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Electroless surface polymerization of ordered conducting polyaniline films on aniline-primed substrates

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Abstract

Ordered conducting polyaniline films were obtained by electroless surface polymerization of aniline molecules on $C_6H_5NHC_3H_6Si(OMe)_3$-modified substrates. Dense, smooth and strongly adhered films with thickness in the range of 50 nm to 1 μm were isolated. The polymer films were in their conducting state and were homogeneously doped. Complete protonating/deprotonating of polyaniline films took only several seconds, and this process could be repeated several times without affecting the adhesion and conductivity of the polymer films. Infrared, X-ray diffractometer and transmission electron microscopy data revealed the ordering of polyaniline chains, which have the domain size of a couple of hundred angstroms. The room temperature conductivity of the 1 μm polyaniline film was 0.5 S/cm. These polymer films were very stable, their conductivities did not change even after staying in ambient atmosphere for 4 months. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ordered conducting films; Electroless surface polymerization; Polyaniline

1. Introduction

Conducting polymers have been extensively studied during the past couple of decades. Issues were focused on the processibility, crystallinity, structure regularity and applications. Thin films of conducting polymers with their interesting optical and/or electronic properties have potential applications in optoelectronic and molecular electronic devices [1,2]. The techniques used for fabrication of conducting polymer thin films include the electrochemical growth of polymers on modified electrode surfaces [3–6], Langmuir–Blodgett deposition [7], self-assembly of polycation and polyanion of polymer derivatives [8] and spin coating [9]. However, the polymer films prepared by these methods are either not well oriented or involve complicated experimental procedures. Thus, the preparation of highly oriented polymers with commercially viable methods remains a challenge. However, high-quality, well-defined thin films are essential for studying the electronic, magnetic or optical properties of these materials.

On the other hand, "molecular self-assembly" phenomenon has been applied to generate materials with novel optical and electrical properties [10]. It was believed that self-assembled monolayer (SAM), which has desired control on the order at the molecular level, was considered as a potential technique for the construction of future advanced materials [11]. In the literature, there are few papers discussing the electrochemical studies of self-assembled monomer-containing monolayers on various substrates. Those existing include discussion of the alkoxy-silane-pyrrole on SiO_2 [12], and thio-tailed thiophene [13–16], pyrrole [17–22] and aniline [23,24] on gold. However, those articles focused mainly on the electrochemical polymerization of polymers on the monomer-modified electrodes. Issues of polymer orientation and thickness-related conductivity were not clearly addressed and, to the best of our knowledge, there was no report regarding the in situ electroless surface polymerization of the conducting polymer films on insulating substrates. We had reported the primary results on the deposition of polyaniline [25] films on SiO_2 substrates. In this article, we report, in detail, the studies of the preparation methods, formation mechanism and properties of conducting polymer films on silane-modified substrates. The ordering of the polymer chains is specially addressed. The method described here has the advantages of electroless polymerization, such as simple reaction setup, choice of various substrates for different applications and the ability to obtain easily a large area film. In addition, this preparation method offers a good opportunity for synthesizing better ordered, good adhesion

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conducting polymer films for structure characterization and technical applications.

2. Experimental section

2.1. Reagents

$FeCl_3$ and $(NH_4)_2S_2O_8$ were purchased from the Aldrich Co. and used as received. $C_6H_5NHC_3H_6Si(OMe)_3$ was purchased from the United Chemical Technologies Inc., PA. Ultrapure water and HPLC grade solvents were used in the reactions.

2.2. Substrates

Glass slide and (100)-oriented p-type Silicon wafer (purchased from Topsil Co.) with resistivity higher than 2000 Ω cm.

2.3. Surface modification of the substrates

The glass and silicon wafer substrates were treated with a mixture (7/3 in volume) of concentrated H_2SO_4 and 30% H_2O_2 (caution: piraha solution is a very dangerous solution with high oxidation power) at 90°C for 30 min. The acid-treated substrates were then washed with copious amounts of water and blown dried with nitrogen gas. In the glove box, the clean substrate was dipped in $C_6H_5NHC_3H_6Si(OMe)_3$/MeOH solution (11 mM) for 20 h, washed with MeOH thoroughly, and then dried with nitrogen gas at room temperature.

