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Selective Microsphere Adsorption and Metallization on Photopatterned Polycation Single-layered Adsorption Films

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ABSTRACT: Multivalent cationic molecular and macromolecular adsorbates with plural pyridinium groups were adsorbed irreversibly on a substrate surface taking a negative charge, giving their single-layered adsorption film showing high desorption resistance toward deionized water. The desorption resistance of the adsorbates toward aqueous electrolyte solutions could be controlled by photochemical means such as photodimerization and photodegradation. The desorption suppression and promotion by the photochemical means was due to increasing and decreasing the number of cationic adsorption sites per molecule, respectively. Positive- and negative-type micropatterning, consisting of the surface adsorption, the imagewise exposure, and the development, could be carried out on the basis of the desorption promotion and suppression. The photopatterned adsorption films were available as templates for selective microsphere adsorption and metallization by electroless deposition. In this review, the recent studies done by the author and co-workers were described. [doi:10.1295/polymj.PJ2005260]

KEY WORDS Polycation / Monolayer / Adsorption / Electroless Deposition / Microsphere / Pattern / Photochemistry /

Wiring circuit boards having metallic wires of 10 μm to 1 mm in width are widely used in house electric appliances. Most of the wiring boards are manufactured currently by photolithography using an organic photoresist material. There are two categories of subtractive and additive methods in electroless plating for preparing conductive metallic wires on an insulating substrate. In the subtract method, a ternary plate consisting of a photoresist layer, a metal layer and a substrate layer is used. The photoresist layer is formed by spin-coating or laminating. The photoresist layer is exposed imagewise to actinic light. Either exposed or unexposed region of the photoresist layer is removed by a developer solution, and unnecessary regions of the metal layer are removed by an etchant solution. It is necessary to collect and reuse metal species in a waste solution caused by the etching process. Therefore, another additive method trends to spread gradually.

The additive method is a method for forming a conductive metallic pattern on an insulating substrate additively. An example is given.¹ A positive-type photoresist layer on a substrate is exposed imagewise to actinic light, and its exposed regions are developed. The substrate with a relief-shaped photoresist layer is immersed in a solution containing a colloidal catalyst for electroless deposition, and the catalyst is ad-

sorbed on a surface of the substrate entirely. The surface is exposed entirely to the actinic light once again. A colloidal catalyst adsorbed on convexly curved parts of the relief-shaped photoresist layer is washed away by the developer solution. As a result, the colloidal catalyst is left on a substrate surface in accord with the initial photopattern shape, where electroless deposition can be induced. The photoresist layer has a thickness of sub-micrometers to several tens of micrometers usually. The thick photoresist layer is disposed of as industrial waste in the manufacturing process. The industrial waste composed of organic photoresist material and developer is burned, which causes emission of carbon dioxide and harmful organic substances. To achieve green sustainable chemistry, the industrial standpoint is that an alternative method capable of reducing sufficiently harmful industrial waste is desired in the manufacture of the wiring circuit board.

Site-selective surface adsorption or formation of a colloidal plating catalyst is a successful key to preparing patterned metal wires on an insulating substrate in the additive method. The use of a self-assembled monolayer (SAM) having a thickness of a few nanometers has been drawing attention as a new additive method. According to the report by Calvert and co-workers,² the photopatterned SAM derived from phen-

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yltrichlorosilane is available as a template in Ni electroless deposition on a silicon wafer with a native oxide layer. Ni electroless deposition takes place selectively on the unexposed SAM surface patterned by exposure to 193 nm deep-UV light. The selective metallization is responsible for selective adsorption of a colloidal Pd/Sn catalyst on the unexposed phenyl-terminated SAM surface rather than the UV-exposed silanol-terminated substrate surface. The reason why the selective adsorption of the colloidal catalyst occurred still remains unclear. Dressick and coworkers evolve the initial work done by the research group of Calvert. The coordination bond generating between surfaces of amino- or pyridyl-terminated alkoxy silane SAM and a Pd/Sn colloidal catalyst is useful for selective surface adsorption of the plating catalyst.³⁻⁶ In these cases, the SAM works as a surface promoting catalyst adsorption.

