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Citation: *J. Appl. Phys.* **102**, 014906 (2007); doi: 10.1063/1.2752145

View online: <http://dx.doi.org/10.1063/1.2752145>

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Incorporation of cobaltocene as an *n*-dopant in organic molecular films

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(Received 16 March 2007; accepted 25 May 2007; published online 10 July 2007)

Electrical or chemical doping of molecular films is an efficient means of improving and controlling charge injection and carrier transport in organic devices. Recent work demonstrated that bis(cyclopentadienyl)cobalt(II) (cobaltocene, CoCp₂) efficiently dopes a tris(thieno)hexaazatriphenylene (THAP) derivative, as shown by a 0.56 eV shift of the Fermi level toward the empty states and an increase of current density by a factor of 10³ over undoped THAP devices. In this work, a combination of x-ray photoemission spectroscopy and Rutherford backscattering is used to elucidate the details of dopant incorporation into bulk films. Cobaltocene is observed to codeposit into the THAP matrix in a controllable manner, with preferential adsorption of the dopant onto the surface of the host film. In the case of CoCp₂-doped tris(8-hydroxyquinolino) aluminum (Alq₃) films, negligible amounts of the dopant are found in the bulk matrix and on the film surface, resulting in minimal improvements in the electrical characteristics of doped Alq₃ films. The process of CoCp₂ adsorption onto a film surface or the evolving surface of a growing film which leads to dopant incorporation is likely assisted by charge transfer from cobaltocene to the host material, resulting in ion pairing between the dopant and host. © 2007 American Institute of Physics. [DOI: 10.1063/1.2752145]

I. INTRODUCTION

Electrical or chemical doping of molecular organic films is an efficient means of improving and controlling charge injection and carrier transport in organic devices. Although highly oxidizing molecular *p* dopants such as fluorinated tetracyanoquinodimethane (F₄-TCNQ) have been widely used,^{1–5} practical applications of *n* doping have largely been limited to incorporating high concentrations of alkali and other electropositive metals and compounds, which leads to the presence of unstable and diffusible metal ions in the sample.^{6–12} In some cases this form of *n* doping is accompanied by decomposition of the organic transport material.¹⁰ Although these issues regarding diffusion and doping efficiency can be resolved in principle by employing larger organic dopants, the synthesis, handling, and delivery of molecules with sufficiently low ionization energy (IE) for efficient electron transfer to most host materials of interest are often difficult.^{13–17}

We recently reported on a means of dispensing in ultra-high vacuum (UHV) a volatile organometallic complex, bis(cyclopentadienyl)cobalt(II), also known as cobaltocene (CoCp₂), without exposure of the air-sensitive complex to ambient conditions.¹⁸ This electron-rich molecule was used as an *n* dopant in a matrix of tris{2,5-bis(3,4-bis(trifluoromethyl)phenyl)thieno} [3,4-*b,h,n*]-1,4,5,8,9,12-hexaazatriphenylene (THAP). In this system, the relative values of the IE of cobaltocene (4.0 eV) and the electron affinity (EA) of THAP (4.6 eV), as determined by ultraviolet photoemission spectroscopy (UPS) and inverse photoemis-

sion spectroscopy (IPES), respectively, suggest an efficient electron transfer from dopant to host [Fig. 1(a)]. Indeed, *n*-type doping was confirmed by a 0.56 eV shift of the Fermi level (E_F) in THAP toward the lowest unoccupied molecular orbital (LUMO) [Fig. 1(b)] and a 10³-fold increase in the current density through doped THAP films.¹⁸

Despite this evidence of efficient *n* doping of THAP by CoCp₂, insufficient data were available in our initial study to determine the precise doping concentration of the films. By assuming a uniform doping profile in the host matrix, it was calculated that films deposited at a rate of 1 Å/s in a partial pressure of 10⁻⁷ Torr of CoCp₂ should comprise about one dopant molecule per host molecule. However, comparison of the intensities of the Co 2*p* and N 1*s* core level peaks observed using x-ray photoemission spectroscopy (XPS) indicated a cobaltocene:THAP ratio of 1:1.6. A precise determination of the doping concentration by chemical analysis was further hindered by the possibility of preferential CoCp₂ absorption on the surface after film preparation. In view of these difficulties, the issue of dopant diffusion also remained unresolved.

