Chemical deposition of ordered conducting polypyrrole films on modified inorganic substrates

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In-situ deposition of conducting polypyrrole thin films on an insulating substrate has been achieved by chemical polymerization of pyrrole on a modified surface. The surface modification agent was a silane compound bearing a pyrrole group; $C_4H_4NC_3H_6Si(OMe)_3$ which attached to the SiO_2-Si surface *via* molecular self-assembly. A monolayer of silane-bearing pyrrole molecules was formed on the surface. Polymer films formed on the silane-modified surfaces showed better adhesion compared to those on the unmodified surfaces. IR, UV–VIS–NIR and XPS data revealed that the films were in their conducting state and homogeneously doped. The thickness and conductivity of the resulting films were controlled by the preparation conditions, such as choice of solvent, deposition time and pyrrole to oxidant ratio. Polypyrrole films with thickness in the range 410–5500 Å adhered firmly on the surface. The room-temperature conductivity of the films can be up to 1.6 S cm^{-1}. Some of the polypyrrole films showed anisotropic conductivity which indicates that the pyrrole molecules on the surface induced regular deposition of polypyrrole chains on the substrate.

Conducting polymer films have attracted wide attention owing to their interesting optical and electronic properties.[1] Polypyrrole films are one of the important conducting polymers as they are characterized by high conductivity.[2] In general, polypyrrole film are prepared by electrochemical polymerization using highly conducting electrodes.[3] In most cases, adhesion between the polymer and the conducting substrate (electrode) is poor because of weak physical interactions between them. Therefore polypyrrole can be easily peeled off as a free standing film.[4] Electrochemical deposition of conducting polymer films on electrode surfaces is not a well defined process.[5] A generally accepted mechanism for the anodic polymerization of heteroarenes is the formation of soluble oligomers which eventually precipitate on the electrode surface, forming nucleation sites, and film growth thereafter. Polymerization kinetic studies[6] also indicated that the early stages of deposition depend on the solubility of oligomers formed and the rate-determining step is the oxidative incorporation of monomers or oligomers into the growing polymer chains. Therefore the resulting film is randomly oriented and amorphous. However, high-quality well defined thin films are essential for studies of electronic, magnetic and optical properties of these materials. On the other hand, molecular self-assembly has been applied to prepare materials with interesting optical and electrical properties.[7] It is believed that self-assembled monolayers (SAM) which have desired control on the molecular level, should be considered as a potential technique[8] for the construction of more highly ordered materials. Therefore, we used a methoxysilane compound bearing a pyrrole group to assemble a layer of pyrrole on a silicon oxide surface. The pyrrole molecules on the surface can act as nucleation sites to grow ordered conducting polypyrrole films with good adhesion between the polymer film and the substrate.

In the literature, an electrochemical study of self-assembled alkoxysilane–pyrrole monolayers on a silicon substrate has been reported.[9] However, whether formation of a monolayer of silane occurred, the order of the polypyrrole films grown on the modified surface and thickness-related conductivity were not clearly addressed. Although Gregory *et al.*[10] had reported the coating of conducting polymers on unmodified textile composites, they focused only on the reaction kinetics and the conductivity of the fibres. There are no reports related to the chemical deposition of conducting polypyrrole, on large-area surface-modified inorganic substrates. Recently, we have reported[11] the chemical deposition of an ordered conducting polyaniline film on silane-modified substrates. Here we study the chemical deposition of conducting polypyrrole films on a $C_4H_4NC_3H_6Si(OMe)_3$-modified silicon oxide surface. Optimal reaction conditions are investigated and the effect of the self-assembled silane layer on the deposition of polypyrrole films and the thickness related conductivity are reported.

Experimental

(a) Chemicals

$C_4H_4NC_3H_6Si(OMe)_3$, (100) oriented p-type silicon wafer (from Topsil, with an oxide layer of *ca.* 100 Å and resistivity $>2000\ \Omega$ cm), $FeCl_3$, $H_2O_{2(aq)}$, H_2SO_4 were purchased from commercial suppliers and used as received. Pyrrole and all solvents (HPLC grade) were distilled over molecular sieves before use.

(b) Surface modification of substrates with the silane compound

The substrates were first treated with 7 : 3 (v/v) of concentrated H_2SO_4 and 30% H_2O_2 at 90 °C for 30 min to clean the surface and produce terminal hydroxy groups.[12] The acid-treated substrates were then washed with copious amounts of water and blown dry with nitrogen. In a glove bag, the clean substrate was dipped in a solution of $C_4H_4NC_3H_6Si(OMe)_3$ in MeOH (9.0 mM) for 24 h, then removed and washed with MeOH thoroughly and dried at room temperature.