Sugimura and coworkers demonstrate the selective formation of a palladium nanoparticle on an H-terminated silicon wafer surface using an octadecyltrimethoxysilane SAM as a surface preventing catalyst formation.^{7,8} Exposure to 172 nm vacuum ultraviolet light (VUV) causes the SAM on a silicon wafer with a natural oxide layer to be decomposed by photo-oxidation. A natural oxide layer appearing in VUV-exposed regions of the SAM is removed by an etchant solution, and an hydrogen-terminated silicon surface is formed. A palladium nanoparticle working as a plating catalyst in Ni electroless deposition is formed selectively on the hydrogen-terminated silicon surface by immersion in an aqueous solution containing palladium chloride. In this case, limitation of substrate choice often prevents from utilizing the SAM.

Selective adsorption of a colloidal catalyst in the former is the promising way to carry out selective electroless deposition on a variety of insulating polymer substrate surfaces. The complete control of catalyst adsorption is a key in success in this case. However, there are few guidelines to achieve completely the selective adsorption of a colloidal catalyst. More concentrated studies of adsorption affinity between surfaces of an organic monolayer and a colloidal catalyst should be conducted. This review deals with recent studies of organic single-layered adsorption films designed for an adsorption template of colloidal materials by the author and coworkers. Photoreactive cationic molecules and polymers were utilized as a new class of adsorbates, because the involatile cationic adsorbates soluble in environmentally benign water and ethanol have distinctive advantages in the industrial standpoint. Their single-layered adsorption film worked as templates in organic and inorganic microsphere adsorption and electroless deposition.

SELECTIVE SURFACE ADSORPTION OF MICROSPHERES BY ELECTROSTATIC INTERACTION

Microspheres and nanoparticles are dispersed in an aqueous solution because their outermost surface takes a negative or positive charge. If a solid substrate surface having both positively and negatively charged regions could be prepared, a charged particle would be adsorbed on the surface regions taking its opposite charge by electrostatic attraction. In contrast, the charged particle would be hardly adsorbed on the surface regions showing the same charge by electrostatic repulsion. The hypothesis was a principle idea of achieving selective surface adsorption of a colloidal material dispersed in an aqueous solution. Most SAM surfaces derived from alkoxy silanes and alkanethiolates with a functional group show a negative zeta-potential value in a neutral aqueous solution, although amino-terminated alkoxy silane SAMs show a positive zeta-potential value in an acidic aqueous solution of pH 3 due to protonation.⁹ It is difficult to prepare positively charged substrate surface by the formation of a SAM derived from a commercially available reagent.

When a silica, metal oxide or polymer substrate taking a negative charge in an aqueous solution is immersed in an aqueous solution containing a low-molecular-weight surfactant molecule having a hydrophobic long-chain alkyl tail and a hydrophilic onium polar head such as a quaternary ammonium and pyridinium group, its adsorbed monolayer is formed at an interface between the surfactant-containing solution and the substrate.¹⁰ The adsorbed monolayer is collapsed readily by rinsing the substrate with adsorbate-free deionized water. The monolayer-forming molecule is almost desorbed from the substrate surface due to its reversible adsorption as illustrated in Figure 1a. On the other hand, an electrostatically adsorbed monolayer formed from a high-molecular-weight polycation on a negatively charged surface shows high desorption resistance toward deionized water. The desorption resistance arises from multipoint adsorption of the polycation having plural adsorption sites as illustrated in Figure 1b. The difference in desorption between the low-molecular-weight cationic molecule and the high-molecular-weight polycation brings us into two simple questions: How many cationic adsorption sites at least does one cationic molecule need to show high desorption resistance toward deionized water? Is it possible to control the desorption resistance by a photochemical mean?

UV-visible absorption spectral measurements allowed us to answer the first question. We prepared two kinds of cationic adsorbates as shown in Figure 2.

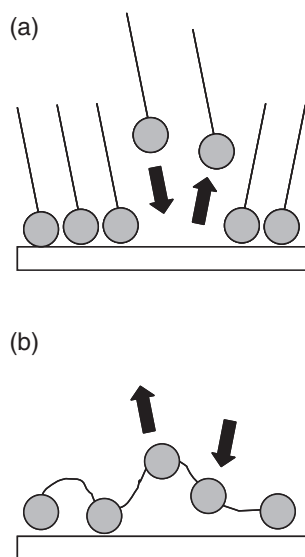


Figure 1. Illustrations of (a) reversible adsorption of a low-molecular-weight cationic molecule and (b) irreversible adsorption of a high-molecular-weight polycation due to its multipoint adsorption.