In the present work, a variety of cobaltocene/THAP samples are investigated using XPS and compared to data obtained with Rutherford backscattering (RBS), which provides a depth profile of the elemental composition of the films. Results indicate that controlled bulk doping of THAP by CoCp₂ is achieved by varying the partial pressure of the dopant from 10⁻⁷ Torr (30%) to 5 × 10⁻⁹ Torr (<1%). Cobaltocene concentrations within that range have been shown to produce similarly efficient doping effects in THAP.¹⁸ Investigation of spatially doped THAP layers showed no discernable diffusion of CoCp₂ through the film.

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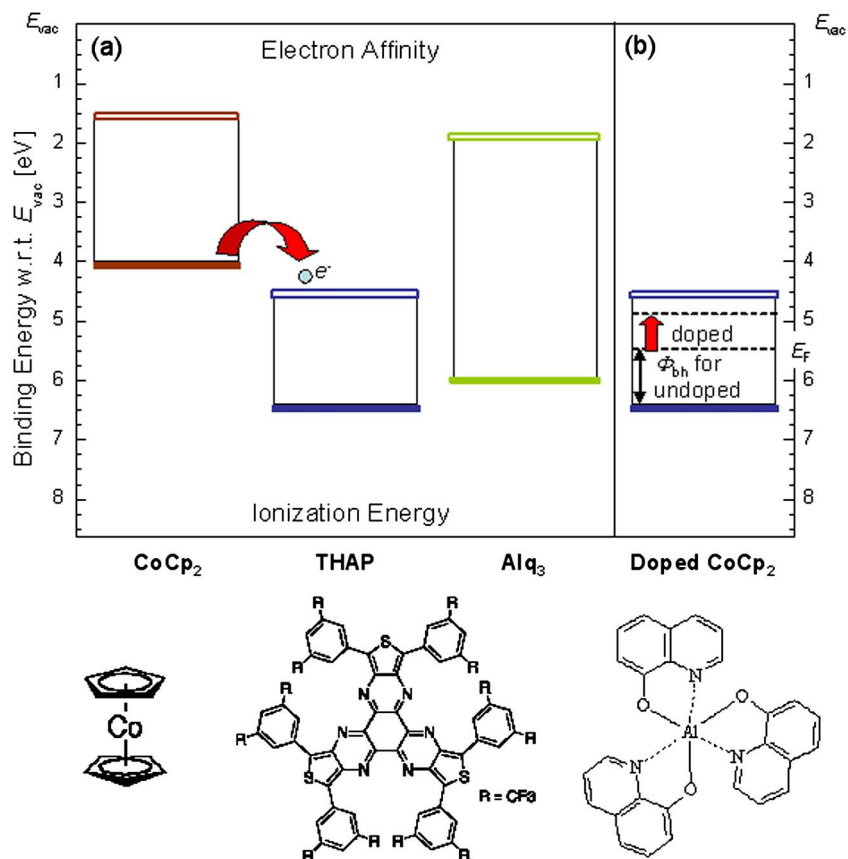


FIG. 1. (Color online) Schematic diagrams illustrating (a) the energetically favorable electron transfer from the HOMO of cobaltocene to the LUMO of THAP and the large energy difference between the dopant HOMO and the Alq₃ LUMO. (b) The effect of this doping on the E_F position in a THAP film (Ref. 18). The molecular structures of the dopant and host are shown on the insets.

Incorporation of cobaltocene into a more commonly used electron-transport material, tris(8-hydroxyquinolino)aluminum (Alq₃), is also studied, and the results are compared with those obtained for THAP. The inefficient incorporation of CoCp₂ in Alq₃, which has an EA of only 2.1 ± 0.2 eV as measured with IPES,¹⁹ is linked to the nearly 2.0 eV barrier for electron donation from dopant to host in this system. A small 0.2 eV shift of E_F in doped Alq₃ and a minor improvement in device performance are attributed mainly to the modification of the energy-level alignment at the anode-Alq₃ interface.

