

# Energy-level alignment at interfaces between metals and the organic semiconductor 4,4'-N,N'-dicarbazolyl-biphenyl

I. G. Hill,<sup>a)</sup> A. Rajagopal, and A. Kahn

*Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544*

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We have used ultraviolet photoemission spectroscopy to study the formation of interfaces between the organic semiconductor, 4,4'-N,N'-dicarbazolyl-biphenyl (CBP), and the metals Au, Ag, and Mg. Each interface was studied by depositing the organic on the metal, and by depositing the metal on the organic. The two methods produced inequivalent interfaces, except in the case of Au/CBP. The position of the highest occupied molecular orbital relative to the Fermi level and the magnitude of the interface dipole were measured for each interface. The barrier to electron injection from each metal was estimated using the magnitude of the measured optical gap. An interface dipole, of magnitude nearly independent of the metal work function, was formed when CBP was deposited on a metal surface. The position of the Fermi level within the CBP gap was found to vary strongly with the metal work function. © 1998 American Institute of Physics. [S0021-8979(98)05218-9]

## I. INTRODUCTION

Organic light-emitting devices (OLEDs) have attracted a great deal of attention during the past decade.<sup>1</sup> OLEDs can be made with virtually any visible emission wavelength by choosing an appropriate organic emissive material. The devices are very efficient, and are compatible with relatively low-temperature deposition processes. Devices may be grown on a large number of substrates, including flexible plastics. These characteristics make OLEDs attractive for their potential use in inexpensive large-area displays.

OLEDs contain one or more organic layers sandwiched between two metallic contacts—one used as a hole injector, and the other as an electron injector. The hole/electron injecting contacts are typically made from high/low work-function metals to minimize their respective injection barriers, following the Schottky–Mott model.<sup>2</sup> The use of low work-function cathode metals, such as Ca and Mg, has been successful, but the resulting devices tend to be unstable due to rapid oxidation of the contact material.<sup>3</sup> Furthermore, the process of carrier injection has been found to be more complicated than is described by this model. Electronic states within the gap of the organic, formed through chemical interactions between the organic and metal, have been found to determine the injection properties of some interfaces.<sup>4–6</sup>

Recently, the use of thin cathode interface layers, such as Al<sub>2</sub>O<sub>3</sub>,<sup>7</sup> LiF,<sup>3</sup> and aromatic diamines [including 4,4'-N,N'-dicarbazolyl-biphenyl (CBP)]<sup>8</sup> have been shown to improve the injection characteristics of higher work-function metals, like Al and Ag, to the point where the resulting performance rivals that of the low work-function metals. Suggested explanations for this behavior include tunneling across the cathode interface layer,<sup>3,7</sup> and the formation of “microtip” structures due to the rough interface morphology in the case of Ag on CBP.<sup>8</sup>

We have studied the interface formation between CBP and three metals, Mg, Ag, and Au, using ultraviolet photoemission spectroscopy (UPS). We have used this technique to measure the carrier injection barriers and the interface dipoles, and to look for evidence of gap states indicating chemical interaction between the metal and the organic.

## II. EXPERIMENT

All measurements and depositions were performed in an ultrahigh vacuum system (UHV) (base pressure  $< 1 \times 10^{-10}$  Torr), consisting of a main analysis chamber and a sample preparation chamber. The analysis chamber was equipped with an x-ray source (Al and Zr anodes), a He discharge lamp, and a double-pass cylindrical mirror analyzer. The resolution of the UPS system was  $\approx 150$  meV, determined from the width of the Fermi level observed on polycrystalline Au.

The organic compound was purified *ex situ* by several cycles of gradient sublimation, and was thoroughly degassed after being placed in the UHV preparation chamber. Organic thin films were deposited from heated effusion cells at rates ranging from 5 to 20 Å/min. The pressure during organic deposition was  $\leq 10^{-9}$  Torr. Metals were evaporated from heated tungsten filaments (Au and Ag) or a heated crucible (Mg). Au and Ag were deposited in the analysis chamber at pressures  $\leq 10^{-9}$  Torr, and Mg was deposited in the preparation chamber at  $\leq 10^{-8}$  Torr. All thicknesses were determined by timed depositions calibrated using a quartz-crystal microbalance. No correction was made for sticking coefficients. The substrates used for all samples were gold films deposited on Si(100) wafers. All depositions were performed at room temperature.

