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Pyrrole-Substituted Alkyl Silanes as New Adhesion Promoters on Oxidic Substrates

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Summary: ω-(Pyrrol-1-yl alkyl) dimethylchlorosilanes with different chain length were synthesized and characterized with IR, NMR and elemental analysis. The growth of self-assembled monolayers of ω-(pyrrol-1-yl alkyl) dimethylchlorosilanes on oxide surfaces has been investigated. The order gradually improved with adsorption time and highly ordered SAMs were obtained for nearly 2 days adsorption time. Characterization of the films has been performed with contact angle measurements, ellipsometry, SPR and grazing incident FTIR. The chemical deposition of polypyrrole on the modified surface was investigated. The thickness of polypyrrole layer was influenced by the concentration of monomer, the deposition time, and the ratio of monomer to oxidant.

Keywords: monolayer; polypyrrole; ω-(pyrrol-1-yl alkyl) dimethylchlorosilanes

Introduction

Many varieties of conducting polymers have been described in the last decades [1]. Especially, the electrochemically synthesized conducting polymer films have been extensively investigated because of their wide range of useful applications such as microelectronic devices [2], chemical sensors, biosensors [3, 4], and corrosion protection [5]. Polypyrrole films are one of the important conducting polymers and their films are prepared by electrochemical polymerisation using highly conducting electrodes [6]. However, in most cases, adhesion between the polymer and the conducting substrate (electrode) is poor because of weak physical interactions between them. Generally, polypyrrole can be peeled from the substrate to give freestanding films [7, 8]. Researchers have tried to use adhesion promoter molecules to modify the electrode to increase the adhesion between the substrates and the polymer films [9]. Wrighton and co-workers used N-(3-trimethoxysilyl) pyrrole as a surface modification agent to improve adhesion of polypyrrole films and n-type Si [10]. F. Faveralle et. al reported the chemical polymerisation of polypyrrole

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on glass fibre modified with pyrrole-substituted organotrialkoxysilane coupling agents as adhesion promoter between polypyrrole and glass fibre [11]. Recently, the synthesis and application of several substituted pyrroles as adhesion promoters were described, e.g., pyrroles with thiol group on Au [12-17]. Nevertheless, none of these researchers systematically investigated the effect of alkyl chain length on the properties of the monolayer of pyrrolyl-alkyl dimethylchlorosilanes and the chemical deposition of conducting polypyrrole on surface modified inorganic substrates.

In this paper, the properties of the monolayer were studied with various techniques including contact angle measurements, ellipsometry, surface plasmon resonance spectroscopy (SPR), grazing incident FTIR and X-ray photoelectron spectroscopy (XPS). The chemical deposition of polypyrrole on the modified substrates was described and the layer thickness could be adjusted.

EXPERIMENTAL

Substances

Several ω-(pyrrol-1-yl alkyl) dimethylchlorosilanes with different chain length were used as adhesion promoters for grafting polypyrrole layers onto silicon. The synthesis details will be described elsewhere.

6-(pyrrol-1-yl hexyl)dimethylchlorosilane	PMCS-6
8-(pyrrol-1-yl octyl)dimethylchlorosilane	PMCS-8
11-(pyrrol-1-yl undecyl)dimethylchlorosilane	PMCS-11
16-(pyrrol-1-yl hexadecyl)dimethylchlorosilane	PMCS-16

Surface modification of substrates with the silane compounds

Silicon substrates were first treated with 3:1(v/v) of concentrated H_2SO_4 and 30% H_2O_2 at 90° for 30min to clean the surface and produce terminal hydroxyl groups [18]. The acid treated substrates were then carefully washed with water and blown dry with argon. The clean substrate was dipped in a solution of silane compound in bicyclohexyl (10mM) for 48h, washed with chloroform, and thoroughly ultrosonicated for 20min and dried with argon.