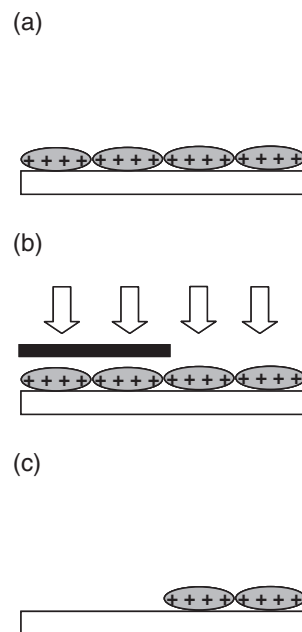


Figure 3. Schematic representation of negative-type photopatterning of an adsorbed monolayer. (a) Surface adsorption of the tetracation **2** susceptible of [2+2]photodimerization on a silica plate. (b) Pattern UV-exposure with 313 nm light causing the photodimerization. (c) Development with an electrolyte aqueous solution.

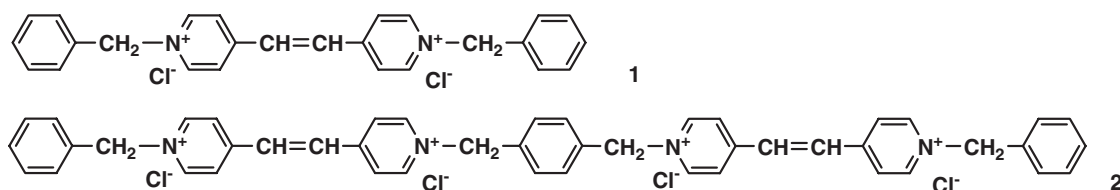


Figure 2. Chemical structures of (a) a dication and (b) a tetracation susceptible of [2+2]photodimerization.

4,4'-(1,2-ethenediyl)bis[1-(phenylmethyl)pyridinium chloride] **1** and 1,1'-[1,4-phenylenebis(methylene)]-bis[4-[2-[1-(phenylmethyl)pyridinium-4-yl]ethenyl]pyridinium chloride] **2** were designed as a dication molecule and a tetracation molecule having two and four pyridinium adsorption sites, respectively. The desorption behavior of **1** and **2** adsorbed on a silica substrate was monitored by following the change in absorbance as a function of the immersion period in deionized water at 20 °C. The tetracation **2** was hardly desorbed from a silica surface by deionized water, while the dication **1** was desorbed readily. The difference between their desorption behaviors unequivocally suggested that at least four pyridinium groups were necessary for one cationic molecule to exhibit high desorption resistance toward deionized water. In contrast, it was found that removal of the tetracation **2** is achievable by washing a silica plate adsorbing **2** in a 1 mol dm⁻³ NaCl aqueous solution for 5 min due to ion exchange.¹¹ Taking into account the fact that the tetra-

cation has two [2+2]photodimerizable bis(pyridinio)-ethylene moieties¹² leading to stepwise photopolymerization, we investigated whether the photodimerization caused the desorption resistance toward the NaCl aqueous solution to be enhanced. First, the surface adsorption of **2** was carried out by immersing a silica plate in an aqueous solution of **2** and washing thoroughly with deionized water, giving an adsorbed monolayer of **2** on the silica plate. Second, the adsorbed monolayer was exposed imagewise to 313 nm UV-light causing the photodimerization through a photomask. Third, the adsorbed monolayer in unexposed regions was removed by immersion in a 1 mol dm⁻³ NaCl aqueous solution. Selective adsorption of negatively charged colloidal silica particles of 73 nm in average diameter by electrostatic interaction allowed us to visualize the photopatterned adsorbed monolayer of the tetracation **2** left in the UV-exposed regions. As illustrated in Figure 3, it was found that as a result of the photochemical increase in electrostatic adsorption

sites per molecule due to photodimerization, the desorption of **2** in the UV-exposed regions was suppressed markedly so that photolithographic patterning of its adsorbed monolayer is achievable by development with the aqueous electrolyte solution. In this way, the tetracation **2** susceptible of [2+2]photodimerization was available as a photoreactive adsorbate to prepare negative-type adsorbed monolayer photopatterns.¹³

