# Thickness Control of Polycationic Single-Layer Adsorption Films by Mix Proportion of Poor Solvent to Good Solvent

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We designed a new polycationic adsorbate of poly(4-vinylpyridine-co-1-dodecyl-4-vinylpyridinium bromide) to achieve selective surface metallization by electroless plating. In this study, we investigated the thickness of the single-layer adsorption film formed from the polycationic adsorbate on a negatively charged substrate surface by immersing once the substrate in an EtOH/H<sub>2</sub>O solution of the polycationic adsorbate. To measure the film thickness, the adsorption films were irradiated with vacuum-ultraviolet (VUV) light at 172 nm through a photomask and the VUV-exposed films were decomposed selectively. The thickness of the adsorption film was determined by measuring a topographical shape of the photopatterned film on a substrate surface using an atomic force microscope. The adsorption film prepared from good solvent ethanol had a thickness of  $0.8 \pm 0.1$  nm. As a mix proportion of poor solvent water was increased, the film thicknesses were increased. In the case of 80 wt% H<sub>2</sub>O content, the adsorption film of  $2.4 \pm 0.6$  nm in thickness was formed. It was found that the thickness of the single-layer adsorption film was readily tunable by changing a mixing ratio of poor solvent to good solvent in the film preparation.

Key words: single-layer adsorption film, polycation, thickness control, good solvent, poor solvent

#### 1. INTRODUCTION

The photolithography of a thick polymer photoresist layer on a micrometer scale has been widely adopted to fabricate printed-wiring circuit boards in home electric appliances. In the manufacturing process, development to remove the photoresist layer is performed using an aqueous solution containing harmful organic substances. A copious amount of organic wastes containing photoresist and harmful organic substances should be reduced from a standpoint of green sustainable chemistry.

One approach to reduce the organic wastes in the manufacturing process will be to use a photopatterned self-assembled monolayer having a thickness of several nanometers. Dressick and Calvert have demonstrated that self-assembled monolayers (SAMs) bearing amino, pyridyl, phenyl, and chloromethylphenyl groups are available for selective metallization of substrate surfaces.<sup>[1]</sup> The selective metallization is achieved by site-selective adsorption of Pd/Sn nanospheres as plating catalysts on photopatterned SAM surfaces, which leads to electroless deposition of cupper and nickel metals. Their studies are concentrated on overcoming an optical limit in lateral resolution that current photoresist systems have.

To reduce the organic wastes in the manufacturing process of printed-wiring circuit boards, we have recently proposed the utilization of single-layer adsorption films of polycationic adsorbates formed from mild green solvents of ethanol and water.<sup>[2]</sup> A polycation of poly(1-dodecyl-4-vinylpyridinium bromide) is adsorbed by a negatively charged silica surface through multipoint electrostatic adsorption. The irradiation with vacuum-ultraviolet (VUV) light at 172 nm decomposes surface-adsorbed polymer species. As a result, VUV-exposed silica surfaces with negative charge and unexposed polymer surfaces with positive

charge are formed on a silica substrate by imagewise irradiation.  $SDS-SnO_x$  colloids with negative charge (SDS: sodium dodecyl sulfate) are adsorbed preferably on the positively charged film surfaces by cooperative attractions of electrostatic interaction and van der Waals interaction. The selectively adsorbed SDS-SnO<sub>x</sub> colloids form metallic palladium catalysts by redox reactions, which cause selective electroless deposition of nickel-phosphorus (Ni-P) alloy.

On the basis of the principle mentioned above, we have first demonstrated that the single-layer adsorption film of the polypyridinium adsorbate is available for surface-assisted selective metallization. However, the novel method for preparing metallic wires on a substrate surface has several problems. First, the SDS-SnO<sub>x</sub> colloids of about 500 nm in diameter are too large. Therefore, a lateral resolution of deposited Ni-P alloy is limited up to 100 µm. The lateral resolution of conductive wires should be reduced at least to 10 µm for home electric appliances. Secondly, the electroless plating method is in an old-fashioned way, consisting of SnO<sub>2</sub> sensitization, PdCl<sub>2</sub> activation and electroless deposition. It is preferable to avoid the use of tin compounds such as SnOx by current environmental standards.

Taking particular note of coordination of  $Pd^{2+}$ species in an acidic  $PdCl_2$  aqueous solution to surface pyridyl groups,<sup>[1,3]</sup> we designed a new polycationic adsorbate of poly(4-vinylpyridine-*co*-1-dodecyl-4vinylpyridinium bromide) for cupper electroless plating. It was anticipated that the cationic copolymer, abbreviated as p(py-pym), possesses pyridinium groups as multipoint electrostatic adsorption sites to negatively charged substrate surfaces, pyridyl groups as coordination sites to  $Pd^{2+}$  species, and hydrophobic dodecyl groups as controllers of its film thickness.

