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Self-doping and partial oxidation of metal-on-organic interfaces for organic semiconductor devices studied by chemical analysis techniques

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The performance of organic electronic devices, such as organic light emitting diodes, transistors, or organic solar cells, depends critically on the chemical composition of the metal/organic and organic/metal interfaces which inject or extract charges into or from the device. By combining a number of techniques, such as x-ray photoemission spectroscopy (XPS) sputter depth profiling, XPS itself, secondary ion mass spectrometry, and laser desorption/ionization time-of-flight mass spectrometry, we investigate the reasons for differences in charge injection from metallic bottom and top contacts into either preferentially hole or preferentially electron transporting materials. We find that the deposition of metal onto organic semiconductors creates an organic-inorganic mixed interlayer in between the organic bulk material and the metal. In the case of electron injection, this interlayer acts as highly doped injection layer, while for hole injection, no significant improvement is visible. In addition to the self-doping, some cathode materials form partially oxidized metal-on-organic interfaces caused by oxygen in the residual gas. Depending on the evaporation conditions, the oxygen content varies. The effect of the oxygen incorporation, the origin, and the binding behavior in between the metal-on-organic interlayer is investigated and discussed. In contrast, organic materials evaporated on top of metals create an abrupt interface, where no self-doping effect is observed. © 2008 American Institute of Physics. [DOI: 10.1063/1.3018716]

I. INTRODUCTION

Devices based on organic semiconductors have recently gained considerable interest due to advantageous properties such as large area, low cost, and flexibility. Organic light emitting diodes (OLEDs) are currently intensively investigated due to their application possibilities in displays and lighting. A key point in many OLED applications is flexibility in terms of emission direction and electrode configuration. For instance, the adaptation to *n*-channel amorphous silicon thin film transistors as driver electronics for active matrix displays requires the inversion of conventional OLED stacks such that electrons may be injected from the bottom contact into a *n*-type organic semiconductor. Since silicon backplanes are usually opaque, the OLEDs need to be top emitting, i.e., one needs inverted top emitting OLEDs to be developed.¹ Efficiencies of inverted top emitting OLEDs and electron injection from the bottom can be improved by using highly reflective metals or alloys with low work function as cathodes.^{2–4} The performance of OLEDs may be further enhanced by using an efficient charge injection layer or even a

highly doped charge transporting layer, which may, e.g., consist of an electron transporting host material coevaporated with an electron donating material as a dopant.⁵

Nevertheless, inverted OLEDs show a significant drop of efficiency as compared to conventional OLEDs. This phenomenon is widely known but the reasons are still not sufficiently explained.^{3,4} Even the use of additional injection layers (e.g., 1 nm of LiF) does not overcome the asymmetric injection behavior of electrons from the top and bottom electrodes in an organic device.⁶ One of the key topics for enhancing the performance of inverted top emitting OLEDs is the improvement of charge injection from transparent indium tin oxide (ITO)^{1,4,7} or other top contact anodes (e.g., semitransparent metal^{8,9}) without destroying the underlying organic layer during electrode deposition. It is known that low work function cathode materials such as Ca, Mg, or the alkaline metals improve electron injection into electron transporting layers (ETLs). This is due to the good match of their work functions with the lowest unoccupied molecular orbital level of the ETL.^{10,11} On the other hand, the low ionization potential causes a high reactivity of these metals, leading to oxidation processes even during the vacuum evaporation process. The origin and the role of such an oxidic interlayer are still under discussion. Some groups detected oxygen on top of the processed metal-on-organic interfaces, mainly with x-ray photoemission spectroscopy (XPS)^{12,13} or photoluminescence measurements, e.g., by detecting photoactivated Ag₂O.¹⁴ Oxygen containing organic compounds were found

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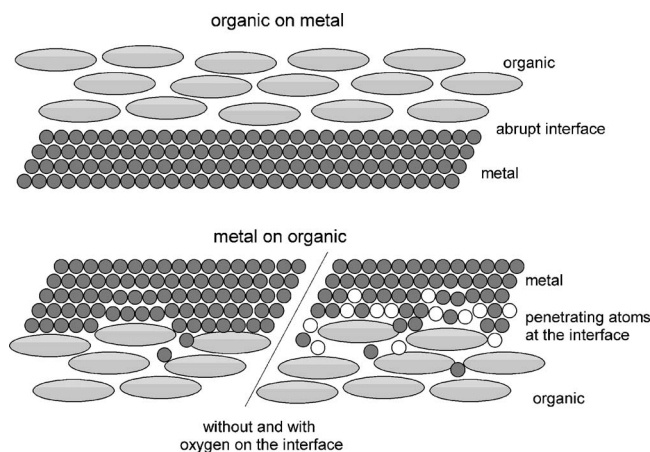


FIG. 1. Schematic view of organic-on-metal and metal-on-organic interfaces. Note that the organic-on-metal interface remains abrupt, while the metal-on-organic interface creates a doped interlayer with (hollow symbols) or without possible oxygen incorporation.

as oxygen sources at organic/metal interfaces.^{15–17} Additional work was done to show the influence of different metals on organic materials by investigating interface dipoles and Fermi level alignment by ultraviolet photoemission spectroscopy (UPS) measurements and the chemical shift of XPS core level signals as a function of the reactivity and the coverage of different metals.^{13,18,19} Nevertheless, these results confirm the theory of improved electron injection into organic material even with highly reactive metals.^{13,15,20} For example, several groups showed improved charge injection into organic devices by using a thin (1 nm) Al_2O_3 interlayer between ETL and cathode.^{21,22} In the light of possible reactions by evaporating “hot” metals onto organic material, the resulting metal-on-organic interfaces need to be investigated. Beyond OLED development, this is of general interest also for organic field effect transistors,^{23,24} organic memory devices,²⁵ and organic solar cells (OSCs).^{26,27} Such a penetration of hot atoms into an underlying organic layer and the formation of additional gap states in the organic material were already briefly discussed by Rand *et al.* for OSCs.²⁷ A similar formation of gap states is observed by the diffusion of deposited Li down to 80 nm into an underlying organic material.²⁸ This behavior may occur similarly during the deposition of a layer sequence organic/LiF/Al, where the evaporation of the metal will cause a chemical reaction (of) in the underlying LiF, resulting in a diffusion of Li into the organic.^{6,29}

In this paper, we focus on metal/organic and organic/metal interfaces at different single carrier devices, i.e., organic devices carrying exclusively either holes or electrons. We prove that metal atoms penetrate the organic layers during evaporation and act as electron donating dopants (Fig. 1). We use laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF-MS) (Ref. 30) as a mass selective method, depth profiling XPS, and depth profiling secondary ion mass spectrometry (SIMS), as well as XPS and UPS as surface-sensitive analysis tools. We find different compounds consisting of acceptor-donor complexes, which are created at the metal-on-organic interfaces. These metal-organic complexes may be formed in the presence of penetrating atoms.³¹

If this is the case, atoms “dope” the topmost organic layer of a device. We will show that such complexes are not formed when depositing organic material onto metal surfaces.