The second question was “Is it possible to control the desorption resistance by a photochemical mean?”. The answer was “Yes” as mentioned above. The desorption resistance of **2** could be improved by the [2+2]photodimerization causing the number of its cationic adsorption sites to be increased. Then, we investigate whether it is possible to deteriorate desorption resistance by reducing cationic adsorption sites by photodegradation as the opposite method of positive-type photopatterning. For the purpose, we designed a photodegradable multivalent cationic molecule **3**¹⁴ shown in Figure 4a. There are two major reasons: First, the cationic adsorbate **3** has a cyclopentasilane ring as a photodegradable moiety and plural quaternary pyridinium groups as multipoint adsorption sites. It is anticipated that the photodegradable cyclopentasilane unit is decomposed to smaller products by photocleavage of Si–Si bonds caused by UV-exposure with 254 nm light. Second, the role of the cationic pyridinium units in the adsorbed monolayer is anticipated to separate into adsorption sites tethered to a negatively charged substrate surface and adsorption-free sites to promote surface adsorption of microspheres taking a negative charge.

The photodegradation of **3** adsorbed on a silica plate was caused by exposure to UV light emitting

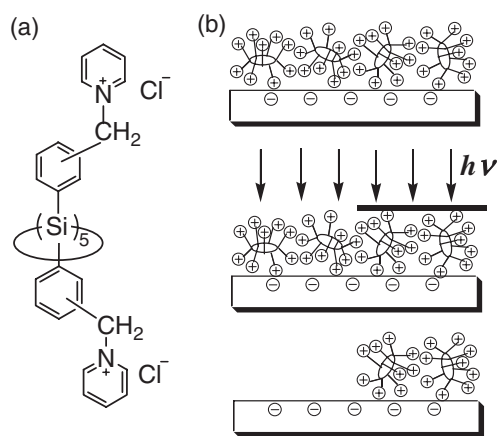


Figure 4. Chemical structure of (a) a photodegradable multivalent cationic adsorbate **3** and schematic representation of (b) positive-type photopatterning of its adsorbed monolayer on a substrate surface. The figure is cited from *Langmuir* **2003**, *19*, 8771 (Nakagawa, M. *et al.*).

from a low-pressure mercury lamp, which could be monitored by following the change in absorbance of its adsorbed monolayer by UV-visible absorption spectroscopy. Desorption of fragmented photoproducts from a silica or poly(ethylene terephthalate) substrate surface by deionized water could be confirmed by zeta-potential measurements of the substrate adsorbing **3** before and after UV-exposure. The adsorbed monolayer of **3** on the substrate showing a positive zeta-potential value almost altered to a bare substrate surface showing a negative zeta-potential value after UV-exposure. It was found that the photodegradation of **3** on the substrate lowered markedly its desorption resistance toward deionized water. Consequently, the positive-type photopatterning of the adsorbed monolayer, which consisted of surface adsorption, image-wise UV-exposure and development, could be carried out as illustrated in Figure 4b. A thus treated substrate surface with a photopattern of the adsorbed monolayer was available as an adsorption template for both a carboxy-modified poly(styrene) microsphere taking a negative charge and an amino-modified poly(styrene) microsphere taking a positive charge. Furthermore, binary microsphere arrays in accord with a photopattern shape of the adsorbed monolayer could be prepared by immersion in aqueous dispersion of the amino-modified microsphere and then in aqueous dispersion of the carboxy-modified microsphere due to control of electrostatic attraction and repulsion.¹⁴

SELECTIVE SURFACE METALLIZATION BY ELECTROLESS DEPOSITION

By photolithographic patterning of a cationic adsorbed monolayer on a substrate, we could prepare the micropatterned adsorption template composed of a positively charged surface of the cationic monolayer and a negatively charged surface of the bare substrate. According to electrostatic attraction and repulsion, poly(styrene) microspheres taking a charge could be adsorbed selectively in accord with the micropatterned template. The interfacial electronic phenomena led us to investigate whether the adsorption template was available to a colloidal catalyst used in nickel-phosphorus (Ni–P) electroless deposition. It was anticipated that the electroless deposition would take place as illustrated in Figure 5. The negatively charged substrate surface would be plated in the case of a positively charged colloidal catalyst, while the positively charged film surface would be plated in the case of a negatively charged colloidal catalyst.