Here, we investigated the formation of a single-layer



**Figure 1.** Chemical structure of poly(4-vinylpyridine -*co*-1-dodecyl-4-vinylpyridinium bromide).

adsorption film from the cationic copolymer p(py-pym)on surfaces of a silica plate and a surface-oxidized silicon wafer by UV-visible absorption spectral measurement and zeta-potential measurement. It was found that the thickness of the single-layer adsorption film could be measured by photolithography using vacuum-ultraviolet (VUV) light at 172 nm and atomic force microscopy. Moreover, we revealed that the film thickness was successfully tunable by a mix proportion of poor solvent H<sub>2</sub>O to good solvent EtOH in the film preparation.

### 2. EXPERIMENT

#### 2-1. Materials

Deionized water with a resistivity of 18.0 M $\Omega$  cm was prepared by a Mili-Q system and used throughout. Ethanol was purchased from Wako Pure Chemical Industries and distilled prior to use. Fused silica plates and silicon wafers (antimony-doped type, Si(100)) were purchased from Nippon Rika Glass Co., Ltd. and Toshiba Ceramics Co., Ltd. respectively. A surface of the substrates was cleaned by irradiation with 172 nm VUV light emitting from a Xe excimer lamp (Ushio UER20-172A) under a pressure of 1000 Pa for 5 min.

Poly(4-vinylpyridine-co-1-dodecyl-4-vinylpyridinium bromide), abbreviated as p(py-pym), was synthesized by the reaction of poly(4-vinylpyridine) (Aldrich, Mw = 7.0x  $10^4$ , Mn = 3.1 x  $10^4$ , Mw/Mn = 2.3) with 1-bromododecane in 2-propanol at 105 °C for 24 h. The reaction mixture was poured into ethyl acetate to give precipitate. The precipitated product was purified by twice reprecipitation with ethanol as good solvent and ethyl acetate as poor solvent, followed by drying in vacuo. The molar ratio of pyridinium groups to pyridyl groups in the copolymer was confirmed by <sup>1</sup>H-NMR measurement in DMSO- $d_6$  using  $\alpha$ -proton of the pyridinium groups (8.9 ppm) and  $\beta$ -proton of the pyridyl groups (6.7 ppm). The cationic copolymer having the molar ratio of 0.3 to 0.7 as shown in Figure 1 was used in this study.

### 2-2. Film preparation and photopatterning

Five types of EtOH/H<sub>2</sub>O mixed solutions containing  $10^{-2}$  unit mol dm<sup>-3</sup> p(py-pym) were prepared. The mix proportions of the EtOH/H<sub>2</sub>O solutions were 0, 20, 40, 60, and 80 wt% H<sub>2</sub>O. Hydrophilic cleaned silica plates (10 x 30 x 1 mm) or silicon wafers (10 x 10 x 0.5 mm) with a contact angle below 5° were immersed once in each mixed solution at 30 °C for 1 h under gentle agitation (100 times min<sup>-1</sup>). The substrates were rinsed with pure mixed solution and dried by blowing N<sub>2</sub> gas. Adsorbed silica plates were subjected to UV-visible spectral measurement and zeta-potential measurement.

Adsorbed silicon wafers were subjected to zeta-potential measurement and photopatterning. Photopatterning of an adsorption film formed on a silicon wafer was carried out by VUV-exposure through a photomask made of synthetic silica. The photopatterned adsorption film was observed by atomic force microscopy.

#### 2-3. Physical measurement

UV-visible absorption spectra were taken on a weak spectrophotometer (MAC-1, JASCO). absorption Sessile contact angles for water were measured with a contact angle meter (CA-X, Kyowa Interface Science Zeta-potential measurement of substrate Co., Ltd.). surfaces before and after polymer adsorption was carried out at  $25 \pm 1$  °C using an electrophoretic light scattering spectrophotometer (ELS-8000, Otsuka Electronics). The detailed procedures were described in our previous paper.<sup>[4]</sup> Surface morphology of the photopatterned adsorption film was probed by an atomic force microscope (Nanoscope IV). The measurement was carried out in a tapping mode using a silicon tip (Nano Device) with a resonance frequency of ca. 150 kHz.

## 3. RESULTS AND DISCUSSION

3-1. Formation of a single-layer adsorption film followed by zeta-potential and UV-visible spectral measurements

To investigate the effect of the mix proportion of poor solvent to good solvent on formation of a single-layer adsorption film, we prepared five types of adsorption films by immersing a silica plate in 0, 20, 40, 60 and 80 wt% H<sub>2</sub>O-containing EtOH/H<sub>2</sub>O mixed solutions of  $10^{-2}$  mol dm<sup>-3</sup> polycationic adsorbate p(py-pym). The adsorption film on a silica plate was subjected to zeta-potential and UV-visible absorption spectral measurements.