II. EXPERIMENT

Experiments were conducted in a three-chamber UHV system equipped for organic and metallic film growth (growth chamber), coevaporation of host and dopants and *in situ* current-voltage (I - V) measurements (preparation chamber), and UPS and XPS (analysis chamber). Cobaltocene was loaded under a purged nitrogen environment as received from Sigma-Aldrich into a quartz ampoule and sealed onto a leak valve. The apparatus was then mounted onto the UHV preparation chamber ($p_{\text{base}} = 2 \times 10^{-10}$ Torr) without exposing the contents of the ampoule to air. The high vapor pressure of cobaltocene results in spontaneous sublimation under vacuum at room temperature, with the partial pressure controlled by the leak valve.

THAP was synthesized as previously described²⁰ and placed into two thermal evaporation cells: one in the preparation chamber for the growth of doped THAP films and one in the growth chamber ($p_{\text{base}} = 1 \times 10^{-9}$ Torr) for deposition

of undoped films. THAP, which sublimates at 350 °C at 10^{-9} Torr, was thoroughly outgassed prior to use. Unless otherwise specified, all films were grown on poly-3,4-ethylenedioxythiophene-polystyrenesulfonate (PEDOT:PSS, Baytron 8000) spun onto indium tin oxide (ITO)/glass substrates at 4000 rpm for 60 s. The ITO was prepared by mechanical and solvent cleaning and exposed to UV ozone for 1 h. The 50-nm-thick PEDOT:PSS films were annealed at 180 °C for 1 h and immediately transferred from the nitrogen glove box into vacuum using a sealed nitrogen container.

XPS was conducted in the analysis chamber ($p = 6 \times 10^{-11}$ Torr) using the AlK α x-ray source ($h\nu = 1486.6$ eV). The detection limit of the technique was estimated to be on the order of a few molecular percent with a spectral resolution of 0.9 eV. A control sample of pure CoCp₂ was condensed onto a sputter-cleaned platinum substrate that was cooled to 77 K by a closed-cycle helium refrigerator and examined with XPS at low temperature. Doped films of THAP with a thickness of 6 nm were prepared at room temperature by depositing the host material at 1 Å/s under different partial pressures (p_d) of cobaltocene: 10^{-7} , 5×10^{-8} , and 5×10^{-9} Torr. A sample used to investigate the effects of preferential surface adsorption of CoCp₂ was prepared by exposing an undoped 6 nm THAP film to a cobaltocene partial pressure of $p_d = 10^{-7}$ Torr for 5 min.

To investigate the process of dopant diffusion in the host film, a 5-nm-thick film of THAP doped at 10^{-7} Torr of CoCp₂ was grown on Au followed by the deposition of 20 nm of pristine THAP (interface-doped sample). The sample was kept in the growth chamber in the absence of cobaltocene for 16 h so that the pressure in the preparation

chamber could recover to 5×10^{-9} Torr. The sample was then transferred through the preparation chamber, which likely still contained trace amounts of CoCp_2 , and into the analysis chamber for XPS analysis. After an initial scan, the sample was then annealed at 50°C for 30 min and at 60°C for an additional hour, with XPS performed after each annealing step.

To supplement the XPS data, RBS experiments were performed by Evans Analytical Group (Sunnyvale, CA) using a 2.275 MeV He^{2+} ion beam incident on the sample at 75° from the sample normal. Backscattered He atoms were collected with an RBS detector 20° offset from the incident beam. Experimental conditions allowed for a spatial resolution of 25 nm and a Co detection limit of 0.05 at. % (5 mol %). The hydrogen concentration was simultaneously determined by hydrogen forward scattering (HFS) with the detector positioned 75° from the sample normal in the forward scattering direction. Four samples were prepared at Princeton using the aforementioned UHV system on Si(100) substrates: (i) 100 nm of pristine THAP; (ii) 100 nm of doped THAP grown with $p_d=10^{-7}$ Torr; (iii) 100 nm of doped THAP grown with $p_d=10^{-9}$ Torr; (iv) 30 nm of doped THAP ($p_d=10^{-7}$ Torr) underneath 70 nm of undoped THAP and annealed to 60°C for 1 h. The samples were removed from vacuum, sealed in containers under N_2 , shipped to Evans Analytical, and transferred into the RBS apparatus with minimal exposure to ambient air.