(c) Chemical deposition of polypyrrole films on silane-modified substrates

In a typical reaction, the modified substrate was dipped in 1.5 M pyrrole–MeOH solution, and an equal volume of 1.5 M $FeCl_3$–MeOH solution was added. The mixture was stirred at room temperature for 20 h and the substrate then removed from solution, washed with solvent to remove the loose powder attached on the film surface, and blown dry with nitrogen. Other parameters for deposition of polypyrrole films were as follows: pyrrole (C_4H_4NH) concentration = 0.25–2.50 M; pyrrole to $FeCl_3$ ratios 0.25–4 : 1; solvents, H_2O, CH_3OH, C_2H_5OH, C_3H_7OH, CH_3CN, THF, $CHCl_3$ and benzene; reaction atmosphere, air or nitrogen (glove bag); deposition time, 10 min to 85 h; reaction temperature, 0 °C and room temperature.

(d) Physicochemical studies

Fourier transform IR (FTIR) spectra were recorded for pressed KBr pellets or films on Si substrates using a Bio-Rad 155 FTIR spectrometer. Polarized IR absorption spectra were taken by placing the KRS-5 wire grid polarizer between the IR source and sample. Ellipsometric studies were performed with a computer interfaced J. A. Woollam Co. Control Module EC-1000 ellipsometer over the wavelength range 400–1000 nm and an incident angle of 70°. X-Ray photoelectron spectroscopy studies were carried out using a Perkin-Elmer PHI-1600 ESCA/XPS spectrometer and a Perkin-Elmer PHI 670 Auger Nanoprobe. The thicknesses of polypyrrole films were measured with a Dektak^3 surface profile measuring system. The scan length is 5 mm and the thickness was calculated from the average thickness of the length scanned. UV–VIS–NIR spectra were obtained on a Varian Cary 5E spectrometer. Scanning electron micrographs were taken using a Hitachi S-800 electron microscope at 15 kV. Samples for SEM imaging were mounted on Al stubs with graphite paint without further coating.

(e) Charge transport measurements

Direct current electrical conductivity measurements were performed on compressed pellets (1.2 cm diameter) of powders and films on substrates (1.2 cm × 1.2 cm square plate) in the usual four-point geometry.[13] The four points on the sample surface were in a line at an equal spacing of 2 mm. Each point was adhered to a gold wire (using silver paste) for the current and voltage electrode. An appropriate current (1 nA to 1 mA) was maintained on the two outer electrodes. The floating potential across the two inner electrodes was measured to determine the conductivity.[14]

Results and Discussion

Formation of monolayer silane on the surface of the substrate

The strategy for deposition of a conducting polypyrrole film on an insulating substrate is shown in Scheme 1. The deposition of silane compounds on the SiO_2-Si substrate was achieved by dipping the clean substrate in 9 mM $C_4H_4NC_3H_6Si(OMe)_3$–MeOH solution. The surface absorbed water as well as a trace amount of water in the solvent and reaction environment catalysed the reaction between methoxy groups in the silane with the OH groups on the surface.[9,15] Optical ellipsometry was used to measure the thickness of the silane compound on the surface during reaction. It was found that after reacting for 24 h, the thickness of silane on the SiO_2-Si surface was *ca.* 11 Å in accord with the presence of a monolayer. X-Ray photoelectron studies were performed to further confirm the presence of the silane on the substrate. The XPS spectrum of the modified surface showed a nitrogen 1s peak at a binding energy of 399.5 eV, close to that of nitrogen in polypyrrole.[16] Moreover, by electron microscopy, the surface of silane-treated substrate was as flat as that of the bare substrate. There is no obvious aggregation on the surface which implied that the silane was homogeneously dispersed on the substrate. The formation of a monolayer of silane on the substrate has a significant influence on the properties of the polypyrrole deposited on it (vide infra). If the moisture of the glove bag was too high or if the reaction time was too long, multilayers of silane were obtained. Polypyrrole films deposited on multilayer silane-modified surfaces, while showing good adhesion were very inhomogeneous and had low conductivity. Therefore only the properties of polymer films deposited on monolayer silane-modified surfaces are discussed further.

