Photoelectron Transmission through Organized Organic Thin Films

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Direct evidence for ballistic electron motion through organized organic thin films was observed. Photoelectrons were injected from a thin silver film coated with organic films, prepared by the Langmuir-Blodgett method, and the energy distribution of the electrons transmitted through the layer was measured. Electrons with energy above ca. 0.8 eV were transmitted without alteration through an organic layer that contains up to five monolayers, each about 20 Å thick.

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The conductive properties of systems on the nanoscale are difficult to obtain. Little is known on the subject despite its importance in any attempt to produce molecular electronic devices, in biological processes as well as for the understanding of the high conductance through organic layers as measured with scanning tunneling microscopy (STM) [1]. The tunneling voltage used in those STM measurements (0.4–1 V) [2] are compatible to the photoelectron energy range in the present study. It is also believed that the tunneling current in the STM measurements originates from the substrate and the organic molecules only appear as a perturbation to the tunneling process [3]. This mechanism is analogous to the photoelectron transmission measurements presented here.

In addition, the interaction between electron with subexcitation energies and condensed matter in general is still not a completely understood phenomenon [4]. This work presents the first direct evidence for ballistic electron motion through organized organic thin films (OOTF) when photoelectrons are injected from a thin silver film coated with OOTF. The measured energy distribution of the electrons transmitted through the layer serves for obtaining the conduction properties of the OOTF.

The effect of adsorbents on photoelectrons emitted from surfaces has been studied for almost a century [5,6]. Adsorbents serve to modify the work function [7,8], and, therefore, the field has important practical implications. The effect of organic adsorbent on the photoelectric effect has been the focus of less attention, and only a few works on the subject have been published [9,10]. Recently, the photoelectron energy distribution was measured for electrons produced from a Pt(111) surface covered with several layers of water [11]. It was found that the transmission probability decreases exponentially with an increasing number of water layers, but is independent of the energy of the electrons. In the current work the effect of OOTF on the energy distribution of photoelectrons emitted from silver film is presented for the first time. OOTF have the advantage of being well defined in terms of orientation and packing on the surface. In addition, due to their nature, it is possible to modify the layer thickness in a controlled manner, layer after layer. Although electron transport properties of OOTF were studied very extensively in the past [12,13], it was always done by measuring the total current, without the ability to monitor the electron energy distributions. In these past studies one measured the current versus voltage applied on electrodes in contact with the OOTF.

In the present study, the OOTF were prepared by the Langmuir-Blodgett method [14] and transferred on a quartz microscope slide coated with 150 nm of silver. Cadmium stearate (CdSt), $[CH_3(CH_2)_{16}COO^-]_2Cd^{2+}$, and arachidic acid (ArAc), $CH_3(CH_2)_{18}COOH$, were used as the organic films. The slide coated with the OOTF was inserted into an UHV chamber pumped to below 10^{-8} mbar by adsorption and ion pumps. A frequency doubled Nd:YAG pumped dye laser at 223 nm (5.56 eV) and an energy of 0.1 μJ was used as the light source. The photoelectron kinetic energy distribution was measured via the retarded field method. A grid made of nickel was placed 3 mm in front of the silver/OOTF coated slide. The grid could be biased with a negative or positive voltage relative to the silver surface which was kept at ground potential. A newly developed microsphere plate (MSP made by El-Mul, Israel) was placed 5 mm after the grid and biased by 200 V relative to it. The MSP serves as an electron multiplier, in the same way as does a regular microchannel plate. The close proximity of the grid and the silver surface ensures high collection efficiency and nonperturbed collection of the low energy electrons. An anode placed after the MSP collected the amplified electron signal, which was processed by a boxcar integrator (stanford instruments). Much care was given through all the studies to the linearity of the measurements and to avoiding nonlinear effects due to too intense laser pulses.

