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Adhesion Promoters for Polythiophene

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Abstract:

Polythiophene layers have been grafted onto silicon, iron, platinum and titanium for applications as organic semi-conducting films on solid surfaces.
In general, the adhesion between the polymer films and substrates is insufficient for technical and microelectronic applications. The use of adhesion promoters between substrate and polymer and enables the formation of a strongly bonded composite. The polymers were synthesized by chemical or electrochemical surface polymerization.

1 Introduction

Polythiophene (PT) and its derivatives continue to attract great interest in the field of conducting polymers for both fundamental studies and potential electronic applications [1].
Highly ordered conjugated molecules on semiconductors are very important for building molecular devices such as metal-oxide-semiconductors (MOS) structures. Self-assembling which takes place through the interaction between the head group of the molecule and the substrate is one of the convenient techniques for the formation of homogeneous organic monolayers [2, 3]. Two possible methods can be used: the coating of the substrate with the polymer itself or the use of an adhesion promoter between substrate and conductive polymer. For the formation of self-assembled monolayer (SAM) films of oligothiophenes, the solubility of the polymer is crucial. The conductivity increases with the number of the thiophene moiety, but the solubility in the solvents decreases. An improvement in the solubility is reached by the introduction of a long chain substituent in the third position of the thiophene ring [1].
The second method was used in this study involving the development of adhesion promoters between the substrate and conducting layer.

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2 Aim and scope

The aim of this study was the creation of new materials based on polythiophene layers, that are applicable as conductive and intrinsic polymer layers for microelectronics and sensors or as interfaces for further metallization processes. In general, the direct adhesion between the polymer films and substrates is insufficient for technical and microelectronic applications. It is also not possible to electropolymerize non-conductive substrates. We chose some metal substrates including platinum or titanium as electrodes for electropolymerization.

Thiophene terminated self-assembly layers were synthesized as adhesion promoters to make polythiophene more compatible towards diverse metal substrates [4,5]. The adhesion promoters are self-assembly molecules that are able to react spontaneously with the substrate surface. They contain a surface-reactive group, an alkyl spacer and a polymerizable group on the layer surface. Different anchor groups were chosen depending on the substrates: for silicon the trichlorosilyl group was used and for reactive metals the phosphonic acid group. The appropriate 3-substituted thiophene derivatives were synthesized: ω-(3-thienyl) alkyltrichlorosilanes und 2-(3-thienyl) ethyl phosphonic acid.

Figure 1: Adhesion promoters for SiO_2 and metal-substrates

The polymerizable group on the surface is the thiophene ring. These thiophene terminated SAMs adsorbed onto silicon-wafers or metal surfaces allowing the in-situ polymerization and the formation of (semi)-conducting polymer layers.

The first step is the adsorption of the adhesion promoter onto the pre-treated substrate surface. Surface-active analytical methods including contact angle, FTIR- and XPS measurements gave information about the conformation of the monolayer and the composite.

The second step is the in-situ chemical or electrochemical polymerization of the thiophene ring with different thiophene monomers (3-methylthiophene, 2-(3-thienyl) ethyl acetate).

Differential scanning calorimetry (DSC) investigations of the synthesized polymers show whether copolymers are produced. AFM and SEM-images give a picture of the surface properties of these layers. Impedance measurements show the conductive behaviour of the films. The properties of the polymer films depend on the monomer ratios and the conditions of polymerization.

3 Experimental

All reagents used, solvents and substances were of reagent grade quality and were obtained from commercial sources. The solvents bicyclohexyl (99.0 %, Aldrich), chloroform (99.9 %, Merck) and toluene (99.9 %, Merck) were HPLC-grade and used without further purification. The other solvents were dried and distilled.

The synthesized compounds were characterized by their melting or boiling points, FT-IR-, ^{13}C-NMR-, ^{31}P-NMR-spectroscopy and elemental analysis.

METTLER TG 50 instrument was used for the differential scanning calorimetry (DSC). The spectral investigations were made with a BRUKER DRX500 NMR INSTRUMENT. Elemental analyses were carried out with a Carlo Erba CHNS-O EA1108 elemental analyser.

