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Effect of electrostatic screening on apparent shifts in photoemission spectra near metal/organic interfaces

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Photoemission spectra of very thin organic films differ from that of thicker bulklike films. In particular, the binding-energy shifts in molecular orbitals at metal/organic interfaces vary as a function of the organic overlayer thickness. Using a simple image-charge model it is found that electrostatic screening can have a significant effect on the final-state relaxation energy. Good agreement between experimental results and theoretical calculations for a variety of dielectric substrates indicate that reported thickness dependent energy-level shifts in organic overlayer spectra can be accounted for by electrostatic screening. Models of organic interfaces based on photoemission spectra of organic thin films should therefore be re-examined.

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In the study of organic interfaces photoelectron spectroscopy (PES) has been extensively used to study the electronic structure of organic thin films deposited on various inorganic substrates. It is often observed that the PES spectra of very thin organic films differ from that of thicker bulklike films. In particular, the binding-energy shifts in molecular orbitals at metal/organic interfaces have been reported to vary as a function of the organic overlayer thickness. The spectral features of the organic overlayer are found to shift to higher binding energy with increasing film thickness.[1–4] The interpretation of these apparent thickness dependent organic overlayer spectra have, however, remained a source of contention.[5–7] More than two decades ago a similar debate was waged over the interpretation of PES spectra of the $\mathrm{Si/SiO_2}$ interface. Shifts on the order of $\sim$1 eV in the $\mathrm{SiO_2}$ spectral features were observed between thin and thick $\mathrm{SiO_2}$ layer films.[8–10] It is now well established that these apparent thickness dependent shifts are a result of electrostatic screening effects on the final-state relaxation energy.[11–13] However, in the case of metal/organic interfaces the effect of electrostatic screening on PES spectra has in general been overlooked.

In this paper, we demonstrate that the experimentally observed binding-energy shifts for a prototypical organic semiconductor on various conductive substrates are consistent with electrostatic screening. Although several authors have qualitatively discussed electrostatic screening at metal/organic interfaces,[14,15] this work provides detailed theoretical calculations quantifying the direction and magnitude of the apparent binding-energy shifts, including valence-band features, for an amorphous organic semiconductor. Good agreement between experimental results and theoretical calculations for a variety of different metallic and dielectric substrates strongly suggests that many of the reported thickness dependent energy-level shifts in organic overlayer spectra are a result of electrostatic screening. Therefore many models of the energy-level alignment at organic interfaces based on PES spectra of organic thin films need to be reexamined.

The substrates used in this study were selected to represent a range of dielectric properties. Au, Cu, and Ag thin films were prepared on Si(100) as described elsewhere.[16] H-terminated Si(100) was prepared by several cycles of UV ozone treatment and etching in 5% hydrofluoric acid.[17] Highly orientated pyrolytic graphite (HOPG) was freshly cleaved prior to use. After sample preparation, substrates were immediately loaded into a PHI 5500 Multi-Technique system attached to a Kurt J. Lesker multiaccess chamber ultrahigh vacuum cluster tool.[18] The base pressure of the entire system was $\sim 10^{-10}$ Torr. The metallic substrates were $\mathrm{Ar^+}$ sputter cleaned until the C 1s and O 2p signals vanished and consistent work function measurements were obtained. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed at a photoelectron take-off angle of 90° and with a -15 V bias applied to the sample.[19] Peak positions were determined using a polynomial fit to the top 5% of the peak.[20]

To calculate the effect of electrostatic screening on the final-state relaxation energy we applied a classical dielectric continuum model. We consider a system of three dielectric layers, with permittivities of ε_1, ε_2, and ε_3, in contact with each other as shown in Fig. 1: a semi-infinite substrate slab $(z<0)$, an organic overlayer of thickness $d(0<z<d)$ and the vacuum above the organic thin film $(z>d)$. The reflection coefficients at the dielectric boundaries are defined as,