In Fig. 1, the signal observed at the anode of the MSP is shown as a function of the retarding potential on the grid for photoelectrons emitted from a bare silver film, and from silver coated by one and three layers of ArAc. In the case of pure silver and silver coated with a single monolayer, the dependence of the signal on the retarding field could be well fitted by the known Fowler law [15], for a retarding field above 0.4 eV. In order to obtain

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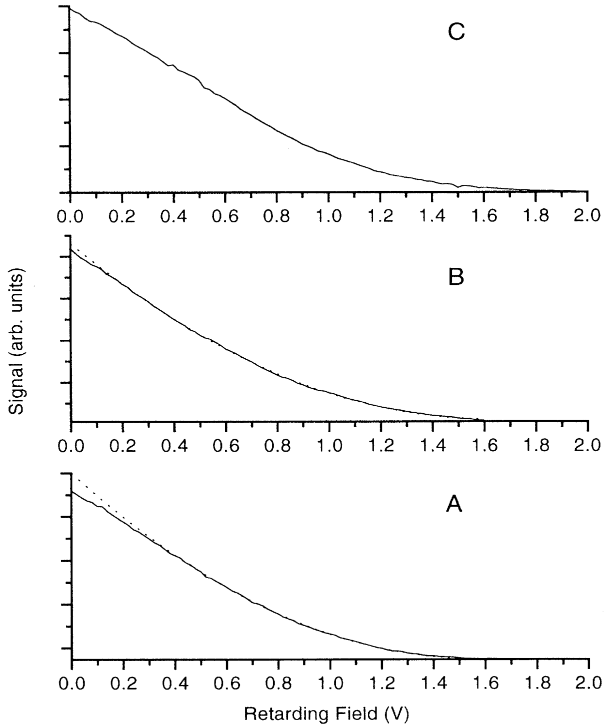

FIG. 1. The signal as measured on the anode from (A) bare silver surface, silver coated with one (B), and three (C) layers of arachidic acid. The dotted lines refer to the signal as predicted by Fowler's law.

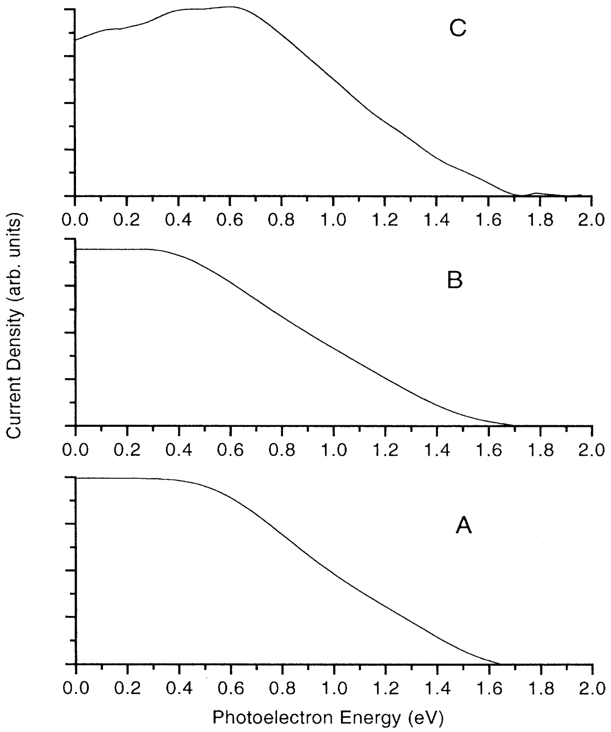

FIG. 2. The electron energy distribution obtained by differentiating the signal presented in Fig. 1. The electron energy is shown for bare silver (A) and silver coated with one (B) and three (C) monolayers of arachidic acid.

the electron energy distribution, the signal observed is differentiated [16]. Figure 2 presents the electron current density as a function of the electron energy, for the data as presented in Fig. 1. Some reduction in the number of low energy electrons is seen when the silver is coated with three layers having a thickness of about 60 Å. In Fig. 3, the current density is presented when the silver surface is coated with one, three, and five layers of CdSt. Here clearly, as the number of layers increases, less low energy electrons are measured, while the high energy part of the distribution remains almost unchanged. The results were not altered as the substrate with the OOTF was heated up to 415 K. At this temperature the OOTF melt, and the relative orientation of the chains is lost. By changing the conditions in the Langmuir-Blodgett trough, while lifting the CdSt, it was possible to obtain films in which the headgroups of the CdSt were not aligned perpendicular to the metal surface. Namely, in this case, the direction of the dipolar moment of the $Cd^{2+}(COO^{-})_2$ groups is not aligned normal to the silver surface. In this case the electron energy distributions obtained are similar to that obtained with ArAc, and no significant depletion of the low energy electrons was observed. These findings suggest that the order or alignment of the organic chains is not playing an important role in transmission of the electrons through the layers, however, the orientation of the headgroups is important.