For the Alq_3 experiments, prepurified undoped and doped ($p_d=10^{-7}$ Torr) Alq_3 layers were deposited onto clean Al substrates for analysis with UPS ($h\nu=21.22$ eV) and XPS. Current-voltage measurements were performed on Al/200 nm organic/Al diode devices where the organic layer consisted of (i) pristine Alq_3 , (ii) Alq_3 deposited with $p_d=10^{-7}$ Torr of cobaltocene, and (iii) pristine Alq_3 in which 15 nm of the bottom interface is doped with CoCp_2 at a pressure of 5×10^{-8} Torr. Another sample consisting of 100 nm of Alq_3 deposited onto Si(100) with $p_d=10^{-7}$ Torr was also prepared for RBS analysis.

III. RESULTS AND ANALYSIS

A. XPS on doped THAP

The Co 2*p* core levels measured on a pristine cobaltocene film and on doped THAP films deposited under decreasing partial pressures of cobaltocene are shown in Figs. 2(a)–2(d). The core level measured on the interface-doped sample used for diffusion studies is plotted in Fig. 2(e), with subsequent annealing steps shown in Figs. 2(f) and 2(g). Finally, the spectrum corresponding to an undoped THAP film, the surface of which was exposed to a cobaltocene pressure of 10^{-7} Torr for 5 min, is displayed in Fig. 2(h).

The pure cobaltocene film shows two main core levels at binding energies (BEs) of 783 and 797 eV, which correspond to the spin-orbit split Co 2*p*_{3/2} and Co 2*p*_{1/2} levels. The peaks appear to be broadened by the addition of higher BE components at 786 and 799 eV. These peaks likely represent interface molecules that have been “oxidized” by electron transfer to the Pt substrate, while the dominant peaks correspond to neutral CoCp_2 molecules in the bulk of the film.

