

## Area-selective Fabrication of Polyaniline/Poly(styrenesulfonic acid) Composite Ultrathin Films on Micropatterned Aminosilane Grafted Surfaces

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Micropatterning of ultrathin films was achieved using area-selectively immobilized PSS as the template. (Polyaniline (PANI) /poly(styrenesulfonic acid) (PSS)) composite ultrathin films on Si-wafers were area-selectively fabricated based on ionic interaction between PSS and aniline. (PANI/PSS) composite ultrathin films were characterized by X-ray photoelectron spectroscopy (XPS), ultraviolet-visible-near infrared (UV-Vis-near IR) spectroscopy, and scanning force microscopy (SFM). Spectroscopic analyses indicated that anionic PSS adsorbed on positively-charged patterned aminosilane surface plays an important role as the template for polymerization of aniline. SFM observation revealed that ca. 2  $\mu\text{m}$  width, ca. 5-10 nm thick (PANI/PSS) composite micropattern were successfully fabricated on the micropatterned Si-wafer.

Key words : polyaniline, poly(styrenesulfonic acid), aminosilane, ultrathin film, micropattern

### 1. Introduction

In recent years, PANI ultrathin film has been paid great attention since it shows excellent stability, wide range of functional properties, such as optical and electronic properties.<sup>1</sup> Therefore, PANI is expected as novel high functional conductive materials, which will be substituted for metallic materials. So far, films of PANI have been prepared by using 'self-assembly method'.<sup>2</sup> One can prepare the multi-layer of PANI and polymer electrolyte by using this method. However, this method needs a large number of processes to prepare sufficient films to utilize as electronic devices, and the conductivity of PANI multi-layer film prepared by this method was not greater than  $1 \text{ S cm}^{-1}$ .

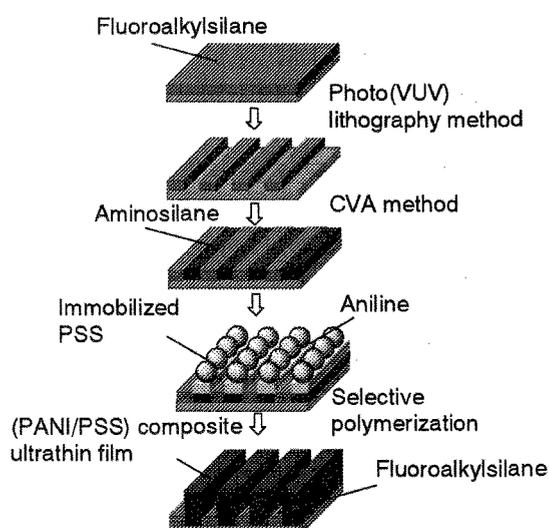
In the present paper, the authors report the preparation of micropatterned (PANI/PSS) composite ultrathin films on the amino-terminated monolayers, and characterization of their morphologies and physicochemical properties. Scheme 1 shows the processes to fabricate micropatterned (PANI/PSS) composite ultrathin films. This method is based on matrix polymerization, which utilizes PSS as the template molecules for PANI.<sup>3</sup>

### 2. Experimental Section

#### 2.1 Micropatterning of organosilane monolayers.

The Si wafer substrates were placed in a mixed solution of concentrated  $\text{H}_2\text{SO}_4$  and 30 %  $\text{H}_2\text{O}_2$  (70:30 (v/v)) to dissociate the siloxane bonds on the substrate surface. Then, the substrates were photochemically cleaned by a vacuum ultra violet (VUV,  $\lambda=173 \text{ nm}$ ) treatment under pressure less than 15 mmHg for 3 min. An excimer lamp (Ushio Electric, Co., Ltd., UER20-172V,  $\lambda=172 \text{ nm}$ ) served as the light source.

3- (2-aminoethylaminopropyl)dimethoxysilane [AEAPDMS,  $\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OMe})_2\text{CH}_3$ , Chisso Co., Ltd.], and hexadecafluoroethyltrimethoxysilane [FHETMS, Pinnacle Chemicals, Co., Ltd.] were used as surface modifier. Modified Si surfaces were prepared based on chemical vapor adsorption (CVA) method.<sup>4</sup> The cleaned Si-wafers were placed together with a glass cup filled with 0.2 ml FHETMS or 0.05 ml AEAPDMS liquid diluted with 0.35 ml absolute toluene into a Teflon™ container. The container was sealed with a cap and heated in an oven maintained at 373 K. In this study, reaction time for CVA was 2 h. After taking out the samples from a container, immediately, the substrates were rinsed by ethanol or absolute toluene. The substrates were dried under room



Scheme 1 Schematic representation of preparation method for micropatterned (PANI/PSS) composite ultrathin film.

temperature for 24 h in vacuo.