II. EXPERIMENTAL DETAILS

A. Sample preparation

Sample structures A–R and T–Z (see Table I) were prepared in an ultrahigh vacuum (UHV) multichamber evaporation tool (BesTec GmbH) without breaking the vacuum during processing, while sample S was made in a UHV single-chamber evaporation tool (Kurt J. Lesker). While samples A–R were produced at a constant base pressure of 10^{-8} mbar, the base pressure for metal evaporation was varied for samples S–Z (see Table I). Commercial ITO and molybdenum tantalum (MoTa) substrates were used, which were cleaned subsequently in acetone and ethanol using an ultrasonic bath, dried under a stream of nitrogen, and afterward treated in ozone plasma. A similar wet cleaning process without the ozone plasma cleaning was performed for the LDI targets (material: Fe). The amorphous silver foil (MaTeck) (used for the UPS samples O and P) was sputter cleaned in UHV prior organic thin film deposition.

The evaporation rate for all organic materials was $0.3 \text{ \AA/s}$, a value commonly used for organic device preparation. The metal evaporation rate (Al, Ag, and Au) was set to $1\text{--}2 \text{ \AA/s}$. The following set of materials — all of them prototypic for state-of-the-art OLEDs^{32–35} — was studied in this work: Cs, 4,7-diphenyl-1,10-phenanthroline (BPhen), 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBi), tris(2-phenylpyridine)iridium [Ir(ppy)₃], tris(1-phenylisoquinoline)iridium(III) [Ir(piq)₃], 4,4'-bis[(1-naphthyl)phenylamino]-1,1'-biphenyl (NPD), tris(8-hydroxyquinolinato)-aluminum (Alq₃), 2,2',7',7'-tetrakis(*N,N*-diphenylamino)-9,9'-Spiro-bifluorene (Spiro-TAD), 4,4',4''-tris(carbazol-9-yl)-triphenylamine (TCTA), iridium(III) bis(2-methyldibenzo-[f,h]quinoxaline)(acetylacetonate) [Ir(MDQ)₂(acac)], *N,N,N',N'*-tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD), and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ). For the chemical structures see Fig. 2.

B. Measurements

Samples A–F, Q, and R, as well as X–Z were measured completely under inert conditions, while all other samples need to be handled in air (less than 5 min) for inserting them into the vacuum chambers of the different analysis tools. The LDI-TOF-MS spectra were collected as described elsewhere.^{30,36} SIMS measurements were performed with Cs⁺ ions in a device equipped with a quadrupole mass-to-charge analyzer (PHI 6800, Physical Electronics) at a typical primary beam current of 80 nA. The sputtered area is 0.49 mm^2 , while the measurement area is 0.09 mm^2 at the center of the sputter crater. XPS depth profiling was done at a PHI 5600 CI instrument, equipped with a hemispherical analyzer with an acceptance diameter of $800 \text{ }\mu\text{m}$, working at pass energy of 29 eV. For excitation, nonmonochromated Mg *K* α x rays (350 W) were used. Depth sputtering was accomplished by using Ar⁺ ions with an energy of 3.5 keV at a scan area of 4 mm^2 . UPS measurements were performed

TABLE I. Layer structures of samples A–Z. Layer thickness in nm. Doping: 8 wt% for Ir(ppy)₃ and 10 wt% for the Ir(MDQ)₂(acac) emitters, 4 mol% for F₄-TCNQ.

Sample	Device	Layer structure
A	<i>pin</i> OLED (noninverted)	Glass/Ag (>80)/MeO-TPD:F ₄ -TCNQ (45)/Spiro-TAD (10)/TCTA:Ir(ppy) ₃ (5)/TPBI:Ir(ppy) ₃ (10)/BPhen (10)/BPhen:Cs (25)/Ag (15)
B	<i>nip</i> OLED (inverted)	Glass/Ag (>80)/BPhen:Cs (40)/BPhen (10)/TPBI:Ir(ppy) ₃ (10)/TCTA:Ir(ppy) ₃ (5)/Spiro-TAD (10)/MeO-TPD:F ₄ -TCNQ (30)/Ag (15)
C (and D)	e only device with Al or Ag	ITO/Al [or Ag] (15)/BPhen:Cs (15)/BPhen(100)/BPhen:Cs (15)/Al [or Ag] (50)
E (and F)	h only device with Ag or Au	ITO/Ag [or Au] (20)/MeO-TPD:F ₄ -TCNQ (10)/MeO-TPD (200)/MeO-TPD:F ₄ -TCNQ(10)/Ag [or Au] (40)
G (and H)	LDI sample	Fe target/Al [or Ag] (15)/BPhen (20)
I (and J)	LDI sample	Fe target/BPhen (20)/Al [or Ag] (15)
K (and M)	LDI sample	Fe target/MeO-TPD [or Spiro-TAD] (20 nm)/Ag (15)
L (and N)	LDI sample	Fe target/Ag (15)/MeO-TPD [or Spiro-TAD] (20)
O	UPS sample	Ag foil/BPhen:Cs (15)/Ag (5)
P	UPS sample	Ag foil/BPhen:Cs (5)
Q	<i>nip</i> OLED w/o Ag interlayer	MoTa/Ag (30)/BPhen:Cs (50)/BPhen (10.8)/NPD:Ir(MDQ) ₂ (acac) (20)/Spiro-TAD (10)/MeO-TPD:F ₄ -TCNQ (35)/Ag (15)
R	<i>nip</i> OLED with Ag interlayer	MoTa/Ag (30)/BPhen:Cs (2)/Ag (1.5)/BPhen:Cs (2)/Ag (1)/BPhen:Cs (46)/BPhen (10.8)/NPD:Ir(MDQ) ₂ (acac) (20)/Spiro-TAD (10)/MeO-TPD:F ₄ -TCNQ (35)/Ag (15)
S	OLED SIMS sample	Glass/ITO/ <i>p</i> -side (Ref. 35) (100)/Spiro-TAD (10)/NPD:Ir(piq) ₃ (20)/BPhen (10)/BPhen:Cs (80)/Al (100) (metal chamber pressure: 10 ⁻⁷ mbar)
T (and U)	XPS sample	Glass/BPhen [or BPhen:Cs] (80)/Al (80) (metal chamber pressure: 10 ⁻⁸ mbar)
V	XPS sample	Glass/BPhen (80)/Al (80) (metal chamber pressure: 10 ⁻⁶ mbar)
W	LDI sample	Fe target/BPhen (20)/Al (15) (metal chamber pressure: 10 ⁻⁶ mbar)
X; Y; Z	Intrinsic Alq ₃	ITO/Alq ₃ (100)/Al (100) (metal chamber pressure: X, 1.8 × 10 ⁻⁷ mbar; Y, 3.3 × 10 ⁻⁶ mbar, Z: 4.6 × 10 ⁻⁶ mbar)