Samples were prepared by depositing an organic ( $\approx 100$  Å) or metal ( $\approx 200$  Å) film on a substrate. This surface was then studied using UPS, to determine the ionization energy (IE) and highest occupied molecular orbital (HOMO) position relative to the Fermi level in the case of organic films, or

<sup>a)</sup>Corresponding author; electronic mail: ianhill@ee.princeton.edu

the work function (WF), in the case of metallic films. The IE and WF are defined as the energy difference between the vacuum level and the top of the HOMO or the Fermi level, respectively. The top of the HOMO is estimated by linearly extrapolating the low binding energy side of the HOMO peak to the zero intensity base line. The position of the vacuum level is determined by adding the photon energy to the low-energy secondary electron cutoff collected with the sample at a negative bias ( $-3$  V) to overcome the contact potential between the sample and detector. The lowest energy secondary electrons emerge from the sample at the vacuum level. A hypothetical electron originating at the vacuum level, photoexcited by the same photon energy, would therefore have a kinetic energy one photon energy above that of the lowest energy secondary electrons. These parameters, as well as the shape of the photoemission spectra, were used to assess the quality of the films.

Organic or metal overlayers were then deposited on the original film. UPS spectra were collected as a function of overlayer thickness to determine the vacuum level shift, the position of the HOMO, and to study the evolution of the spectral shape. Both the metal on organic and organic on metal interfaces were studied for each combination.

### III. RESULTS

#### A. Au/CBP interfaces

UPS data and level offset diagrams for the CBP on Au system are shown in Fig. 1. The clean polycrystalline Au film was found to have a WF of 4.9 eV. Deposition of 4 Å of CBP caused an immediate  $\approx 0.4$  eV downward shift of the vacuum level, corresponding to the formation of an interface dipole, with the dipole vector pointing from the Au film into the (positive) CBP layer. Accompanying this shift was the appearance of spectral features characteristic of the CBP overlayer. Further deposition resulted in a slight increase in the vacuum level shift, which saturated at 0.5 eV at 16 Å, increasing CBP feature intensities, and diminishing Au features. At 64 Å the spectrum was characteristic of bulk CBP. The IE of the CBP surface was 6.3 eV, and the top of the HOMO was 1.9 eV below the Fermi level. The position of the lowest unoccupied molecular orbital (LUMO) cannot be measured using UPS, and has been estimated using the measured optical gap of CBP.<sup>9</sup>

Figure 2 contains the UPS and band offset data obtained from the study of Au deposition onto a CBP film. The IE of the initial CBP film was 6.2 eV, and the top of the HOMO was initially 1.8 eV below the Fermi level. 4 Å of Au produced an abrupt upward shift of 0.3 eV in the position of the vacuum level. The relative positions of the Fermi level and HOMO of the clean film are fixed by the substrate Au/CBP interface. The Fermi level was therefore, not expected, or observed, to shift within the CBP gap upon Au deposition. The direction of the associated surface dipole was the same as that found in the CBP on Au system. 18 Å of Au produced spectra characteristic of bulk Au, although the WF was found to be 4.7 eV, which is 0.2 eV lower than that of the Au film studied above.