3.1 Syntheses

[11-(3-thienyl) undecyltrichlorosilane] (TUTS) was synthesized via a Ni-catalyzed coupling reaction between 3-bromothiophene and 10-undecene-1-yl magnesium bromide, followed by hydrosilylation of the 3-(10-undecene-1-yl) thiophene. Freshly distilled and cleaned TUTS was stored under an argon atmosphere. Additional storage took place in a desiccator over silica gel before use [4].

2-(3-thienyl) ethyl phosphonic acid was synthesized via a Michaelis-Arbusov reaction from 2-(3-thienyl) ethyl bromide [6].

3.2 Preparation of substrates

The Si substrates were non-doped polished silicon (100) wafers (cut into different pieces 10x10 mm, 15x10 mm, and 20x15 mm, depending on the characterization method) and polished silicon single crystals for ATR-IR. The substrates were cleaned by a wet chemical treatment in a freshly prepared hot Piranha solution [H_2SO_4/30% H_2O_2 (4:1)] for 30 min, followed by extensive rinsing with distilled water and chloroform, and drying in a stream of argon.

Metal substrates, including Ti, Fe, Pt, were used as plates (15x15 mm), ultrasonically cleaned in acetone, polished and stored under argon.

3.3 Preparation of adhesion promoter films

All films were prepared under ambient laboratory conditions. The Si substrates were immersed into a diluted solution of TUTS in bicyclohexyl for various periods of time. This deposition was carried out in an Erlenmeyer flask, which was pre-heated under vacuum and fluted with dry argon before use.

The samples were rinsed with chloroform, distilled water, and once more with chloroform before being dried in a stream of argon.

The metal substrates were coated with 2-(3-thienyl) ethyl phosphonic acid by immersing in a solution of the adhesion promoter. The samples were kept in a desiccator after rinsing with the solvent and drying in a stream of argon.

3.4 Analytical tools

- *FTIR-ATR spectroscopy of ultrathin layer*

ATR (attenuated total reflection) IR spectra were obtained at a 45° incidence on 50x20x5 mm silicon single crystals by using a BRUKER IFS 66 spectrometer equipped with a liquid nitrogen cooled MCT-detector. All ATR-spectra were recorded at a resolution of 2 cm^{-1} collecting 256 scans. Spectra were run in a dry atmosphere and were referenced to background spectra previously determined for the crystal under the same conditions. The sample chamber was purged for 2 h with nitrogen before the ATR-IR measurements.

- *Raman Spectroscopy*

Raman spectra were taken with Renishaw Raman Imaging Microscope System 2000 under ambient laboratory conditions. The spectra were recorded at a resolution of 0,87 cm^{-1} at a range of 100 to 3000 cm^{-1}.

- *Scanning Electron Microscopy – SEM*

SEM images were made by using a Zeiss DSM 982 Gemini with an Schottky-FE-Cathode. The pressure in the system of the probe chamber during the measurements was between $1x10^{-6}$ and $1x10^{-7}$ hPa. The magnification of the images were between 5000 and 50000.

- *Atomic Force Microscopy – AFM*

The morphology of the layers was investigated by AFM. A Digital Instruments, Nano Scope III in the Tapping Mode™ was used and a silicon cantilever with integrated tip. The Tapping mode was chosen in order to reduce interactions of the tip sample and to avoid lateral forces during scanning. All measurements were performed in air at 22°C and 50% RH. The surface profile of the samples was quantified on images of the same size and pixel resolution, using the built-in roughness and section analysis software.

- Impedance Measurements

The polymer films that were electrochemically grafted on the electrodes were measured using IM5d Impedance Measuring Instrument from Zahner Electric. The impedance spectra were obtained between the potential ranges from 500 mV to –800 mV in steps of 10 mV.

4 Results

4.1 Synthesis of conducting layers

Two different types of adhesion promoters were chosen for the bonding of the polymer layers on the several substrates.