using a hemispherical electron spectrometer Phoibos 100 (Specs) equipped with a He I (21.22 eV) discharge lamp. To collect the secondary electrons, a bias of −8 V was applied and the achieved energy resolution is 150 meV. The vacuum conditions in the metal evaporation chamber were checked with a residual gas analyzer from Pfeiffer Vacuum (QSM PTM25253).

III. RESULTS AND DISCUSSION

A. Self-doping of metal atoms in organic layers

Using the doping concept of organic charge transport layers, the emission zone in OLEDs can be adjusted for an optimal micro-optical light outcoupling for certain wavelengths by simply varying the transport layer thicknesses without changing the electrical behavior of the device.³⁷ Using this option, we show in Fig. 3 the device characteristics of a conventional (sample A) and an inverted (sample B) top emitting OLED. The charge carrier transport layers were optimized in both cases for optimum light extraction.⁸ Compared to noninverted devices, inverted OLEDs show a decreased current density and a decreased luminance at a given voltage. Thus, the main difference must be caused by differ-

ent metal/organic and organic/metal interfaces, either by improved hole injection from the bottom and/or electron injection from the top contact of the device.

To understand this difference, we processed the so-called single carrier devices with metal-*n*-type-intrinsic-*n*-type-metal structures for electron injection (samples C and D) and metal-*p*-type-intrinsic-*p*-type-metal structures for hole injection (samples E and F). The current-voltage (*J*-*V*) characteristics of these devices are displayed in Fig. 4, where the electron only devices C and D clearly show a suppressed electron injection from the bottom contact, as compared to the enhanced electron injection through the top side, resulting in an asymmetric (*J*-*V*) curve. Despite the Cs-doped BPhen layers as electron injection layers, the current density is more than one order of magnitude higher for electron injection from the top contact than from the bottom.³²

A different behavior is observed for hole transport materials, where the holes are well injected both from the bottom and the top contacts, which is also seen in Fig. 4. This is not surprising because it is well known that *p*-doping overcomes the main problem of hole injection from the anode

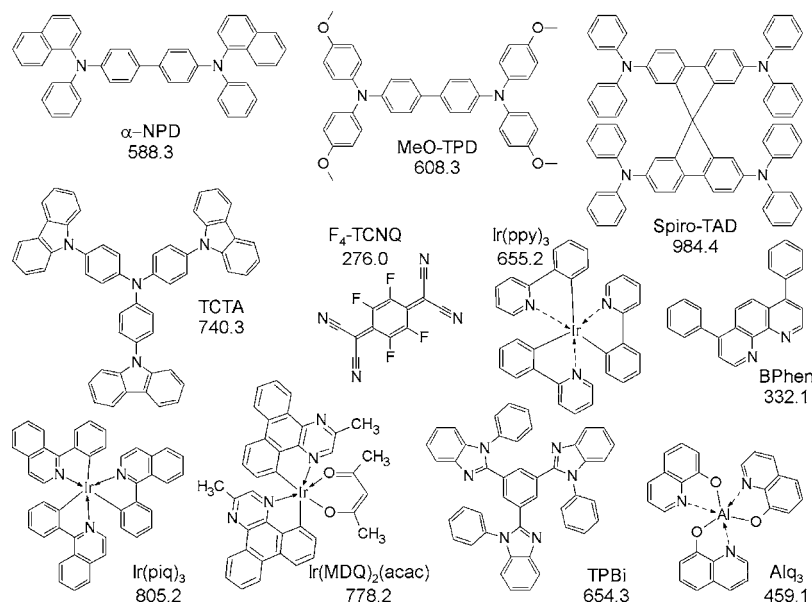


FIG. 2. Chemical structures of the organic materials with their acronyms and monoisotopic masses in g/mol.

material.^{3,8} We exclude internal asymmetries in between the *n*-type-intrinsic and intrinsic-*n*-type interfaces due to the short time delay (less than 5 min) between depositing these layers. The asymmetric behavior, observed on the ETL/metal interfaces in Fig. 4, may be explained as follows: due to metal evaporation, hot atoms penetrate the organic surface²⁴ and may therefore form a mixed interlayer at the topmost tens of angstroms of the organic materials. This means for the interface to the ETL that an additional amount of electron donating material acts as a thin, highly doped injection layer at the organic/metal interface. Wang *et al.*³⁸ demonstrated this behavior of Al as a dopant for ETLs. They also observed that doping of a hole transporting layer (HTL) with electron donating metal atoms causes a hindered injection of holes into the HTL, which demonstrates the hole blocking behavior of Al doping in between HTLs.^{19,38} In contrast, the organic-on-metal interfaces of any organic devices remain abrupt, both for HTLs and ETLs, so a self-doping effect cannot take place.

To prove the theory of self-doping, which is also mentioned in other publications,^{27,39} we used the LDI-TOF-MS method to analyze the different interfaces and to detect such acceptor-donor complexes, especially in the test structures G–J (Table I), which contain the organic semiconductor BPhen, well known as good complexing agent for metals and therefore well suitable for acceptor-donor interactions with penetrated metal atoms.^{40,41} As shown in Figs. 5(c) and 5(d) at the metal-on-organic interfaces, a clear creation of metal-BPhen adducts is observed, caused by the “free” atoms penetrating the organic layer. Al-on-BPhen sample [Fig. 5(c)] shows besides the main signal — protonated BPhen (mass-to-charge ratio of 333.1 amu) — the Al adduct ion [2BPhen+Al]⁺ (at m/z =692.8 amu), where Al forms a complex with two undestroyed BPhen molecules simply by donor-acceptor interaction. A similar effect is seen at the Ag-on-BPhen interface [Fig. 5(d)], where — besides the BPhen oligomers — the metal-organic donor-acceptor adducts [BPhen+Ag]⁺ (m/z =438.9 amu) and [2BPhen+Ag]⁺ (m/z =770.6 amu) are the dominant signals. The additionally ob-

