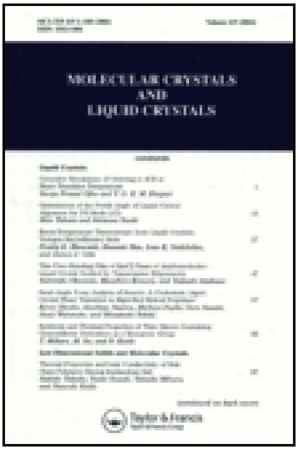

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INVESTIGATION OF TRANSPORT PHENOMENA IN THIN OLIGOTHIOPHENE FILMS IN METAL/ORGANIC/METAL HETERO-STRUCTURES

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Abstract Electrical transport properties of thin films of evaporated end-capped oligothiophene were studied by current/voltage measurements between gold microcontacts. The experiments were performed as a function of dimension of the microstructures, film thickness, chain length of the oligomers, doping state and time. The devices show ohmic behavior and a clear dependence of the conductivities on the inverse chain length. Strong dependence of the conductivities on doping time is observed for different electrode distances. The results are compared with doping experiments on macroscopic thin films.

INTRODUCTION

Organic conjugated polymers and oligomers consisting of pyrrole, thiophene or phenylene-vinylene units have proved to be well-suited as active components in molecular electronic devices (e.g. FETs, sensors, LEDs, etc.)[1] . Most transport experiments were so far carried out using macroscopic polymer or oligomer films prepared by thin film technique. It appears likely that a better understanding of the mechanism of charge transport in molecular layers, and even an improvement of the electronic properties of model devices, becomes possible if the dimensions of such hybrid systems can be reduced to the submicron range. In particular, the distance between contacts, the properties of the interfaces, the character, and degree of order in the molecular material may play an important role.

One way of tackling these questions is to use microfabricated heterostructures. In this paper we present investigations with gold microstructures concerning charge transport properties of oligothiophenes with different chain lengths and the development of conductivity as a function of in situ iodine doping time.

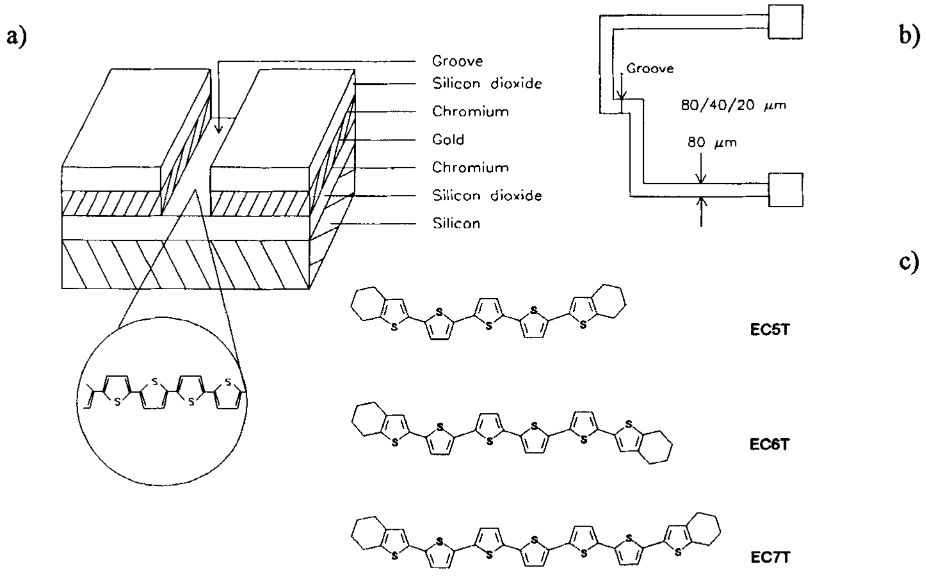


FIGURE 1 (a) Schematic picture of the microstructures used for the measurements of transport properties of organic materials. (b) Actual layout of the microstructure with a strip width of 80 μm. (c) End-capped oligothiophene with chain lengths of n=5,6,7.

DEVICE FABRICATION

The layout of the actually prepared metal microstructures is shown in Fig. 1b. In order to get an insulating, easy cutable substrate, a silicon wafer was coated with 300-400 nm SiO_2 . Photolithographic and lift-off processes were used to define an array of metallic structures (10 nm chromium, 200 nm gold, 10 nm chromium) deposited by thermal evaporation. Apart from the bond pads the whole structure was then coated with a top layer of SiO_2 in order to properly define the electrode area and to reduce the influence of leakage currents. The cutting of the structure and hence the definition of the electrode distance ("groove", see Fig.1b) was carried out by electron-beam lithography and a dry etching process[2]. Electrode distances from 10 μm down to 100 nm have been prepared. The investigations on macroscopic films were performed on structures consisting of a glass substrate which is covered with the organic material and on top two 3 mm long gold electrodes separated by 11 mm.

As active organic material we employed end-capped oligothiophenes (Fig.1c) which represent well-defined conjugated π- systems with controlled chain and conjugation lengths[3]. Moreover due to the cycloalkane caps at the terminal thiophene units further polymerisation of the oligomer in its oxidised state is completely prevented.