Micropatterning was carried out by photolithographic method as follows. This method based on excite-cleavage of C-C bond by irradiation of VUV light.<sup>4</sup> The FHETMS grafted Si substrate was placed in a vacuum chamber. The pressure in the chamber was maintained below 0.6 mmHg. The sample was then irradiated for 15 min with VUV light through a photomask (Toyo Precision Parts MFG, Co., Ltd.) contacting the sample surface. A cylindrical stainless weight served on the photomask in order to contact between the sample surface and the mask. AEAPDMS SAMs were introduced into the patterned substrate surfaces by CVA method.

## 2.2 Preparation of polyaniline / poly(styrenesulfonic acid) composite ultrathin film.

Aniline (99 %, Kanto Chemical, Co., Ltd.) was purified by vacuum distillation. PSS ( $M_w=70k$ , Poly Science, Co., Ltd.) and ammonium persulfate (APS, 98 %, Kanto Chemical, Co., Ltd.) were used without purification. All reactions were carried out at 288 K. In advance, PSS was adsorbed on SAMs by immersing the substrates in 10 or 60 mM PSS aq. for 5 min. Then the substrates were rinsed with distilled water and ethanol, and dried in vacuo. Next, in order to form ion complex between aniline and immobilized PSS, the samples were immersed in 10 mM aniline HCl aq. (pH4) for 10 min. Polymerization of PANI was carried out in HCl aq under several pH conditions for 6 h. It took 1 h to complete the addition of APS 2.5  $\mu\text{mol}$  into the mixture. Prepared (PANI/PSS) composite ultrathin film was rinsed with distilled water and ethanol, then dried in vacuo.

## 2.3 Characterization of ultrathin films

Attenuated total reflection fourier transformation infrared (ATR-FT-IR) spectra were measured at room temperature in dry air using Spectrum One FT-IR spectrometer (PerkinElmer, Co., Ltd.) with H120-0311 HATR unit. ZnSe was used as the optical crystal. All spectra are the sum of 1024 scans, and collected at 0.5  $\text{cm}^{-1}$  resolution.

XPS spectra were obtained on a PHI ESCA 5800 H (Physical Electronics, Co., Ltd.) with an  $\text{AlK}_{\alpha}$  X-ray source that was operated at 14 kV and 24 mA. The pressure in the XPS analysis chamber was maintained at  $10^{-9}$  Torr or lower during data collection. The binding energies were referenced to the  $\text{C}_{1s}$  graphite carbon peaks at 284.7 eV in order to correct for the charging energy shift, and the spectra were deconvoluted into suitable components of a Gaussian-Lorentzian function.

UV-Vis-near IR spectra were measured with UV-3100 PC (Shimadzu, Co., Ltd.) spectrometer. The scan

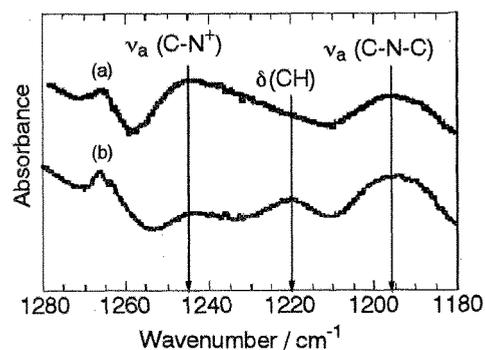


Figure 1 ATR-FT-IR spectra for (a) (PANI/PSS) composite on AEAPDMS monolayer surface, and (a) AEAPDMS monolayer.

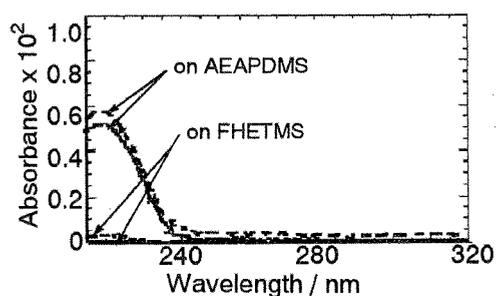


Figure 2 UV-Vis spectra for immobilized PSS and aniline monomer on AEAPDMS and FHETMS SAMs. (Solid line and broken line correspond to PSS and PSS + aniline monomer, respectively.)

rate was 160  $\text{nm min}^{-1}$ , width of slit was 5.0 nm. Fused silica was used as the substrate for measurements.

The surface morphology of (PANI/PSS) composite ultrathin film was observed with atomic force microscopy (AFM) and lateral force microscopy (LFM). AFM observations and LFM measurements were carried out with TMX-2100 (TM Microscopes, Co., Ltd.), at room temperature under constant force mode with a reference force of 0.1 nN.  $\text{Si}_3\text{N}_4$  triangular cantilever with a spring constant of 0.09  $\text{Nm}^{-1}$  was used.