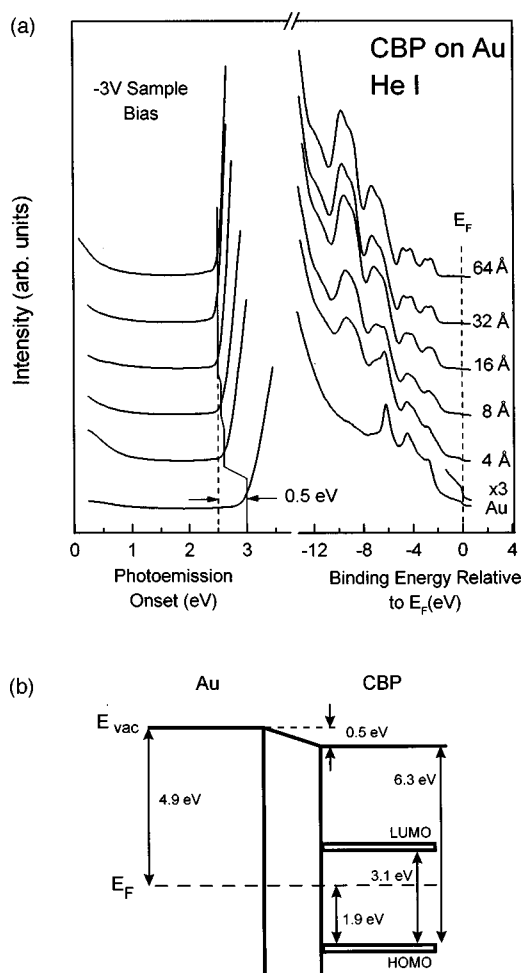


FIG. 1. (a) He I UPS spectra for the CBP deposited on Au system. The bottom spectrum was collected from the clean Au surface. The vacuum level shift, derived from the secondary electron cutoff, is labeled. (b) The parameters extracted from the data in (a) were used to construct an energy diagram for the interface.

#### B. Ag/CBP interfaces

The results of the deposition of CBP on Ag are presented in Fig. 3. The WF of the clean Ag surface was 4.1 eV. Deposition of 4 Å of CBP caused an abrupt  $\approx 0.4$  eV downward shift of the vacuum level, as it did in the CBP on Au system. The shift reached its final value of 0.5 eV at a thickness of  $\approx 16$  Å. The bulk CBP features observed at a thickness of 64 Å revealed the top of the HOMO to be 2.5 eV below the Fermi level, and the IE was found to be 6.1 eV.

Deposition of Ag on CBP revealed a much different behavior than CBP on Ag, as illustrated in Fig. 4. The clean CBP surface had an IE of 6.3 eV, and the HOMO was located 1.9 eV below the Fermi level. Deposition of 8 Å of Ag resulted in a 0.8 eV downward vacuum level shift, accompanied by a 0.5 eV downward shift in the CBP spectral features. The vacuum shift is therefore composed of two components: a 0.5 eV upward shift of the Fermi level within the gap of CBP, and a 0.3 eV interface dipole shift. Prior to Ag deposition, the position of the Fermi level within the gap is determined by the substrate Au/CBP interface  $\approx 100$  Å below the surface. Depositing any metal, other than Au, on this

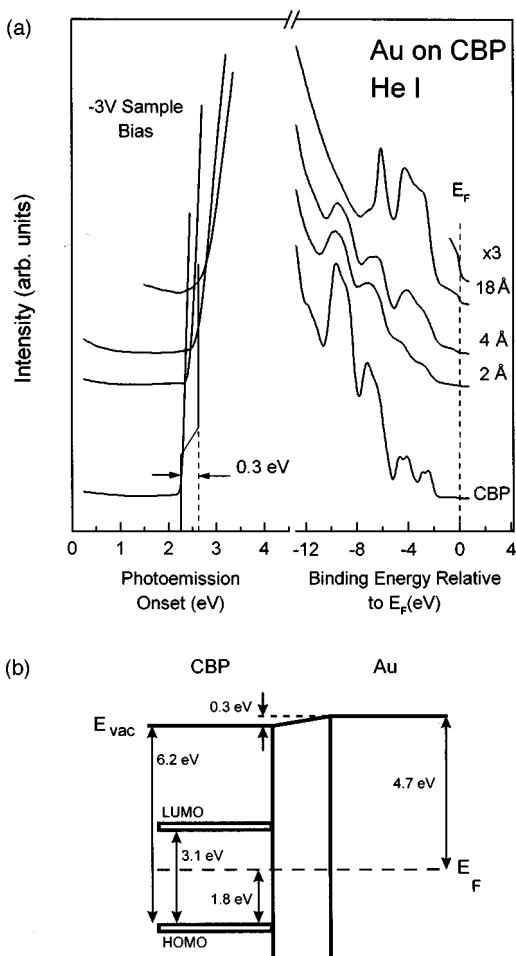


FIG. 2. Same as in Fig. 1, for Au deposited on CBP.

