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# Metallic conductivity in a polyamidine film

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**1 Introduction** The progress of the electronic industry in the past few decades was bound to a design philosophy to construct metal-oxide-semiconductor transistors with smaller and smaller dimensions and denser integrated circuits. However, the further down-scaling of individual devices to the nanometer range collides with fundamental physical laws: the energy bands turn into discrete energy levels with localization effect for carriers. In order to continue the miniaturization of integrated circuits scientists and engineers are searching for novel technologies based on quantum mechanical effects on the nanometer scale. The main aim of molecular-scale electronics is to employ molecular scale components such as single molecules or a small number of molecules as electronic components. For that reason it is crucial to understand the phenomena of high conductivity which is observed in some non-conjugated and undoped polymer films placed between metallic electrodes at a film thickness of about 1–2  $\mu\text{m}$  ([1] and references therein). If the electrodes undergo the transition into the superconducting state, a supercurrent flows through the polymer. The proof of this is the observation of Josephson voltage oscillations in a magnetic field [2].

In this contribution we discuss experimental results which deal with metallic conductivity in partially conjugated and undoped polyamidine thin films which are inter-

preted in the framework of a model where an electrification effect due to metallic electrodes plays the significant role in the resulting metallic conductivity in sandwich structures metal – polyamidine – metal. In accordance with the model [3] the main reason for metallic conductivity in dielectric polyamidine films is the collapse of the HOMO/ LUMO gap of macromolecules (here HOMO – is the highest occupied molecular orbital and LUMO – is the lowest unoccupied molecular orbital) in a strong internal electrical field inside the polymer.

**2 Experiment** Polyamidine (Fig. 1) was synthesised by the method described in [4]. A droplet of 5% mass solution of polyamidine in pure alcohol was deposited onto one electrode. We used polished metals as bulk electrodes made from Au, Pt, Sn, In, Nb, or as thin metallic films made from Au, Sn, or In evaporated onto a glass substrate. After heat treatment at 90–100  $^{\circ}\text{C}$  for 1 hour, the major part of the solvent was removed and polymer films with a thickness of 0.8–2.0  $\mu\text{m}$  were obtained.

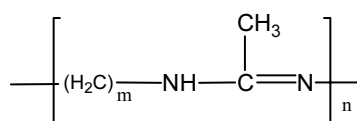
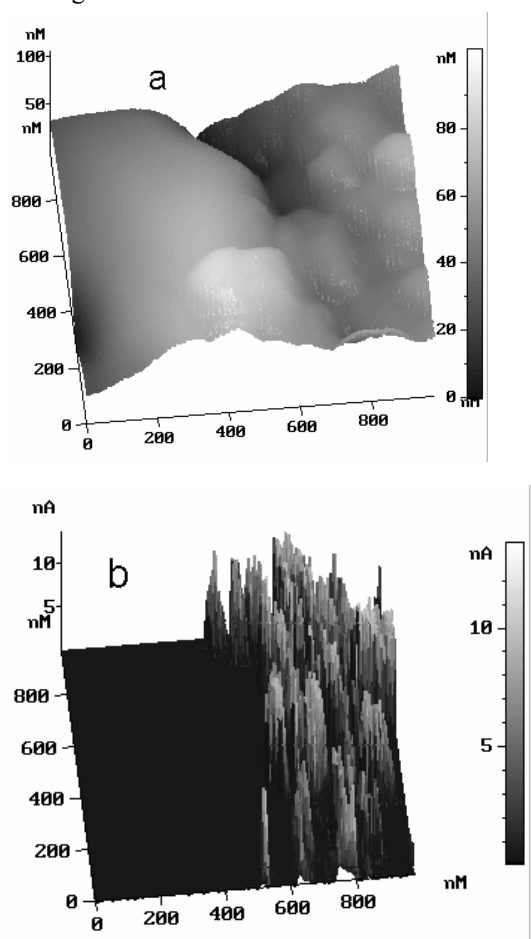


Figure 1 Chemical formula of polyamidine.

A four-wire method was used for dc-conductivity measurements at low temperature.

We investigated simultaneously the surface topography of the polymer film and the current distribution by the atomic force microscope (Solver P47, NTMDT) in the spreading resistance mode at room temperature. The radii at the ends of the used Au-tip and highly doped diamond tip were about 30 nm and 50 nm, respectively. Consequently the contact area between the tips and the polymer surface was different in the two cases. At different points on the polymer surface we also investigated the current-voltage characteristics (CVC).