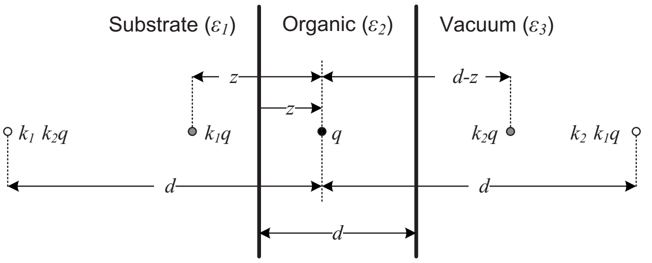

FIG. 1. Dielectric continuum model of an organic overlayer on a substrate with point charge $q=e$ in the organic layer. ε_1, ε_2, and ε_3 are the permittivities of each layer and k_1 and k_2 are the reflection coefficients at the dielectric boundaries. The image charges shown are from the $n=0$ term of Eq. (2).

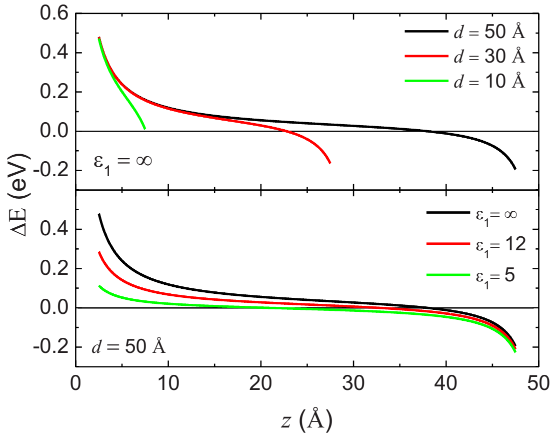

FIG. 2. (Color online) Correction to the binding energy as a function of the position (z) in the organic film for different organic layer thickness (d) and substrate permittivity (ε_1). The permittivity of the organic was taken as $\varepsilon_2=3.0$

$$k_1=\frac{\varepsilon_2-\varepsilon_1}{\varepsilon_2+\varepsilon_1} \quad \text{and} \quad k_2=\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}. \tag{1}$$

A metal can be substituted for the dielectric substrate by using a jellium slab, in which case $k_1=-1$. The correction to the final-state relaxation energy can be calculated by solving Poisson's equation. For an excitation in the second dielectric layer (i.e., the organic film) we obtain,

$$\Delta E=-\frac{e^2}{16\pi\varepsilon_0\varepsilon_2}\sum_{n=0}^{\infty}(k_1k_2)^n\left[\frac{k_1}{z+nd}+\frac{k_2}{(n+1)d-z}+\frac{2k_1k_2}{(n+1)d}\right], \tag{2}$$

where e is the electron charge and ε_0 is the permittivity of free space. Equation (2) represents the binding-energy shift due to an infinite series of image charges, reflected in the two dielectric interfaces; for a complete derivation see Ref. 21. A similar approach was used to describe the electrostatic screening at the Si/SiO$_2$ interface[11] and for physisorbed rare-gas multilayers[22] on various substrates.

Figure 2 shows the calculated correction to the binding energy as a function of the position z in the organic overlayer for different film thicknesses d and substrate permittivity ε_1. To calculate the net effect of the z dependent binding-energy shift on PES spectra of the organic overlayer the contribution to the measured signal from different depths in the organic are summed, following the procedure from Ref. 11. The sum includes the attenuation due to the electron mean-free paths over the escape depth in the organic. The total shift in the binding energy for a thin organic overlayer is referenced to that of a thick overlayer. This approach avoids the energy artifacts due to the artificial divergence of classical electrostatics near the vacuum interface for the dielectric continuum model.[11] Similarly, the sum is terminated a finite distance near the substrate interface. The minimum distance was taken as the mean substrate-molecule separation of ~2.5 Å,[23–25] corrected by ~0.5 Å for metallic substrates[26,27] based on the overlap of charge density at the interface estimated from calculations for a jellium slab. Figure 3 shows the net correction to the binding energy as a function of organic film thickness d for different photoelectron escape depths λ. The inset shows calculated model spectra for two different film thicknesses on a metallic substrate. Due to the exponential dependence of the signal intensity on the depth in the organic layer, the shifted peaks are only slightly asymmetrically broadened.