2.4. Electroless surface polymerization of the aniline on the aniline-primed substrates

The silane-modified substrate was dipped into the acidic solution, which contained aniline and oxidant at 0°C for polymer film deposition. The reaction parameters are listed below:

Concentration of acid: 0.012–1.2 M HCl(aq).
Monomer ($C_6H_5NH_2$) concentration: 0.075–0.6 M.
Molar ratio of monomer/oxidant: 6/1–1/2.
Solvents: H_2O, MeOH, CH_3CN.
Oxidants: $(NH_4)_2S_2O_8$, $FeCl_3$.
Reaction time: from 3 min to 72 h.
Reaction temperature: 0°C and room temperature.

2.5. Protonation/deprotonation of polyaniline films

Polyaniline films on the substrates were dipped in 0.01 M HCl(aq) (or 0.01M NH_4OH(aq)) for 5 min, washed with distilled water and blown-dried with N_2 gas. For very thin film, washing will cause the deprotonation of polyaniline. Therefore, thin polyaniline film was blown-dried with N_2 gas without washing. The doping (protonation)/dedoping (deprotonation) completeness was judged by the changes of the film colors and the UV/Vis/NIR absorption spectra.

2.6. Physicochemical studies

Fourier transform infrared (FT-IR) spectra were recorded as pressed KBr pellets or films on Si substrate using a Bio-Rad 155 FT-IR spectrometer. The attenuated total reflectance (ATR) spectra were obtained from Bio-Rad FTS185 FT-IR with a linearized MCT detector and a reflection accessory from Specac Analytic Inc. Static contact angles were measured with a home-made goniometer at room temperature and ambient humidity. Water was used as a probe liquid. A 2 μl water droplet was placed on the substrate with a syringe. The angle was obtained by estimating the tangent to the drop at its intersection with the surface, and three measurements were taken for the reported contact angle readings. Ellipsometric measurements for monolayer silanes were made on a computer interfaced J. A. Woollam Co. Control Module EC-1000 ellipsometer using the continuous wavelengths from 400 to 700 nm and an incident angle of 70°. The thickness of polymer films was measured with a Dektak ST surface profile measuring system. The scan length is 10 mm and the thickness is calculated from the average thickness of the length scanned. UV/Vis/NIR spectra were obtained from a Varian Cary 5E spectrometer under both transmission and reflection modes. X-ray powder diffraction studies were carried out with an Inel X-ray diffractometer (XRD) using Cu-Kα radiation at 45 kV and 40 mA. The coherence length was determined from the half-width of the diffraction peaks using the Scherrer formula [26]. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGA-7 thermal analysis system using dry nitrogen as carrier gas at a flow rate of 30 psi pressure. The TGA experiments were conducted from room temperature to 900°C with a linear heating rate of 5°C/min. Scanning electron microscopy (SEM) and energy disperse spectroscope (EDS) studies were performed with a Hitachi S-800 at 15 kV. The samples for SEM imaging were mounted on metal stubs with a conducting tape without further coating. X-ray photoelectron spectroscopy (Auger/ESCA) studies were carried out on a Perkin–Elmer 670PHI Xi spectrometer (with thermal field emitter and a Cylindrical Mirror Electron (CMA) energy analyzer) and a Perkin–Elmer PHI-590AM ESCA/XPS spectrometer system with a spherical capacitor analyzer. The X-ray sources were Al-Kα at 600 W and Mg-Kα at 400 W.

2.7. Charge transport measurements

Direct current electrical conductivity measurements were performed on compressed powder sample or films on substrates in the usual four-point geometry [27,28]. The four points on the sample surface were in 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 (ranged from 1 nA to 10 mA) was maintained on two outer electrodes. The floating potential across two inner electrodes was measured to determine the conductivity [29]. The conductivities of polymer thin films were also measured with the van der Pauw method. Four contact points were arranged in the four corners of the sample surface. Each point was adhered to a gold wire (using silver paste) for the current and voltage electrode. A current was applied on either of the two electrodes, and the floating potential across the other two electrodes was measured to determine the conductivity [30].

3. Results and discussion

3.1. The spontaneous absorption of monolayer aniline-containing silane on the surface of the substrates

To adhere aniline on a solid substrate, we grafted the surface with a silane compound bearing an aniline molecule. This reaction was carried out by modifying the substrate's surface with $C_6H_5NHC_3H_6Si(OMe)_3$ via molecular self-assembly. The formation of a monolayer aniline–silane on the substrate was confirmed with the contact angle, XPS and optical ellipsometer data. After treating with the silane compound, the surface contact angles of the silicon wafer increased from 30 to 60°. This result was consistent with the deposition of organic molecules on an inorganic surface [31,32]. The thickness of the silane layer was 14 ± 2 Å, which was reasonable for monolayer deposition. XPS spectra of the aniline–silane-modified surfaces revealed an N_{1s} peak at 399.5 eV, which is similar to the binding energy of nitrogen in an amine site of the emeraldine base [33]. The fact that ATR-IR spectra of silane–aniline-modified SiO_2/Si showed two well-defined broad peaks at 2874 and 2948 cm^{-1} further support the formation of an organic monolayer.

