gap states" emission originates from nonmetallic indium nanoclusters inert to the CuPc and residing at the CuPc surface with their photoemission signal simply superposed to the photoemission spectrum of the CuPc beneath. We emphasize that we do not disclaim the formation of gap states in general. For example, alkali metals or metals with high affinity to oxygen deposited on oxygen containing organic films may produce a high concentration of gap states. However, the emerging gap states are paralleled by a distortion of the molecular electronic structure, which is reflected by the significantly altered line shape of the valence band.[2,4,6,17,18,34,46]

C. Work function

The evolution of the work function (Fig. 4) can be also qualitatively rationalized by the final effect of indium nanoclusters. We have shown above that the core levels of the nonmetallic nanoclusters shift toward higher BE. The shift, however, applies for the entire photoemission spectrum of the nanoclusters and thus their secondary electron emission cutoff, which is only another part of the photoemission spectrum, shifts in the same fashion. The shift of the cutoff toward higher and lower binding energy is interpreted as the work function decrease and increase, respectively. As only indium nanoclusters are charged, a question arises which part of the surface—either indium or the CuPc—determines the work function of the In/CuPc system. Koller *et al.*[45] showed in their study that a surface, which is electronically inhomogeneous on the nanoscopic scale, i.e., consisting of areas with distinct work functions, shows the work function being an area average of the local work function. It follows that the initial abrupt drop of the work function is due to the high-BE shift of the photoemission spectra induced by the formation of nonmetallic nanoclusters upon the first indium deposition. With the increased indium deposition, the nonmetallic nanoclusters are gradually eliminated in favor of metallic ones (note the decreasing signal ratio of the nonmetallic to the metallic component with the indium coverage in the In 4*d* spectrum) and this results in the gradual increase in the work function toward the tabulated value of indium.

D. Supplemental remarks

The question arises whether the molecular orientation in the CuPc film may affect its reactivity with indium. We remind the reader that the molecular orientation was near upright in this study, while rather lying molecules were claimed in Ref. 16; the lying molecules forming the film's surface may expose their π bonds and thus facilitate the reaction with indium. In view of the closed similarities in both experimental photoemission data and our previous discussion, we assume that indium does not react with CuPc irrespective the molecular orientation.

Even though each metal-organic system should be evaluated individually, extreme trends may be characterized as follows: (a) metals reactive to organic film wet the surface of the molecular film instead of diffusing into it, since presumably a stable reacted interface is formed;[17] in contrast, (b) clustering may dominate over the in diffusion for metals weakly interacting with the organic film.[10,12,23] The clustering of the metal on the organic film surface may be understood in terms of relation of the substrate's and the adsorbent's surface free energies. Since metals show the high free surface energy compared to organic films, the evaporated metals do not wet the organic surface, they form clusters instead.[12] Obviously, this occurs provided that no chemical reaction takes place between the metal and the organic substrate. The surface free energy of metals can be decreased via their oxidation; such ultrathin semimetallic films wet the surfaces of organic layers and may be inserted between the standard metallization and the organic film.[47] Noteworthy, the growth of a metal with high affinity to oxygen such as aluminum under high vacuum conditions—as opposed to the evaporation under ultrahigh vacuum—is sufficient to avoid clustering and to ensure the formation of a wetting film.[3,12]

Here, a remark on the diffusion of metals into organic film as evidenced from photoemission would be relevant. A departure from the laminar growth adversely affects the overlayer thickness evaluation. The metal clustering—if occurring—produces an inferior signal of the evaporated metal incommensurate to its amount on the surface, since the photoemission is rather an area averaging technique. It may therefore be difficult to differentiate effects of clustering and in diffusion. Other arguments supporting the latter have been based on the increased relative intensity of metal-related features in the VB spectra, i.e., the presumed gap states, with respect to the organic film features like the HOMO upon increased photon energy. Since the higher photon energy results in the extension of the probing depth, the relative increase in metal-related features obtained at higher photon energy is believed to reflect metal species diffused into the organic film, so to speak making their concentration in the bulk of the organic film higher than on the surface (e.g., Ref. 14). However, such analysis ignores different photon energy dependence of photoionization cross sections of particular elements; usually, the cross section of C 2*p*, which is often associated with the HOMO, drops faster with the photon energy than the cross section of energy levels of metal elements.[48] Such relations can be nicely illustrated, e.g., by probing the valence band of metal-containing molecules with different photon energies.[27] In fact, the effect of varying cross section may strongly dominate the effect of the increased probing depth. It follows that conclusions on the metal diffusion into organic film drawn from photoemission characterization may not be conclusive without considering photoionization cross-section evolutions and may lead to spurious effects.

V. SUMMARY

We have presented a photoemission study on the initial stages of formation of the indium-on-CuPc contacts. Core levels of indium, carbon, and nitrogen, and valence band were monitored during the formation of the interfaces. Even though the In 4*d* and the valence band revealed a high-BE shifted component and emerging gap states upon indium deposition, respectively, the C 1*s* and N 1*s* core level and all molecular orbitals in the valence band suggest no reaction. The apparent inconsistency was explained by the formation of isolated indium nanoclusters on the CuPc surface evidenced by SEM; an insufficient screening of a photohole during the photoemission process due to the small size of nanoclusters produces the high-binding-energy shift of their photoemission spectra. The effect is tantamount to the chemical shift induced by chemical bonding. Particularly, if the cluster distribution contains both nonmetallic and metallic clusters, their manifestation in the core-level photoemission spectrum may be indistinguishable from a reacted interface.

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