ω-(3-Thienyl) undecyltrichlorosilane is spontaneously adsorbed from solution onto different substrates like Si/SiO_2, Fe/Fe_2O_3, Ta/Ta_2O_5, Ti/TiO_2, Al/Al_2O_3. However, the compound is extremely sensitive towards moisture and contains chloride that causes corrosion of the metal substrates.2-(3-thienyl) ethyl-phosphonic acid forms stable layers on most of the investigated substrates with the exception of Si/SiO_2.

The adsorbed adhesion promoter layers were characterized with ATR-IR spectroscopy. In the case of TUTS the characteristic methylene vibrations of the alkyl chain are at 2923 cm^{-1} and 2853 cm^{-1}. The layers are not highly ordered because of the terminal thiophene group.

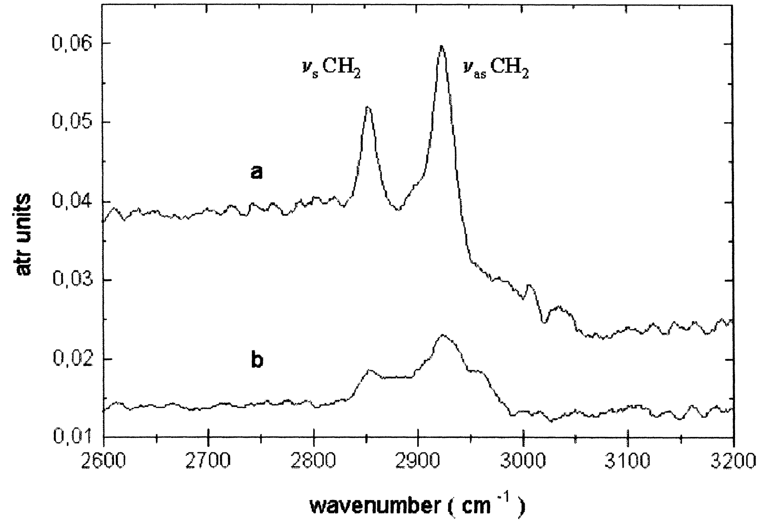

Figure 2: ATR spectra of adsorbed TUTS on SiO_2 [4]

Further reactions can now be carried out on the substrate surface. The in-situ polymerization of thiophene and its derivatives produces conductive polymer layers which can be characterized.

The surface polymerization can be undertaken either chemically or electrochemically. The principle of these reactions is shown in figure 3. $FeCl_3$ was used as an oxidative coupling reagent for the chemical polymerization, we used as. The terminal thiophene groups of the adhesion promoter take part in the polymerization process and a stable composite can be formed consisting of the conducting polymer, adhesion promoter and substrate.

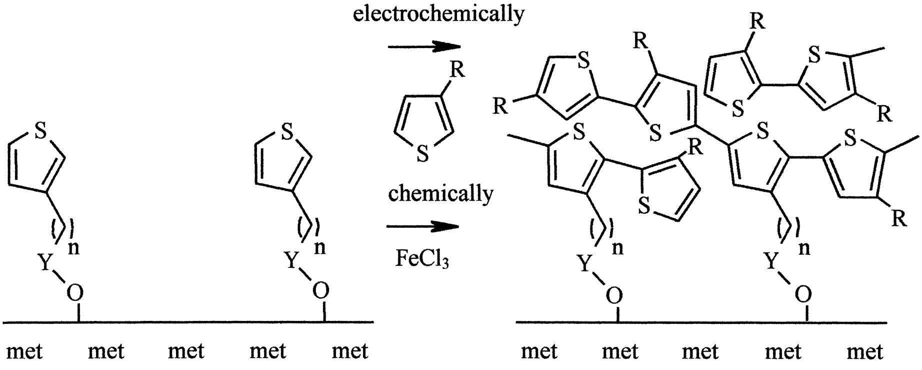

Figure 3: Principle of surface polymerization via an adhesion promoter

For electro-polymerization, the electrodes were coated with the adhesion promoter and polymerised at the corresponding oxidizing potential.