3.2. Electroless surface polymerization of polyaniline films on aniline-primed surface

The surface polymerization of polyaniline films was carried out by reaction of the aniline-primed substrates with aniline in the presence of an oxidant, such as $(NH_4)_2S_2O_8$ or $FeCl_3$. The pendant aniline functionality was to be used as the initiation site for polymerization and also served as a covalent anchor for the growth of polyaniline chains on the surface. The formation of polyaniline films were characterized and confirmed with IR spectra. The observed characteristic vibration peaks of polymer films were very similar to the pressed KBr pellets of polymer powders in their conducting states. The UV/Vis/NIR spectra of polyaniline films on the monomer-primed quartz substrate showed a polaronic absorption peak at ca. 800 nm, further confirming that the films were on the protonated state [34–36]. However, the absorption tail which extended to the whole NIR region was not observed in the protonated film on modified substrate, even after treating with HCl(aq). The electronic absorption spectra indicated that there are isolated polarons existing in the polyaniline chains. The presence of isolated polarons may be due to a special arrangement of polyaniline chains on the modified substrate.

3.3. Optimal conditions for the deposition of polymer films

3.3.1. The effects of the silane modification

We found that the polymer films grown on aniline-primed substrates had much better adhesion compared to those grown on unmodified substrates. Thin polyaniline films on silane-modified substrate passed our peeling test. (The peeling test was performed with Scotch tape. In some thick films, a small area of light green or black color was observed in the tape; however, the film never came off completely.) On the other hand, polymer films deposited on unmodified substrates were easily washed off with splash water. Under SEM, the resulting polyaniline films have smooth surface, and there was no fibril morphology, as observed in electrochemical polymerized polymer [37,38]. The solubility test indicated that there are some polyaniline chains directly bonded to the substrate [25].

3.3.2. The effects of reaction conditions

The properties of the polymer films can be tuned from the preparation conditions, such as monomer concentrations, ratios of monomer to oxidant, solvents, oxidants, reaction times and reaction temperatures. We found that polyaniline films prepared from acidic aqueous solution had the smoothest surface and the highest conductivity. The optimal mole ratio of oxidant to monomer for preparing high-quality (smallest surface roughness films with high conductivity) polyaniline films was 1. However, it was reported [39] that in the preparation of bulk polymer the highest conductivity polyanilines can be obtained with the molar ratio of $(NH_4)_2S_2O_8$/aniline as low as 0.25. This result implied that the mechanism for the deposition of polymer film on the modified substrate was different from that which happened in solution [39]. Moreover, when the deposition of polyaniline film was carried out in H_2O using $FeCl_3$ as an oxidant, only a brown thin film of poor quality was formed on the substrate. If $FeCl_3/CH_3CN$ was used as an oxidant, no film was formed. This was due to the lower oxidation power of $FeCl_3$ compared to $(NH_4)_2S_2O_8$/HCl(aq). Nevertheless, it was reported [40] that polyaniline prepared from chemically oxidized aniline with $FeCl_3/H_2O$ or $(NH_4)_2S_2O_8$/HCl(aq) showed the similar optical and charge transport properties. The distinct quality of polyaniline films we obtained by using these two types of oxidant further supported that the in situ surface polymerization of the polyaniline film on a modified surface was different from the chemical polymerization of the polyaniline powder in the bulk solution [39–41]. The mechanism of deposition of polymer chains on the modified substrates will be described later in this article.

The thickness and, therefore, the conductivity of the polymer films can also be tuned by reaction conditions.

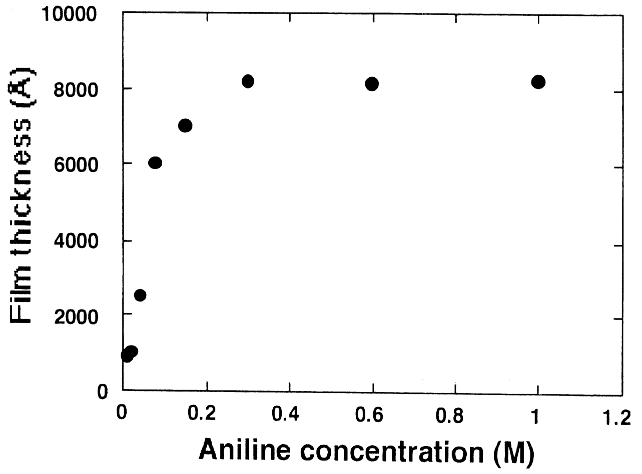


Fig. 1. The effect of aniline concentration on the thickness of polyaniline films on aniline-primed substrates.