Under the assumption of the absence of elastic and inelastic scattering, the probability of the electrons to be transmitted through the OOTF as a function of their energy, can be deduced by the ratio between the current densities obtained for silver coated with OOTF and bare silver [Fig. 2(a)]. In Fig. 4 the results shown in Fig. 3 are plotted as a transmission function. The results clearly indicate that as the OOTF are comprised of more layers, less low energy electrons are transmitted through the film. However, the energy distribution of the high energy electrons (above ca. 0.8 eV) is not affected by the film.

The transmission function for the five layers could be simulated from the transmission function for one and three layers, by assuming that the electron transmission is affected only by a quasi-one-dimensional potential barrier caused by the static dipole moments of the headgroups. Two types of barriers had to be assumed, one corresponding to the interface between the headgroup and the metal surface, and the other corresponding to the interface between the headgroups of two organic layers. The probability to cross the metal/headgroup barrier $[P_{SM}(E)]$ can be obtained from the transmission function for the surface covered with one layer. The probability to cross

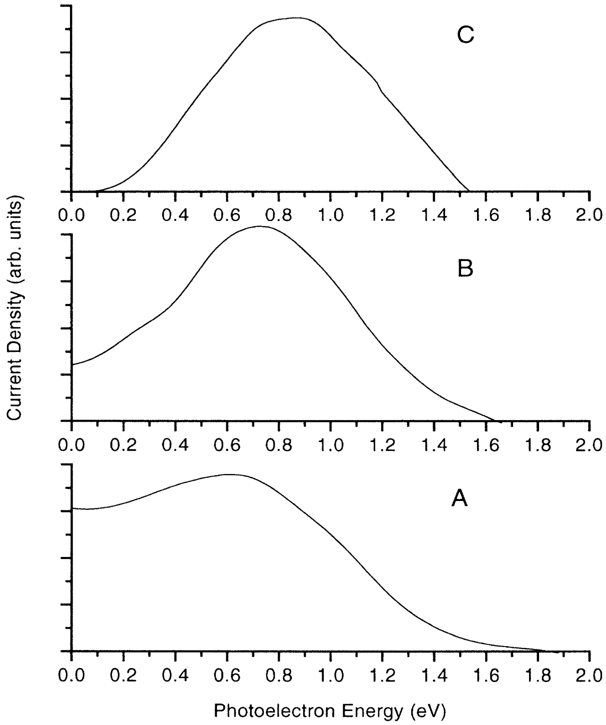

FIG. 3. The electron energy distribution of photoelectrons from silver coated with one (A), three (B), and five (C) monolayers of cadmium stearate.

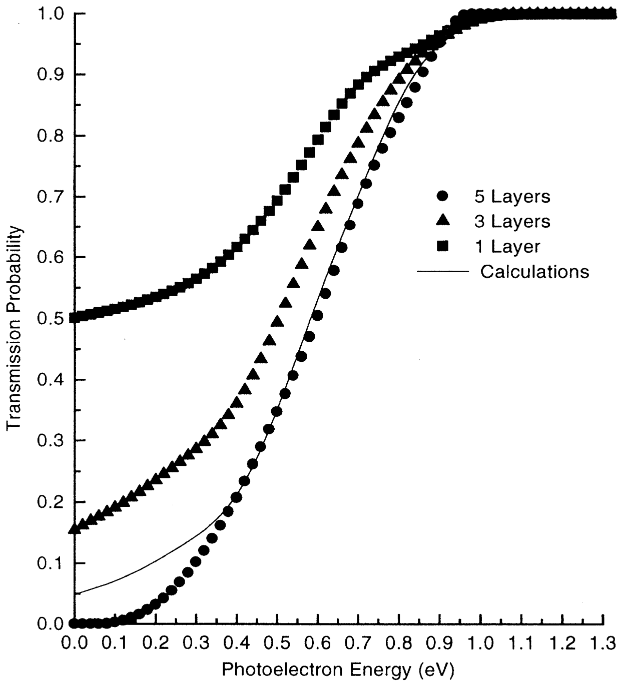

FIG. 4. The transmission function of electrons through one (squares), three (triangles), and five (circles) layers on CdSt. The solid line is a model fit to the transmission through five monolayers obtained as discussed in the text.

