Scanning tunneling microscopy and spectroscopy of Langmuir–Blodgett films of ion-exchange polymers: 2D conductivity, resonant tunneling, and charge superstructure

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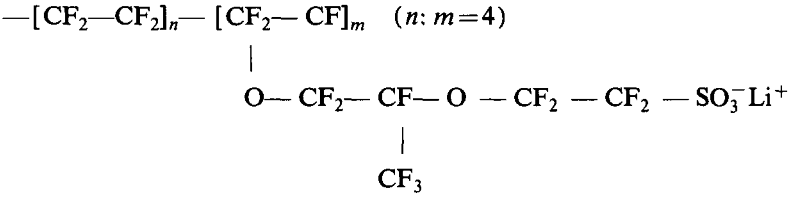
Scanning tunneling microscopy and scanning tunneling spectroscopy (STM–STS) have been used to study monomolecular layers of an ion-exchange polymer. In a study of films containing an odd number of layers, an anomaly was found on the plot of $dI/dV(V)$: a conductance peak on the order of 150–200 mV wide near zero bias voltage. In addition, the results reveal a 3×2 surface reconstruction corresponding to a charge density wave and an oscillatory current–voltage characteristic. Generation of the feedback system of the microscope can arise in negative-slope regions on the current–voltage characteristic. The observed effects can be explained by noting that the density of states is determined by a superposition of effects stemming from the 2D nature of the conductance and a charge density wave.

This letter reports the use of scanning tunneling microscopy–spectroscopy (STM–STS) to study Langmuir–Blodgett films of an ion-exchange polymer with the structural formula



$$-[CF_2-CF_2]_n-[CF_2-\underset{\underset{\displaystyle O-CF_2-\underset{\underset{\displaystyle CF_3}{|}}{CF}-O-CF_2-CF_2-SO_3^-Li^+}{|}}{CF}]_m \quad (n:m=4)$$

The purpose of preparing films of this sort was to obtain 2D conducting layers separated by a nonconducting fluorinated polymer. The test samples were prepared in the following way. The polymer was dissolved in a 1:10 DMFA–dichloromethane mixture to a concentration of 1 mg/ml and then deposited on the surface of water. After the solvent was evaporated off, the monolayer was compressed to 30 mN/m and transferred to the surfaces of crystals of highly oriented pyrolytic graphite by the Langmuir–Blodgett method. The substrate with the film was then placed in a 1:1 water–alcohol solution of $AgNO_3$ (10 g/liter) and held there for 30 s. In this step, Li^+ cations in the film were replaced by Ag^+ cations from the solution. The resulting

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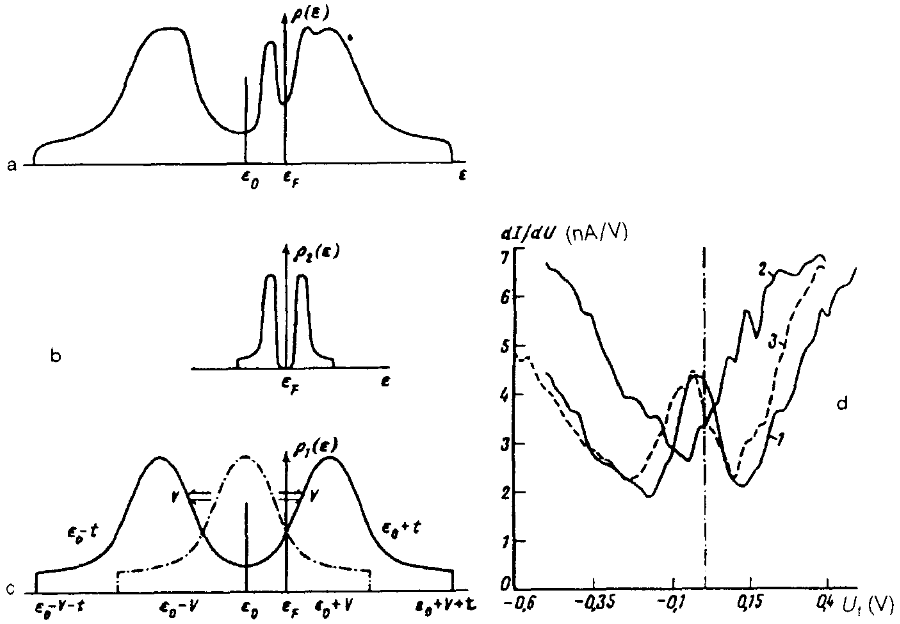

FIG. 1. Parts a, b, and c are explained in the text proper. d: Conductance versus the bias voltage, dI/dV, found for Langmuir–Blodgett films consisting of the following numbers of layers, for the following parameter values. 1—One layer, $U_t = -10$ mV, $I_t = 0.8$ nA, modulation voltage $U_{\text{mod}} = 50$ mV; 2—two layers, × 10 mV, 0.8 nA, 50 mV; 3—three layers, 15 mV, 0.8 nA, 50 mV.

films thus contained ion layers consisting of SO_3^- sulfo groups and Ag^+ cations. These ion layers were separated by layers of the fluorinated polymer about 15 Å thick. The area per Ag^+ cation in the monolayer was 22 Å^2.