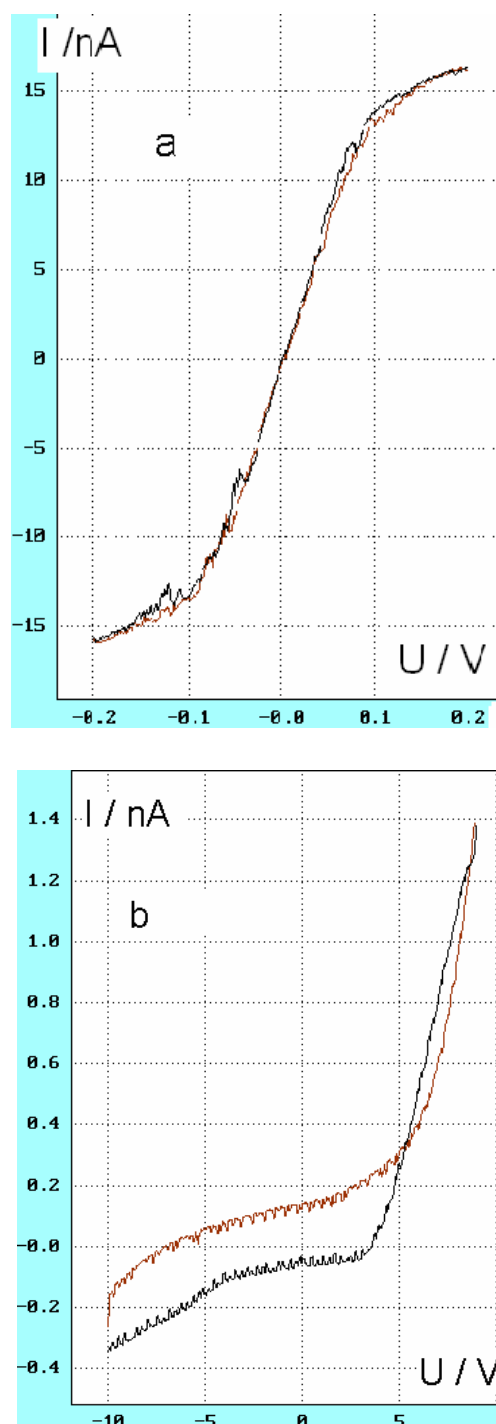
**3 Results and discussion** Earlier it was observed that if the AFM tip has a radius of about 30 nm in polyamidine films with a thickness about 1  $\mu\text{m}$  placed on a Pt substrate, there was no current topography up to a tip voltage of as high as 10 V.



**Figure 2** a) AFM surface topography of a polyamidine film of one micron thickness on a bulk platinum substrate measured with  $R_{\text{tip}} = 50$  nm; b) distribution of the current at  $U = 0.1$  V applied to the tip.

If we now increase the contact area between the metal and the polymer up to a radius of 50 nm the current

through the polymer channels appears even if the applied voltage is only 0.1 V, Figs. 2(a, b). The brighter grey tone, shown in Fig. 2a corresponds to higher points of the polymer film surface and in Fig. 2b to the largest values of current.



**Figure 3** a) CVC measured in brighter spots corresponding to Ohm's law behavior; b) reversible On/Off current switching at points of the polymer surface topography corresponding to dark tones.

As seen from Fig. 2, there exists a correlation between the surface topography and the current distribution: a measurable current was observed only at surface points which were predominantly higher than the mean surface and there was no current on the relatively smooth surface (left part of Fig. 2b).

One can assume that in places where high conductivity was observed, a reconstruction of the macromolecular structure takes place. Our experiment also shows that in the dark tones of the polymer surface there is reversible On/Off switching at electric field strengths less than the threshold field, whereas in the brighter spots we see Ohmic behaviour, Figs. 3(a, b).

The same correlation between the AFM surface topography and the current distribution was observed with other electrodes.

It is well known that insulators and in particular polymers will acquire charge if they are touched by a metal. This means that they have energy levels within their energy gap. The experiment shows that many polymers may charge negatively or positively depending on whether the work function of the contacting metal is small or large. Therefore, the insulator must contain empty states that can accept electrons from the metal, as well as occupied states that can donate electrons. The energy of both kinds of electron states (traps) must be close to the Fermi energy of the contacting metal; that is in the range of 4 - 5 eV below the vacuum level [5].

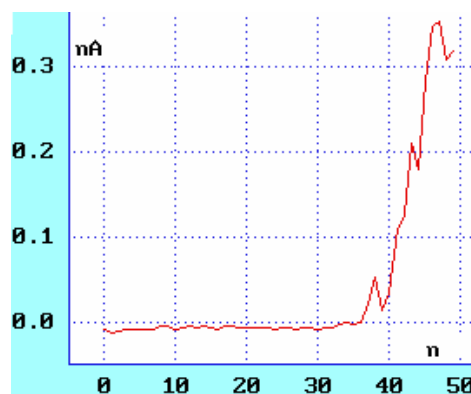
Donor and acceptor traps are the result of various kinds of defects, such as chemical groups [6], cavities and entanglements, unsaturated bonds, and molecular oxygen [7]. We investigated the influence of polymer defects on the phenomenon of the onset of metallic conductivity and concluded that, the more defects (such as unsaturated bonds, cavities entanglements etc.), the greater the probability of metallic conductivity in the polymer film between the metallic electrodes.