both the metal/headgroup and headgroup/headgroup barriers ($P_{SM}P_{MM}$) equals the transmission function of the three layer system. Hence, for the case of five layers, the probability for the electrons to pass through one metal/headgroup and *two* headgroup/headgroup barriers [$P_T(E)$] is given by $P_5(E) = P_{SM}(E)P_{MM}^2(E)$, when $P_{MM}(E)$ is the probability of the electron to pass through the headgroup/headgroup barrier. The model calculation is presented in the form of a solid line that fits extremely well the observed data for the five layer system. The deviation between the experimental result and the model at electron energies below 0.35 eV is due to the role of phonons in absorbing the electron energy. Electron-phonon collisions were not taken into account in the model; however, it is expected that this process will be important for electron energies below 0.4 eV. It is interesting to note that the electron-phonon collisions account for only about 5% of the loss of the electrons in this energy range. This means that on the time scale that the electron is in the organic layers (<50 fsec), the electron-phonon interaction is not efficient enough to affect the electron energy distribution.

The results point to the importance of the dipole produced by the Cd^+ and COO^- in blocking the transmission of low energy electrons. However, the dipole barrier is efficient in blocking electrons only when it is aligned perpendicular to the metal surface. When unordered layers of CdSt were deposited on the surface, where the dipole moment is not aligned perpendicular to the surface, their effect on the electron energy distribution was similar to that of the ArAc.

The obtained results indicate clearly that in the case of CdSt, the low energy electron (up to about 0.8 eV) are affected by the OOTF; however, electron with higher kinetic energy are fully transmitted without going through any energy or momentum transfer processes. When the OOTF does not contain the metal ion, the transmission probability is larger even for the low energy electrons; however, the qualitative behavior is similar. While some of the low energy electrons are blocked, there is no effect whatsoever on electrons with kinetic energy above about 0.8 eV.

The success in fitting the transmission function for five monolayers (in Fig. 4), except in the very low end of the energy distribution, indicates that indeed there are two types of barriers for the slow electrons, the metal/monolayer barrier and the barrier formed between the organic layers themselves. The data could not be fitted with any success when a single barrier was assumed. The metal/monolayer barrier is composed from the dipole created between the metal atom and the metal film and in addition a dipole in the opposite direction exiting between the metal ion and the two COO^- groups. On the other hand, the monolayer/monolayer barrier is created by the existence of two dipoles pointing away from each other, each one of them is due to the charge separation between the metal ion and the two adjacent COO^- groups.

Usually, the process of low energy electron transmission through a polar dielectric material is controlled by inelastic collisions [4], which eventually causes thermalization of the electrons [17]. The data presented above indicate that in the case of OOTF, on the scale of up to about 10 nm, inelastic collisions are unimportant. This conclusion is in good agreement with a recent classical simulation study which claims that inelastic scattering is an inefficient process for photoelectrons passing through a thin adsorbed layer [18]. The inefficiency of the inelastic collisions can be rationalized by the large energy gap between the phonon energies and the electronic transition energies in OOTF. The first electronic excited states in OOTF lies at about 5 eV, while the highest phonon energy is about 0.4 eV. Hence, there is no mechanism for efficient energy transfer between the electrons and the organic films. Hence we must conclude that the electron transmission through the OOTF is controlled by two parameters, the barriers caused by the high dipole moments of the headgroups and the ability to transfer energy to phonons. The role of the phonons is emphasized in the misfit of the calculated curve at the lower energy part of the electron energy distribution (Fig. 4). Since in the model on which the calculations were based only the barriers were taken into account, we do expect the calculation, at the lower energy end, to indicate higher transmission probability than actually observed.

In the retarded field method, as applied by us, the velocity component perpendicular to the surface is measured. The observation that while there is depletion in the low energy electron population, the distribution of the higher energy electrons is not altered (Fig. 3) indicates that not only inelastic collisions between the electrons and the OOTF are unimportant on the scale of the layer thickness, but also elastic scattering does not play an important role. If the direction of the electron velocity would be altered, the energy distribution, as measured by the retarded field method, would show a decrease in the average electron energy. This is because the main contribution to the high energy tail in Fig. 3 is a result of electrons emitted perpendicular to the surface. Any change in their direction will necessarily result in lowering the velocity component in this direction appearing as an effective decrease in the energy. The "hole" in the electron energy distribution observed for five layers of CdSt, indicates that no electron scattering (elastic or inelastic) occurs on the scale of a single monolayer. Any such scattering would necessarily fill the hole, by reducing the velocity component normal to the surface. The fact that the high energy part of the distribution is unchanged even for five layers, indicates a ballistic electron motion of the high energy electrons (above ca. 0.8 eV), on the length scale of the film (about 10 nm).

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