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Chemical Deposition of Ordered Conducting Polyaniline Film via Molecular Self-Assembly

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Optoelectronic and molecular electronic[1] materials are the frontiers of today's material research. This is probably the main reason for the interest in polymeric thin films. Among them, conducting polymer films[2] have attracted wide attention due to their unique properties, such as easy synthesis by chemical methods and reversible and adjustable conductivity. Although numerous applications have been proposed for conducting polymers films, some difficulties, such as material processing, nonreproducible properties, and the poor adhesion between polymer film and substrate remain as limitations to their practice applications. Recently, the "molecular self-assembly" phenomenon has been applied to prepare materials with novel optical and electrical properties.[3] It is believed that self-assemble monolayers (SAM), which have desired control on the order at the molecular level, should be considered as a potential technique[4] for the construction of future advanced materials. On the other hand, silanization as a method of surface modification has had an extensive history of the use in electrochemistry.[5] The construction of a monolayer by functional silane molecules which assemblies spontaneously onto selected surface to give a high degree of orientation akin to the classical Langmuir−Blodgett films[6] is known. Therefore, silane-bearing aniline compounds can be used to assemble a monolayer of aniline on the surface. This silane-modified surface may offer an environment to grow ordered conducting polymer films with good adhesion between polymer films and substrates.

In the literature, electrochemical studies of self-assembled monomer-containing monolayer on various substrates have been discussed, for example, alkoxysilane pyrrole[7] on SiO_2/Si, thiol-tailed thiophene,[8] pyrrole,[9] and aniline[10] on gold surface. However, the ordering of polymer and thickness-related conductivity were not clearly addressed, and to our best knowledge, there is no report regarding the chemical deposition of conducting polymers on modified substrates. On these bases we are investigating the chemical deposition of conducting polyaniline films on a modified silicon oxide surface. The chemistry of the preparation can be represented as Scheme 1: the effects of silane monolayer on the properties of polyaniline films and the thickness related conductivity are reported.

The substrates[11] used for chemical deposition of polyaniline film were first treated with a silane com-

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(2) (a) *Application of Intrinsically Conducting Polymers*; NATO Advanced Research Workshop October, 1992, Vermont. (b) *Synth. Met.* **1995**, *71*.

(3) Ulman, A. *An Introduction to Ultra-thin Films from Langmuir−Blodgett to Self-Assembly*; Academic: San Diego, CA, 1991.

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(5) (a) Mose, P. R.; Weir. L. *Anal. Chem.* **1975**, *47*, 1882. (b). Murray, R. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13, p 191. (c) Lenhard, J. R. Murray, R. W. *J. Electroanal. Chem.* **1977**, *78*, 195−201.

(6) Netzer, L.; Iscovici, R.; Sagiv, J. *Mol. Cryst. Liq. Cryst.* **1983**, *93*, 415.

(7) Simon, R. A.; Ricco, A. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 2031−2033.

(8) Kowalik, J.; Tolbert, L.; Ding, Y.; Bottomley, L.; Vogt, K.; Kohl, P. *Synth. Met.* **1993**, *55*, 1171.

(9) (a) Sayre, C. N.; Collard, D. M. *Langmuir* **1995**, *11*, 302−306. (b) Willicut, R. J.; McCarley, R. L. *Langmuir* **1995**, *11*, 296−301. (c) Gorman, C. B.; Biebuyck, H. A.; Whitesides, G. M. *Chem. Mater.* **1995**, *7*, 526−529.

