Controlling Schottky energy barriers in organic electronic devices using self-assembled monolayers

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We demonstrate tuning of Schottky energy barriers in organic electronic devices by utilizing chemically tailored electrodes. The Schottky energy barrier of Ag on poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-1,4-phenylene was tuned over a range of more than 1 eV by using self-assembled monolayers (SAM's) to attach oriented dipole layers to the Ag prior to device fabrication. Kelvin probe measurements were used to determine the effect of the SAM's on the Ag surface potential. *Ab initio* Hartree-Fock calculations of the molecular dipole moments successfully describe the surface potential changes. The chemically tailored electrodes were then incorporated in organic diode structures and changes in the metal/organic Schottky energy barriers were measured using an electroabsorption technique. These results demonstrate the use of self-assembled monolayers to control metal/organic interfacial electronic properties. They establish a physical principle for manipulating the relative energy levels between two materials and demonstrate an approach to improve metal/organic contacts in organic electronic devices. [S0163-1829(96)52744-X]

Electronic devices made from conjugated organic materials have potential fabrication, mechanical, and cost advantages.[1] Organic light emitting diodes (LED's) are particularly promising[2–4] and transistors,[5] photodetectors,[6] and other devices have also been demonstrated.[7] In organic LED's, electrons and holes are injected from metal contacts into an undoped organic material where they subsequently recombine emitting light. In order to achieve efficient injection, it is necessary that both the electron and hole injecting contacts have small Schottky energy barriers.

Contacts can be a serious problem that can limit the performance and stability of organic electronic devices such as LED's. Metal/organic Schottky energy barriers have been shown to follow ideal Schottky behavior; that is, the electron (hole) Schottky barrier is determined by the energy difference between the metal work function and the electron affinity (ionization potential) of the organic material.[8,9] Therefore, low work-function metals are used for electron injection and high work-function metals are used for hole injection. The work functions of metals which can be used for contacts span a relatively restricted range from about 3 to 6 eV. The electron affinities and ionization potentials of organic materials often lie outside these values and therefore it is desirable to extend the effective range of work functions for contact metals.

In this paper, we demonstrate that the Schottky energy barrier between a metal and a conjugated organic material can be manipulated by the insertion of an oriented dipole layer between the metal and the organic material. We specifically consider Ag electrodes and the electroluminescent conjugated polymer poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV). Self-assembled monolayer (SAM) techniques were used to attached a monolayer of polar molecules to the surface of the Ag electrode. Because of the ordering inherent in the SAM

structure, the molecular dipoles are oriented relative to the metal surface. This chemically tailored electrode is then used in the fabrication of the organic electronic device.

Schematic energy level diagrams of metal/organic interfaces which illustrate the approach are shown in Fig. 1. Figure 1(a) represents the untreated metal/organic interface, i.e.,
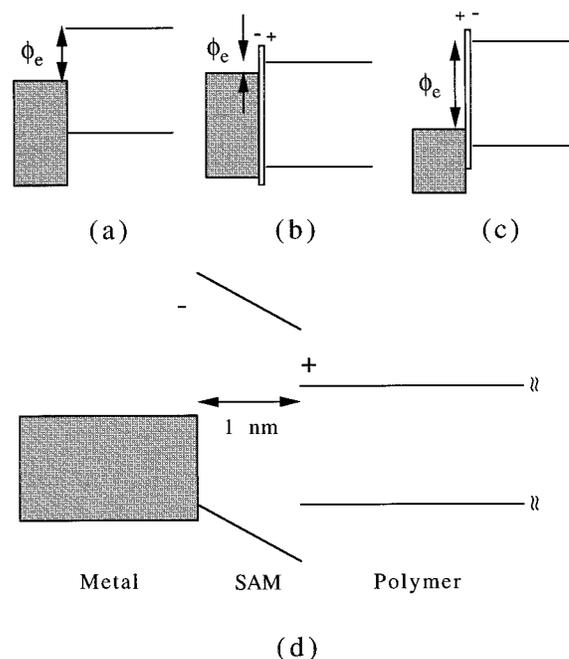

FIG. 1. Schematic energy level diagrams of metal/organic interfaces: panel *a*, untreated interface; panel *b* (panel *c*), dipole layer which decreases (increases) the electron Schottky energy barrier; and panel *d*, magnified view of the interface.