Experimental results. To determine the electronic structure of the Langmuir–Blodgett (LB) film of the ion-exchange polymer, we studied it in the ordinary $Z(x, y)$ topographic mode of STM and also under conditions involving measurement of the spatial distribution of the first derivative of the tunneling current with respect to the bias voltage, $dI/dV(x, y)$. In addition, the tunneling current was measured as a function of the change in the gap size, $I(\Delta z)$, and as a function of the bias voltage, $I(V)$; the first derivative of the latter function, $dI/dV(V)$, was also measured. These measurements were made at fixed points on the surface. The measurement procedure for all measurement regimes is described in Refs. 1 and 2. The experiments were carried out in an air atmosphere on samples with various numbers of layers in the LB film: from 1 to 16

In our study of films containing odd numbers of layers, we observed an anomaly on the plot of $dI/dV(V)$: a conductance peak on the order of 150–200 mV wide near zero bias voltage (curves 1 and 3 in Fig. 1d). Curve 1 in Fig. 3 shows the corresponding $I(V)$ curve. This anomaly was not found for films with an even number of layers, and the curve of $dI/dV(V)$ had the shape shown by curve 2 in Fig. 1d.

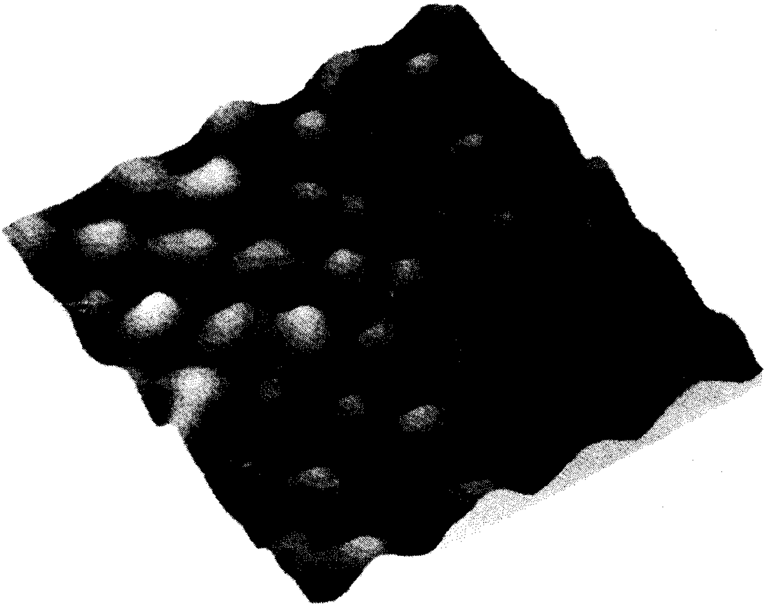

FIG. 2. Image of the surface of a film consisting of three layers, recorded under conditions corresponding to measurements of the conductance $dI/dV(x,y)$. The dimensions of this image are 70×74 Å. The gray scale or the scale of brightness gradations is arbitrary. This image was recorded at $I_t=0.8$ nA, $U_t=-50$ mV, and a modulation voltage $U_{\text{mod}}=50$ mV.

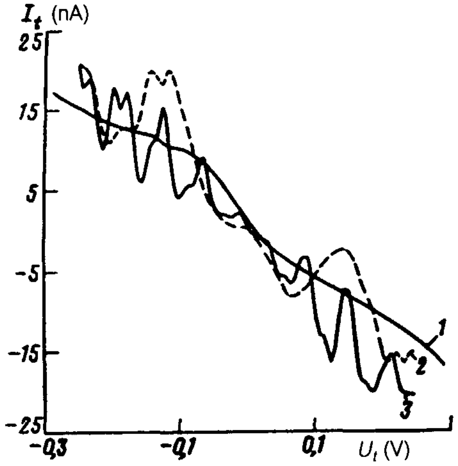

FIG. 3. Current–voltage characteristics $I(V)$ recorded for a three-layer Langmuir–Blodgett film, for various values of the initial tunneling current and the bias voltage: 1) $U_t=15$ mV, $I_t=0.8$ nA; 2) -30 mV, 0.8 nA; 3) -10 mV, 0.8 nA.