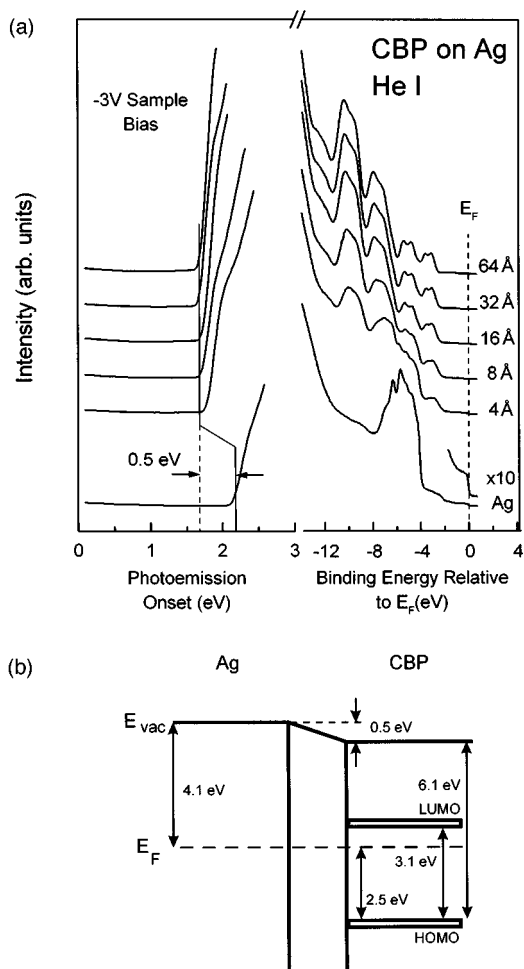


FIG. 3. Same as in Fig. 1, for CBP deposited on Ag.

surface should therefore cause the Fermi level to shift within the CBP gap. The dipole shift corresponds to a dipole vector pointing from the CBP towards the Ag, which is the direction *opposite* that observed in the case of CBP on Ag. It was believed that this contrasting behavior might be attributed to a chemical interaction between the hot metal atoms with the relatively soft organic surface that may not occur during the lower temperature deposition of the organic on a room-temperature metal film. However, x-ray photoelectron spectroscopy studies of the Ag( $3d$ ) and C( $1s$ ) levels revealed no evidence of chemical interactions. Finally, the deposition of 256 Å of Ag on CBP did not completely quench the CBP features, perhaps indicating that Ag islands form which do not completely cover the CBP surface.

### C. Mg/CBP interfaces

The results of our studies of the CBP on Mg system are shown in Fig. 5. A clean film of Mg was deposited, and its WF was measured to be 3.8 eV. Deposition of CBP on the Mg surface resulted in a 0.4 eV downward shift of the vacuum level at 64 Å exposure. This shift was not as abrupt as observed in the CBP on Au/Ag systems which saturated after 16 Å nominal coverage. The concomitant growth of intensity of the CBP features was much slower than the previous systems, indicating that the sticking coefficient of CBP

on Mg may be much smaller than on Au or Ag. The top of the HOMO was found to be 2.6 eV below the Fermi level at 64 Å nominal coverage.

The UPS data from our study of Mg on CBP are presented in Fig. 6. Exposure of the clean CBP surface to the Mg flux caused a 0.2 eV downward shift of the HOMO position with respect to the Fermi level, accompanied by a 0.4 eV downward shift of the vacuum level. Increasing Mg exposure tended to smear the CBP features, but their intensities remained quite high, even after exposure to 256 Å of Mg. At this coverage there was no clear Fermi step in the UPS spectrum. These observations indicated that there was very little Mg present on the surface. The Mg may diffuse into the CBP film, or have a low sticking coefficient on the surface. Given that the initial CBP film was  $\approx 100$  Å thick, and was exposed to a Mg flux corresponding to a 256 Å thickness at the Mg bulk density, we favor the latter explanation. This is also supported by the empirical observations of device growers, who commonly use a Mg/Ag alloy to insure adhesion of Mg-based cathodes in organic semiconductor devices.