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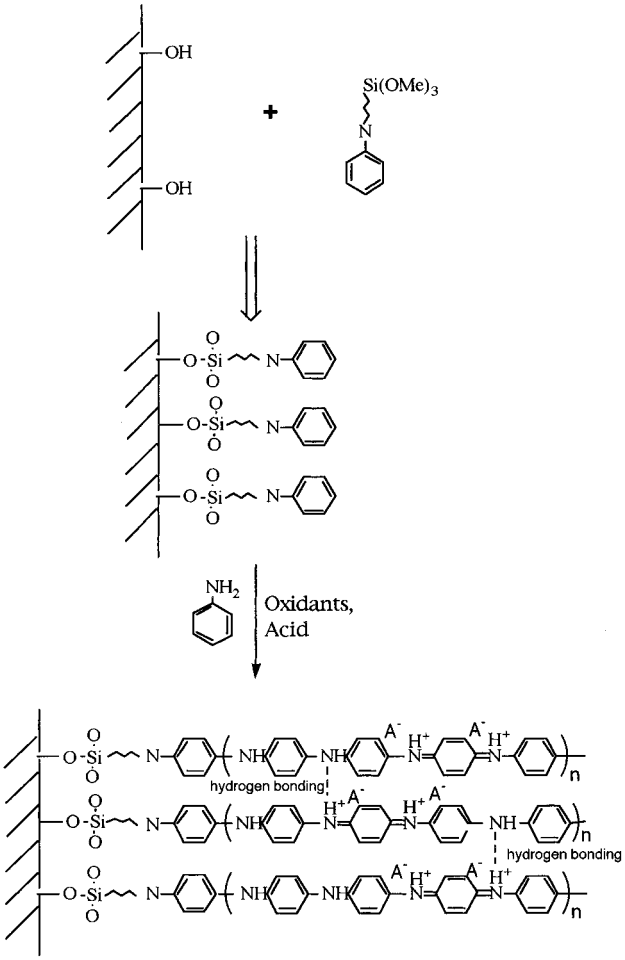
Scheme 1. Chemical Deposition of Polyaniline Chains on Modified Surface



pound; $C_6H_5NHC_3H_6Si(OMe)_3$[12] (*I*). A monolayer of silane-bearing aniline was formed on the substrate via molecular self-assembly. The formation of a monolayer of organic silane was characterized by contact angle, optical ellipsometry measurements, and XPS studies. After treating with **I**, the contact angle of of the substrate increased from 30 to 60°, consistent with the deposition of organic molecules on inorganic surfaces. The thickness of the layer measured from an ellipsometer is ca. 10 Å, accounting for the formation of monolayer silane. The XPS spectrum of the **I**-modified surface showed a very weak N^{1s} peak at binding energy of 399.5 eV which is close to the bonding energy of nitrogen in the amine site of emeraldine base.[13]

Chemical deposition of the polyaniline films on **I**-modified substrates was performed by dipping the substrate in aniline/HCl aqueous solution at 0 °C and then $(NH_4)_2S_2O_8$/HCl(aq) was added.[14] The pendant aniline on the surface served as a mediate to covalently anchor the polyaniline chain on the substrate. The resulting films had good adhesion due to the chemical bonding between the substrate and polymer film. The formation of conducting polyaniline films was confirmed with IR and UV/vis/NIR studies. The IR spectrum showed the characteristic peaks of conducting emeraldine salt and the electronic absorption spectrum also showed a distinguishable peak at ca. 820 nm, indicating the existence of localized polarons.[15] The absorption tail, indicating the free carriers,[16] which extended to the whole near-IR region was not observed. The results suggested that the structure of polyaniline films made by this method is similar to that made by electrochemical polymerization.[17] The scanning electron micrograph, shown in Figure 1, of the film with thickness of 1 μm exhibits a dense and continuous surface, similar to a Langmuir−Blodgett processed polyaniline film.[18] The fibril morphology as often observed in electrochemically

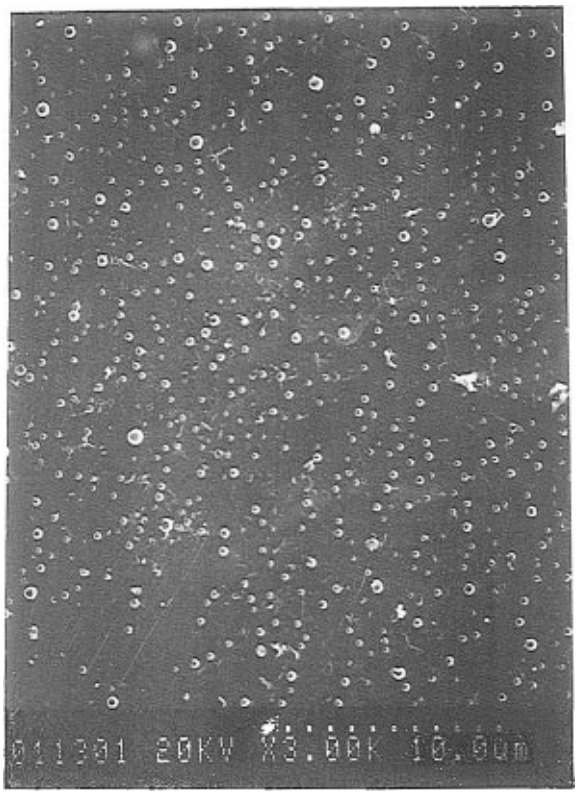


Figure 1. SEM photography of polyaniline film on $C_6H_5NHC_3H_6Si(OMe)_3$-modified SiO_2/Si substrate.