Physicochemical studies

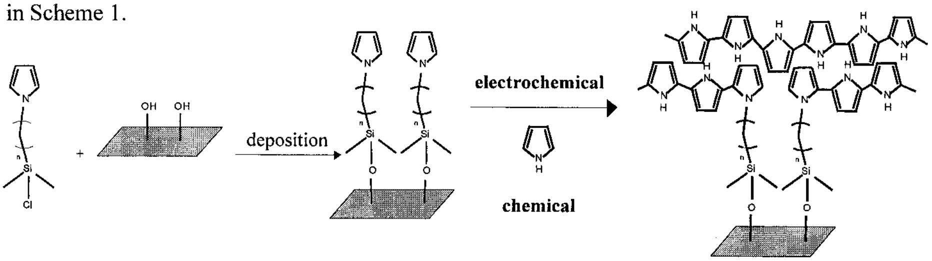
KRÜSS DSA10 goniometer (drop shape analysis) was used for contact angle measurements. Ellipsometric studies were preformed with a computer interfaced DRE GmbH ELX-02C ellipsometer over the wavelength 623nm and an incident angle of 70°. XPS studies were carried out using a Physical Electronics PHI 5700 ESCA system. UV-VIS spectra were obtained on a Perkin-Elmer Lambda 35 UV/VIS spectrometer. Nanoscope Dimension 3100 from Veeco/USA was used for AFM measurements, which was run in tapping mode. The thickness of polypyrrole films were measured with Dektak surface profile measuring system.

Chemical deposition of polypyrrole films on silane-modified substrates

In a typical reaction, the modified substrate was dipped in 1.7M oxidant /H_2O solution, and a two times volume of 0.1M pyrrole-MeOH solution was added. The mixture was stirred at room temperature for 1h and then the substrate was removed from solution. It was washed with solvent to remove the loose polymer attached on the film surface, and blown dry with argon.

RESULTS AND DISCUSSION

The strategy for deposition of a conducting polypyrrole film on an insulating substrate is shown in Scheme 1.

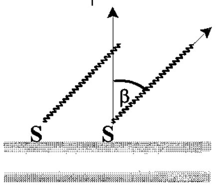


Scheme 1. Polymerisation of pyrrole via template modified surface

The deposition of silane compounds on the oxide substrate was achieved by dipping the clean substrate in 10mM ω-(pyrrole-1-yl alkyl) silanes/bicyclohexyl solution. The static contact angle showed that the longer alkyl chain of ω-(pyrrole-1-yl alkyl) silanes lead to high hydrophobicity of the surface. Optical ellipsometry was used to measure the thickness of the silane compounds on the oxide surface. It was found that the thickness of ω-(pyrrole-1-yl alkyl) silanes on silicon dioxide surface is not proportional to the chain length of the alkyl group and that they are smaller than the size of ω-(pyrrole-1-yl alkyl) silanes calculated from molecular models (Tab.1).

Table 1. Contact angles and thickness of monolayer.

Compounds	**PMCS-6**	**PMCS-8**	**PMCS-11**	**PMCS-16**
Contact angle [°]	86.7	98.1	101.7	103.4
Layer thickness [nm]	0.95	1.22	1.47	2.59
Calculated length [nm]	1.42	1.53	2.05	2.69
Tilt angle [°]	48.2	37.9	44.2	15.8



$$\cos\beta = \frac{\text{Layer thickness}}{\text{Molecule length}}$$

Fig. 1: Definition of tilt angle of adsorbed monolayer

These results indicated that ω-(pyrrole-1-yl alkyl) dimethylchlorosilane molecules are not closely packed on the oxide surface, due to two methyl groups at the silicon atom except for the derivative with 16 carbons spacer length. Grazing incident FTIR was measured to study the order of the monolayer. The IR spectra are shown in Figure 1. The order in the PMCS-8 layers can be assessed from the position of the CH_2-stretching vibration. As shown in previous studies [19-22], the frequency of the CH_2-stretching vibration is characteristic for long-chain SAM's indicating close packed structures. For completely disordered structures, the frequency of the CH_2-stretching is close to that of a liquid alkane ($\nu_{as}\sim$ 2924 cm^{-1}). For well-ordered SAMs, the frequency is shifted to lower wavenumbers, and it is close to that of a crystalline alkane (ν_{as} ~ 2915-2918 cm^{-1}) [23]. The data of Fig. 2 show that CH_2-stretching of 8-(pyrrol-1-yl octyl) dimethylchlorosilane is 2918 cm^{-1}. This indicates SAMs with a high degree of order.