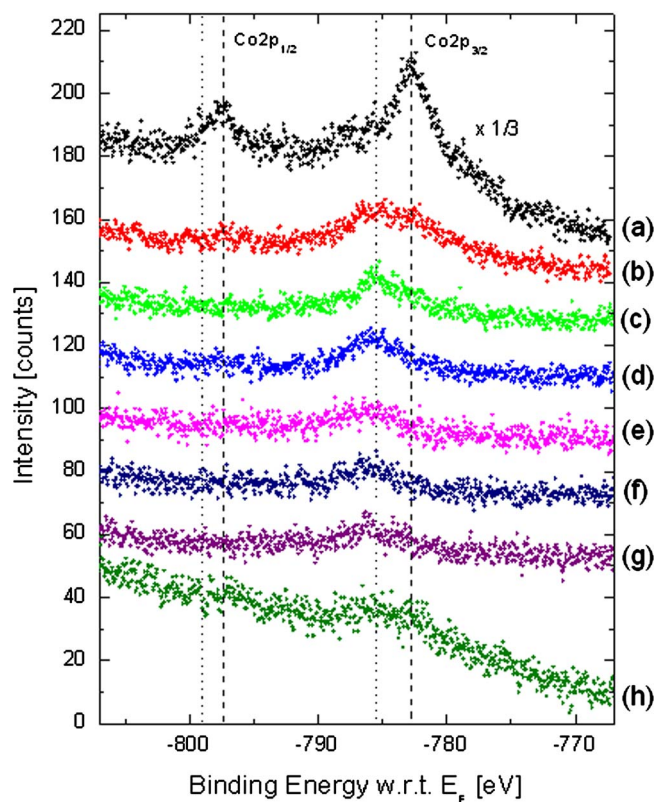


FIG. 2. (Color online) Co 2*p* core levels measured by XPS on (a) a pure cobaltocene film on Pt, 6 nm of THAP deposited on PEDOT:PSS under a cobaltocene partial pressure of (b) $p_d=10^{-7}$ Torr, (c) $p_d=5 \times 10^{-8}$ Torr, and (d) $p_d=5 \times 10^{-9}$ Torr, (e) An interface-doped sample consisting of 5 nm of doped THAP ($p_d=10^{-7}$ Torr) underneath 20 nm of pristine THAP, Sample (e) annealed at (f) 50°C for 30 min, and (g) 60°C for an additional 1 h. (h) an undoped layer of THAP with the surface exposed to $p_d=10^{-7}$ Torr of cobaltocene for 5 min.

These Co peaks and associated shifts serve as useful markers to understand the spectra of the doped THAP films. In these spectra [Figs. 2(b)–2(d)], the overall intensity of the Co 2*p* peaks decreases as the concentration of cobaltocene exposure is reduced, and the dominant unoxidized Co components shift toward the oxidized positions observed above. This transition occurs as the concentration of donor CoCp_2 molecules decreases and the fraction of ionized dopants increases.

The XPS measurement on the undoped THAP sample simply exposed to a partial pressure of CoCp_2 [Fig. 2(h)] indicates the presence of a significant amount of Co adsorbed onto the film surface. We note that an ~ 0.3 – 0.5 eV shift in the vacuum level of THAP is observed when this surface is exposed to CoCp_2 . Assuming full ionization of the dopants and a dipole model, this shift is indicative of a surface charge concentration (or dopant coverage) of $\sim 10\%$. Therefore, all dosages above 0.1 L, and, in particular, all the exposures to residual CoCp_2 encountered here, result in a CoCp_2 saturated surface. By comparing the XPS intensity from the surface Co to that obtained from the “heavily” bulk doped film [Fig. 2(b)], more than half the observed intensity in the doped film can be attributed to surface-adsorbed cobaltocene. The problem is of course more prominent in lightly doped samples, with nearly all of the cobalt intensity observed in the mod-

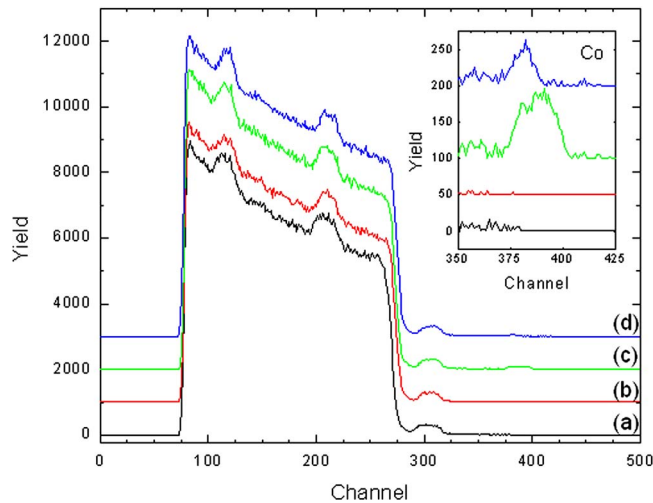


FIG. 3. (Color online) RBS spectra of various samples of THAP: (a) 100 nm of undoped THAP deposited on Si(100); 100 nm of THAP deposited in a cobaltocene partial pressure of (b) $p_d=10^{-9}$ Torr, and (c) $p_d=10^{-7}$ Torr; (d) 30 nm of doped THAP ($p_d=10^{-7}$ Torr) underneath a 70 nm layer of pristine THAP. The channel (energy) range corresponding to the Co signal is expanded in the inset.

erately and lightly doped THAP samples resulting from the surface contribution. Unfortunately, using XPS to rigorously quantify the doping concentration incorporated into the bulk film by subtracting the surface component is difficult because the spectroscopic contributions of surface dopants relative to that of the bulk dopants decrease with increasing doping concentration. The cobalt signal in an undoped film is entirely due to the surface-adsorbed cobaltocene, whereas the proportion of surface to bulk cobaltocene in heavily doped films is very small. Since the surface contribution of the Co signal is strongly correlated with the doping concentration, correction for this signal by assuming a constant surface component will overcorrect for highly doped samples and undercorrect for lightly doped samples.