The polymer thickness could be adjusted between 3 and 250 nm depending on the reaction conditions.

4.2 Characterization of polymers

The polymer layers grafted onto the substrates were characterized by Raman spectroscopy, Atomic Force Microscopy, SEM and impedance measurements.

4.2.1 Grafting of polythiophene onto SiO_2

The Raman spectrum of polythiophene grafted onto SiO_2 showed three characteristic bands for polythiophene (see figure 4).

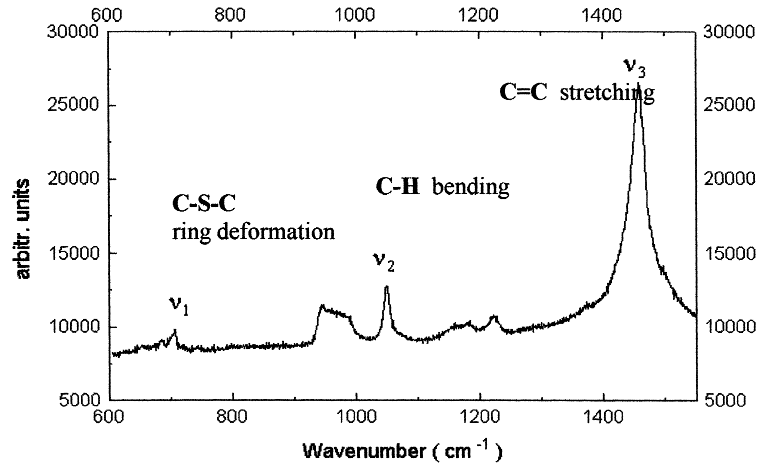

Figure 4: Raman spectrum of polythiophene grafted onto SiO_2

The AFM image of polythiophene grafted onto a Si-wafer is shown in figure 5. The layer has a relatively homogeneous and dense surface with a shell-like structure. A roughness analysis gave values of R_{ms} = 1,73 nm and R_a = 1,35 nm.

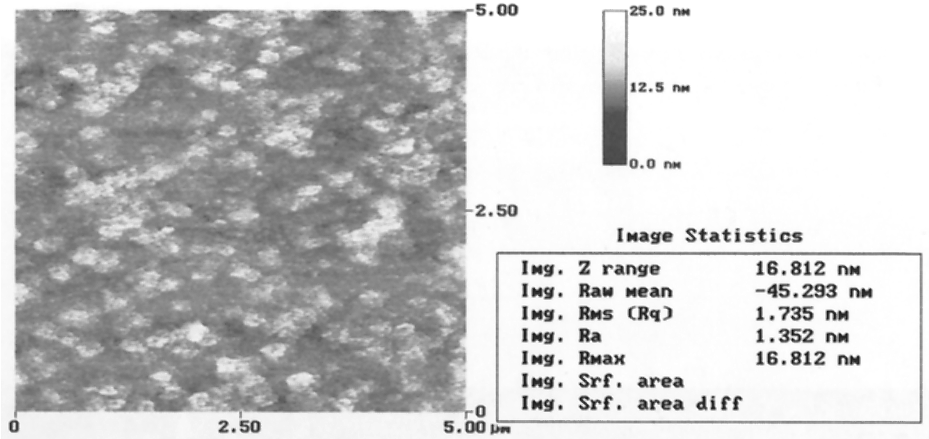

Image Statistics

Img. Z range	16.812 nm
Img. Raw mean	-45.293 nm
Img. Rms (Rq)	1.735 nm
Img. Ra	1.352 nm
Img. Rmax	16.812 nm
Img. Srf. area	
Img. Srf. area diff	

Figure 5: AFM Image of polythiophene grafted onto SiO_2

By comparison, the surface of the adhesion promoter layer of TUTS (see figure 6) on SiO_2 is very homogeneous, i.e. free of holes and aggregates, and smooth [4]. A roughness analysis yields a R_{ms} value of 0.22 nm and R_a of 0.17 nm. These values are in good agreement with literature data (R_a=in the range of 0.1 nm) for octadecyl trichlorosilane layers on SiO_2 substrates [7, 8].