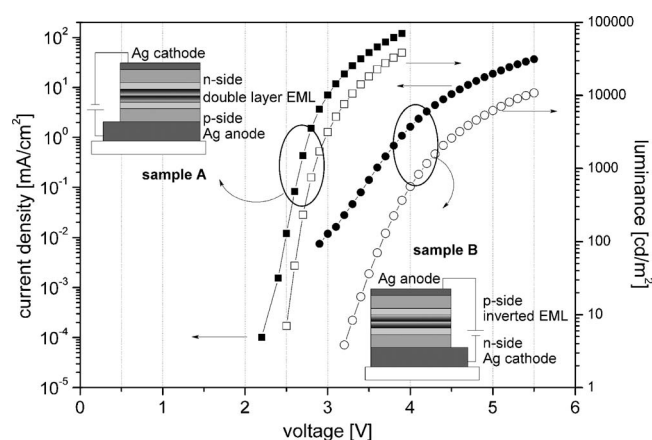


FIG. 3. *J*-*V* and *L*-*V* characteristics of samples A and B. The noninverted top emitting diode A shows a higher current and a higher luminance at a given voltage than the inverted sample B. The insets show schemes of the layer structures of samples A and B.

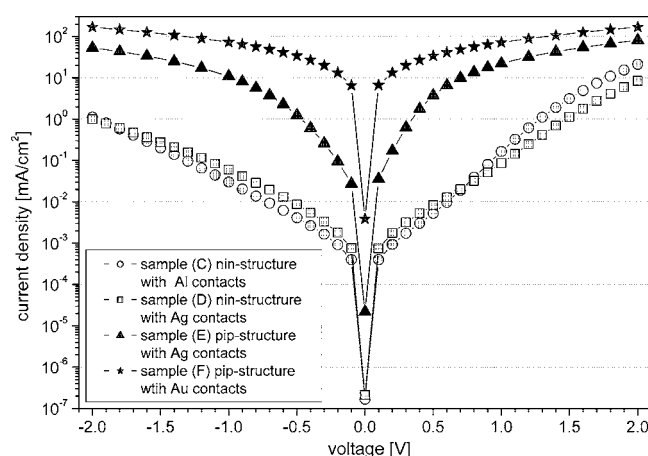


FIG. 4. *J*-*V* characteristics of the electron only devices C (with Al top and bottom contacts) and D (with Ag contacts) and of the hole only devices E (Ag contacts) and F (Au contacts).

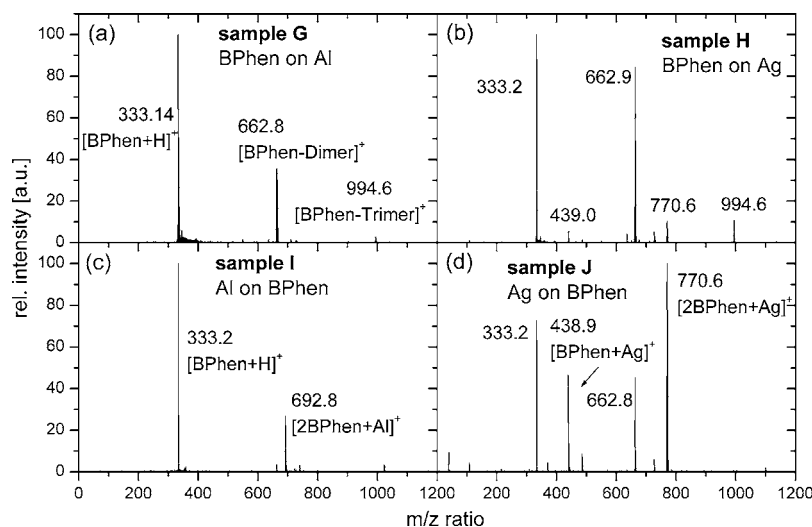


FIG. 5. LDI-TOF-MS spectra of (a) sample G: BPhen (332.1 g/mol) on Al (27 g/mol), (b) sample H: BPhen on Ag (107 g/mol), (c) sample I: Al on BPhen, and (d) sample J: Ag on BPhen. The samples were taken in the positive detection mode at 200 $\mu\text{J}/\text{pulse}$ and show the major generation of the BPhen-metal adducts for the metal-on-organic samples, where the metal adducts, seen on the organic-on-metal samples are negligible.

served BPhen oligomers were created by photochemical reactions during the LDI process, as shown elsewhere.³⁰ It is quite interesting to see that Al does not form complexes with the single BPhen molecule. This is reasonable because Al appears in the ionized state as a threefold charged ion. Nevertheless, both contact metals show similar electron injection behaviors into the underlying ETL (Fig. 4). In Figs. 5(a) and 5(b) samples G and H are presented, where the organic material is evaporated on top of either Al or Ag. The spectra show only the formation of BPhen related ions, especially $[\text{BPhen}+\text{H}]^+$ at 333.1 amu, its dimer $[2\text{BPhen}-2\text{H}+\text{H}]^+$ at 662.8 amu and the trimer at 994.6 amu.

It is important to note that BPhen does not form metal adducts with the Al layer underneath upon laser light exposure (sample G). Similar results are seen at the BPhen-on-Ag interface (sample H), where the metal adduct ion intensity is very low. The slight adduct ion generation is due to the photoelectric properties of Ag, which enables the metal to donate electrons very easily under light exposure, which is why the organic molecules may form a minor amount of donor-acceptor complexes with Ag. Therefore, weak signals of the

Ag-BPhen adduct at $m/z=439$ amu and the adduct $[2\text{BPhen}+\text{Ag}]^+$ at 770.6 amu are seen besides the main BPhen ions [Fig. 5(b)].