More interestingly, when the silane–pyrrole monolayer was treated with oxidant, a shoulder on the N 1s XPS appeared, as shown in Fig. 1. This indicated that the monolayer of the pyrrole on the surface can be polymerized by an oxidant without the presence of external pyrrole molecules. Unfortunately, this could not be observed by IR spectroscopy.

Effect of the silane monolayer on the deposition of polypyrrole films

Polypyrrole films deposited on silane-modified substrates show much better adhesion compared to those on unmodified substrates. Thin films up to 5500 Å in thickness adhered tightly to the silane-modified substrate. 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 solvent. Under SEM, Fig. 2, a polypyrrole film on

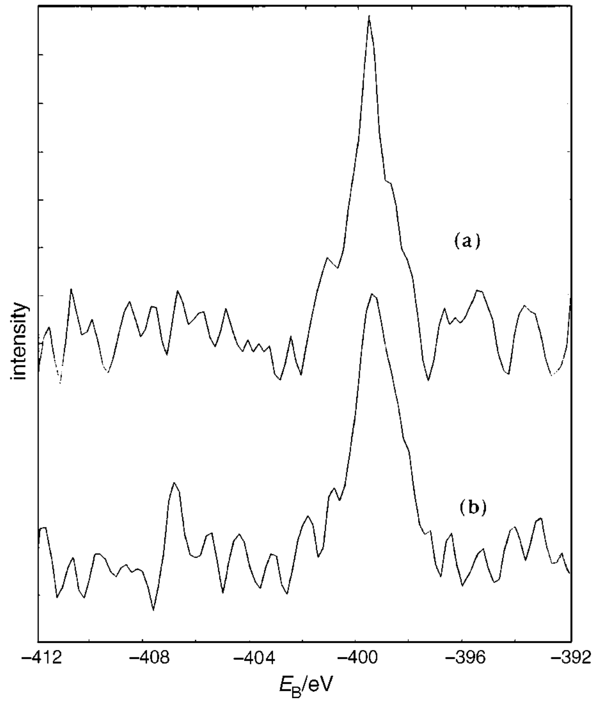
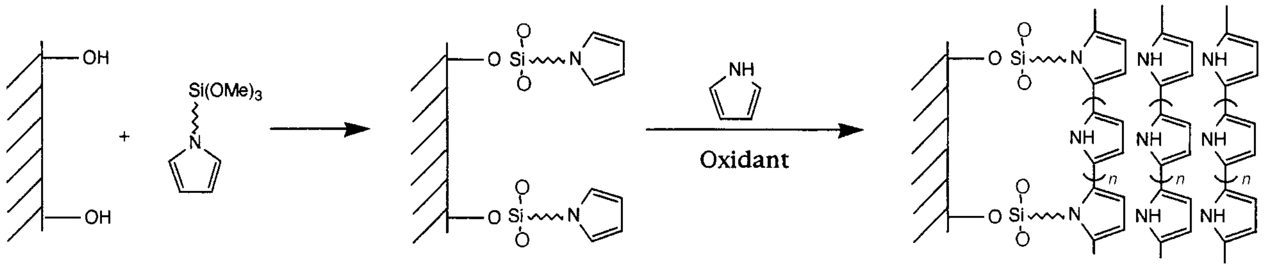


Fig. 1 High-resolution XPS spectra of the N 1s region of the silane–pyrrole monolayer assembled on the SiO_2-Si surface (a) before and (b) after treatment with oxidant



Scheme 1 Fabrication of a conducting polypyrrole film on a silane-modified substrate

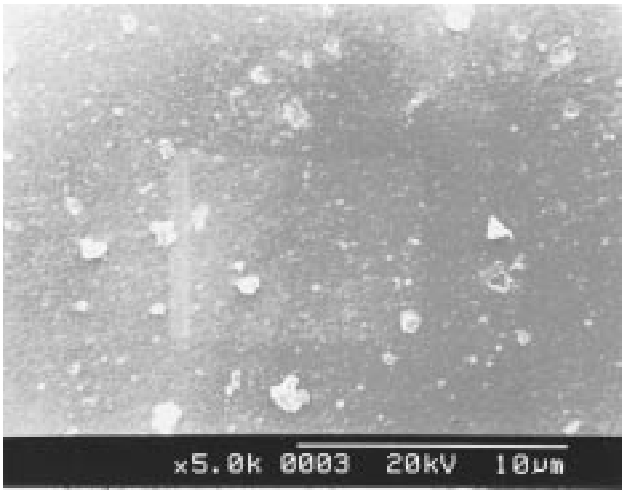


Fig. 2 SEM micrograph of polypyrrole films (*ca.* 5000 Å) on a silane-modified silicon substrate

a silane-modified substrate showed a continual and dense phase, similar to electrochemically polymerized polypyrrole films on Fe electrodes.[3a] Most of the polypyrrole chains are probably not directly bonded to the pyrrole molecules on the surface (Scheme 1). However the formation of pyrrole molecules on the surface of the inorganic substrate increases the interaction between the organic polymer and the substrate, and therefore increases the adhesion between them.