When the molar ratio of the monomer to the oxidant was kept constant, the thickness of the films increased when the monomer concentration was increased up to 0.3 M. The deposition of a polymer film was the result of two competing reactions: free aniline molecules reacting to surface-bonded anilines and the coupling of the free aniline molecules in solution. Higher aniline concentration apparently increased the chance of reaction between aniline molecules in solution and anilines on the surface, resulting in thicker films. The thickness of polymer film can also be controlled by the reaction time. It was found that the thickest film was obtained after deposition for 1 h, and the thickness remained similar when the deposition time was increased up to 24 h. This is because of all the aniline molecules in solution having polymerized within 1 h. This conclusion was supported by the fact that the amount of polyaniline powder recovered from the reaction vessel was independent of the deposition time after 1 h. The polyaniline chains formed in the solution could not adhere firmly to the surface of the polymer-deposited substrate. Therefore, the thickness of the polyaniline films did not increase with deposition time after 1 h. By controlling the aniline concentration and reaction time, polyaniline films as thin as 90 nm can be obtained, see Fig. 1. It was worth noting here that the thickest polymer film we obtained from the reaction conditions presented in this article is 1 μm. Nevertheless, thicker films can be obtained by immersing the polyaniline film in a fresh aniline/oxidant solution. The surface morphology and adhesion of this ”double deposition or double layers” polyaniline film is rough and poor. Work on the preparation and characterization of “double layers” polymer films is in progress.

3.4. The properties of polyaniline films grown on aniline-primed substrates

3.4.1. The degree of doping

Chemical deposition of polyaniline films was generally prepared from casting emeraldine base/NMP (1-methyl-2-pyrrolidinone) solution on substrate, followed by acid doping [42,43]. However, only the vicinity of the polymer surface region can be doped by this doping method [44]. On the other hand, polyaniline films prepared by our method were homogeneously protonated through the entire film thickness as revealed by depth profile ESCA and SIMS studies. The process of protonating/deprotonating of polymer films on the substrate was finished in less than half a minute, and this process could be repeated several times without affecting the adhesion and conductivity of the