The interface-doped THAP sample appears at first to exhibit some evidence of dopant diffusion since detectable amounts of Co are present at the surface [Fig. 2(e)]. However, the intensity of the Co signal is comparable with that

found for surface-exposed undoped THAP samples. After 30 min of annealing at 50 °C, no appreciable change is observed in the XPS spectra. Furthermore, the peak intensity decreases after an additional hour of annealing at 60 °C, suggesting that physisorbed cobaltocene may be driven off the surface in the process. Therefore, it is unlikely that appreciable cobaltocene diffusion occurs in THAP films.

B. RBS on doped THAP

To resolve the questions regarding doping concentration and diffusion raised by the presence of surface-adsorbed CoCp_2 , RBS data are obtained for (a) undoped, (b) lightly doped (10^{-9} Torr), (c) highly doped (10^{-7} Torr), and (d) interface-doped ($p_d=10^{-7}$ Torr for 30 nm) THAP films (Fig. 3). Since the Co signal is expected to appear at higher channel numbers, i.e., at higher kinetic energies—due to its larger atomic mass as compared to the other elements present in the matrix (H, C, N, F, and S)—that part of the RBS spectra is magnified in the inset of Fig. 3. By fitting the data to theoretical models and iteratively adjusting the elemental concentrations,²¹ the film composition versus depth can be determined and is shown in Table I. The highly doped sample shows a uniformly distributed 0.27 at. % concentration of Co, which corresponds to nearly 30 mol % doping. This is in good agreement with the data observed by XPS, which indicated 38% doping when uncorrected for the surface contribution of cobaltocene. In the THAP sample grown under a low partial pressure of CoCp_2 , no significant concentration of Co is detected, which is in agreement with the fact that the intensity of the XPS Co $2p$ peak of the lightly doped sample is comparable to that of the surface-exposed undoped sample. Indeed, estimations based solely on the growth parameters of the lightly doped THAP samples would suggest a doping concentration of only 1%, which is below the detection limit of both XPS and RBS for their specific systems. Unlike in the XPS results, which show the presence of Co due to surface-adsorbed cobaltocene on low-doped samples, this surface component is not observed in RBS. The RBS signal is integrated over a much larger depth than the XPS signal, i.e., the spatial resolution of RBS is ~ 25 nm, which

TABLE I. Atomic concentration (at. %) of various elements present in different films as determined by modeling of the RBS data. The lightly doped THAP film was deposited under a cobaltocene partial pressure of $p_d=10^{-9}$ Torr, while the highly doped films indicate a partial pressure of $p_d=10^{-7}$ Torr. The interface-doped THAP film has a 30-nm-thick highly doped region near the bottom interface and pure THAP above.

Element	Concentration (at. %)					
	Undoped THAP	Lightly doped THAP	Highly doped THAP	Interface-doped THAP		Highly doped Alq_3
				<30 nm	>30 nm	
Co	0.0	0.0	0.27	0.25	0.0	0.0
C	56.3	54.3	53.53	55.05	55.3	52.0
H	0.0	0.0	0.27	0.25	0.0	33.0
N	7.0	7.0	7.00	7.00	7.0	5.0
S	2.7	2.7	2.70	2.70	2.7	—
F	22.0	22.0	21.50	22.00	22.0	—
Al	—	—	—	—	—	2.0
O	—	—	—	—	—	8.0