The oligomer films were prepared by vacuum sublimation under UHV conditions with evaporation rates from 0.01 to 0.1 nm/s leading to film thicknesses from 88 nm to 240 nm. Doping with iodine vapour in air and at room temperature was performed after removing the devices from the vacuum chamber and introducing them into a specially constructed doping chamber with electrical feedthroughs for in situ measurements. The conductivities were determined by current/voltage measurements with applied voltages in the range from -1V to 1V using a semiconductor analyzer (HP 4145B).

RESULTS AND DISCUSSION

As-prepared Devices

The conductivities of non doped (not intentionally doped) devices and macroscopic films were determined immediately after removing them from the vacuum preparation chamber. The values for macroscopic films in the thickness range from 130-300 nm are $5.7*10^{-6}$ S/cm for EC7T, $4.9*10^{-7}$ S/cm for EC6T, and $2.4*10^{-7}$ S/cm for EC5T. Microstructures with 1 µm electrode distances showed slightly lower values of $2.2*10^{-6}$ S/cm for EC7T, $2.9*10^{-7}$ S/cm for EC6T, and $3*10^{-7}$ S/cm for EC5T in the same thickness range (100-220 nm). The obtained values are comparable with those from normal oligothiophene films[4]. Measurements on EC6T in microstructures as narrow as 0.1 µm did not show any dependence of the conductivity on the electrode distance. Thus the influence of space charge current on the measured transport properties which would lead to a dependence of the conductivity on the inverse square of the electrode distance[5] can be neglected.

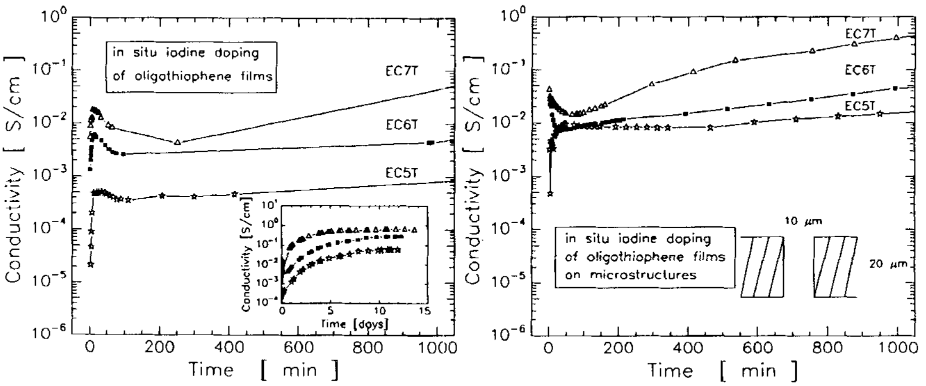
Analysing the conductivity in terms of the chain length of the oligomers leads to a logarithmic dependence of the conductivity on the inverse chain length 1/n as is demonstrated in Fig. 3b for the macroscopic films and for the microstructures. A dependence on inverse chain length was also observed for the onset of the optical absorption (~ band gap), for the redox potentials of these oligothiophenes[3], and for the electro- and photoluminescence emission energies of recently prepared light emitting diodes[6].

The increase of the conductivity which depends on the carrier mobility μ and the carrier density n_c ($\sigma = e n_c \mu$) with growing chain length may be due to an increase of carrier mobility as was observed for alkyl substituted oligothiophenes [7] in field effect transistors or to a larger density of thermally activated charge carriers from impurities, i. e. non intentionally enclosed doping ions (e.g. oxygen).

Iodine doped Devices

In our previous work on electrical measurements of doped EC4T devices [8] we found a strong dependence of the conductivity on dedoping time as has been observed for other thiophene based organic films [9]. From this we concluded that it would be valuable to investigate the development of the conductivity by doping in situ. Figure 2 displays the conductivity of macroscopic oligothiophene films for doping times up to 1000 min (a) and for ECnT films in 10 μm microstructures (b) for doping times up to 1000 min. The macroscopic films show a logarithmic increase of the conductivity within the first minutes, reaching a maximum at about 8 minutes , followed by a slight decrease for the next 100 minutes and then a subsequent increase of conductivity. The values after 1000 minutes are $5*10^{-2}$ S/cm for EC7T, $5*10^{-3}$ S/cm for EC6T, and $9*10^{-4}$ S/cm for EC5T. As can be seen in the inset of Fig. 2a the conductivities of the films still increase for times up to 10 days leading to maximum values of $6*10^{-1}$ S/cm for EC7T, $2.5*10^{-1}$ S/cm for EC6T, and $5*10^{-2}$ S/cm for EC5T.

The development of the conductivities with doping time is different for the ECnT films on microstructures. The increase of conductivity for EC7T and EC6T was not observed in the experiment leading to the conclusion that it occurred within the first minute. Again a slight decrease of the conductivities during the first 20 to 50 minutes is observed, followed by an increase up to 1000 minutes. The values after 1000 min of iodine doping are 4.5*10^{-1} S/cm for EC7T, 4.5*10^{-2} S/cm for EC6T, and 1.5*10^{-2} S/cm for EC5T. Thus for the same doping time the conductivities of ECnT films on 10 μm microstructures are a factor 10 higher compared to macroscopic films.