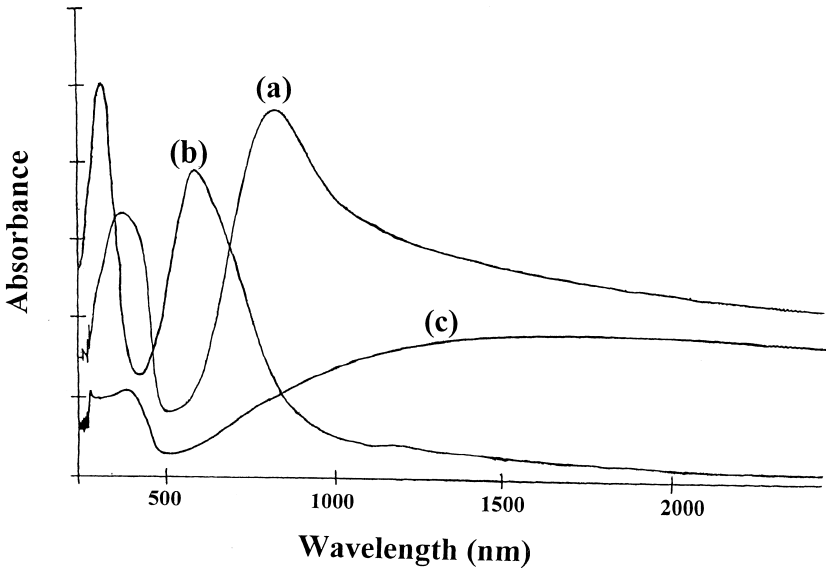
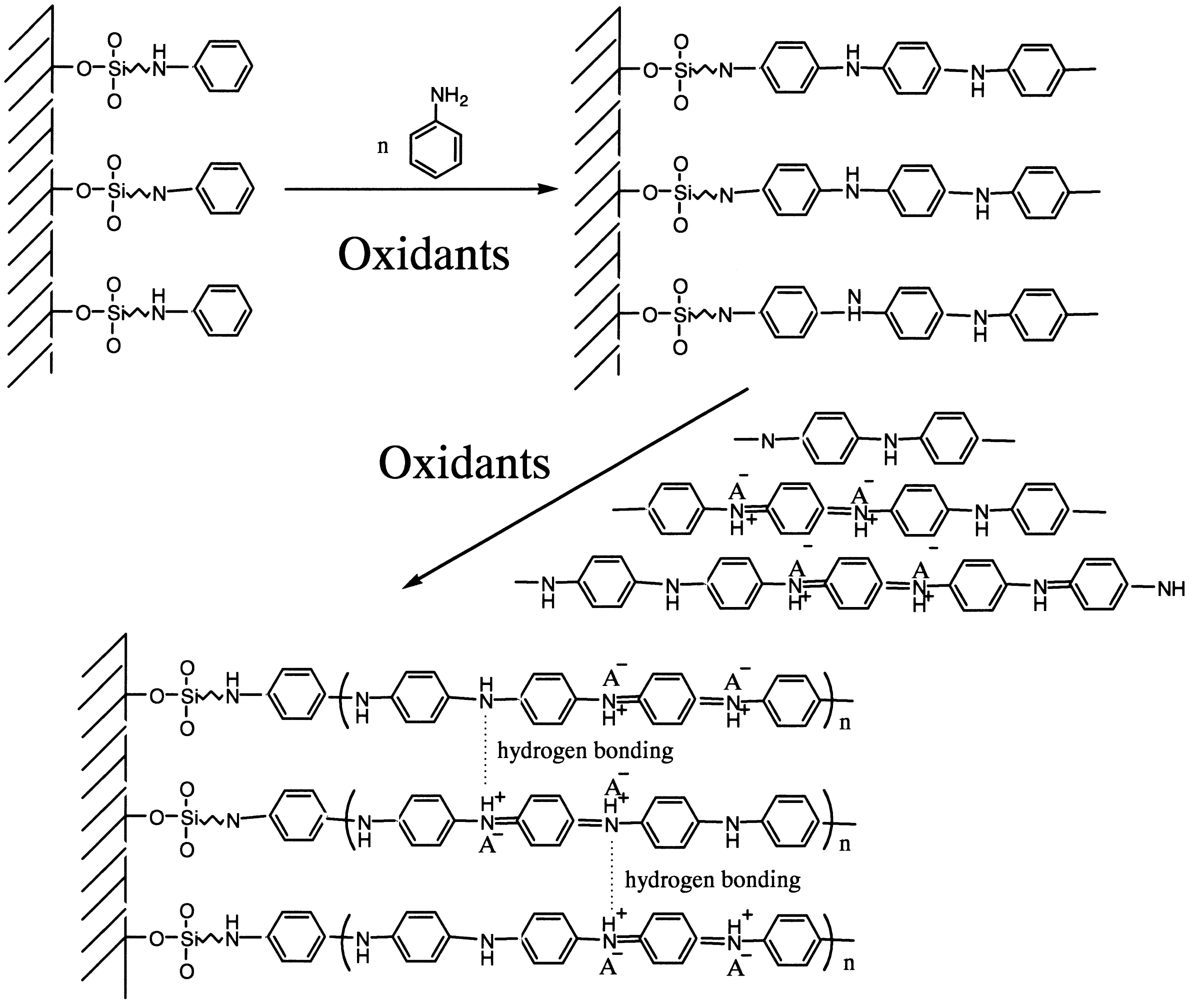


Fig. 2. UV/Vis/NIR spectra of: (a) as-prepared polyaniline film (on aniline-primed glass); (b) polyaniline film treated with NMP; and (c) polyaniline film treated with NMP and then with HCl(aq).



Scheme 1. Chemical deposition of ordered polyaniline film on aniline primed substrate.

polymer films. The thermal stability of the polyaniline films on substrates was tested with a TGA analyzer, or a hot stage with controlled heating; the color change was observed using an optical microscope. The green film (ca. 200 nm thickness) was stable at temperatures up to 120°C, then the deprotonating proceeded. The color of the film became darker and then turned to dark purple at ca. 200°C where the deprotonation completed. Bulk polyaniline [45] required several minutes to complete the doping/dedoping process and deprotonated at ca. 150°C. Compared to the bulk polyaniline, the polyaniline films we prepared were more sensitive to the changes in the environment. Nevertheless, the conductivities of both thin and thick polyaniline films did not change after being kept in ambient atmosphere for over 4 months.