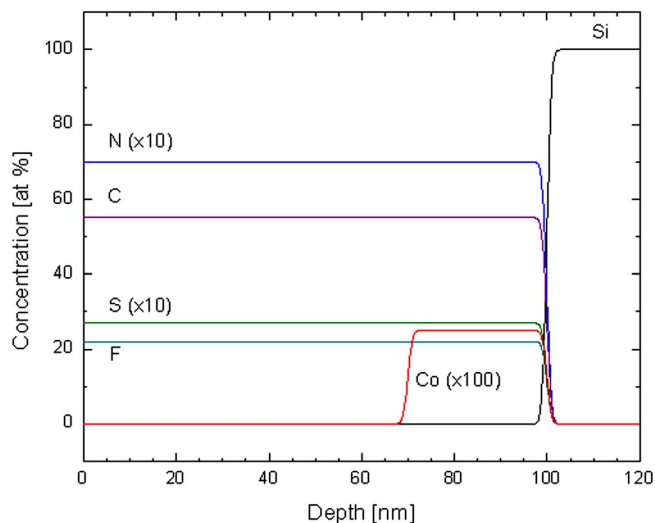


FIG. 4. (Color online) Atomic concentrations as a function of depth as determined by analysis of the RBS spectra for the interface-doped THAP film.

is more than an order of magnitude larger than the electron mean free path in XPS. Nevertheless, other evidence of doping, such as the pronounced shift in E_F and significant improvement in device performance,¹⁸ indicates that low doping concentrations are attainable.

With regard to diffusion, interpretation of the RBS spectra for the interface-doped sample shows no discernable concentrations of cobaltocene in the THAP film beyond the intentionally doped region confined to 30 nm at the interface. Table I summarizes the elemental concentrations found in the doped (<30 nm) and undoped (>30 nm) regions of the film, and Fig. 4 illustrates the relative concentrations of Co, N, S, F, and C as a function film depth. The depth profiling of the film shows uniform concentration of the elements related to THAP and a sharp, well-defined region at the organic-Si(100) interface with a finite concentration of cobaltocene. The spatial confinement of cobalt to the established region indicates that minimal diffusion of cobaltocene occurs in the THAP matrix.

C. Incorporation of cobaltocene in Alq₃

Alq₃ is an electron-transport material of great interest in organic optoelectronics. However, its EA (2.1 ± 0.2 eV) is significantly lower than that of THAP, making n doping considerably more challenging. Despite the energy misalignment between the Alq₃ LUMO and cobaltocene highest occupied molecular orbital (HOMO) (Fig. 1), we investigated the incorporation of cobaltocene in Alq₃ with the possibility that a sufficiently large dopant density might result in measurable n doping of the host.¹⁴

The UPS spectra of (a) undoped Alq₃ and (b) Alq₃ deposited under 10^{-7} Torr of cobaltocene are shown in Fig. 5. A 0.2 eV shift of the spectrum toward higher binding energy, which is equivalent to an upward shift of the Fermi level in the gap, is observed in the doped spectrum and suggests some n doping effect. Furthermore, I - V characteristics (inset of Fig. 5) measured on Al/(200 nm)Alq₃/Al diodes fabricated using (a) undoped, (b) uniformly doped (p_d

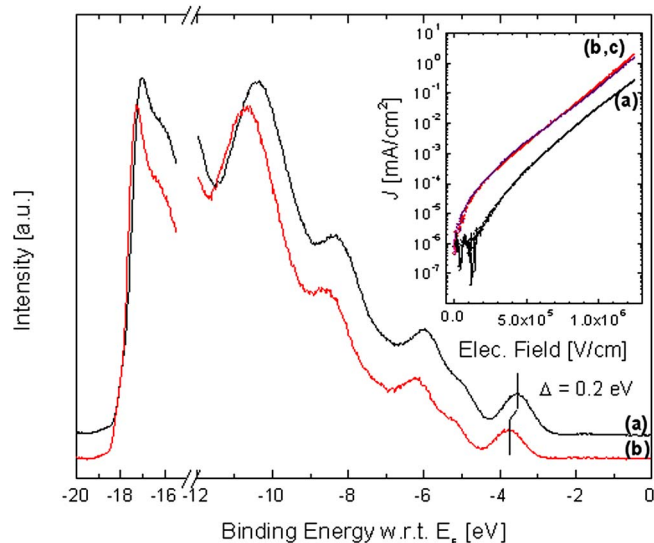


FIG. 5. (Color online) UPS spectra of (b) cobaltocene-doped Alq₃ ($p_d = 10^{-7}$ Torr) showing the 0.2 eV shift compared to (a) undoped Alq₃. The I - V characteristics for (a) undoped, (b) doped, and (c) interface-doped Alq₃ devices are plotted in the inset.