(10) (a) Rubinstein, I.; Rishpon, J.; Sabatani, E.; Redondo, A.; Gottesfeld, S. *J. Am. Chem. Soc.* **1990**, *112*, 6135. (b) Sabatani, E.; Redondo, A.; Rishpon, J.; Rudge, A.; Rubinstein, I.; Gottesfeld, S. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 287−294.

(11) The substrates (silicon wafer and glass) were treated with 7:3 (v/v) of concentrated H_2SO_4 and 30% H_2O_2 at 90 °C for 30 min, then washed with copious amount of water, and blow dried with nitrogen gas.

(12) In a glovebox, the clean substrate was dipped in 11 mM $C_6H_5NHC_3H_6Si(OMe)_3$/MeOH solution for 13.5 h, then taken out, washed with MeOH thoroughly, and dried at room temperature.

(13) Kang, E. T.; Neoh, K. G.; Khor, S. H.; Tan, K. L.; Tan, B. T. G. *J. Chem. Soc., Chem. Commun.* **1989**, 695.

(14) The concentration of aniline is 0.075−0.6 M, and the concentration of HCl(aq) is 1.2 M. The deposition time ranged from several seconds to 24 h, and the mole ratios of aniline to $(NH_4)_2S_2O_8$ was varied from 6 to 0.33.

(15) (a) Kulszewicz, I. *Macromolecules* **1995**, *28*, 610−613. (b) Xia, Y.; Wiesinger, J. M.; MacDiarmid, A. G.; Epstein, A. J. *Chem. Mater.* **1995**, *7*, 443−445. (c) Chinn, D.; DuBow, J.; Li, J.; Tanata, J.; Josowicz, M. *Chem. Mater.* **1995**, *7*, 1510−1518.

(16) (a) Shavklette, L. W.; Wolf, J. F.; Gould, S.; Baughman, R. H. *J. Chem. Phys.* **1988**, *88*, 3955−3961. (b) M. Wan *Synth. Met.* **1989**, *31*, 51−59. (c) Kabumoto, A.; Shinozaki, K. *Synth. Met.* **1988**, *26*, 349−355.

(17) (a) Shavklette, L. W.; Wolf, J. F.; Gould, S.; Baughman, R. H. *J. Chem. Phys.* **1988**, *88*, 3955−3961. (b) M. Wan *Synth. Met.* **1989**, *31*, 51−59. (c) Kabumoto, A.; Shinozaki, K. *Synth. Met.* **1988**, *26*, 349−355.

(18) Ram, M. K.; Sundaresan, N. S.; Malhotra, B. D. *J. Phys. Chem.* **1993**, *97*, 11580−11582.

polymerized polyaniline[17b,19] was seen in the thin film with thickness of 1000 Å.

The thickness and electric properties of the polymer films can be tuned by preparation conditions such as monomer concentrations, ratios of monomer to oxidant, deposition time, and/or types of oxidants or solvents used. The data showed that when the mole ratio of monomer to oxidant was kept constant, the higher the monomer concentration, the thicker the film was obtained. On the other hand, if the concentration of aniline was kept constant, a thinner film was obtained with a higher mole ratio of aniline to oxidant. When the concentration of aniline is 015 M and aniline to $(NH_4)_2S_2O_8$ ratio is 1, the maximum thickness (1 μm)[20] is obtained after deposition for an hour and a similar thickness retained even when the deposition time was increased to 24 h. This is probably due to that all aniline molecules in the solution have polymerized to polyaniline within an hour. It can be supported by the fact that the amount of polyaniline powder recovered from the reaction vessel is independent of the deposition time after 1 h. The polyaniline chains formed in the solution cannot adhere firmly on the surface of the polymer-deposited substrate; therefore the thickness of the film did not increase with longer deposition time. For all the reaction conditions we have investigated so far, the best quality polyaniline film was obtained from acidic aqueous solution using ammonium peroxosulfate as an oxidant with an aniline-to-oxidant ratio equal to 1.