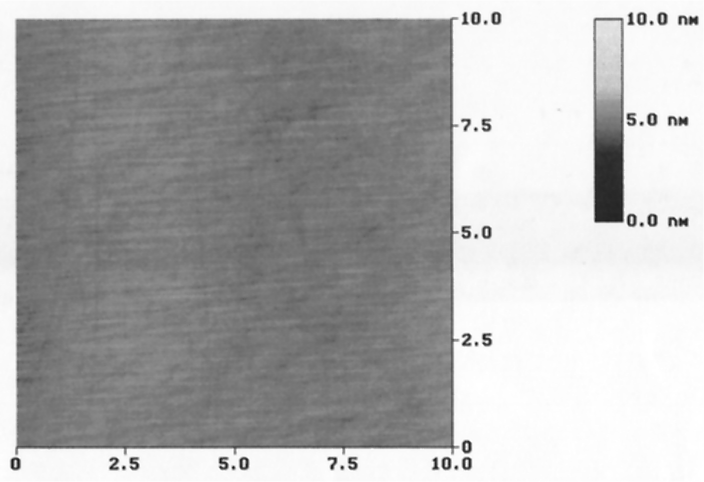

Figure 6: AFM image of [11-(3-thienyl) undecyltrichlorosilane] (TUTS) adsorbed onto SiO_2

4.2.2 Grafting of thiophene copolymers onto metal substrates

In order to study the possible copolymerization between different monomers (e.g. thiophene and thiophene acetate), attempts were made to chemically polymerize different compositions (1:1, 1:9 and 9:1) of these monomers.

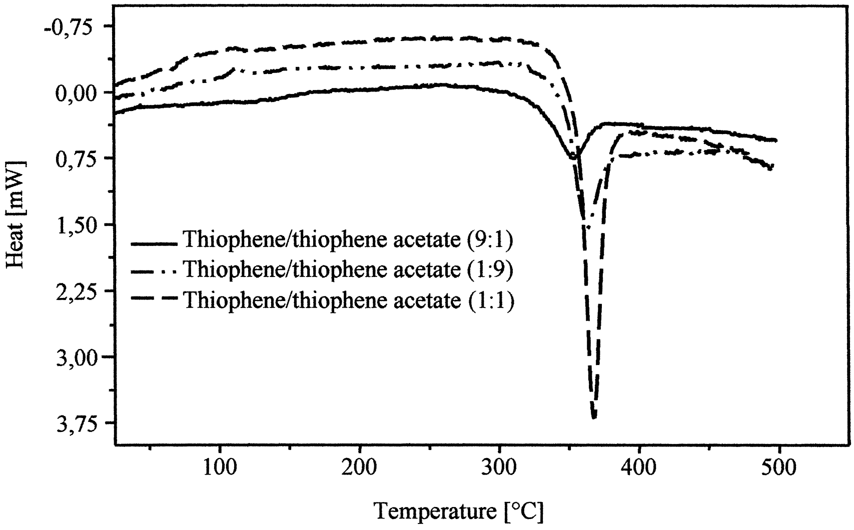

Figure 7: DSC analysis of different thiophene copolymers

The DSC scans (see figure 7) show single sharp peaks in a nitrogen atmosphere and it can be concluded that copolymers were formed. If only homo-polymers were synthesized from several monomers, two or more peaks would be found. There is a slight shift in the decomposition temperature of the copolymers depending on the monomer mixture composition.

The conducting properties of several copolymers were investigated using impedance measurements [9]. There are different possibilities for representing impedance measurements: The Bode plot illustrates the dependence of impedance and phase angel on frequency. It is obtained by measuring at different potentials. In figure 7 the Bode plot of the copolymer thiophene/thiophene acetate (9:1) on platinum was measured in a potential range of 450 mV to –800 mV. There is a regular decrease of impedance from –800 mV to 450 mV indicating that the film shows semi-conducting behaviour.