3.4.2. The optical properties

The UV/Vis/NIR spectra of polyaniline film deposited on the modified glass substrate showed a broad well-defined peak centered at 800–840 nm, indicating the existence of localized polarons as shown in Fig. 2. The absorption tail which was related to the free carrier [46] showed up only after the polyaniline film was dipped in NMP for 30 s, taken out, blown dry with N_2 gas and then reprotonated with HCl(aq). If the film was deprotonated with a weak base, such as NH_4OH(aq), and then reprotonated with 1.2 M HCl(aq), only a defined polaron absorption was observed. Secondary doping of polyaniline with an inert solvent had been reported by MacDiarmid and Epstein [47] several years ago. The variation of optical properties after treating with secondary dopant was similar to what we observed here. However, they found that NMP is not a good secondary dopant for polyaniline. This result suggested that the structure of the polyaniline films we prepared may be different from that casted from the polymer solution. The function of NMP is not to solvate the counter anions of the polymers as a typical secondary dopant does. Its function may just break the hydrogen bonding (see Scheme 1, the functionality of aniline–silane for the deposition of polyaniline film) between polyaniline chains, leading to more delocalized polarons; therefore, the absorption of a free carrier was detected.

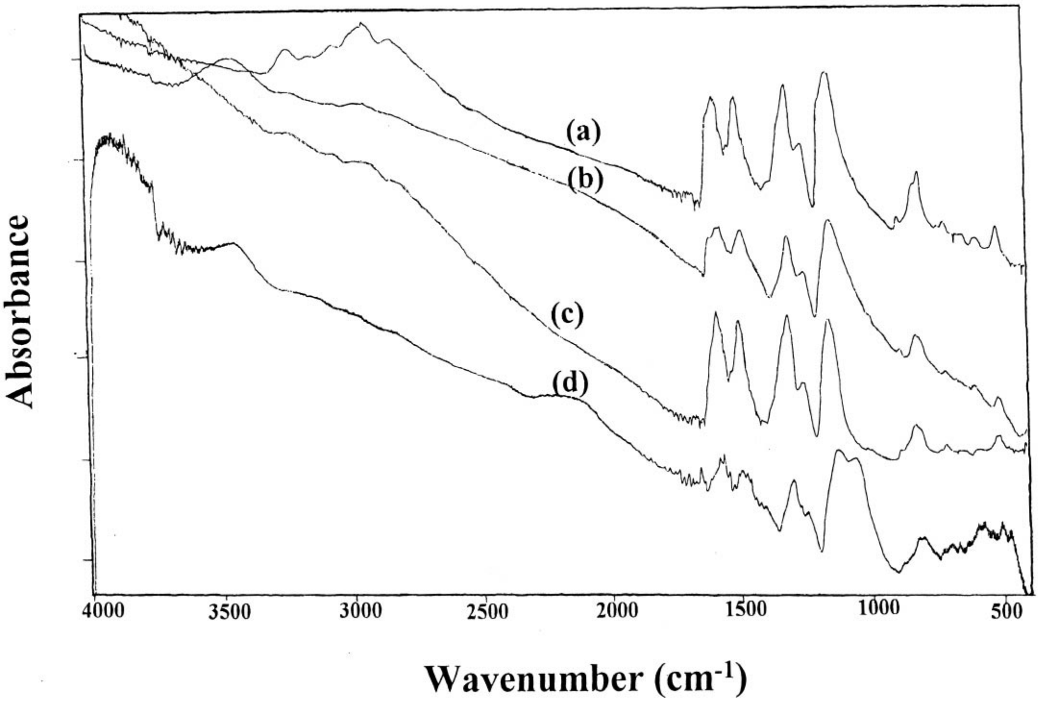


Fig. 3. IR spectra of polyaniline: (a) as prepared polymer film deposited on aniline-primed SiO_2/Si substrate; (b) chemically prepared polyaniline powder (KBr pellet); (c) solution-casted film (protonated); and (d) polyaniline powder scraped from the aniline-primed substrate (KBr pellet).