To demonstrate the idea, we prepared poly(4-ethenyl-1-dodecylpyridinium bromide), QP4VP-C12, as a readily synthesized polycation adsorbate. The single-layered adsorption film could be formed on a silica

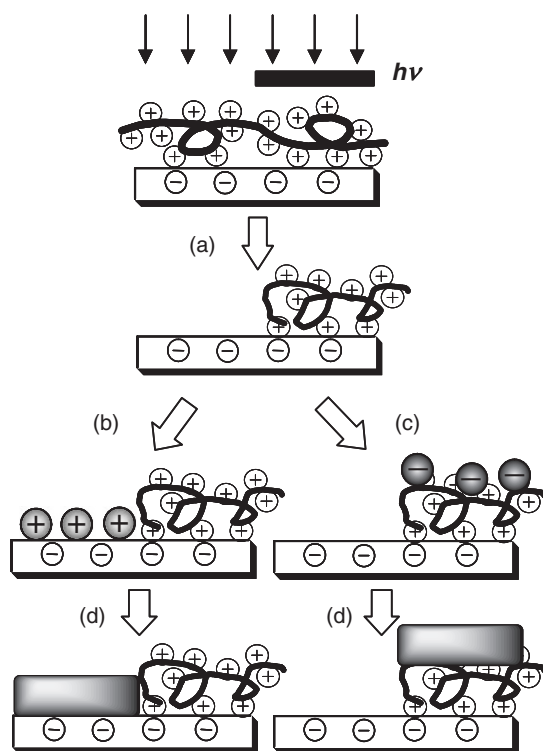


Figure 5. Schematic illustration of selective surface metallization by electroless deposition involving (a) photodegradation of a polycation single-layered adsorption film on a negative substrate surface, selective adsorption of a colloidal catalyst taking (b) a positive charge and (c) a negative charge, and (d) electroless plating. The figure is cited from *Langmuir* **2004**, *20*, 9845 (Nakagawa, M. *et al.*).

plate by its immersion in the ethanol solution containing QP4VP-C12, followed by rinsing with ethanol and drying. Vacuum ultraviolet light (VUV) at 172 nm emitting from a Xe excimer lamp was used for the positive-type photopatterning, because the adsorption film could be removed by photo-oxidation.¹⁵ The photopatterned adsorption film fabricated by VUV-exposure through a photomask was subjected to Ni–P electroless deposition using two kinds of SnO_x colloidal catalyst precursors surrounded with a cationic surfactant of cetyltrimethylammonium chloride (CTAC) and an anionic surfactant of sodium dodecylsulfate (SDS). The CTAC- SnO_x colloid exhibited a positive zeta-potential value of 50 ± 1 mV, while the SDS- SnO_x colloid showed a negative zeta-potential value of -60 ± 2 mV. In the case of the negative SDS- SnO_x colloid, Ni–P electroless deposition took place preferentially on the polycation adsorption film left in unexposed regions. The result was very consistent with that observed in the above selective adsorption of negatively charged poly(styrene) microspheres. According to the simple experimental result, it seemed that the selective adsorption of the SDS- SnO_x colloid took place on the charge-patterned surface by electrostatic attraction generating between surfaces of the positive-

ly charged adsorption film and the negatively charged SDS- SnO_x colloid.