## IV. DISCUSSION

### A. CBP on metals

A summary of our results for CBP on metal surfaces can be found in Fig. 7. The position of the Fermi level with

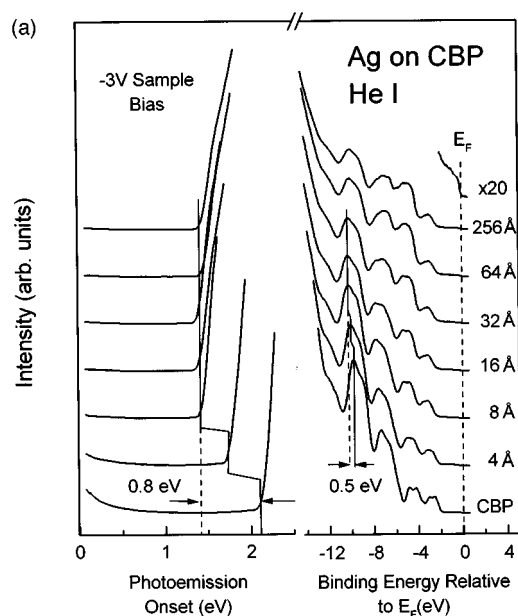


FIG. 4. Same as in Fig. 1, for Ag deposited on CBP.

respect to the HOMO is found to vary strongly, and linearly, with the metal WF. The magnitude of the surface dipole was found to be relatively insensitive to the WF of the metal. One inconsistency in these results may be noted—if the magnitude of the surface dipole is constant, one would expect the magnitude of the slope in Fig. 7(a) to be 1, not 0.63. This discrepancy is due to the IE of the CBP film varying from 6.0 eV on Mg to 6.3 eV on Au. This difference in IE may be a result of differing surface morphologies, or may indicate that the 64 Å films are not representative of the bulk CBP electronic properties. Sample charging prohibits much thicker films from being studied. Further study is required to fully understand this discrepancy.

Ishii and Seki have found similar behavior of the dipole for ZnTPP on metals.<sup>10</sup> They argue that a constant value of the surface dipole indicates that it cannot be due to chemical bonding, as this would be metal dependent. They further suggest that an electrostatic interaction, due to the image potential at a metal surface, may explain why the dipole shift is independent of the metal work function. In such a scenario, the outermost electrons of a molecule at the surface experience an attractive force toward the metal surface due to their image potentials. This additional electrostatic potential would cause a redistribution of the electronic charge on these molecules, with the resulting center of the (negative) electronic charge distribution being closer to the metal sur-

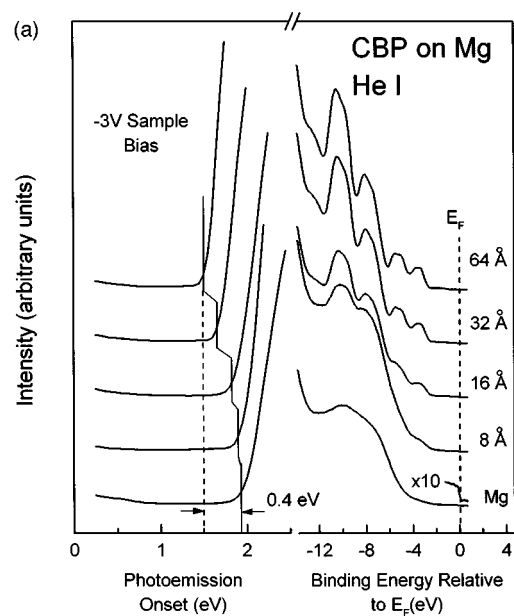


FIG. 5. Same as in Fig. 1, for CBP deposited on Mg.

face than the (positive) nuclear charge distribution, resulting in an electric dipole pointing away from the metal surface. The image potential of an electron at a metal surface decays as  $1/r$ , so only the first layer of organic molecules would effectively contribute to this effect. This explanation is qualitatively satisfying, as it explains the orientation of the dipole, its abruptness, and its constancy. At this time, however, it is not known if the observed magnitude of the dipole is reasonable.