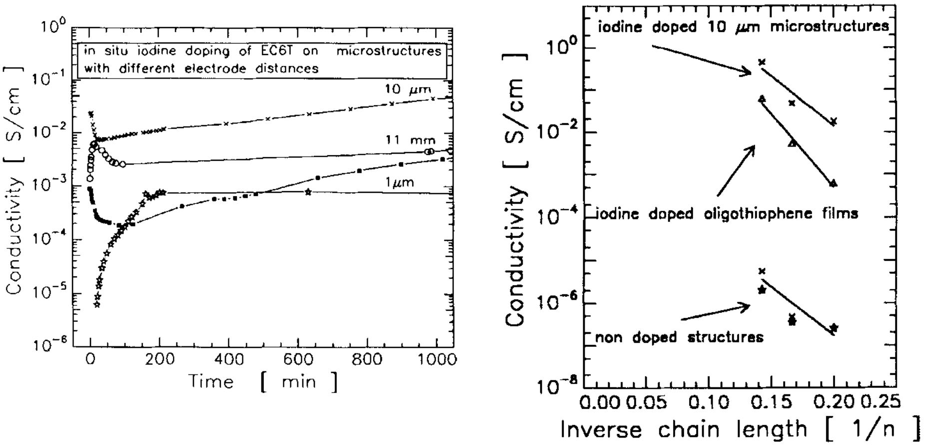


a) b)

FIGURE 2 (a) Conductivities of macroscopic ECnT films (thicknesses: EC7T 244 nm, EC6T 150 nm, EC5T 150 nm) in dependence on in situ iodine doping time. The inset shows the development of the conductivities for doping times up to 15 days. (b) Conductivities of ECnT films (EC7T 88 nm, EC6T 122 nm, EC5T 122 nm) on 10 μm microstructures in dependence on doping time.

Unfortunately it was not possible to dope the microstructures up to 15 days like the macroscopic films (which have a completely different layout) due to the high corrosive potential of iodine vapour to the metallic stripes, which even appears to be enhanced by the organic film.

By reducing the electrode distance down to 1 μm the measured conductivity becomes more sensitive to the individual sample differences and geometric influences. Fig. 3a shows the iodine doping of EC6T on structures with different electrode distances of 11 mm (which refers to the macroscopic film), 10 μm, and 1 μm (two devices as example), all in the same thickness range of the organic film (100-150 nm). One of the 1 μm microstructures (marked by filled squares) yielded the same dependence of the conductivity on time as the 10 µm structure in the first doping minutes which was then followed by a stronger increase for subsequent doping. It is likely that the narrower structure reacted much faster on exposure by doping reagents which hence is not resolved on the experimental time scale. Nevertheless the conductivity value measured for this sample ($3*10^{-3}$ S/cm after 1000 minutes) are by a factor of 10 lower than those from 10 µm structures but in the same range as for the macroscopic film. The second 1 µm sample (marked by stars) revealed a strong dependence on the individual preparation parameters although it was prepared in the same manner. Slightly different evaporation rates of the organic film, different roughness of the electrode surfaces or of the underlying substrate may have contributed to a different degree of order or morphology of the films.



a) b)

FIGURE 3 (a) Conductivities in dependence on iodine doping time for 100 -150 nm thick EC6T films on microstructures with different electrode distances down to 1 µm.(b) Conductivities in dependence on the inverse chain length 1/n for the different oligothiophenes for non doped and iodine doped (doping time 1000 min) macroscopic films and 10 µm microstructures.

Fig. 3b shows the observed dependence of conductivity on the inverse chain length for non doped and iodine doped (1000 minutes) macroscopic films and for 10 μm microstructures. There seems to exist a proportionality of $\ln \sigma \sim 1/n$, the reason of which is not yet clear. At first glance one may speculate that this is due to the dependence of the charge carrier density n_c on the size of the band gap which scales with the inverse chain length $1/n$. However, it is less likely that the relative position of the dopant levels also sales with $1/n$. Thus other mechanisms have to be considered, for instance a dependence of the carrier mobility on the film morphology which may vary with the length of the oligothiophenes. Further experiments concerning, e.g., the variation of temperature or preparation parameters, are required. It is nevertheless remarkable that the slope of $\ln \sigma$ versus $1/n$ is almost equal for the non doped and iodine doped samples independent of the geometric layout. This may lead to the conclusion that although swelling of organic films upon doping is observed, conformational or morphological changes upon doping which may affect the carrier mobility in, and hence the conductivity of the oligothiophene films do not occur or at least are independent of the chain length for these longish oligomers.

CONCLUSION

Non doped and iodine doped end-capped oligothiophenes in macroscopic films and microstructures show a logarithmic dependence of the conductivities on the inverse chain length. The conductivities of non doped devices are independent of the film thickness and electrode distances down to 100 nm. The conductivities of iodine doped devices show a strong dependence on the in situ doping time and geometric parameters. Iodine doped microstructures with small electrode distances are very sensitive to the preparation parameters.

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