A silica surface cleaned by VUV-exposure exhibited a negative zeta-potential value of -85  $\pm$  1 mV in a 10 mmol dm<sup>-3</sup> NaCl aqueous solution at pH 7. In contrast, all surfaces of silica substrates after immersion in p(py-pym)-containing solutions and multiple rinses exhibited positive zeta-potential values under the same condition. In the case of ethanol as good solvent, the zeta-potential value was 19  $\pm$  2 mV. As a mix proportion of poor solvent H<sub>2</sub>O to good solvent EtOH was increased, the zeta-potential value observed for p(py-pym) adsorption films was increased as shown in Figure 2. These results obviously suggested that a single-layer adsorption film of the polycation p(py-pym) was formed on a silica surface with negative charge on the basis of our previous study.<sup>[4]</sup>

To estimate quantitatively the amount of adsorbed p(py-pym) polycation, we measured UV-visible absorption spectra of silica plates adsorbing p(py-pym). A characteristic absorption band centered at 260 nm was observed for all the UV-visible spectra. The absorption band was attributable to a  $\pi - \pi^*$  transition band of pyridyl and pyridinium groups in the polycationic adsorbate. The absorbance at 260 nm plotted against an H<sub>2</sub>O content in the mixed solutions was indicated in Figure 2. The absorbance at 260 nm was larger, as the H<sub>2</sub>O content in the EtOH/H<sub>2</sub>O mixed solutions was increased. The absorbance is equal to the average amount of the adsorbed polycation per a probed area.



**Figure 2.** (i) Absorbance at 260 nm and (ii) surface zeta potential of p(py-pym)-adsorbed silica plates at pH7 as a function of H<sub>2</sub>O content in EtOH/H<sub>2</sub>O mixed solutions.

Therefore, the increase of the absorbance at 260 nm indicated clearly that the amount of adsorbed p(py-pym) was increase with an increase of the poor solvent H<sub>2</sub>O in the mixed solutions.

Organic polycations and polyanions are adsorbed by oppositely charged substrate surfaces, to give an adsorption film. Based on the principle, electrostatic layer-by-layer deposition can be carried out to fabricate multilayer films of polyelectrolytes. Caruso et al. report that a mix proportion of poor solvent EtOH to good solvent H<sub>2</sub>O in adsorption solutions for electrostatic layer-by-layer depositions significantly influences the amount of deposited polyelectrolytes.[5] It is revealed that the amount and the thickness of polyelectrolyte multilayers are markedly increased with an increase of the amount of poor solvent in mixed adsorption solutions by quartz crystal microbalance measurement and surface plasmon resonance spectroscopy. The increase of adsorbed amount is considered to be due to a coil-globule transition<sup>[6,7]</sup> of a polymer main-chain. Theoretical Rubinstein,<sup>[8]</sup> Dünweg,<sup>[9]</sup> and Kremer<sup>[10]</sup> works hv suggest that polyelectrolyte chains in poor-solvent-rich solution form globule conformation through "necklace-like" structures consisting of globules separated by stretched segments or strings. Minko et al. have observed single molecule structures of polyelectrolytes reflecting the macromolecular conformation such as necklace-like structures by AFM.<sup>[7]</sup> These previous works obviously imply that the thickness of a single-layer adsorption film formed from a charged polymer on a substrate surface would be increased, as a mix proportion of poor solvent to good solvent is increased in a mix solution for adsorption.

3-2. Photolithography of a single-layer adsorption film

Multilayer films prepared by layer-by-layer depositions are usually measured by optical measurements such as ellipsometry and surface plasmon resonance spectroscopy. Topological heterogeneity on a nanometer scale is completely neglected, because the film thickness is optically determined as an average value in such optical measurements. Although atomic force microscopy is a powerful tool to probe a topological surface shape of organic ultrathin films, it is



**Figure 3.** Schematic outlines of photopatterning a polycationic single-layer adsorption film on a substrate surface.

usually difficult to measure the thickness of organic ultrathin films, unless organic thin films are rubbed off by an ATM probing tip.

We have recently reported that a single-layer adsorption film of poly(1-alkyl-4-vinylpyridinium halide) on a silica plate could be decomposed completely by irradiation with vacuum-ultraviolet (VUV) light at 172 nm under a reduced pressure.<sup>[2]</sup> Taking note of the fact, we hit upon an idea to measure the thickness of such single-layer adsorption films. The idea is illustrated in Fig. 3. First, a single-layer adsorption film of p(py-pym) is formed on a surface-oxidized silicon wafer with a roughness of 0.08 nm by immersion in an EtOH/H2O solution containing p(py-pym). The adsorption film was exposed selectively to VUV light through a photomask. The adsorbed p(py-pym) polycation in VUV-exposed areas is decomposed. By measuring a topological shape of the photopatterned adsorption film by atomic force microscopy, we might determine the thickness of the adsorption film.