The formation of polypyrrole films was identified by IR and UV–VIS–NIR data. Both spectra showed the characteristic absorption patterns of polypyrrole.[17,18]

Properties of the polypyrrole films

The degree of doping and doping homogeneity of the polypyrrole film (*ca.* 4000 Å thickness) were characterized by Auger depth profile analysis (Fig. 3). Polypyrrole films contain only C, N and Cl atoms, while the dopant (counter anion) is Cl^-. The atomic ratio of Cl to N (the degree of doping) is 0.33 which suggested that the polypyrrole is fully doped.[19] Furthermore, the Cl/N ratio is similar throughout the film, indicating the degree of doping of the polypyrrole film is homogeneous.

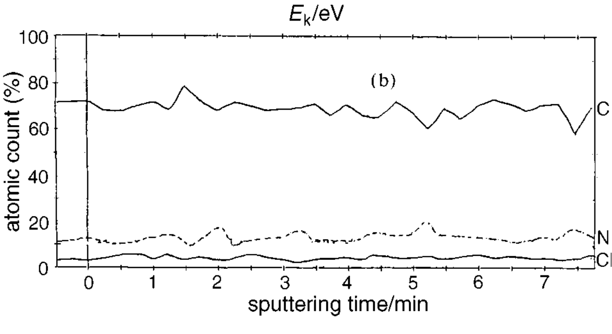


Fig. 3 Auger spectra of the as-prepared polypyrrole film: (a) survey scan, (b) depth profile analysis

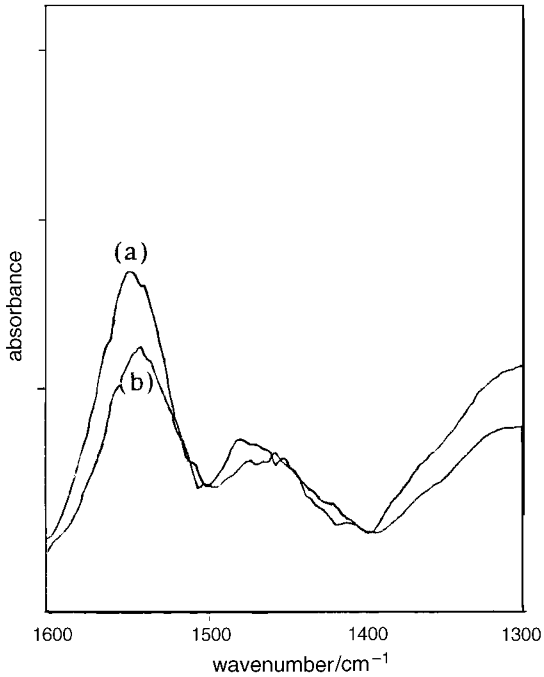


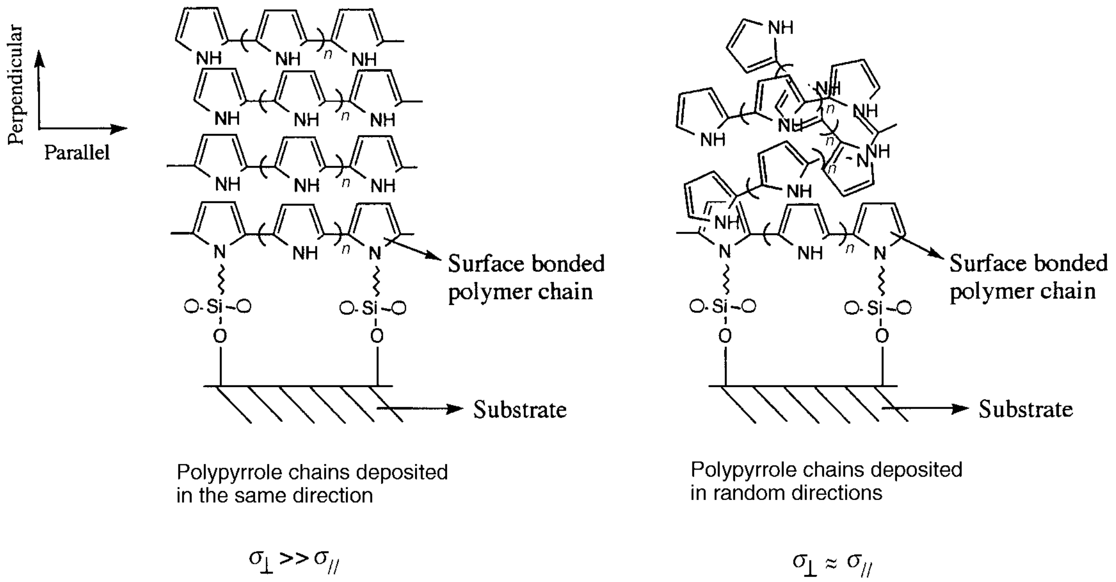
Fig. 4 PIRAS spectra of a polypyrrole film on a silane-modified silicon substrate: (a) polarized in parallel direction; (b) polarized in perpendicular direction