However, two unperceivable events occurred in the Ni–P electroless deposition. The first event is that the amount of deposited Ni–P alloy obviously decreased, as the length of the alkyl group (n) included in poly(4-enethyl-1-alkylpyridinium halide), abbreviated as QP4VP-C n , was shorter. Four kinds of adsorption films prepared from QP4VP-C1 (methyl), QP4VP-C3 (propyl), QP4VP-C6 (hexyl) and QP4VP-C12 (dodecyl) exhibited a positive zeta-potential value of 59 ± 8 , 57 ± 6 , 41 ± 2 , and 24 ± 1 mV, respectively, in a HCl acidic aqueous solution of pH 3. The VUV-exposed film surface equal to a bare silica surface showed a zeta-potential value of about -27 mV. It is assumed that the QP4VP-C1 adsorption film with the highest positive zeta-potential will promote Ni–P deposition, because the amount of adsorbed SDS- SnO_x colloid is largest. The second event is that Ni–P electroless deposition took place on the positively charged QP4VP-C6 and QP4VP-C12 adsorption films with long-chain alkyl groups rather than the negatively charged silica surface, in the case of the positively charged CTAC- SnO_x colloid surrounded with the cationic surfactant cetyltrimethylammonium chloride. The unperceivable events put into our head some effect of the alkyl chain length (n) in the polycation adsorbates QP4VP-C n . Inductively coupled plasma atomic emission spectroscopy (ICP-AES) allowed us to confirm that the hydrophobic interaction generating between the long-chain dodecyl group in the QP4VP-C12 adsorption film and the long-chain alkyl group included in the surfactant.¹⁵ We revealed that, in addition to electrostatic attraction, the hydrophobic interactions among the long-chain alkyl groups enhanced significantly the adsorption stability of the surfactant-surrounded SnO_x colloids, followed by much nucleus formation of a zerovalent Pd catalyst useful for the Ni–P electroless deposition.

Several problems arose in the Ni–P electroless deposition using QP4VP-C12 as a plate-promoting polycation adsorbate and the SDS- SnO_x colloid as a catalyst precursor. First, site-selectivity of the Ni–P deposition was incomplete. The Ni–P deposition took place partially on VUV-exposed substrate regions, because the negatively charged SDS- SnO_x colloid in large size was adsorbed even on the VUV-exposed regions in addition to the unexposed regions. Highly selective adsorption of the colloidal catalyst will be achieved, if a monodisperse colloidal catalyst in size can be used. Second, the SDS- SnO_x colloid of 550 nm in average size was too large to carry out fine electroless plating. As the result, the resolution of the width of Ni–P wires was limited up to $30 \mu\text{m}$. Third, the use of stannum compound is not favor in present

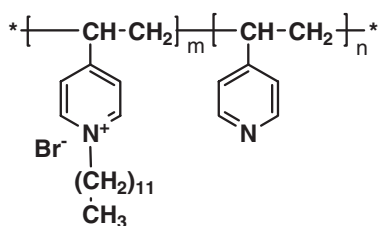


Figure 6. Chemical structure of poly(4-ethenylpyridine-co-4-ethenyl-1-dodecylpyridinium bromide), QP4VP₃₀.

industrial plating processes. All of the arisen problems were responsible for the use of SnO_x colloid. For the reason, we designed a new polycation adsorbate available to Sn-free electroless deposition.^{16,17}

The chemical structure of the newly designed polycation adsorbate, poly(4-ethenylpyridine-co-4-ethenyl-1-dodecylpyridinium bromide), was shown in Figure 6. The polycation is abbreviated as QP4VP₃₀. Its pyridinium group will work as an adsorption site to a negatively charged substrate surface in multipoint adsorption. Its pyridyl group will work as a coordination site to a divalent palladium species. Its long-chain dodecyl group will work as a thickness controller. Ethanol is a good solvent for the polycation, while water is a poor solvent because of hydrophobicity arising from the long-chain dodecyl group. It is anticipated that the thickness of the single-layered adsorption film prepared from the good solvent becomes thin, because the polycation is solvated sufficiently. As a mix proportion of the poor solvent water to the good solvent ethanol is increased, the polymer conformation in the mixed solution is probably changed to a hold and aggregated structure like globule owing to the hydrophobic interaction among the dodecyl groups. The single-layered adsorption film is probably thicker in this situation. Thus, the hydrophobic dodecyl group will work as a thickness controller in the preparation of the single-layered adsorption film. To measure the thickness of the single-layered adsorption film prepared on a silicon wafer with a native oxide layer, the film was irradiated with 172 nm light through a photomask and decomposed by photo-oxidation. The film thickness was determined by measuring a topographical shape of the photopatterned film on the substrate by atomic force microscopy. The result was shown in Figure 7. In the case of the good solvent ethanol, the adsorption film had a thickness of 0.8 ± 0.1 nm. As the mix proportion of water to ethanol was increased, the film thickness was increased gradually up to 2.4 ± 0.6 nm in the case of 80% H₂O on weight. It was possible to tune readily the thickness of the single-layered adsorption film by changing the mix proportion of the solvent used in the film preparation by immersion.¹⁷