H-S(CH$_2$)$_9$CH$_3$

2.24 D

H-S(CH$_2$)$_{10}$NH$_2$

1.77 D

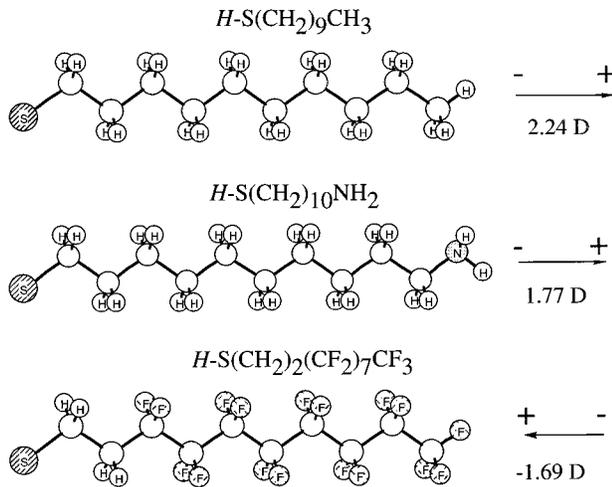*H*-S(CH$_2$)$_2$(CF$_2$)$_7$CF$_3$

-1.69 D

FIG. 2. Molecular structure of the neutral radicals for the three SAM's used in the study. Also shown are the results of *ab initio* Hartree-Fock calculations of the molecular dipole moments of the three neutral radicals.
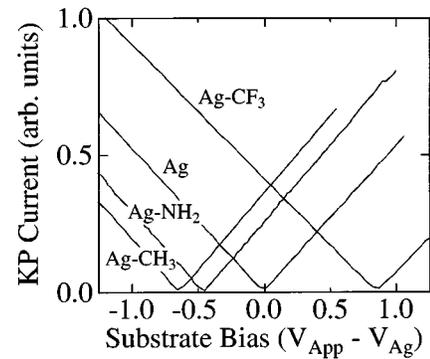

FIG. 3. Kelvin probe current as a function of substrate bias for a pristine Ag electrode and for Ag electrodes modified by the three SAM's. The applied substrate bias has been shifted by the difference in the surface potentials of the Kelvin probe tip and the pristine Ag substrate.

there is no SAM dipole layer on the metal. The electron Schottky energy barrier ϕ_e is the energy difference between the metal Fermi energy and the lowest unoccupied single-electron state of the organic film. Figures 1(b) and 1(c) show the effect of inserting an oriented dipole layer between the metal and the organic film. In Fig. 1(b), the dipole layer is oriented so that the electron Schottky energy barrier is decreased and in Fig. 1(c), the dipole layer is oriented so that the electron Schottky energy barrier is increased. Figure 1(d) is a magnified view of the interface showing a 1-nm-thick SAM with an electric field across it representing the effect of the dipole layer. In this work, we demonstrate control of the metal/organic Schottky energy barrier utilizing SAM's to insert an oriented dipole layer between the metal and the organic material.

Three thiol adsorbates, shown in Fig. 2, were used to form the self-assembled monolayers: CH$_3$(CH$_2$)$_9$SH[CH$_3$ SAM], NH$_2$(CH$_2$)$_{10}$SH[NH$_2$ SAM], and CF$_3$(CF$_2$)$_7$(CH$_2$)$_2$SH[CF$_3$ SAM]. When the thiol adsorbate forms a monolayer film on the surface of Ag, the hydrogen attached to the sulfur is removed and the sulfur bonds to the Ag. Also shown in Fig. 2 are the results of *ab initio* Hartree-Fock calculations of the molecular dipole moments of the neutral radicals (i.e., the thiol with the hydrogen removed) of the adsorbates. These adsorbates were chosen because their self-assembly properties have been extensively studied and they are known to form dense, well-ordered monolayers on the (111) surface of the column *Ib* metals[10–17] and because the set includes molecules with dipole moments of both signs. Employing adsorbates with opposite dipole moments demonstrates control of the Schottky energy barrier; a SAM with one sign of the dipole moment decreases the electron Schottky energy barrier while a SAM with the opposite sign of the dipole moment increases the electron Schottky energy barrier.