To date, many metal/organic interfaces have been studied by UPS. The existence of an interface dipole shift is a common feature of all such interfaces. The dependence of the interface dipole magnitude on the metal work function varies from organic to organic. For instance, if the magnitude of the interface dipole is plotted as a function of the metal work function, the slope of the resulting linear relationship is found to be  $\approx 1$  for PTCDA,<sup>11</sup>  $\sim 0.2$  for  $\text{Alq}_3$ <sup>11</sup> and is between 0.5 and 0.9 for  $\alpha$ -NPD,  $\text{H}_2\text{TPP}$ , and  $\text{H}_2\text{T}(4\text{-Py})$ .<sup>10</sup> The current study has shown that the corresponding slope for CBP/metal interfaces is  $\approx 0$ , as was found for ZnTPP/metal interfaces.<sup>10</sup> The origins of these dipole shifts are not currently understood, but the spectroscopic measurements have clearly demonstrated their existence. The common assumption of vacuum level alignment clearly breaks down at these interfaces.

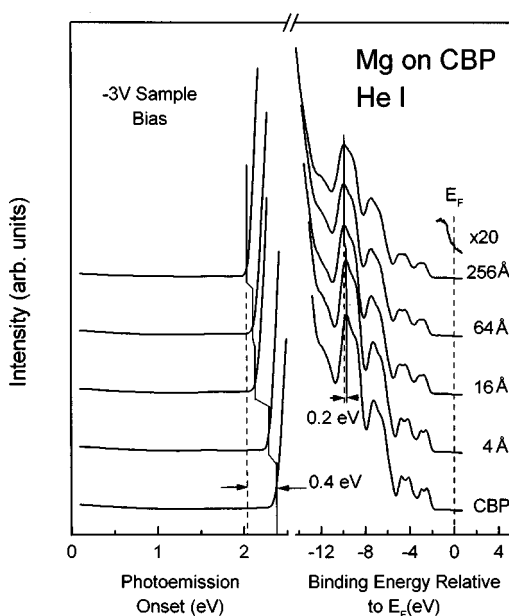


FIG. 6. Same as in Fig. 1(a), for Mg deposited on CBP. A metallic Mg overlayer was not formed, so an interface energy diagram is not included.

## B. Metals on CBP

Studies of organic thin films on metals<sup>5,6,10</sup> are much more common than the reverse.<sup>4,12,13</sup> In general, the interfaces formed are not equivalent. The asymmetry is due to the differences in heats of adsorption and surface bond strengths of the organic and the metal.<sup>12</sup> When depositing an organic on a metal, the strongly bonded surface atoms are not affected by the low-energy organic molecules, which are typically evaporated at relatively low temperatures. In contrast, the molecules in an organic film form a weakly bonded van der Waals solid, which are easily disturbed by the deposition of energetic metal atoms from a high-temperature evaporation source. The organic surface may, therefore, be modified by the deposition of metal atoms, and the metal atoms may diffuse into the organic layer. The deposition of an organic on a metal typically results in an abrupt interface, while the interfaces formed by depositing metals on organics are often broad and not well defined.

The deposition of Au on CBP resulted in an abrupt interface, which appeared to be equivalent, within experimental error, to the deposition of CBP on Au. Au has also been found to produce abrupt interfaces when deposited on perylenetetracarboxylic dianhydride (PTCDA).<sup>5,6</sup> The spectral features of CBP were completely quenched by a few atomic layers of Au, indicating that the metal wets the surface, and the UPS spectrum of the CBP+18 Å Au surface was characteristic of bulk Au. The position of the Fermi level and the magnitude of the surface dipole agree within experimental error with the values obtained for the CBP on Au surface.