To carry out photolithography of the adsorption film, we should first determine VUV-exposure time to remove the adsorption film completely. We have reported that surface zeta-potential measurement is a reliable tool to confirm complete removal of an adsorption films on a substrate surface,<sup>[2]</sup> although contact angle measurement for water is commonly used. To determine the VUV-exposure time required for film removal, an adsorption film placed under a synthetic silica plate was exposed to VUV light at 172 nm under a pressure of 1000 Pa at different exposure time and subjected to surface zeta-potential measurement in a 10 mmol dm<sup>-3</sup> NaCl aqueous solution at pH 7. As a result, it was found that the positive zeta-potential value of 46  $\pm$  2 mV exhibited by the thickest p(py-pym) adsorption film prepared from a 80 wt% H<sub>2</sub>O solution turned to a negative zeta-potential value of -85 ± 1 mV after VUV-exposure for 20 min. The negative value was identical to that exhibited by a cleaned surface-oxidized silicon wafer before use, indicating that the VUV-exposure time for 20 min at least was required for the film removal. Accordingly, the adsorption film was exposed selectively to VUV light for 20 min through a photomask of a synthetic silica grade. Latent images of the hydrophobic photopatterned adsorption film could be visualized by a condensation figure method.<sup>[11]</sup>

3-3. Measurement of the film thickness by atomic force microscopy (AFM)

Surface morphology of the photopatterned



Figure 4. AFM images of photopatterned adsorption films on a substrate surface. A  $H_2O$  content in an EtOH/ $H_2O$  solution was (a) 0 wt% and (b) 80 wt%. Cross section profiles c,d were obtained from original AFM images a,b respectively.

adsorption films prepared from EtOH/H<sub>2</sub>O mixed solutions was probed by AFM in a tapping mode. Figure 4 shows the topographical image and the cross section profile of the photopatterned adsorption films. The parts (a) and (b) indicate the AFM images prepared from 0 wt% and 80 wt% H<sub>2</sub>O-containing mixed solutions, respectively. As seen in Figure 4, grooved microstructures in accord with a photomask shape could be clearly observed. The thickness of the adsorption film was measured from the cross sectional profile as shown in Fig. 4(c-d). In the case of the 0 wt% H<sub>2</sub>O content, the thickness of the adsorption film was observed for the adsorption film prepared from the 80 wt% H<sub>2</sub>O-containing solution.

The thicknesses of the adsorption films prepared from EtOH/H2O mixed solutions were plotted against an H<sub>2</sub>O content. The results were indicated in Fig. 5. The thickness was increased stepwise, as the content of H<sub>2</sub>O poor solvent was increased in the mixed solutions. It was worthy of note that the adsorption film in the case of 40 wt% H<sub>2</sub>O content was thicker than the adsorption film in the case of 0 wt% H<sub>2</sub>O content. Similarly, the zeta-potential value of  $28 \pm 2$  mV in the case of 40 wt% H<sub>2</sub>O content was significantly larger than zeta-potential value of 19 + 2 mV in the case of 0 wt% H<sub>2</sub>O content as indicated in Fig. 2. Taking account of the fact that an increase of adsorption-free cationic sites not contributing to substrate-adsorption sites causes an increase of a positive zeta-potential value,<sup>[12]</sup> the increase of the positive zeta-potential in the case of 40 wt% H<sub>2</sub>O was probably due to a structural transformation of the polycationic adsorbate p(py-pym) in the mixed solutions. The structural transformation of the polycationic adsorbate is probably due to coil-globule transition<sup>[6-10]</sup> or polymer micelle formation.

#### 4. CONCLUSION

We described the thickness of the single-layer adsorption film formed from a polycationic adsorbate of



**Figure 5.** (i) Absorbance at 260 nm and (ii) film thickness as a function of  $H_2O$  content in EtOH/ $H_2O$  mixed solutions.

poly(4-vinylpyridine-co-1-dodecyl-4-vinylpyridinium bromide) designed for surface-assisted selective electroless plating. To measure the film thickness, we proposed а novel method consisting of VUV-photolithography and atomic force microscopy. The film thickness was increased as the mix portion of poor solvent H<sub>2</sub>O to good solvent EtOH was increased. It was found that the film thickness was tunable by The method for changing the mix proportion. measuring the thickness by VUV-photolithography and atomic force microscopy will be commonly available for organic ultrathin films such as Langmuir-Blodgett monolayers and self-assembled monolayers in addition to single-layer adsorption films. The effect of the film thickness on Cu electroless deposition is under investigation in detail.

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