More interestingly, we found that some thin (<2000 Å) polypyrrole films deposited on silane monolayer-modified substrates showed anisotropic conductivity. This conducting anisotropy can be as high as several hundred times. The anisotropic conductivity of the films implied that the structure of the polypyrrole film has some regularity as confirmed by polarized IR absorption spectroscopy (PIRAS) as shown in Fig. 4. The dichroic ratio ($A_\perp/A_\parallel$) is 1.38. PIRAS is a classical technique[20] for investigating chain orientations in polymers. The non-equal integrated absorbances indicated that the polypyrrole film prepared by our method shows a preferred spatial orientation.[21] One of the possibilities for the formation of a spatially oriented polymer film is that most polypyrrole chains were deposited in the same direction as shown in Scheme 2. This possibility was further supported by the fact that polypyrrole films deposited on unmodified substrate or multilayer silane-modified substrates did not show anisotropic conductivity. The average room-temperature conductivity of oriented film is two orders of magnitude higher than that of a randomly oriented polymer film of similar thickness. These polymer films are not very stable and start to degrade upon standing in an ambient atmosphere over 3 days.

The mechanism for the deposition of polymer films is not well understood. Most likely the pyrrole molecules on the surface initiate the polymerization as well as intercepting chains growing in solution, as evidenced by the change of the XPS spectrum when the silane–pyrrole monolayer was treated with oxidant (*vide supra*).

Optimal conditions for chemical deposition of polypyrrole films on silane-modified substrates

In general, polypyrrole is not soluble in common organic solvents and *in situ* polymerization/formation of polypyrrole film is a necessary procedure for practical applications of this polymer. However, chemically polymerized polypyrrole is always a powder or a very poor-quality film.[22] The chemical preparation of high-quality polypyrrole films on inorganic substrates remains a challenging technique. We investigated the best procedure to prepare good quality polypyrrole films. It was found that the best polymer films were obtained by dipping the surface-modified Si substrate in monomer solution



Scheme 2 The possible orientations of polypyrrole chains in the polypyrrole film

prior to addition of the oxidant solution. This method has the advantage of dispersing the monomer on the substrate first, followed by combining them together with the aid of the oxidant.

The solvent used in the polymerization procedure also affected the quality of the resulting polymer films. The electric properties of polypyrrole have been reported to be dependent on the reaction solvent, reaction time and concentration of oxidant.[18] We found that polymer films obtained from hydroxy-containing solvents have better conductivities and smaller surface roughness. Table 1 lists the relative permittivity of various solvents and the conductivity of the resulting polypyrrole films. The data show that polymer films obtained from solvents with higher relative permittivities had higher conductivities. It is believed that the polymerization of polypyrrole proceeds *via* two mechanisms: a σ-radical[23] or π-radical pathway.[24] Both mechanisms involve the formation of cationic intermediates. Solvents with higher relative permittivity will stabilize such intermediates, favouring the growth of polymer chains, and resulting in better quality films. The conductivities of the polypyrrole films prepared in water were not as good as those prepared in methanol, despite the higher relative permittivity of the former. Water is a relatively reactive molecule, and polymer films prepared from aqueous solution, while showing good adhesion, had a higher number of structural defects, resulting in lower conductivity. Although acetonitrile also has a high relative permittivity, polypyrrole films prepared from acetonitrile had the highest surface roughness; this is probably why the film showed the lowest conductivity.