The polyaniline films grown on a **I**-modified surface had much better adhesion compared to that grown on unmodified substrate. A thin film of the former can stand the peeling test,[21] but the latter can be washed off easily with splash water. It took only several seconds to completely protonate or deprotonate the polyaniline film on the modified substrate. The protonating/deprotonating process can be repeated several times without affecting the adhesion and conductivity of the film. Furthermore, a conducting polyaniline film for various applications was generally prepared from casting emeraldine base/NMP (1-methyl-2-pyrrolidinone) solution on substrate, followed by acid doping.[22] However, only the vicinity of the surface region can be doped with this doping method.[23] On the other hand, the degree of protonation of polyaniline films prepared by our method is very homogeneous through all film thickness as revealed by profile SIMS studies shown in Figure 2.

To address whether the polyaniline was chemically bonded or physically attached to the surface, the polymer film was first deprotonated with weak base[24] and then dipped into NMP to remove the polymer chains which only physically absorbed on the surface. It was found that there is a layer of polyaniline film with a thickness of ca. 2000−2500 Å still strongly attached on the substrate after this treatment. When the same treatment was performed on the film deposited on unmodified substrate, the polymer film dissolved totally in NMP. The results suggested that the length of polyaniline chains bonded on the modified surface is ca. 2000−2500 Å which corresponds to 400−500 aniline units.[25] The molecular weight of chemically polymerized polyaniline was reported[26] on the order of 64 000 or 690 aniline units. Our result is quite consistent with literature report. We do not have sufficient evidence thus far to show whether the aniline on the surface initiate the polymerization or they just intercept chains growing in solution. However, the XPS spectrum of oxidant-treated silane monolayer did not have any significant difference compared to that before oxidant treatment. Therefore, the aniline on the surface is probably just intercept aniline oligomers growing in solution. The thickness-related conductivity of polyaniline films deposited on silicon substrate is shown in Figure 3. The conductivity of polyaniline films on a **I**-modified substrate is higher than those on unmodified substrate. A similar result was obtained in polypyrrole films[27] prepared with the same method. Surface-bonded polymer chains may have a better regularity, which results in higher conductivity, as also observed by other authors.[28] Regardless of whether the polyaniline films were deposited on modified or unmodified substrates, the thinner the film, the higher the conductivity. The thick films on unmodified substrate were damaged so easily during washing that consequently very low conductivity was observed.

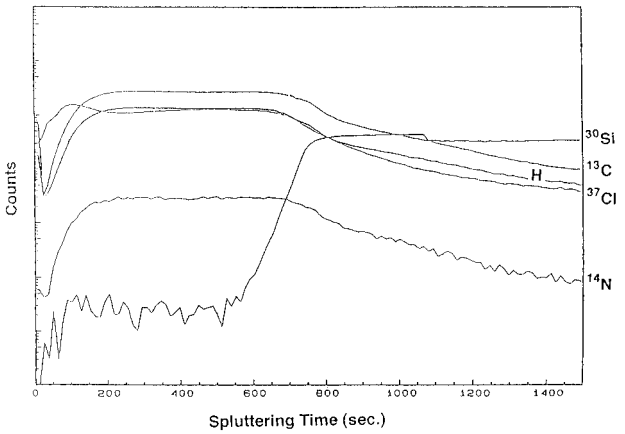


Figure 2. Depth profile SIMS spectrum of polyaniline film (1 μm thickness) on $C_6H_5NHC_3H_6Si(OMe)_3$-modified SiO_2/Si substrate.

The order of polymer film (1 μm thickness) was suggested by an X-ray diffraction study. Contrasted

(19) Kanamura, K.; Kawai, Y.; Yonezawa, S.; Takehara, Z.-I. *J. Phys. Chem.* **1994**, *98*, 2174−2179.

(20) The maximum thickness of polymer film depends on the reaction conditions and deposition procedures. With these specific reaction conditions, the maximum thickness is 1 μm. However, a thicker film can be obtained with different deposition methods.

(21) The peeling test was performed with scotch tape, although in some thick films, a light green color was observed in the tape. Nevertheless, the film never came out altogether.

(22) (a) MacDimard, A. G.; Epstein, A. J. *J. Chem. Soc., Faraday Discuss.* **1989**, *88*, 317. (b) Monkman, A. P.; Adams, P. *Synth. Met.* **1991**, *40*, 87.

(23) Chen, S.-A; Lee, H.-T. *Macromolecules* **1993**, *26*, 3254−3261.

(24) Strong base will break the Si−O bond; the polymer film will fall off.

(25) The exact structure of polyaniline is unknown. However, on the basis of the general chemistry sense and model studies, the polyaniline chains consist of a repeat unit of 10 Å which includes two aniline units: Wu, C.-G.; DeGroot, D. C.; Marcy, H. O.; Schindler, J. L.; Kannewurf, C. R.; Bakas, T.; Papaefthymiou, V.; Hirpo, W.; Yesinowski, J. P.; Liu Y. J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 9229−9242.