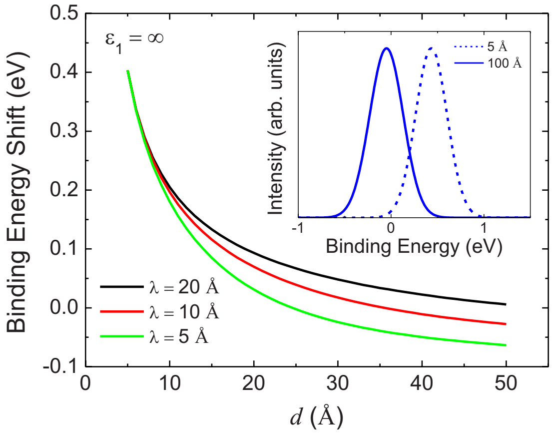

FIG. 3. (Color online) Binding-energy shift as a function of organic film thickness (d) for different photoelectron escape depths (λ). The inset shows calculated model spectra for two different film thicknesses on a metallic substrate.

Typically, the Auger-parameter—the sum of the kinetic energy of the sharpest Auger line and the binding energy of the most intense photoemission peak—has been used to evaluate the effect of electrostatic screening on the final-state relaxation energy near dielectric interfaces. The Auger parameter has the advantage that it is independent of sample charging and energy scale referencing. However, for organic semiconductors shifts in the valence levels are a more useful metric, since the Auger features of C and N are in general too weak to accurately determine changes in the Auger parameter, particularly for very thin organic films. In addition the prolonged exposure to x-rays required to accurately measure the core-level binding energies for very thin organic films using x-ray photoelectron spectroscopy (XPS) can lead to additional binding-energy shifts, which are difficult to correct for. Alternatively, changes in valence levels can be measured using UPS with much greater precision and without x-ray induced binding-energy shifts. More importantly, it is the valence levels of organic molecules that are typically of interest in most studies.[28–31] It is therefore not only more practical, but also more meaningful to evaluate the effect of electrostatic screening on the final-state relaxation energy of the valence levels for organic semiconductors. Most organic semiconductors are amorphous with highly localized electronic states, even for valence levels, due to weak intermolecular van der Waals interactions. The simple image-charge model assuming point charges given by Eq. (2) should therefore be applicable to both core- and valence-level excitations.

Figure 4 shows the evolution of the He Iα ($h\nu=21.22$ eV) valence-band spectra and secondary electron

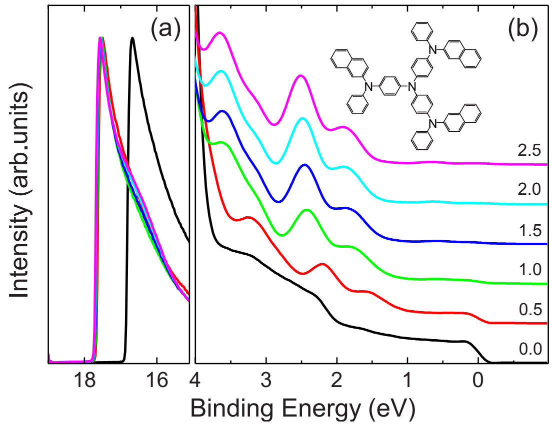

FIG. 4. (Color online) He Iα ($h\nu = 21.22$) valence-band spectra of the Ag/2T-NATA interface showing the evolution of (a) the secondary electron cutoff and (b) the HOMO of 2T-NATA. The 2T-NATA thickness is shown in (b) in nm. The molecular structure of 2T-NATA is shown in the inset.