Table 1 Conductivity of polypyrrole films obtained from various solvents

solvent[a]	ε[b]	σ/S cm^{-1}
water	78.54	$(3.9 \pm 0.5) \times 10^{-2}$
methanol	32.63	$(8.7 \pm 1.0) \times 10^{-2}$
ethanol	24.30	$(5.2 \pm 0.7) \times 10^{-2}$
isopropyl alcohol	15.80	$(9.3 \pm 1.0) \times 10^{-3}$
tetrahydrofuran	7.60	$(4.7 \pm 1.0) \times 10^{-3}$
chloroform	4.81	3.3×10^{-3} [c]
benzene	2.28	2.0×10^{-3} [c]
acetonitrile	37.5	$< 10^{-4}$ [c]

[a] Preparation conditions: pyrrole concentration 1.5 M; pyrrole to $FeCl_3$ ratio = 1 : 1; deposition time 20 h; Si wafer substrate; reaction atmosphere N_2. [b] Relative permittivity. [c] Highest conductivity value obtained from several films.

Effects of deposition time on the thickness of the resulting films

The thickness of the film increased as the deposition time increased during the first 20 hours and then altered irregularly, due to complicated equilibrium processes between polypyrrole chains deposited on and removed from the substrate. It was also found that all pyrrole molecules were polymerized to polypyrrole after 17 h. This was confirmed by the similar amount of polypyrrole powder recovered from the reaction vessel for deposition times > 17 h. The optimal deposition time is that when all monomers in solution are consumed.

Effect of monomer (or oxidant) concentration and monomer to oxidant ratio on the thickness and conductivity of the resulting films

For a constant monomer to oxidant ratio, the effect of monomer concentration on the thickness and conductivity of the resulting films is shown in Fig. 5. It was found that polymer films prepared at a monomer concentration of 1.5 M have the highest thickness and smallest surface roughness. At lower monomer concentrations, the polypyrrole chains have less chance to deposit on the surface while at higher concentrations, the reaction rate is too fast to allow growth of a dense film on the substrate; both circumstances are unfavourable for film growth. The data also showed that at a given deposition time, thicker polypyrrole films show higher conductivity. The

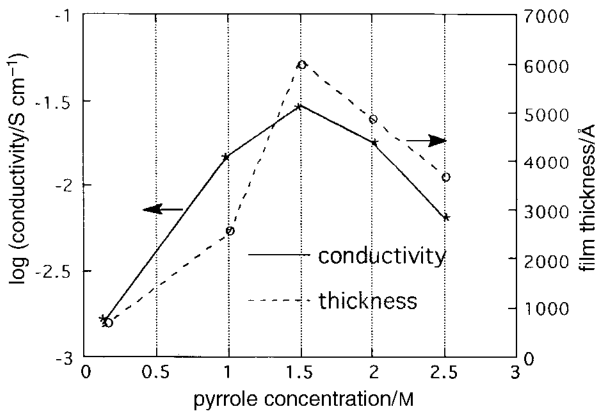


Fig. 5 Effects of pyrrole concentration on the thickness and conductivity of polypyrrole films (deposition time 20 h; solvent MeOH; pyrrole to $FeCl_3$ ratio 1 : 1; reaction atmosphere N_2)

smoothness of the surface will affect the surface conductivity of a thin film. Here, thicker films had smoother surfaces and thus showed higher conductivities.

The mole ratio of monomer to oxidant also affected the quality of the resulting polymer films. In general, the lower the monomer to oxidant ratio, the smaller the surface roughness of the resulting films. However, due to the limited solubility of $FeCl_3$ in methanol, the concentration of $FeCl_3$ can not be higher than 2.5 M. The reaction atmosphere and temperature did not have any obvious effects on the properties of the resulting films. Combining the optimal fabrication conditions, polypyrrole films with thickness of *ca.* 4000 Å and room-temperature conductivity up to 1.6 S cm^{-1} can be obtained.

Conclusion

Many positive points can be emphasized in this study. Molecular self-assembly properties can be used to construct a monolayer of pyrrole molecules on insulating substrates. The silane monolayer acts as a glue to adhere high-conducting, strong-adhesion polypyrrole films on the substrates. The presence of a monomer on the surface induced the regular deposition of polypyrrole chains, which resulted in the polymer films showing anisotropic conductivities. Finally, dense and homogeneously doped polypyrrole thin films can be readily deposited on insulating substrates.

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