3.4.3. Structure and ordering of the polymer chains

The order of the polymer films was investigated with IR spectroscopes, XRD and transmission electron microscope (TEM). The IR spectra of the polyaniline film on silicon wafer showed a number of peaks, named "H-peaks" at 3240, 3154, 3064, 2975 and 2840 cm^{-1}. These "H-peaks" were not observed in the bulk emeraldine salt, polyaniline film made from emeraldine base/NMP solution, then protonated with HCl or polyaniline scraped from the substrates (see Fig. 3). The "H-peaks" were related to the hydrogen bonding between the protonating nitrogen, since the "H-peaks" disappeared after the film was deprotonated and it reappeared when the deprotonated film was reprotonated. The low vibration energy peak at 2840 cm^{-1} also supported the existence of the interchain hydrogen bonding [48,49]. This interchain hydrogen bonding existed only when the

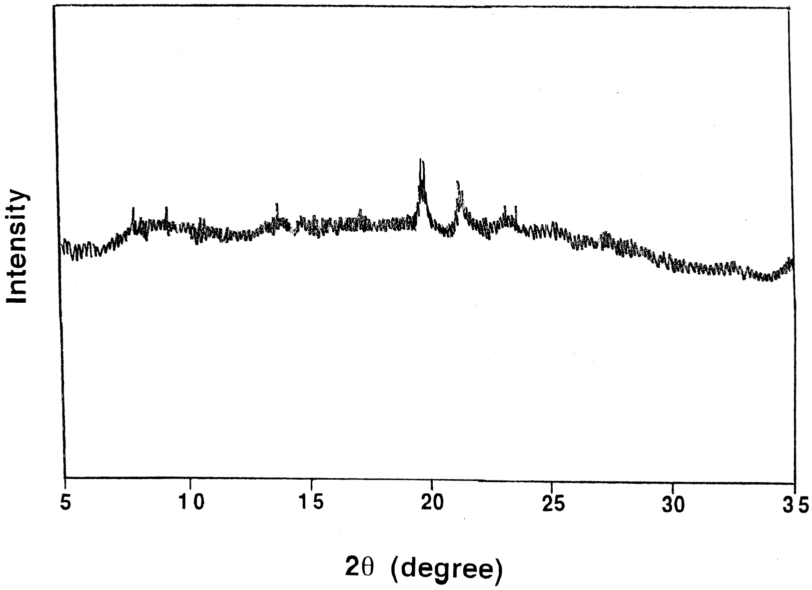
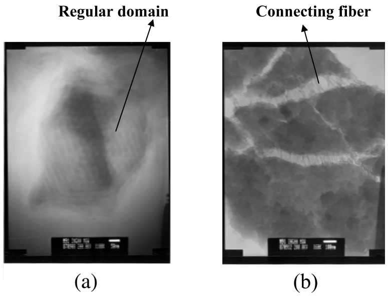


Fig. 4. Grazing angle XRD pattern of polyaniline film on aniline-primed SiO_2/Si substrate.



(a) (b)

Fig. 5. TEM micrographs of polyaniline film scratched from the substrate: (a) the regular domain; and (b) the connection fibers.

polyaniline chains were regularly aligned on the substrate. XRD pattern, Fig. 4 of the as-prepared polyaniline films (1 μm thickness) on the substrate showed two very weak peaks at $2\theta = \sim 20$ and 22° with the domain size of ca. 250 Å. The *d*-spacings calculated from the Bragg's equation were 4.4 and 4.0 Å, corresponding to the width and thickness of benzene ring on aniline, respectively. The presence of these two diffraction peaks, although broad and weak, indicated that the long-range order was existent in these conducting films. Polyaniline film was carefully scratched from the Si substrate with a razor blade, dispersed in methanol, then observed under TEM. We found that there existed a regular domain in the dimension of a couple of hundred angstroms, see Fig. 5a, consistent with the XRD data. However, this regular array was extremely unstable, it was destroyed quickly by the high-energy electron beam. Furthermore, under TEM, we also found that there are fine polymer chains linked to two polymer blocks (Fig. 5b). The result suggested that the polymer chains were connected to each other in some degree.

3.4.4. Charge transport properties

The room temperature conductivity of polyaniline film vs film thickness was shown in Fig. 6. It was found that the conductivity of polyaniline films increased as the film thickness increased in the first couple of thousand angstroms, then decreased as the polymer film became thicker. Polyaniline film as thin as 1000 Å showed a significant conductivity, and the highest conductivity was found on polymer film at ca. 2000 Å. As reported [25] previously, there are polyaniline chains (with thickness at ca. 2000 Å) attached directly on the substrate via silane molecules primed on the substrate. The surface-bonded polymer had better order, and therefore showing higher conductivity. The electron transport in conducting conjugated polymers was accomplished by two different pathways: the intrachain transport and interchain hopping. The former depended on the structural integrity of the individual polymer chains, and the latter relied on the order of polymer chains in the bulk solid. It was believed that for the polyheterocyclic polymer, the interchain transport was dominant [50]. Nevertheless, in the polyaniline, we found that the conductivity depended also on the chain length, at least with the first couple of thousand angstroms. This observation might imply that intrachain charge transport was also important in these polymer films. Variable temperature conductivity (Fig. 6, insert) of polyaniline films on the aniline-primed substrate showed an increasing conductivity with increasing temperature, characteristic of thermal activated behavior. This behavior