The self-assembled monolayers were formed by immersing Ag electrodes in 10^{-3} M solutions of the adsorbate in ethanol. The Ag electrodes were semitransparent (10 nm) films on glass substrates to allow optical access to the diode structures. They were prepared by vacuum sputter deposition and were dominantly (111) oriented. The structure and coverage of the SAM layers on the Ag substrates were consistent with previous work.[11,12] Silver was chosen as the electrode because its work function is well within the MEH-PPV energy gap, which allows the electron Schottky energy barrier to be both increased and decreased.

We determined the electrostatic effect of the dipole layer on the chemically tailored electrodes by measuring the change in their surface potential with respect to pristine Ag using a Kelvin probe. In the Kelvin probe technique, the substrate metal surface and a metallic, vibrating probe tip constitute the two plates of a capacitor. The vibration of the probe tip induces an ac current. The current is nulled when the voltage applied to the tip is equal to the difference in surface potential between the tip and the substrate.

Figure 3 shows the Kelvin probe current as a function of substrate bias (V_{App}-V_{Ag}) for a pristine Ag electrode and for Ag electrodes modified by the three SAM's. The applied substrate bias V_{App} has been shifted by the difference in surface potential between the Kelvin probe tip and the pristine Ag substrate V_{Ag}. The difference V_{App}-V_{Ag} represents the change in surface potential with respect to the pristine Ag electrode. The CH$_3$, NH$_2$, and CF$_3$ SAM's change the surface potential with respect to pristine Ag by -0.70, -0.45, and 0.85 V, respectively. The CH$_3$ and NH$_2$ SAM's decrease the effective work function and the CF$_3$ SAM increases the effective work function of the Ag electrode.

The expected surface potential shift due to a molecular dipole layer has the form

$$\Delta\theta = N\left(\frac{\mu_{mol}}{\varepsilon} + \mu_{Ag^+S^-}\right)$$

where N is the areal density of molecules, μ_{mol} is the dipole moment of the molecule, $\mu_{Ag^+S^-}$ is the screened dipole moment of the Ag$^+$S$^-$ bond, and ε is a static dielectric constant. For the SAM's investigated here N takes on values between about 3 and 5×10^{14} cm^{-2} and ε is between 2 and 3.[10–17] The precise value of $\mu_{Ag^+S^-}$ is hard to estimate, but it is expected to have the sign of the CF$_3$ SAM and to be nearly the same for the three SAM's.[10]

We have studied the dipole moments of the SAM's using *ab initio* quantum chemistry techniques.[18] The adsorbate is viewed as a free thiol in which the S-H bond is replaced by a S-Ag interaction. The molecular geometry of the free thiol is obtained by minimizing the energy at the Hartree-Fock level of approximation using a minimal STO-3*G* basis set.[18] The thiol hydrogen is then removed, and the dipole moment of the resulting radical calculated using a more extensive 6-31*G* basis set.[18] The calculated dipoles listed[19] in Fig. 2 give the correct trends and approximate absolute magnitudes for the measured surface potential shifts of the three SAM films.

Metal/polymer Schottky energy barriers were investigated in diode structures consisting of a semitransparent Ag electrode on a glass substrate, an undoped MEH-PPV polymer layer roughly 50 nm thick, and a top Ca contact. The structures were fabricated in an inert atmosphere using spin casting to produce the polymer film. The top metal contact was vacuum evaporated through a shadow mask to produce diodes with active areas of 4×10^{-2} cm^2. The diode structures were loaded into a vacuum cryostat and measured at room temperature.