To look for similar effects in other material arrangements, we investigated metal/organic layer systems with MeO-TPD, Spiro-TAD, and silver. The two hole transporting materials did not show complexation with the metal atoms. Therefore, the detection of metal-organic adducts cannot be used as a proof of metal incorporation into underlying HTLs. In contrast to the metal-BPhen interfaces, the free atoms do not undergo complexation and therefore they are not bound and are separately detectable as metal ions. In Fig. 6, the LDI spectra of the metal/organic and organic/metal interfaces for MeO-TPD (samples K and L) and Spiro-TAD (samples M and N) are shown. The labeled signals are the Ag ions ($m/z=107$ and 109 amu), MeO-TPD ($m/z=608$ amu), and Spiro-TAD ($m/z=984.8$ amu) and the typical fragments of the organic semiconductors.³⁰ In Figs. 6(a) and 6(c), the signal intensities of Ag are clearly visible when Ag is evaporated on top of the organic materials. In contrast, the LDI spectra of the organic-on-Ag samples [Figs. 6(b) and 6(d)]

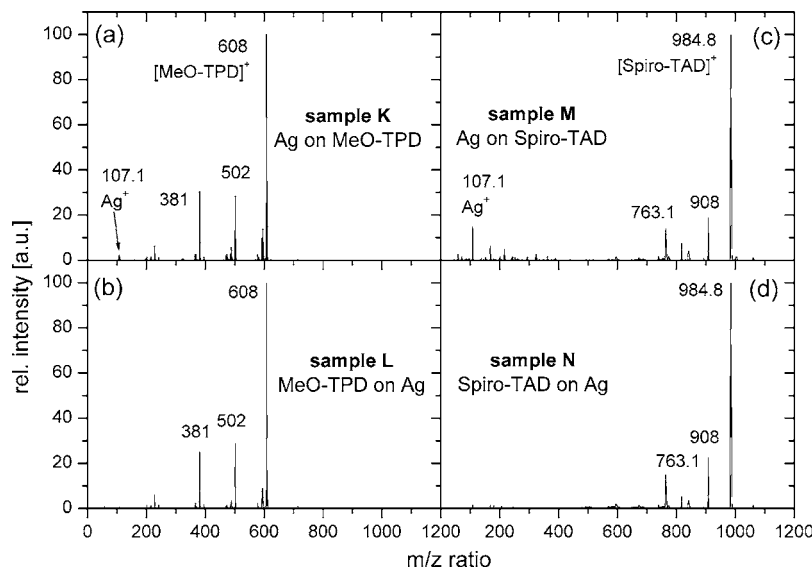


FIG. 6. LDI-TOF-MS spectra of (a) sample K: Ag (107 g/mol) on MeO-TPD (608 g/mol), (b) sample L: MeO-TPD on Ag, (c) sample M: Ag on Spiro-TAD (984 g/mol), and (d) sample N: Spiro-TAD on Ag. Note the intensities for Ag ions in the metal on organic spectra. The spectra were taken in the positive detection mode with 160 $\mu\text{J}/\text{pulse}$ laser intensity.

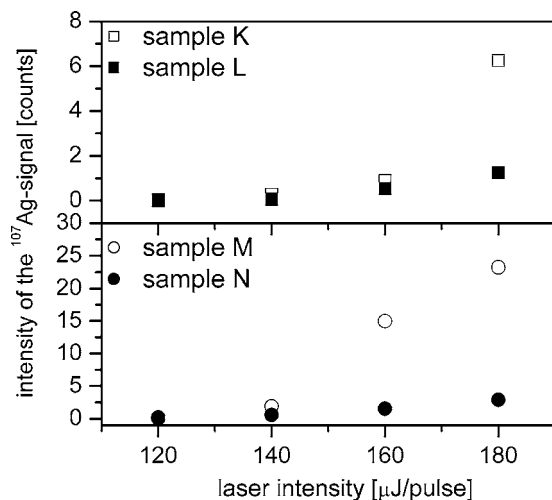


FIG. 7. Signal intensities of the ^{107}Ag ion. Spectra were taken at different laser intensities displaying the detection of the more pronounced free silver atoms on the metal-on-organic interfaces (open symbols) compared to their corresponding organic-on-metal samples (filled symbols).

did not show a clear Ag ion signal. In Fig. 7 the signal intensities of the ^{107}Ag ions are displayed versus the laser intensities. It is clearly seen that due to the existence of free atoms, the ion intensities are increased for the metal-on-organic interfaces. For comparison, the ^{107}Ag ion signal at 180 $\mu\text{J/pulse}$ is five times higher for the Ag-on-MeO-TPD sample K than for the inverted sample L and eight times higher for sample M (Ag on Spiro-TAD) compared to sample N.

To verify our results, we used UPS to look in detail at the interfaces between silver and the Cs-doped BPhen layer. As it is depicted in Fig. 8, sample P (BPhen:Cs on Ag) shows two significant gap states at 2.1 and 0.7 eV, which are caused by the Cs doping of BPhen. Similar gap states are known from Li-doped bathocuproine layers.²⁸ The highest occupied molecular orbital cutoff of BPhen is clearly seen at 4.15 eV. In contrast, sample O (Ag-on-BPhen:Cs) shows the suppression of the gap state induced by Cs doping and the appearance of a single gap state at 1.9 eV. We attribute this gap state to a doping behavior caused by the penetration of Ag atoms into the organic.

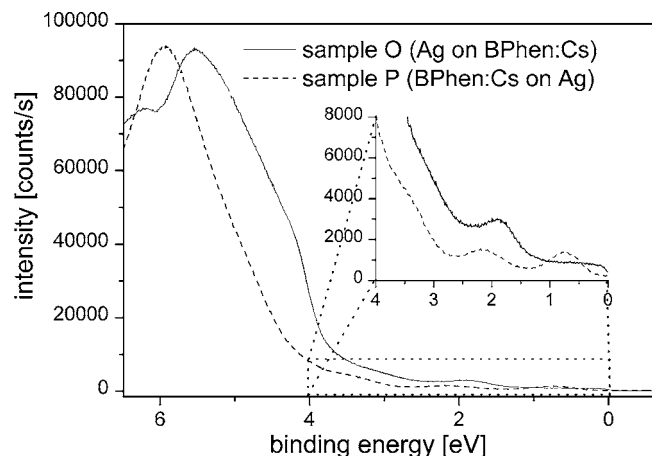


FIG. 8. UPS measurements at the interfaces of samples O and P. The inset shows a closer look to the gap state formation in the BPhen layer due to Cs doping (sample P) and for Ag doping (sample O).

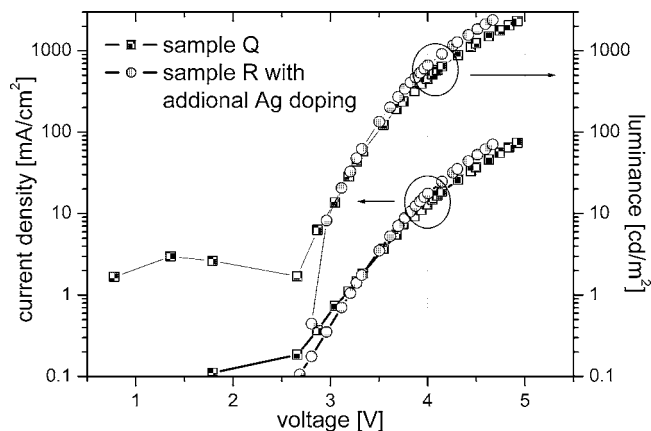


FIG. 9. J - V and L - V characteristics of samples Q and R, where sample R contains a Cs- and Ag-doped ETL. The device structures are seen in Table I.