In a study of an LB film with an odd number of layers under conditions corresponding to measurements of the conductance $dI/dV(x, y)$, we observed an ordered superstructure with typical dimensions of 11.5×11.5 Å. This structure corresponds to a 3×2 reconstruction of the surface (Fig. 2), which was not observed in the topographic regime.

For samples with even numbers of layers, we were not able to obtain reliably reproducible spatial images of the surface of the LB film under any of the regimes described above.

At certain points on the surface, the current–voltage characteristic $I(V)$ had regions with a negative slope (curve 2 in Fig. 3) and oscillations (curve 3 in Fig. 3).

Discussion of results. The experimental data outlined above can be interpreted in the following way. The silver ions in the LB film form a quasi-2D lattice. When there is an odd number of molecular layers, the upper layer is an essentially ideal 2D lattice. The electrons in such a lattice can be described by the Hamiltonian

$$H_0=\sum_{\langle j,i\rangle} t_{ij}a^+_{j\sigma}a_{i\sigma}=\sum_{k\sigma}\epsilon_k a^+_{k\sigma}a_{k\sigma},$$

where t_{ij} is the amplitude for the jump of an electron between nearest lattice sites, and ϵ_k is the energy of an electron in the 2D band. The dashed line in Fig. 1c shows the density of states $\rho_1(E)$ in this 2D system according to the strong-coupling model (the Van Hove singularity has been smoothed over). The film also contains double layers formed by silver ions of neighboring layers. These double layers constitute two sublattices, one on top of the other in a strictly vertical alignment. In the absence of an interaction between sublattices, the behavior of the electrons in each sublattice is described by Hamiltonian H_0. However, since the distance between sublattices is comparable to the lattice constant, the interaction between sublattices must be taken into account. The interaction Hamiltonian is

$$H_{\text{int}}=\sum_{i,j} V\delta_{ij}a^+_{i\sigma}b_{j\sigma}+\text{H.a.}=\sum_{k,p} V\delta_{kp}\,a^+_{k\sigma}\,b_{p\sigma}+\text{H.a.},$$

where i and k refer to one sublattice, and j and p to the other. The electron spectrum is determined by the poles of the Green's functions $G_{kk}(\omega)$ and $G_{pp}(\omega)$, which satisfy the following equations:

$$G_{kk'}=G^0_{kk'}+G^0_{kk}\sum_p V_{kp}G_{pk'},\quad G_{pk'}=G^0_{pp}\sum_{k''}V_{pk'}G_{k''k'},$$

where $V_{pk}=V\delta_{kp}$. Hence

$$G_{kk'}(\omega)=\frac{\delta_{kk'}G^0_{kk}}{1-V^2(G^0_{kk})^2}=\frac{1}{2}\delta_{kk'}\left(\frac{1}{\omega-(\epsilon_k-V)+i\delta}+\frac{1}{\omega-(\epsilon_k+V)+i\delta}\right).\qquad (1)$$

It can be seen from (1) that the interaction leads to a restructuring of the electron spectrum. The width of the band changes from $2t$ to $2(t+V)$ (Fig. 1c).

When the LB film contains an odd number of layers, a 3×2 reconstruction of the charge-density-wave type can occur in the upper layer, as in a purely 2D system. The experimental STM image of a three-layer LB film agrees with this assertion (Fig. 2). This image corresponds to the first derivative of the tunneling current with respect to the bias voltage, dI/dV. In this regime the contrast of the STM image may be much higher than that in the ordinary topographic operating mode of the STM. When there is a charge density wave on the surface of the LB film, the density of states $\rho_2(E)$ is as shown in Fig. 1b. Experimentally, the tunneling actually occurs from both a double layer and a single layer. In the case of an odd number of layers, the final value of the density of states $\rho(E)$ (Fig. 1a) is thus a superposition of $\rho_2(E)$ (Fig. 1b) and $\rho_1(E)$ (Fig. 1c). In the case of a single layer, the background density of states $\rho_1(E)$ may correspond to the density of states of the substrate. In Fig. 1a there is a dip near the Fermi energy E_F, with a size $\approx$250 mV. This dip corresponds to an energy gap in the spectrum when a charge density wave is present. This width of the gap is consistent with the data from other experiments and with theoretical predictions.

In addition to the structural features corresponding to the charge density wave and the double layer, we find on the $I(V)$ curve some regions with a negative slope (curve 2 in Fig. 3) and also oscillations (curve 3 in Fig. 3). These features apparently stem from the formation of collective bound states as the result of interactions of electron states of the tip and the test sample.[1,3] Such states form additional resonance channels for electron tunneling. Since the positions of these levels with respect to E_F and E_F-eV depend on the voltage applied to the tunnel junction, oscillations may occur on the current–voltage characteristics. Current–voltage characteristics and a dI/dV curve like those in Figs. 1 and 3 are frequently observed[4,5] in low-temperature STM studies of superconductors.

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