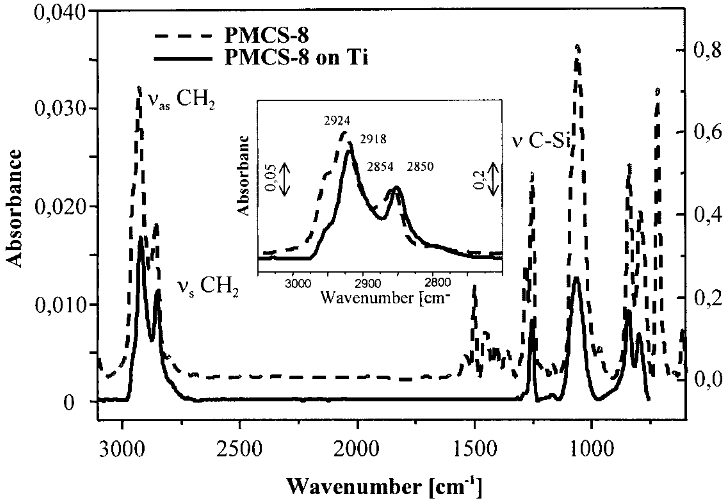


Fig.2: Grazing incident FTIR spectra of PMCS-8

We found that $\nu_{as}CH_2$ is decreasing with the increasing of concentration of solution or adsorption time (Fig. 3). During the adsorption, the early stages of the reactions can be pictured as isolated grafted molecules randomly distributed on the substrate. As the surface coverage increases, the order in the monolayer gradually increase ($\nu_{as}(CH_2)$ decrease), approaching the final highly ordered or the closely packed state.

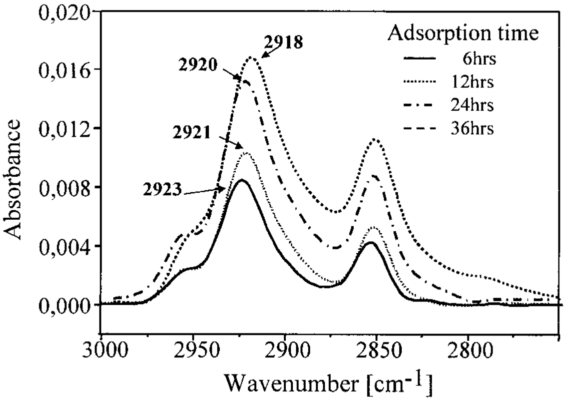


Fig. 3: Grazing incident IR spectra of PMCS-11 on Ti at different adsorption times

Angle-dependent XPS measurements were done to study the orientation of the adsorbed ω-(pyrrole-1-yl alkyl) silane on Ti oxide substrate. The measurements were done at 5°, 20°, 45°, and 85° angles. By varying the detector angle we got information from different depths of the adsorbed layer. Therefore, special marker atoms were used: N from the pyrrole group and Si from the silane group. We calculated I_{Si}/I_N to get an indication how the molecule is oriented on the surface relatively to the detection angle. At a low detector angle more N atoms were observed and at high detector angles more Si atoms. Though, an increase in the Si/N ratio with increasing detector angle indicated that the molecules are oriented with the pyrrole group on top and the silane group attached to the surface (see Fig. 4).