Organic diodes have a built-in electrostatic potential in the organic layer equal to the difference between the metal/organic electron Schottky energy barriers of the two metal contacts,

$$V_0 = (\phi_{e1} - \phi_{e2}),$$

where $\phi_{e1(2)}$ is the electron Schottky energy barrier for metal 1(2). The electron Schottky energy barrier is equal to the difference between the polymer electron affinity and the metal work function if the work function of the metal lies within the energy gap of the polymer. It is zero if the work function of the metal is less than the polymer electron affinity and equal to the energy gap if the work function is greater than the polymer ionization potential.

We use an electroabsorption technique[9,20] to measure these electrostatic potentials and thus determine the Schottky energy barrier in the Ag/polymer/Ca structures. The built-in potential is determined by applying an external dc bias of opposite polarity to the built-in field and measuring the external potential at which the electroabsorption signal is nulled, i.e., the bias necessary to cancel the internal electrostatic potential produced by the different metal contacts.

Figure 4 shows the measured electroabsorption signal $|\Delta T/T|$ as a function of diode bias (V_{App}-V_{Ag}) for a pristine Ag electrode and for Ag electrodes modified by the three SAM's. The applied substrate bias V_{App} has been shifted by the built-in potential in the pristine Ag/polymer/Ca structure. Since the calcium/polymer Schottky energy barrier is constant, the difference, V_{App}-V_{Ag}, represents the change in electron Schottky energy barrier with respect to the pristine Ag electrode. The CH$_3$, NH$_2$, and CF$_3$ SAM's change the electron Schottky energy barrier by -0.60, -0.45, and 0.50 V, respectively. These results demonstrate tuning of the
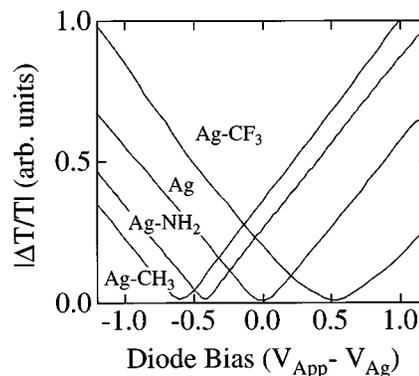

FIG. 4. Electroabsorption signal as a function of diode bias for Ag/polymer/Ca structures with a pristine Ag electrode and for Ag electrodes modified by the three SAM's. The applied substrate bias has been shifted by the built-in potential in the pristine Ag/polymer/Ca structure.

Schottky energy barrier of Ag on MEH-PPV in an organic diode structure over a range of more than 1 eV.

Comparing Figs. 3 and 4 shows that changing the effective work function of the Ag substrate produces a corresponding change in the Ag/polymer electron Schottky energy barrier. The shift of the surface potentials seen in Fig. 3 is essentially the same as that of the Schottky energy barriers seen in Fig. 4 except for the CF$_3$ SAM. The effective work function of the Ag/CF$_3$ SAM film is greater than the ionization potential of MEH-PPV. The electron Schottky energy barrier is saturated at a shift of 0.50 V. This saturation is consistent with previous measurements of Schottky energy barriers in these structures.[8]

The molecules used here to form the ordered dipole layers were chosen because their self-assembly properties have been extensively studied. The dipole moments of these molecules are not particularly large. Molecular dipole moments in excess of 5 D are well known[21] so it should be possible to shift the Schottky energy barrier by substantially more than 1 eV.

In conclusion, we demonstrated tuning of metal/organic Schottky energy barriers in organic electronic devices by utilizing chemically tailored electrodes. The Schottky energy barrier was tuned over a range of more than 1 eV by using self-assembled monolayers to attach well-defined dipole layers to metal contacts prior to fabrication of the device. These results demonstrate the use of self-assembled monolayers to control metal/organic interfacial electronic properties. They establish a physical principle for manipulating the relative energy levels between two materials and demonstrate an approach to improve metal/organic contacts in organic electronic devices.

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