(26) Oh, E. J.; Min, Y.; Wiesinger, J. M.; Manohar, S. K.; Scherr, E. M.; Prest, P. J.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1993**, *55*−*57*, 977.

(27) Chen, C.-Y.; Wu, C.-G., submitted to *J. Mater. Chem.*

(28) (a) Wu, C.-G.; Bein, T. *Science* **1994**, *266*, 1013−1015. (b) Martin, C. R.; Parthasarathy, R.; Menon, V. *Synth. Met.* **1993**, *55*, 1165−1170. (c) Martin, C. R. *Science* **1994**, *266*, 1961−1966.

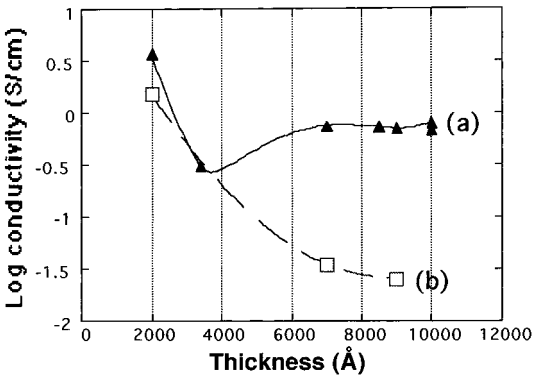


Figure 3. Variation of room-temperature conductivity vs film thickness of (a) films on $C_6H_5NHC_3H_6Si(OMe)_3$-modified SiO_2/Si substrate and (b) films on unmodified SiO_2/Si substrate.

with the amorphous pattern of the film deposited on unmodified substrate or film cast from NMP solution, the XRD pattern of the film on modified substrate showed two very weak peaks at 2θ equal to 20.0 and 21.8°. Although the two peaks were broad and weak, they indicated that the long-range order was existent in this conducting polyaniline film. Furthermore, the IR spectra of the polyaniline films on **I**-modified SiO_2/Si surface showed a group of peaks at 3240, 3154, 3064, 2975, and 2840 cm^{-1}, named "H-peaks". These peaks were not observed in bulk emeraldine salt, protonated polyaniline film made from polymer/NMP solution or deprotonated film on the substrate, as shown in Figure 4. They disappeared and reappeared reversibly in the deprotonation/protonation process. The "H-peaks" may be related to the interchain hydrogen bonding as shown in Scheme 1. The formation of interchain hydrogen bonding of polyaniline film implied that polyaniline chains on the surface arranged in some degree of regularity. More experiments are under way to further address this issue.

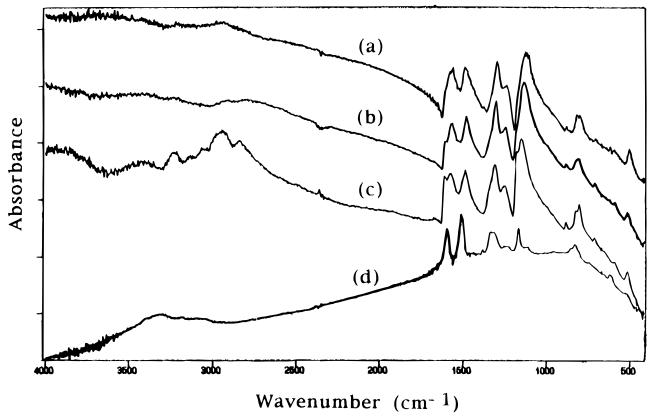


Figure 4. IR spectra of (a) bulk polyaniline (KBr pellet), (b) protonated polyaniline film cast from NMP solution, (c) as-prepared polyaniline film on $C_6H_5NHC_3H_6Si(OMe)_3$-modified SiO_2/Si substrate, and (d) deprotonated polyaniline film on $C_6H_5NHC_3H_6Si(OMe)_3$ modified SiO_2/Si substrate.

In conclusion, the preparation method described here offers a potentially powerful strategy for building good-adhesive, better-ordered conducting polymer thin films with systematic control over both thickness and properties. It was readily adapted to aniline derivatives and other conducting polymer systems, such as polypyrrole. Moreover, the as-prepared polyaniline films were homogeneously protonated. Protonating/deprotonating of the polymer films is very fast and can be repeated several times without damaging the films.

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