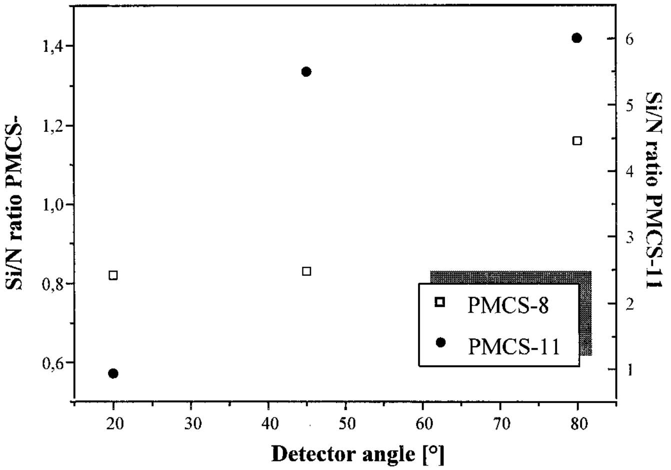
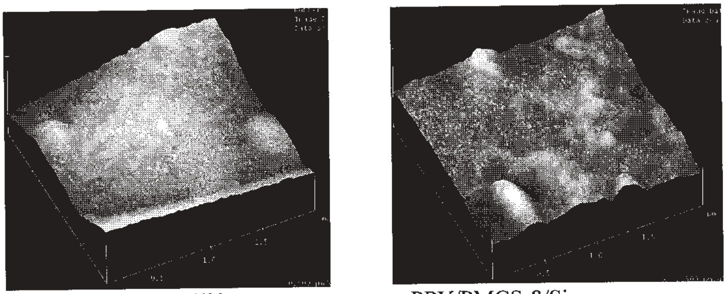


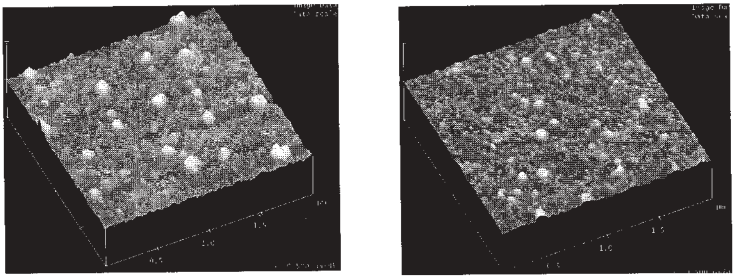
Fig. 4: AR-XPS measurements of adsorbed ω-(pyrrole-1-yl alkyl) silanes: Si/N ratios

There are two methods for deposition of polypyrrole films on the modified substrates, chemical deposition and electrochemical deposition. In this paper, only the results of chemical deposition are given.

Polypyrrole films chemical deposited on a silane-modified substrates show much better adhesion compared to those on unmodified substrates. Thin films up to 400nm in thickness adhered tightly to the silane-modified substrates. On the other hand, when unmodified substrates were used, only loosely attached particles were found on the surface, which could be washed off easily with the solvent. AFM measurements revealed that polypyrrole films deposited over ω-(yrrol-1-yl alkyl) silane with long alkyl chain showed a smoother morphology than that of films deposited over ω-(pyrrole-1-yl alkyl) silane with shorter alkyl chains (Fig.5). Contact angle and ellipsometry data also showed that ω-(pyrrole-1-yl alkyl) silane with long alkyl chains formed more compact and ordered SAMs on the oxide surfaces. The formation of pyrrole molecules on the inorganic surface increased the interaction between the organic polymer and the substrate, and therefore, increased the adhesion between them.



PPY/PMCS-6/Si PPY/PMCS-8/Si



PPY/PMCS-11/Si PPY/PMCS-16/Si

Fig. 5: AFM of polypyrrole deposited on different chain length modified substrate

The formation of polypyrrole was also identified by Raman Spectroscopy (Fig. 6) and UV-VIS data (not shown here), both spectra showed the characteristic absorption patterns of polypyrrole.