Earlier it was experimentally shown that the maximum of charge induced in the polymer does not depend on time. However, in a wide variety of materials the charge can be increased by repeating contact touches. For example, a few hundred contact touches may increase the charge in the polymer by an order of magnitude [5, 8]. There are two mechanisms which can explain this effect:

- i) The first mechanism requires the insulator to be slightly conducting, so that when the contact is removed charge flows away from the contact region into the bulk of the insulator up to several microns [5];
- ii) The second mechanism supposes that the second touch is realised at a slightly different place on the polymer surface, so that the total amount of accumulated charge continuously increases.

In order to check the influence of charge accumulation on the appearance of metallic conductivity, the following experiment was performed [9]. At a location on the polymer surface without Ohmic behaviour a voltage,  $U \leq 300$  mV, was applied, which was much less than the voltage for

a reversible switching (Fig. 4). We performed charge accumulation by repeating the voltage scan many times. At the beginning we only obtained the noise current, but after applying the voltage  $U \leq 300$  mV some tens of times the current sharply increased. This may be explained by the accumulation of charges in a local volume of the polymer film due to the applied voltage cycles. When the applied voltage during the cycle is increased or decreased the charge has time to flow away from the contact region emptying the traps for new charges in the following cycle. Here it should be also taken into account that traps, which belong to the macromolecules, can also move in space due to the motion of macromolecules under the influence of the applied electrical field. This effect is not possible in solids, for example in silicon, because their traps are fixed in a crystalline lattice. It is known that charge acquired by an insulator from a metal that touches it may depend not only on the nature of the insulator but also on the metal and on the type and duration of the contact touch [5]. For example, for almost all polymer insulators a sliding contact is much more effective for the electrification than a permanently touching one.



**Figure 4** Dependence of the current value versus the number (n) of CVC measurement cycles, which were done by an AFM ( $E = 3 \times 10^3$  V/cm,  $R_{tip} \approx 30$  nm) at a point corresponding to dark regions of the polymer surface, see [9], Fig. 2a.

We checked the influence of the type of contact on the starting value of high conductivity. With this aim in mind we produced sliding contacts between the upper gold electrode and the polymer film which were chemically deposited on the metallic gold substrate. Simultaneously, we measured the polymer film resistance under an applied voltage of about 1 V. Apart from a fixed touch contact when the polymer always was in the insulating state, with sliding contacts we observed a crossover from an insulating to highly conductive state at polymer film thicknesses of up to 3-6  $\mu\text{m}$ . Only at a thickness of 3  $\mu\text{m}$  was the high conductive state conserved after stopping the movement of the contact. However, when the metal was removed the conductivity vanished and did not appear again at repeated fixed touch contact with metal, but it reappeared with the

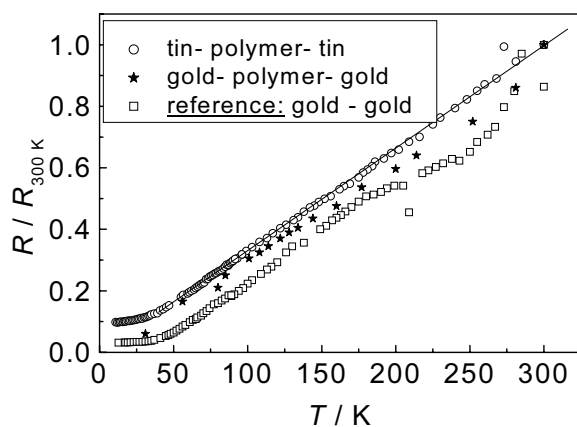
sliding contact. This behaviour is in agreement with a spreading of charge over the surface or into the bulk of the polymer insulator [5]. At the upper end of the range the high conductive state disappeared when sliding of the contact was stopped.

Another illustration that a critical density of charge must be accumulated by the polymer to get high conductivity was provided by experiments on the switching of a polymer to the conductive state under external pressure.

1. First we applied a pressure which was so small that the macromolecular bonds were not yet broken by the deformation.
2. We obtained the high conductive state by field injection of charge.
3. Thereafter, we removed the external pressure and found that the high conductive state disappeared.

These procedures could be repeated up to  $10^8$  times [10, 11]. One can understand the phenomena of Off/On switching cycles in the framework of the electrification model in the following way: compression as well as decompression of the polymer causes plastic deformation which is accompanied by extensive molecular motion [12]. Hence, the charge obtained by the polymer during field injection can move into some local volume between the electrodes due to plastic deformation.