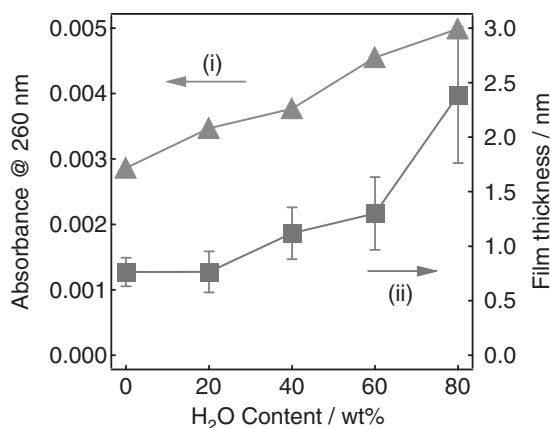


Figure 7. (i) Absorbance at 260 nm and (ii) film thickness of the QP4VP₃₀ single-layered adsorption film on a silicon wafer as a function of H₂O content on weight in EtOH/H₂O mixed solutions used in the film preparation. The figure is cited from *Trans. Mater. Res. Soc. Jpn.* **2005**, *30*, 698 (Suzuki, Y. *et al.*).

X-ray photoelectron spectroscopy allowed us to confirm that the pyridyl group in the polycation worked as a coordination site to a [PdCl₄]²⁻ species in a HCl acidic aqueous solution containing PdCl₂. PdCl₂ is dissolved as [PdCl₄]²⁻ in a concentrated HCl aqueous solution. We assumed divalent palladium species in the HCl acidic PdCl₂ aqueous solution of pH 2.5 used in our study according to the literature reported by Kind and coworkers.¹⁸ It was anticipated that [PdCl₄]²⁻ was the majority species and hydrolyzed [PdCl₃(OH₂)]⁻ and [PdCl₃(OH)]⁻ were the minority species in the PdCl₂ aqueous solution used in our study. The pyridyl and pyridinio moieties of QP4VP₃₀ in the film state gave nitrogen 1s binding energies at 399.1 and 400.1 eV, respectively, before the immersion in the acidic PdCl₂ solution. After the immersion, the binding energy of the pyridyl moiety was only shifted to 399.9 eV. A palladium 3d_{5/2} binding energy appeared at 338.1 eV, indicating that the adsorbed palladium species was divalent and different from [PdCl₄]²⁻. Thus, it was obvious that the Pd–N coordination bond was formed by immersion of the QP4VP₃₀ adsorption film in the PdCl₂ solution.

The micropattern of the adsorption film was prepared by imagewise exposure. Selective metallization by copper (Cu) electroless deposition could be carried out by its immersion in the acidic PdCl₂ solution and a Cu electroless plating bath containing H₂PO₂⁻ as reducing reagent.¹⁶ Cu grains grew on unexposed regions of the micropattern leaving the adsorption film. However, the little amount of Cu deposition was observed for the VUV-exposed regions as can be seen in Figure 8a indicating the SEM image. As can be seen in Figure 8b, it was found that the Cu deposition on the VUV-exposed regions was suppressed when the micropatterned adsorption film after the immersion