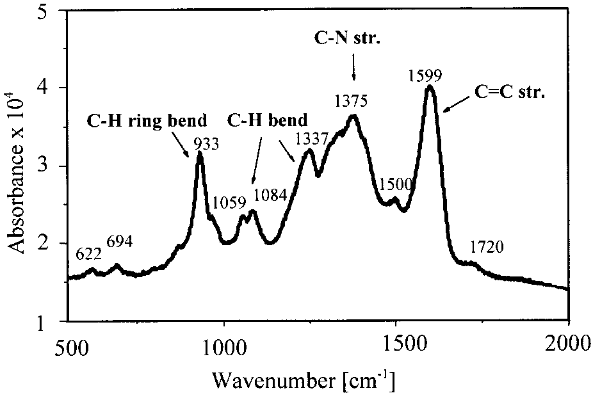


Fig. 6: Raman spectrum of polypyrrole deposited on a silane modified substrate

The thickness of the film increased as the deposition time increased during the first 4 hrs and then reached a plateau, due to complicated equilibrium processes between polypyrrole chains deposited on and removed from the substrate. It was found that the lower the monomer to oxidant ratio, the smaller the surface roughness of the resulting films. For a constant monomer to oxidant ratio, it was found that the polymer films prepared at a concentration of 0.1M have the highest thickness and smallest surface roughness (Fig. 7). At lower monomer concentration, the polypyrrole chains have less chance for deposition on the surface while at high concentration, the reaction rate is too fast to allow the growth of a dense film on the substrate. However, due to the limited solubility of $Na_2S_2O_8$ in water, the concentration of $Na_2S_2O_8$ can not be higher than 0.2M. The reaction atmosphere and temperature did not have any obvious effect on the properties of the resulting films.

The adhesion between polypyrrole film and substrates was tested by peel-out test and ultrasonical test. In every case the film had a good adhesion on the substrate surface.

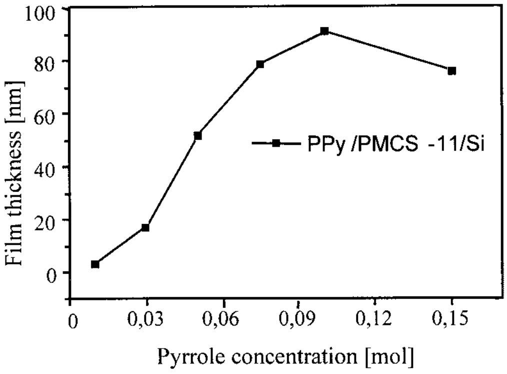


Fig. 7: Effects of polymerisation conditions on the thickness of polypyrrole films (polymerisation time 1h; oxidant $Na_2S_2O_8$; solvent $MeOH/H_2O$ 2:1 v/v; reaction atmosphere air; pyrrole to oxidant ratio 0.17)

CONCLUSION

In this paper, the characterization of ω-(pyrrol-1-yl alkyl) silanes with various alkyl chain lengths, as well as the adsorbed monolayers on oxide substrates and the chemical deposition of polypyrrole over the modified substrates were described. Contact angle measurements showed that hydrophobicity increased with increasing chain length of the adsorbed molecules. Ellipsometry data confirmed that ω-(pyrrol-1-yl alkyl) silane layers formed monolayers on the substrates. The calculation of the tilt angles of the adsorbed molecules revealed that the long chain derivatives formed more compact and well-ordered SAMs on Si substrate. The thickness of the surface polymerised polypyrrole films was influenced by deposition time, monomer to oxidant ratio and monomer concentration. The thickness of polypyrrole films was increased with increasing deposition time during the first 4 hours. At low monomer to oxidant ratios, a small surface roughness and thin polypyrrole films were obtained. ω-(pyrrol-1-yl alkyl) silanes improve the adhesion between polypyrrole layer and substrate. Furthermore, polypyrrole layers deposited over ω-(pyrrol-1-yl alkyl) silanes with long alkyl chains have a smoother morphology than that of layers deposited over ω-(pyrrol-1-yl) alkyl silanes with shorter alkyl chains.

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