## 3. Results and Discussion

### 3.1 Area-selective formation of (PANI/PSS) composite ultrathin films

To characterize the (PANI/PSS) composite ultrathin film on uniform AEAPDMS SAM, ATR-FT-IR measurements were carried out in advance of the microfabrication of (PANI/PSS) composite ultrathin film. Figure 1 shows the ATR-FT-IR spectra for (a) (PANI/PSS) composite on AEAPDMS monolayer surface, and (a) AEAPDMS monolayer. As is shown in Figure 1, the most prominent change of the spectrum is the increase in broad absorption at 1245  $\text{cm}^{-1}$  corresponding to  $\text{C-N}^+$  stretching band.<sup>5</sup> This is due to the formation of protonated nitrogen atoms in polymerized PANI.

Area-selective polymerization of PANI was achieved

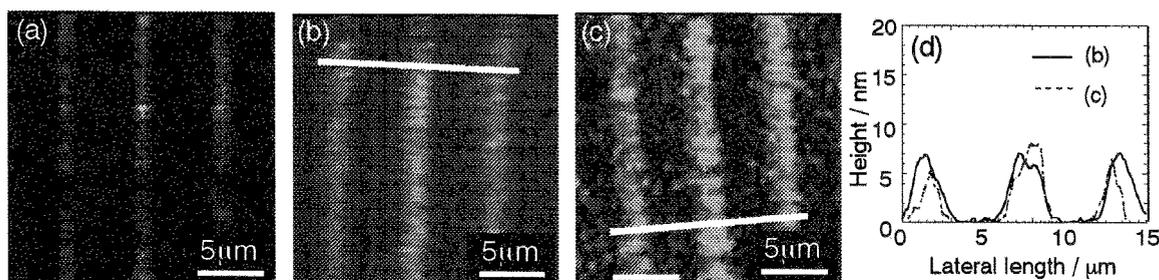


Figure 3 (a) LFM image of (AEAPDMS/FHETMS) patterned surface, AFM images of (b) PSS micropattern, (c) (PANI/PSS) composite micropattern, and (d) their line profiles. ((b) and (c) were prepared from 60 mM PSS aq.)

by electrostatic interaction between PSS and amino-terminated surface. Figure 2 shows UV-Vis spectra of immobilized PSS on fused silica substrates. As can be seen in Figure 2, the absorption band at 224 nm, which is attributed to the  $\pi$ - $\pi^*$  absorption, was observed on AEAPDMS SAMs.<sup>2</sup> On the other hand, the immobilized PSS could not be detected on FHETMS SAMs. These results suggested that adsorption of the initial PSS layer onto the Si wafer is enhanced by electrostatic interactions between the positively charged AEAPDMS surface and negative charges of the PSS. However, the much smaller amount of PSS adsorbed onto the uncharged FHETMS surface suggests that the low surface energy of this SAMs is more effective than electrostatic repulsion for reducing adsorption of PSS.

To characterize microstructure of (PANI/PSS) composite ultrathin film on the patterned (AEAPDMS/FHETMS) surface, AFM observation and LFM measurement were carried out. Figure 3 shows (a) LFM image of (AEAPDMS/FHETMS) patterned SAM, AFM images of (b) PSS micropattern, (c) (PANI/PSS) composite micropattern, and (d) their line profiles. The PSS micropatterns were prepared on the patterned monolayer surfaces from 60 mM PSS aq.. In Figure 3(a), bright areas and dark areas correspond to AEAPDMS and FHETMS monolayer phase, respectively. In Figure 3(b) and (c), immobilized PSS and (PANI/PSS) composite were formed ca. 2 μm width lines on the AEAPDMS monolayer phase spaced by ca. 4 μm lines of the FHETMS monolayer phase, and the thicknesses of these micropatterns were ca. 5-10 nm. The lateral shape of the patterned ultrathin films corresponds to the spacing of the photomask used to prepare the micropatterns of AEAPDMS and FHETMS monolayer phases on the Si substrates by CVA method. In these results, it is obvious that the width and thickness of (PANI/PSS) composite micropattern correspond to that of PSS micropattern formed on the AEAPDMS phase. This area-selective formation of the (PANI/PSS) composite ultrathin film is due to the specific immobilization of

aniline and PSS on the patterned AEAPDMS phase.