cutoff of a Ag thin film during the layer-by-layer deposition of 4,4′,4″-tris[N-(naphthalen-2-yl)-N-phenyl-amino]triphenylamine (2T-NATA) to a total thickness of 25 Å. We chose to use 2T-NATA since it is an amorphous organic semiconductor, which is representative of the most commonly used molecules used in devices.[32,33] The highest occupied molecular orbital (HOMO) of the organic overlayer is found to shift to higher binding-energy with increasing film thickness. The total shift between the first and last deposition is ~0.5 eV. Since the work function of the sample remained constant after the first deposition of organic molecules [see Fig. 4(a)], we conclude that the interfacial dipole is confined to the first monolayer of molecules only, and hence cannot account for the thickness dependent shifts. We also confirmed no charging of the sample by comparing the work function measured by XPS and UPS.

Figure 5 shows the measured position of the HOMO for 2T-NATA as a function of layer thickness for substrates with different dielectric properties. Calculation results for the electrostatic screening induced binding-energy shifts using Eq. (2) are shown as solid lines in the figure. Good agreement between the experimental results and theoretical calculations for a variety of different substrates strongly suggests that electrostatic screening plays an important role in the apparent thickness dependent binding-energy shifts. Even more compelling is the good agreement between substrates with similar dielectric properties (e.g., the different metals).

One obvious implication of electrostatic screening is the measured ionization potential for an organic thin film. For the examples shown in Fig. 5 the work function of the substrate remained constant after the first deposition of organic molecules [see Fig. 4(a)]. However, due to the effect of electrostatic screening the measured position of the HOMO varied with film thickness and dielectric constant of the substrate. As a result the measured ionization potential of the organic also varied from 4.55–5.0 eV depending on the substrate and film thickness. For film thicknesses >2.5 Å the measured ionization potential of the 2T-NATA converged to a constant value of 5.0 eV, in good agreement with transport-based measurements.[32] This finding explains the wide variation in reported ionization potential for the same molecule in literature (i.e., different studies use different substrates and film thicknesses) and also highlights the need for using consistent substrates and film thicknesses when measuring the properties of organic thin films.

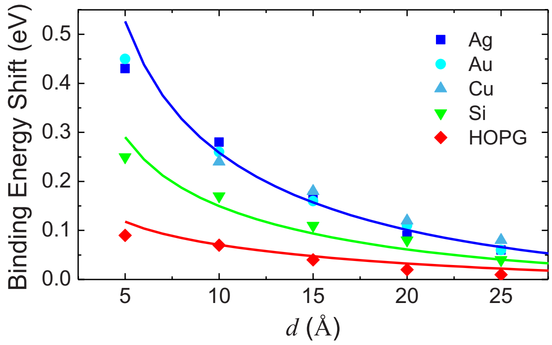

FIG. 5. (Color online) Comparison of the experimental (symbols) and theoretical (lines) binding-energy shift in the HOMO of 2T-NATA as a function of the organic film thickness (d) for various substrates. The photoelectron escape depth $\lambda = 6.4$ Å was determined from the attenuation of the Fermi edge of the Ag substrate with film thickness and is in good agreement with Ref. 35. The permittivity of Si and HOPG were taken as $\varepsilon_1 = 12$ and $\varepsilon_1 = 6$, respectively.

Finally, we have to comment on the validity of the dielectric continuum model to describe the electrostatic screening induced binding-energy shifts for organic thin films. In the present work, the dielectric continuum model yielded satisfactory results since the molecule we used, 2T-NATA, is amorphous with isotropic dielectric properties. However, this simple model may not be sufficient to describe electrostatic screening in well ordered or polycrystalline organic thin films, such as phthalocyanines, where the dielectric properties are anisotropic.[34]

In summary, we have shown that the experimentally observed thickness dependent binding-energy shifts for a prototypical organic semiconductor on various conductive substrates are well explained by electrostatic screening. This finding demonstrates that the spectral shifts observed in PES spectra of organic semiconductors near metal/organic interfaces could easily be caused by electrostatic screening. This brings into question many models of organic interfaces based on PES spectra of organic thin films. In particular, the effects of electrostatic screening must be taken into account when measuring the properties of organic thin films such as the ionization potential.

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