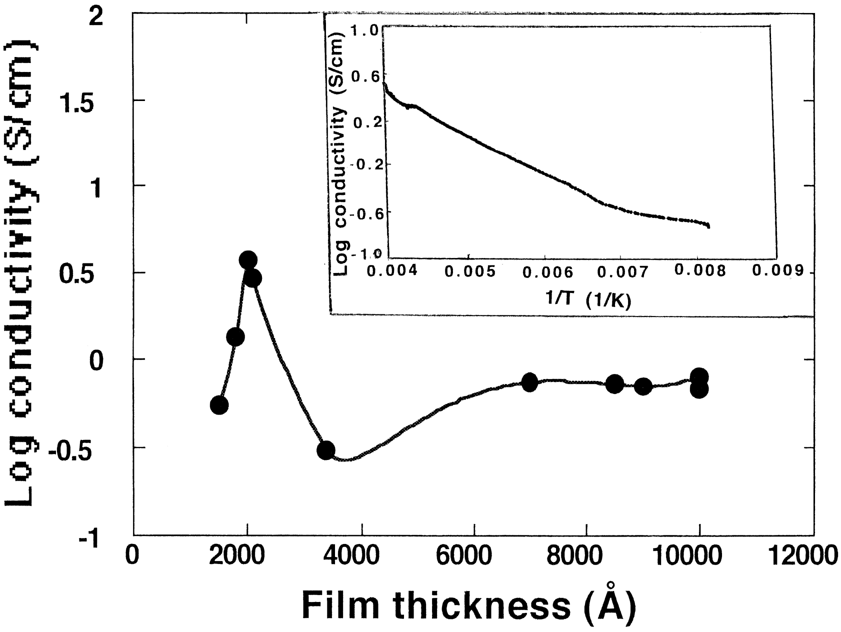


Fig. 6. Room temperature conductivity vs film thickness of polyaniline film (insert: variable temperature conductivity of polyaniline films on aniline-primed substrate).

was also observed in protonated polyaniline prepared from general polymerization methods [51].

3.5. The mechanism for the deposition of polymer chains on the aniline-primed substrates

As proposed in the foregoing section, the growth of polyaniline films can be considered as covalently anchoring polymer chains through the aniline molecules on the surface, based on two following observations:

1. When the polyaniline film was deprotonated with a weak base, and then dipped in NMP to remove the surface attached polymer chains, we found that a layer of film with thickness at ca. 2000 Å did not dissolve in NMP, indicating that some polyaniline chains were directly bound to the surface via silane molecules primed on the substrate.
2. When aniline–silane-treated substrates contacted with the polyaniline suspension for 1 day, no continuous polymer film was formed.

Therefore, the mechanisms of the polymers deposited on the aniline-primed substrates can be rationalized as shown in Scheme 1. The aniline molecules on the modified surface react with the aniline molecules in solution to form longer chain and, at the same time, intercept aniline oligomers growing in the solution and continue growth.

The preparation method presented in this article can be a general synthetic strategy for synthesizing better-quality conducting polymer films for structure characterization and technical applications. Electroless surface polymerization of polyaniline film on other aniline-primed substrate, such as ITO glass can be achieved in a similar method [52]. The good adhesion, smooth, ultra-thin polyaniline film will be a good candidate for use as a hole transport layer in polymeric organic light-emitting diodes [53–55].

4. Conclusions

The preparation method described here offers a potentially powerful strategy for building ordered conducting polymer thin films on various substrates with systematic control over thickness and properties. The monolayer of monomer molecule on the surface acts as a nucleation site for the growth of polymer chains. Therefore, the orientation of polymer films can be regulated by designing properly the monomers on the surface. Optically flat polymer films were adhered tightly to the substrates, and further reactions, such as multiple layer deposition, doping/dedoping reactions, counter anion exchanging and spectroscopic studies could be carried out easily as film on substrate.

Acknowledgements

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