### 3.2 Evaluation of (PANI/PSS) composite ultrathin films.

The influence of the immobilized PSS on the extension of  $\pi$  conjugation in (PANI/PSS) composite was discussed based on UV-Vis-near IR and XPS measurements. The (PANI/PSS) composite was prepared on the uniform AEAPDMS grafted Si wafers. The thickness of PSS ultrathin films, which have been prepared from 60 mM and 10 mM PSS aq., were estimated to be ca. 1 nm and ca. 2-10 nm based on AFM observations, respectively. pH condition was maintained at pH4. Figure 4 shows UV-Vis-near IR spectra for (PANI/PSS) composite ultrathin film prepared from 10 or 60 mM PSS aq.. Absorption at 580 nm is due to the excitation of the quinoid ring on PANI, and absorption over 800 nm was attributed to polaron band on PANI.<sup>7</sup> It is evident that the magnitude of absorbance for quinoid ring of (PANI/PSS) composite prepared from 60 mM PSS aq. is weaker than that from 10 mM aq.. Table 1 shows the relative intensity of the components of  $N_{1s}$  spectra of the same samples corresponding to those in Figure 4. Relative intensity of the  $N^+$  component increase, as the thickness of immobilized PSS increased. From these spectra, it is suggested that an enough thickness of immobilized PSS is necessary to form the highly conjugated (PANI/PSS) composite ultrathin films. In the case of 10 mM, the extension of  $\pi$  conjugation was short in (PANI/PSS) composite ultrathin films owing to the too small amount of immobilized PSS.

To confirm the influence of the pH conditions on polymerization of PANI, UV-Vis-near IR and XPS measurement were carried out. The concentration of PSS aq to prepare the (PANI/PSS) composite ultrathin films was maintained at 60 mM. Figure 5 shows the UV-Vis-near IR spectra for (PANI/PSS) composite ultrathin films prepared under several pH conditions. Table 2 shows the relative intensity of the components in  $N_{1s}$  XPS spectra of the same samples corresponding those in Figure 5. The absorption of polaron band over  $\lambda=800$  nm was extended as the decrease of pH. On the other hand, the absorption of quinoid ring,

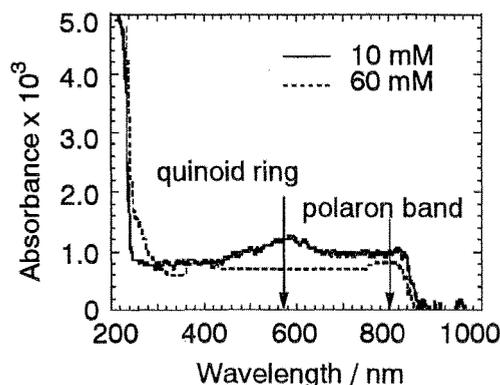


Figure 4 UV-Vis-near IR spectra for (PANI/PSS) composite ultrathin films prepared from 10 mM or 60 mM PSS aq.

Table 1 Relative intensity of the components in  $N_{1s}$  spectra of (PANI/PSS) composite ultrathin films prepared from 10 or 60 mM PSS aq.

Concentration(mM)	NH <sub>2</sub>	-NH-	N <sup>+</sup>
10	-	1.00	0.39
60	-	1.00	0.73

samples corresponding those in Figure 5. The absorption of polaron band over  $\lambda=800$  nm was extended as the decrease of pH. On the other hand, the absorption of quinoid ring, which is observed for PANI with low degree of protonation, decreased with the decrease of pH. In XPS analysis, relative intensity of protonated nitrogen atoms increased with the decrease of pH. These spectral changes suggested that the advance of formation of highly conjugated (PANI/PSS) composite ultrathin films was realized under low pH conditions. From these results, it becomes clear that the low pH condition is also necessary to form the highly conjugated (PANI/PSS) composite ultrathin films.

#### 4. Conclusion

In conclusion, the authors succeeded in area-selective fabrication of (PANI/PSS) composite ultrathin films on the micropatterned (AEAPDMS/FHETMS) monolayer surfaces. The micropatterned ultrathin films were successfully fabricated on the amino-terminated monolayer phase based on electrostatic interaction between PSS and AEAPDMS grafted surfaces. The protonation and the extension of  $\pi$  conjugation in PANI depended on the thickness of immobilized PSS and pH.

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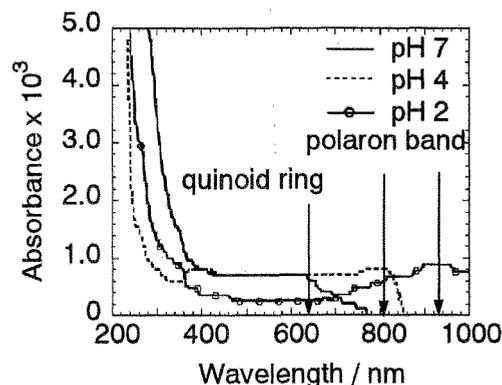


Figure 5 UV-Vis-near IR spectra for (PANI/PSS) composite ultrathin films prepared in several pH conditions.

Table 2 Relative intensity of the components in  $N_{1s}$  spectra of (PANI/PSS) composite ultrathin films prepared under several pH conditions.

pH	NH <sub>2</sub>	-NH-	N <sup>+</sup>
7	0.06	1.00	0.69
4	-	1.00	0.73
2	0.01	1.00	1.17

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