To take advantage of this additional doping, we made an inverted OLED with a Cs- and Ag-doped ETL on top of the bottom contact. This additional doping was done by altering the Cs-doped BPhen layer with thin (1.5 and 1 nm) interlayers of Ag (see sample R in Table I). The idea behind is to dope the BPhen:Cs layer with penetrating Ag atoms. Figure 9 shows the J - V and the L - V characteristics of samples R and Q, where sample Q is an inverted OLED similar to sample R but with a conventionally Cs-doped ETL. In this case, sample Q serves as a reference sample to R. Due to the use of the additional doping with Ag, the J - V and L - V characteristics of sample R show a slight enhancement, as compared to sample Q.

These data allow us to conclude that metal atoms penetrate an underlying organic surface during the evaporation procedure and the penetration causes a doping with electron donating metal atoms. This doping slightly enhances the electron injection from the top metal contact into an electron transporting organic layer but cannot overcome the worse performance of the J - L - V characteristic of an inverted OLED.

B. Oxidation processes at metal-on-organic interfaces

In addition to the self-doping effect of the metal atom penetration, a process of partial oxidation on metal-on-organic interfaces can be observed. To study this topic in detail, we used SIMS and dynamic XPS depth profiling on especially processed samples. In contrast to the samples that were investigated regarding the self-doping behavior, a certain concentration of metal oxide in metal-on-organic interfaces can be detected in different organic semiconductor devices. From Fig. 10, where the positive and the negative SIMS ion spectra of sample S are displayed (see Table I), it is visible that a certain amount of oxygen is detectable. Due to slight changes in the Cs^+ ion primary beam current, the sputter times of the negative and the positive spectra differ from each other. In the negative ion spectra in Fig. 10(a), the ion intensities of $^{12}\text{C}^-$, $^{14}\text{N}^-$, and $^{18}\text{O}^-$ are plotted versus the experimental sputter time. The increased oxygen ion intensity is clearly visible at the aluminum surface, in the aluminum/BPhen interface, and in the ITO (in Fig. 10 the

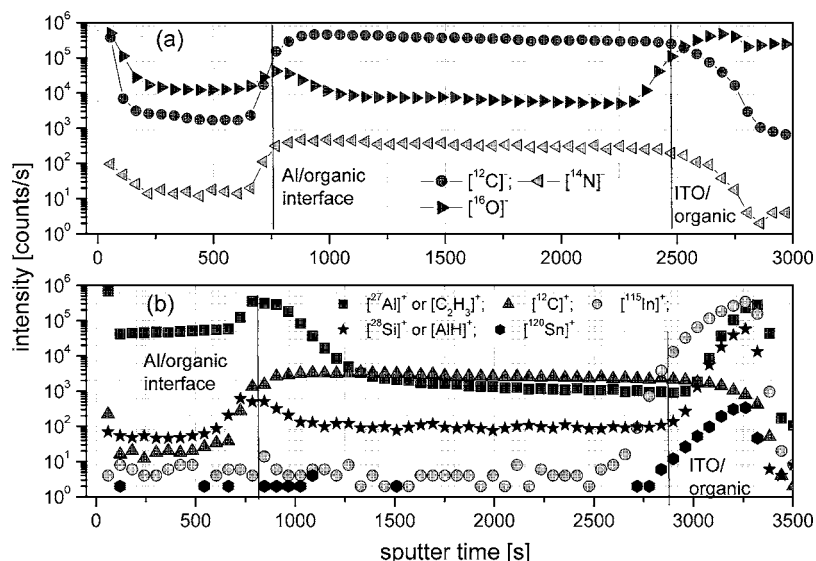


FIG. 10. SIMS measurements of the OLED sample S in negative (a) and positive (b) detection mode. The sputter time represents the sputter depth from the top Al contact to the ITO ground contact. The sputter time in the two graphs differs due to changes in the sputter ion current. The estimated heterointerfaces are displayed by lines. Note the increased intensities of oxygen and the aluminum ion signals at the metal-on-organic interface.

approximate locations of the heterointerfaces are indicated by lines). Due to surface impurities, the ion signal intensities of the first sputtered nanometers have to be neglected. We will therefore concentrate on the increased oxygen concentration between the ETL BPhen and the aluminum metal cathode.

Even in Fig. 10(b), where the positive ions $[^{27}\text{Al}]^+$ (or $[\text{C}_2\text{H}_3]^+$) $[^{12}\text{C}]^+$, $[^{28}\text{Si}]^+$ (or $[\text{AlH}]^+$), $[^{115}\text{In}]^+$, and $[^{120}\text{Sn}]^+$ are displayed, the increased aluminum and silicon ion intensities on the metal/organic interface attract attention. Below we will discuss how aluminum is bound in between metal/organic interfaces and we will show that the oxide creates a more undefined Al_xO_y species than the thermally stable Al_2O_3 . Due to this partial oxidation and the corresponding increased electron accepting behavior of the oxygen containing compounds, the intensity of the Al ion is simultaneously increased. This is clearly visible for the before-mentioned metal-on-organic interface in Fig. 10(b). The increased ion intensity for $[^{28}\text{Si}]^+$ [black stars in Fig. 10(b)] on the metal/organic interface corresponds to the increased generation of $[\text{AlH}]^+$ ions, which have the same mass-to-charge ratio of 28 amu. One can see a similar behavior of such enhanced ion intensity on the organic/ITO interface in Fig. 10(b) for the $[^{27}\text{Al}]^+$ ions (bold squares). Different carbon hydrogen species (such as $[\text{C}_2\text{H}_3]^+$ with $m/z=27$ amu) were created during the sputter process, simultaneously seen as a kind of Al background in the organic part of the OLED.

Important questions are the concentration and the origin of the oxygen content at the metal/organic interfaces. The oxygen concentration can be determined with the help of dynamic XPS depth profiling (see Fig. 11). Standard heterostructures (samples T and U) processed in the evaporation tool with a base pressure of 10^{-8} mbar show nearly no oxygen incorporation at the metal-on-organic interface [see Figs. 11(b) and 11(c)]. Sample V, processed at 10^{-6} mbar, reveals a significant oxygen concentration of about 10 at% at the interface [Fig. 11(d)].

Due to the fact that sample V [Fig. 11(d)] shows no clear oxygen profile, we looked at another sample, in this case a full OLED stack (sample S), which was processed in a single

vacuum chamber with multiple evaporation sources and a base pressure of around 10^{-7} mbar. The XPS depth profile of sample S [Fig. 11(a)] shows a significant oxygen concentration of about 10 at% in between the cathode and the organic interlayer, while in the remaining organic stack and the bulk cathode material no further oxygen is visible.