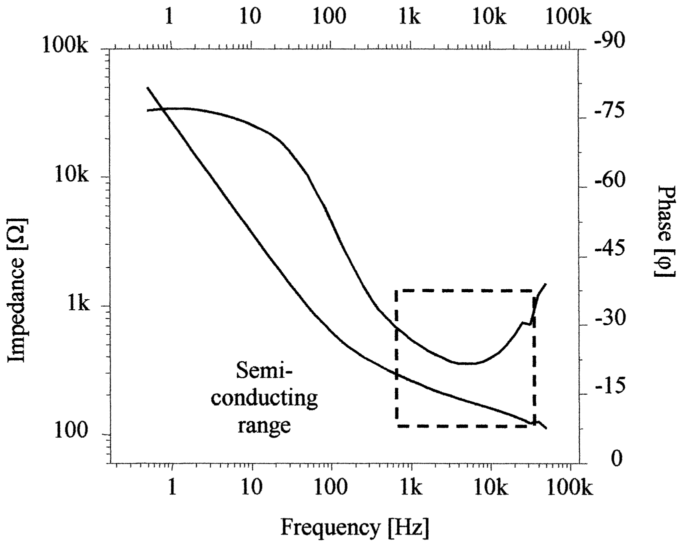

Figure 8: Bode-plot of copolymer thiophene/thiophene acetate (9:1) at 0,5V

Information can be obtained about the kind of the conductor from Mott-Schottky-plot. The Mott-Schottky diagram is obtained when the inverse of the capacitance C_{HF}^2 is plotted against the potential.

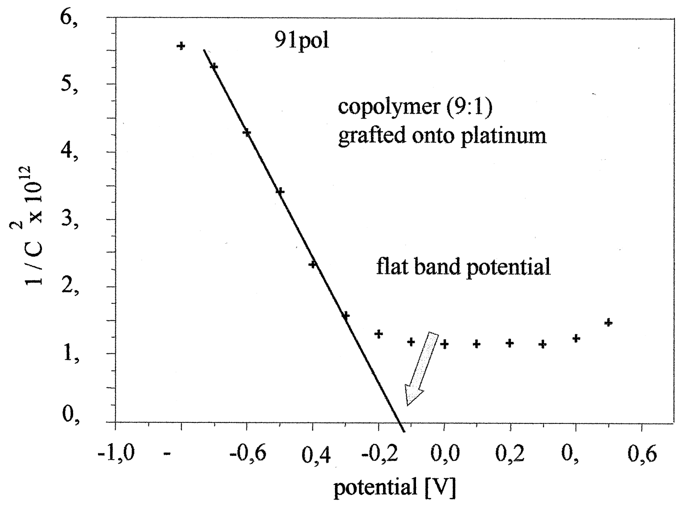

Figure 9: Mott-Schottky-Plott of copolymer (9:1) grafted onto platinum

Figure 9 shows the behaviour of a thiophene/thiophene acetate (9:1) copolymer on platinum. In the region of –0,7 V to –0,1 V the graph follows a linear relationship indicating that the film has semi-conducting properties. The flat band potential can be obtained from Mott-Schottky plot and was found to be E_{fb}= -0,13 V_{SCE}. By comparison, the flat band potential of thiophene is around E_{fb}= 0,5 V_{SCE}.

In general, the flat band potential of the different copolymers thiophene/thiophene acetate varies between E_{fb}= -0,13 V_{SCE} and E_{fb}= -0,29 V_{SCE}.

5 Conclusion

Polythiophene layers were grafted onto several substrates including Si wafers, platinum and titanium by using special adhesion promoters and different monomers. Stable polymer layers were obtained by means of chemical surface polymerization using $FeCl_3$ as oxidising agent. Especially, the copolymers of thiophene and thiophene acetate show the behaviour of a semiconductor with flat band potentials in negative regions.

However, further investigations will be performed to establish the stability, the film thickness and the semi-conducting behaviour of the films.

6 References

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