Our experiments unambiguously showed that in a polymer film there is a direct connection between the electrification effect on the one hand, and the appearance of the high conductive state on the other.



**Figure 5**  $R(T)$  dependences for polyamidine placed between different electrodes in relative units and  $R(T)$  dependence for a Au/Au contact.

We believe that the high conductive state will appear only if the density of charge exceeds some critical value. We attribute the high (metallic) conductivity (Fig. 5) in the polymer film to the vanishing of the HOMO/LUMO gap [3] in separated macromolecules or even in some part of macromolecules which extends from one electrode to another in strong electrical field. This is due to the electrification phenomenon randomly distributed inside the polymer

film. If the HOMO/LUMO gap disappears charge transport from HOMO to LUMO is possible.

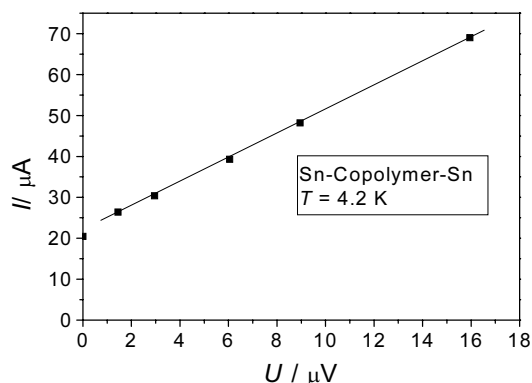
In accordance with this model at least three conditions must be fulfilled:

1. the polymer must be a good insulator, without initial conductivity;
2. there should be enough localised traps for the charges in the polymer;
3. the macromolecules must be packed in such a way that a path for carriers from one electrode to the other is formed.

Due to the possibility of motion of the macromolecules the electrification effect depends on the polymer flexibility and on the temperature which is necessary for charge migration inside the polymer. At some moment in time the charge distribution can be favourable for Off-On – switching. Just in this moment a conducting channel opens which connects the two electrodes resulting in the high conductivity. In this case the resistance will switch randomly between the high-resistance OFF state and the low-resistance ON state. If at the moment of switching conductive paths percolate through macromolecules (which have localised charges that contribute to a critical charge) they immediately lose the charge and an ultra-short time Off-On–Off-switching can take place. It seems that it is this effect that was described by Shlimak and Martchenkov [13].

It is well known that for organic polymers the charge density is in the range of  $10^5$  to  $10^3$  C/m<sup>2</sup>. Contact electrification is a small effect – for example a charge density of  $10^{-4}$  C/m<sup>2</sup> corresponds to one elementary charge for about  $10^4$  surface atoms [5]. Even the charging of a small concentration of traps in the polymer can result in a large inner electrostatic field. For instance, if the charge density is close to  $5 \times 10^{-5}$  C/m<sup>2</sup> it produces such a high field strong enough to enable breakdown in air (the breakdown field is about  $3 \times 10^6$  V/m) [5]. But a charge density of about  $\sim 10^{-3}$  C/m<sup>2</sup> produces a field high enough to get breakdown in the polymer ( $\sim 10^8$  V/m).

To increase the charge density in the polymer one may use polymer compositions, for example co-polymers, where one polymer mainly has localized charges and another mainly produces conductive paths. As example of such a composition, polyamidine can be placed in pinholes of another polymer, for instance polyetherquinoline, Fig. 6. This presents the current-voltage characteristics of such a composition placed between Sn electrodes. As it is seen in the figure, the Josephson behaviour of CVC is observed already at  $T = 4.2$  K, whereas the critical temperature for bulk Sn is known to be  $T_c = 3.72$  K. One can explain this effect by superconductive fluctuations which exist in superconductors in the range  $T_c < T < 2 T_c$ .



**Figure 6** CVC for a Sn-Copolymer–Sn sandwich structure measured at  $T = 4.2$  K.

**4 Conclusion** Our investigations showed that conductivity of a thin polyamide film depends on:

- i) the contact area between the polymer surface and the metallic contacts;
- ii) the type of contact – touch or sliding contact;
- iii) the time of action of the voltage scan.

It was shown that a polymer film switched to the conductive state under external pressure loses its conductivity when the pressure is removed. Correlation was observed between the existence of defects in the polymer matrix and the effect of metallic conductivity. All these findings agree well with the assumption of the accumulation of charge inside the polymer film from the metallic electrodes due to the electrification phenomenon. The metallic conductivity in polymer films is attributed to the vanishing of the HOMO/LUMO gap [3] in macromolecules in a strong electrical field randomly distributed inside the polymer film due to the electrification effect.

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