Oxygen inclusion was discussed in several literature reports. In Refs. 15–17 metals were evaporated on top of oxygen containing organic compounds. These materials were mentioned as possible oxygen sources for the identified oxidation on the metal/organic interfaces. To avoid such an intrinsic oxide contamination, we used BPhen (chemical formula: $\text{C}_{24}\text{H}_{16}\text{N}_2$) instead of oxygen containing compounds. This leads us to the question, where the oxygen comes from and which processing step is responsible for it. To answer these questions, some possible explanations are as follows. (1) Due to the evaporation of the metal from small pieces, the metal oxide covering the metal evaporates first and causes the increase in the oxygen content at the interface. (2) A residual partial pressure of oxygen and water inside the vacuum system reacts with the metal vapor. (3) The oxygen originates from the Cs source, where Cs is evaporated from oxygen containing cesium salt.

To find the right explanation, we look back to the series of metal-on-BPhen samples T (Cs doped) and U (undoped) which were processed and investigated with dynamic XPS. The results of these samples show that Cs doping has no significant influence on the oxidation behavior at the interface [Fig. 11(b)]. The Al-on-BPhen:Cs interface of sample T is nearly oxygen free, which means that the oxygen does not originate from the Cs salt or from a Cs oxide formed by a reaction between Cs and another oxygen source. Furthermore, sample U, without Cs doping and processed at a chamber base pressure of 10^{-8} mbar as well, shows no significant oxygen content on the interface. This points out that oxygen is not originating from a metal oxide, which may cover the metal sticks used for the metal evaporation. In contrast to these results, sample V, evaporated at a base pressure of around 10^{-6} mbar, shows a significant increase in the oxygen concentration. The reason is the origin of oxygen in the

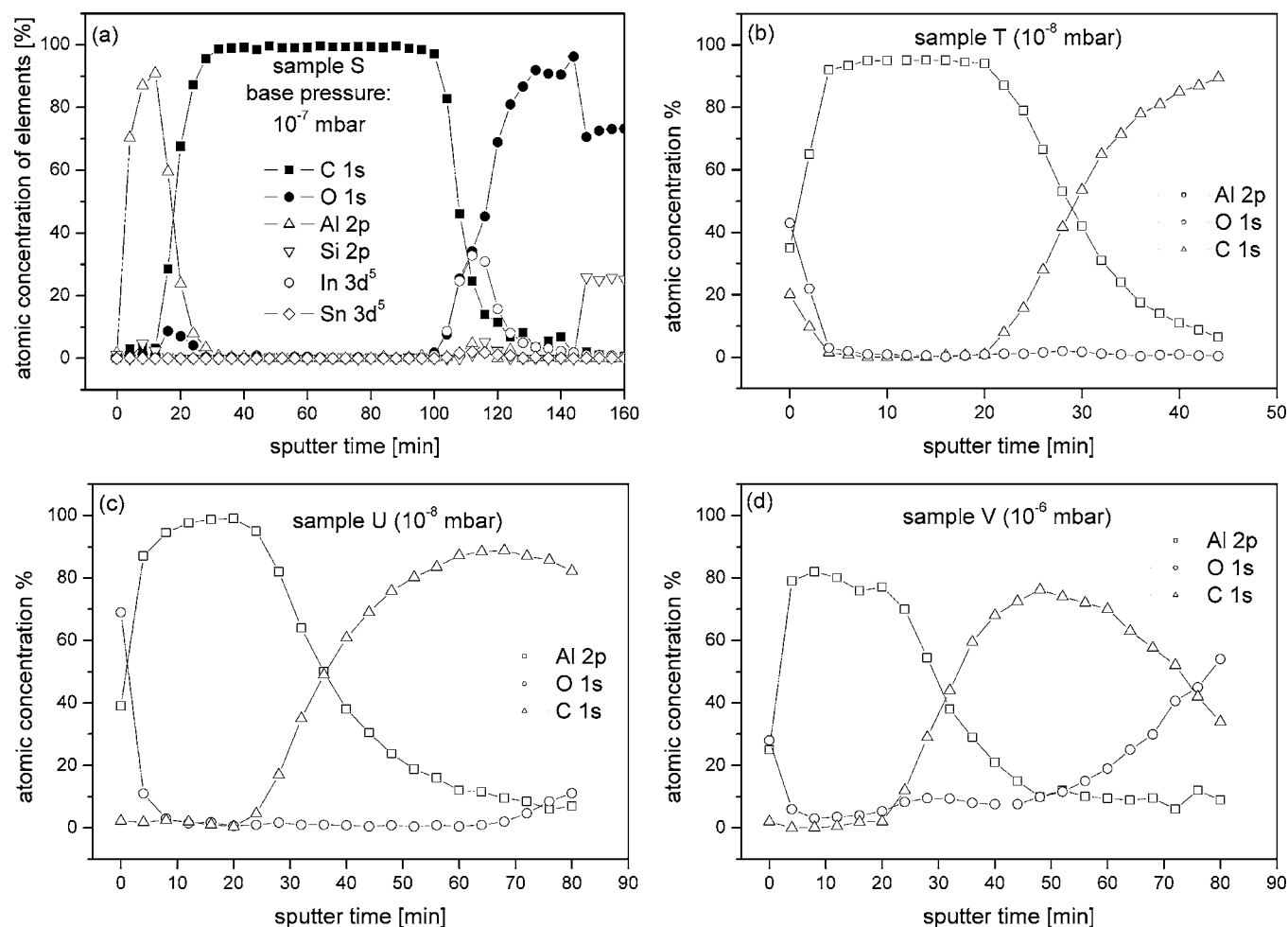


FIG. 11. XPS depth profiles (a) of an OLED (sample S) well pronounced: the oxygen incorporation at the metal-on-organic interface with an atomic concentration of $10 \pm 2\%$. (b) XPS depth profile of sample T, where aluminum was evaporated on Cs-doped BPhen layer at 10^{-8} mbar, (c) Al on intrinsic BPhen grown at 10^{-8} mbar (sample U), and (d) sample V, where Al is deposited at 10^{-6} mbar; note that a small fraction of oxygen is found on the metal-on-organic interface of sample V, while the interfaces of samples T and U remains oxygen-free.

residual partial pressure within the vacuum chamber. A rough estimation yields: a vacuum chamber at 10^{-6} mbar usually contains a residual oxygen partial pressure of about 2×10^{-7} mbar. To prove this, we analyzed our vacuum condition in the metal evaporation chamber with a residual gas analyzer. Even at a total base pressure of 5×10^{-8} mbar, where we do not expect oxygen incorporation into the samples, we measured indeed a low oxygen partial pressure of about 1.2×10^{-9} mbar but a quite high content of water (1.8×10^{-8} mbar). This implies that the amount of oxygen insertion into a metal-on-organic interlayer depends on the oxygen and water partial pressures in the vacuum chamber.