The Mg and Ag on CBP systems did not form abrupt interfaces. The deposition of small quantities ( $\leq 16$  Å) of either Mg or Ag on the clean CBP surface shifted the Fermi level toward the LUMO within the gap of the CBP, and caused the formation of a surface dipole with opposite direc-

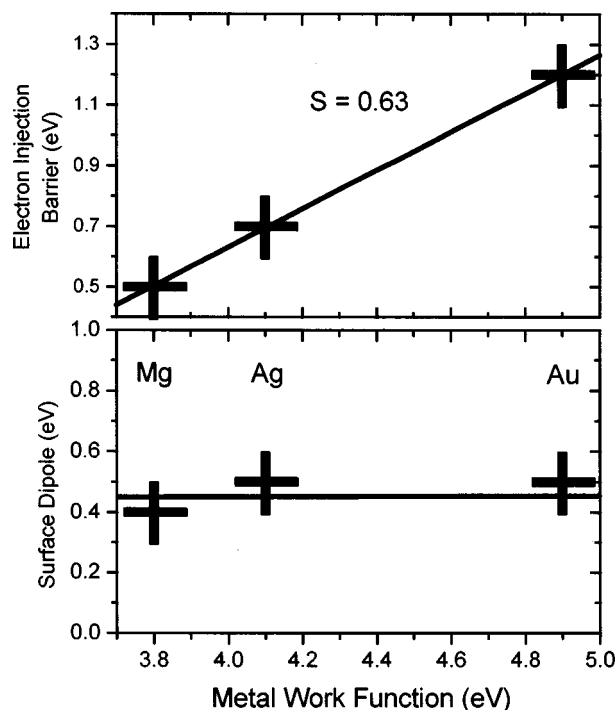


FIG. 7. The data from the studies of CBP on Au, Ag, and Mg are summarized. The top panel shows the barrier to electron injection from the metal to the organic and the  $S$  parameter, which is equal to 0.63. The bottom panel shows the magnitude of the interface dipole, which is found to be insensitive to the metal work function, within the accuracy of the experiment.

tion, when compared to the dipole formed by deposition of the organic on metals. Above these coverages, the Mg and Ag systems differ, in that Ag features, including a well-defined Fermi step, begin to form, indicating the coexistence of CBP and Ag on the surface. The Mg on CBP system does not exhibit any Mg features, even after exposure to 256 Å of Mg. A well-defined Fermi edge is not formed. The final spectrum is indicative of a degraded CBP surface. The movement of the Fermi level may be explained by diffusion of the metal atoms into the surface, which then act as donors, doping the CBP and shifting the Fermi level toward the LUMO, which is the organic equivalent of the conduction band. Ga has been shown to diffuse into tris (8-hydroxy quinoline) aluminum ( $AlQ_3$ ) (Ref. 14) without a significant shift of the Ga 3d core level being observed, consistent with our observations of Ag on CBP. Another explanation for the Fermi level movement may be the formation of defect states at the surface, resulting from the damage caused by incident metal atoms. These states may then pin the Fermi level at the surface.

Ag on CBP has been shown to be an efficient electron injector,<sup>8,15</sup> comparable to Mg on CBP, although our studies of CBP on these metals indicate that there is a substantial barrier to electron injection at these abrupt organic on metal interfaces: 0.5 eV for Mg and 0.6 eV for Ag. The injection characteristics of the real devices cannot be understood simply from the measured spectroscopic injection barriers. We do not see any gap states, indicating a chemical reaction between the organic and the metal, which would assist electron injection through a hopping mechanism.<sup>4-6</sup> Our obser-

vations do suggest that the Ag does not form a smooth layer on the CBP surface, which may support the model of Kanai *et al.* who suggest that the rough interface morphology may assist in electron injection.<sup>8</sup>

## V. CONCLUSION

We have used ultraviolet photoemission spectroscopy to study the formation of interfaces between the organic semiconductor CBP and the metals Au, Ag, and Mg. Each interface was studied by depositing the organic on the metal, and by depositing the metal on the organic. The Au on CBP and CBP on Au interfaces were found to be equivalent, while the deposition of Ag or Mg on CBP resulted in metal island growth, and perhaps diffusion into the organic film. Deposition of CBP on a metal surface results in the formation of an interface dipole indicating electron transfer from the organic to the metal. The magnitude of the dipole is constant, and the position of the Fermi level within the CBP gap, therefore, varies strongly with the metal work function.

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