$= 10^{-7}$ Torr), and (c) interface-doped Alq₃ show an increase in the current of the doped devices by a factor of 10. However, two aspects of these results cast some doubt on the origin of the current increase. First, the magnitude of the E_F shift and the increase in current are far less than the improvements observed for CoCp₂-doped THAP. Second, the I - V characteristics of the uniformly doped and interface-doped devices [(b) and (c) in the inset] are identical over six orders of magnitude.

The relative atomic concentrations in a 100 nm uniformly doped Alq₃ film ($p_d = 10^{-7}$ Torr) as determined by the analysis of the RBS spectrum (not shown) is summarized in the last column of Table I. The RBS data clearly show that any cobaltocene present in the film is below the detection limit of the experiment. This observation is confirmed by XPS, which does not indicate any significant Co intensity. Interestingly, and unlike the case of doping THAP, no surface adsorption of cobaltocene is detected. Since both RBS and XPS data show that cobaltocene does not incorporate significantly into the Alq₃ film, nor adsorb appreciably onto the surface of the film, it is therefore likely that most of the improvements in the I - V characteristics of the “doped” films result from modification of the interface energy-level alignment during deposition of Alq₃ in a background pressure of cobaltocene. Indeed, simple exposure of a pristine Al substrate to cobaltocene reduces its work function by 0.3 eV, which is comparable to the energy-level shifts observed between doped and undoped Alq₃. The effect, in this case, is therefore purely one of electrode modification.

Finally, we can speculate on the different levels of CoCp₂ incorporation in THAP and Alq₃. The volatility of the CoCp₂ molecule, which enables the type of vacuum delivery described in Ref. 18 and used here, may be an impediment to the incorporation in the host matrix. In the case of THAP, the data suggest that incorporation occurs as a gas phase molecule hits the surface of the host film and transfers an elec-

tron to a THAP molecule. The resulting ionized dopants are stabilized by Coulomb interaction with the doped THAP molecules on the film surface and are incorporated, whereas the neutral molecules are not, because of insufficient interaction with the surface. As charge transfer is not energetically favorable with Alq₃, the CoCp₂ molecules do not stick to the surface and are not incorporated in the growing film.

IV. SUMMARY

Expanding on a previous study showing efficient *n*-type doping of THAP by cobaltocene,¹⁸ we performed the XPS and RBS experiments to determine the level of dopant incorporation in the bulk of the host film as compared to the film surface or interface. The results indicate that variable and controlled amounts of CoCp₂ can be included in the THAP matrix and that a non-negligible amount of dopant accumulates on the sample surface. Uniformly doped THAP layers show a constant CoCp₂ concentration throughout the film. The investigation of spatially confined layers of cobaltocene shows excellent spatial stability of the dopants, with no observable diffusion through the film up to temperatures of 60 °C.

However, similar attempts to dope Alq₃ with CoCp₂ do not lead to measurable incorporation of the dopant into the host film nor to appreciable accumulation on the Alq₃ surface. Minor improvement in the *I*-*V* measurements and a slight shift of *E_F* toward the unoccupied states are attributed to the modification of the energy-level alignment at the electrode-organic interface. Finally, the far greater level of incorporation of CoCp₂ in THAP versus Alq₃ is attributed to the charge exchange, which stabilizes the ionized dopant on the film surface during growth.

ACKNOWLEDGMENTS

Support of this work by the National Science Foundation (DMR-0408589) and the Princeton MRSEC of the National

Science Foundation (DMR-0213706) is gratefully acknowledged. Work at the Georgia Institute of Technology was supported by the National Science Foundation (CHE-0211419 and the STC Program under Agreement No. DMR-0120967), Lintec Corporation, and by the Office of Naval Research (N00014-04-1-0120).

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