When looking for possible Al_xO_y compounds, LDI-TOF-MS was used to explain the binding behavior of the oxygen located at the metal-on-organic interface (Fig. 12). Sample W was processed at a metal chamber base pressure of about 10^{-6} mbar. Besides the dominant signals $[\text{Al}]^+$ at $m/z=27$ amu, $[\text{BPhen}+\text{H}]^+$ at $m/z=333$ amu, $[\text{BPhen}+\text{Al}]^+$ at $m/z=359$ amu, and $[\text{2Bphen}+\text{Al}]^+$ at $m/z=691.7$ amu, several oxidized species are detectable. From the group of the partially oxidized Al_xO_y , the ions $[\text{AlO}]^+$ ($m/z=43.3$ amu) and $[\text{Al}_2\text{O}]^+$ ($m/z=70.4$ amu) are visible. Further, the aluminum clusters $[\text{Al}_2]^+$

($m/z=54.4$ amu) and $[\text{Al}_3]^+$ ($m/z=81.4$ amu) and the oxidized metal-organic complexes $[\text{BPhen}+\text{AlO}]^+$ ($m/z=376.0$ amu) and $[\text{2Bphen}+\text{AlO}]^+$ ($m/z=709.2$ amu) are visible.

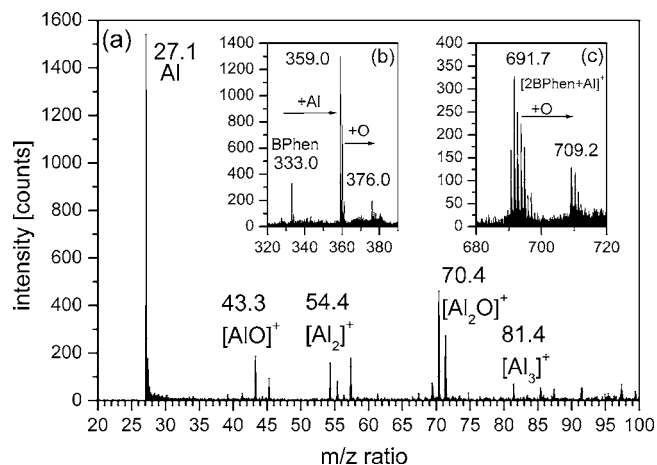


FIG. 12. LDI-TOF-MS spectra of the Al-on-BPhen sample W processed at 10^{-6} mbar of the metal chamber base pressure. Note the different aluminum oxide species in the lower mass region (a) and the different aluminum-oxide-BPhen adducts in (b) and (c).

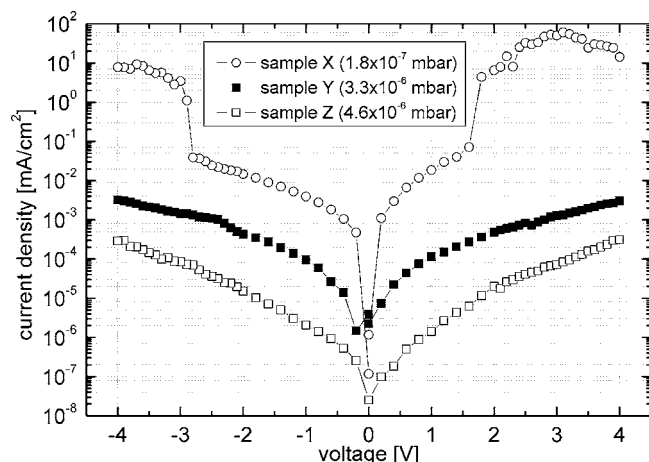


FIG. 13. J - V characteristics of three ITO/Alq₃/Al samples, where Al is evaporated at different vacuum conditions; note that the higher the chamber pressure, the higher the oxygen incorporation, and therefore the lower the current density of the device.

Looking at the XPS depth profile of sample S [Fig. 11(a)] where the oxygen is located at the metal-on-organic interface, it is very likely that the oxygen containing interlayer is created during the first seconds of aluminum evaporation. The “hot gas” of aluminum atoms reacts with the residual partial pressure of oxygen in the evaporation chamber. After a certain time of metal evaporation, the partial pressure of oxygen decreases, so that aluminum is evaporated as pure metal. Due to the effect that the reaction directly relates to the pressure and therefore to the amount of oxygen in a vacuum chamber, the distance between a metal evaporator and the sample is crucial for the oxygen incorporation. In contrast to Refs. 21 and 22, where Al₂O₃ (1 nm) was used as interlayer, we did not observe an improved charge injection due to the insertion of an oxygen-rich interlayer. In Fig. 13 the J - V characteristics of samples X–Z, where the metal is evaporated at different vacuum conditions (pressure), show a clear dependence on the oxygen content at the metal-on-organic interface. The higher the pressure in the evaporation tool, the higher the amount of oxygen at the interface, resulting in a decreased current density. The current jump (at 1.8 and –2.9 V for device X) and the negative differential resistance known from Alq₃ devices disappear in the presence of an oxidized interface.^{42,43}

IV. CONCLUSIONS

Using the example of inverted and noninverted OLEDs and their corresponding hole and electron only devices, we studied the differences between charge injection from top and bottom metallic electrodes into organic materials. It is obvious that electrons are better injected from the top contact than from the bottom into the electron transporting organic material. A reason for this is the self-doping effect during the metal evaporation on top of an organic layer. This behavior was proven by LDI-TOF-MS and UPS, where formation of metal-organic complexes between Al and the ETL BPhen was found. Additionally, a major generation of free atoms in HTLs was observed in contrast to their corresponding

organic-on-metal samples. While the penetration of metal atoms also occurs on HTLs, the self-doping effect has no significant influence on the devices.

By means of SIMS and XPS depth profiling, metal-on-organic interfaces were analyzed. Some samples showed a partial oxidation of the metals at the metal-on-organic interface. The incorporated oxygen originates from a rest partial pressure of oxygen and water in the evaporation tool creating oxidized aluminum of different stoichiometries. LDI-TOF-MS was used to analyze the composition of the oxygen-rich metal-on-organic interfaces, revealing a complex behavior of different bound compounds.

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