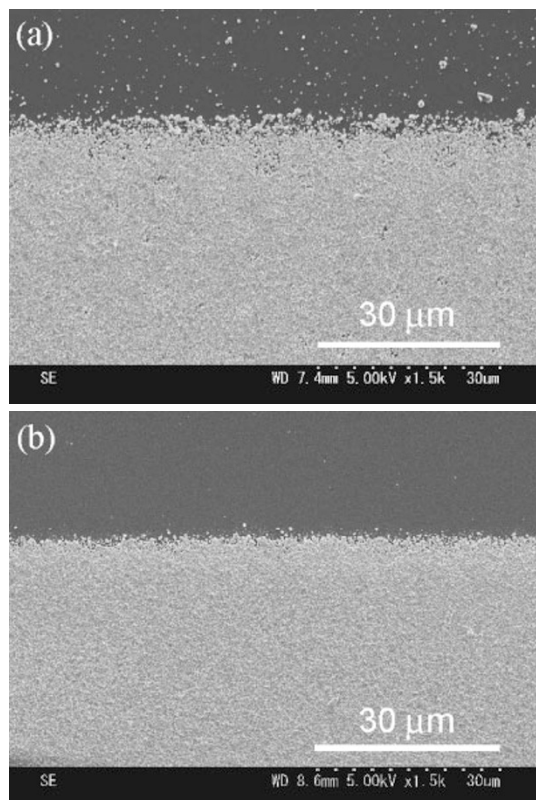


Figure 8. Scanning electron microscope images (a, b) of Cu grains on the micropatterned QP4VP₃₀ single-layered adsorption film formed by Cu electroless deposition using the HCl acidic PdCl₂ aqueous solution; (a) the PdCl₂-treated adsorption film without rinsing with a 1 mol dm⁻³ NaCl aqueous solution and (b) the PdCl₂-treated adsorption film after rinsing with the NaCl aqueous solution.

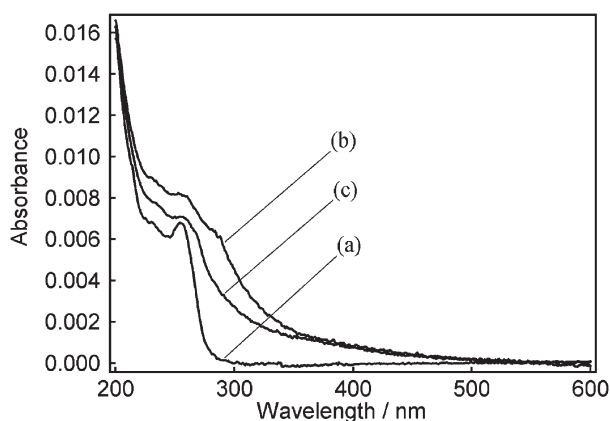


Figure 9. UV-visible absorption spectra of (a) the QP4VP₃₀ adsorption film and the PdCl₂-treated adsorption film (b) before and (c) after rinsing with a 1 mol dm⁻³ NaCl aqueous solution for 3 min.

in the PdCl₂ solution was washed with a 1 mol dm⁻³ NaCl aqueous solution. Figure 9 indicates the UV-visible absorption spectra of the PdCl₂-treated adsorption film on a silica plate before and after rinsing with the NaCl aqueous solution. The absorption band

around 300 nm responsible for divalent mono palladium species such as [PdCl₄]²⁻ was decreased by rinsing with the NaCl aqueous solution. The decrease in the absorption band clearly means that electrostatically adsorbed [PdCl₄]²⁻ species was removed from the polycation adsorption film. In contrast, divalent palladium species forming a Pd–N coordination bond with the pyridyl group still remained after rinsing with the NaCl aqueous solution. The rinse with the NaCl aqueous solution was important to form fogging-free Cu electroless deposition on the unexposed regions leaving the adsorption film. It was assumed that the electrostatically adsorbed [PdCl₄]²⁻ species was removed into the Cu plating bath by ion exchange. The [PdCl₂]²⁻ species in the plating bath would be reduced by the reducing reagent H₂PO₂⁻, giving a zerovalent palladium nanoparticle showing catalytic ability. The palladium nanoparticle and/or Cu grains formed by the catalyst in the bath would be adsorbed on the VUV-exposed regions equal to a bare substrate surface. The detail is under investigation. The Cu wire formed on the unexposed regions was conductive, and the resistivity was approximately 10 times as high as that of Cu bulk ($1.68 \times 10^{-6} \Omega \text{ cm}$). The lateral resolution of the Cu wires could be achieved approximately up to 10 μm.

The selective metallization using the photopatterned QP4VP₃₀ adsorption film by Cu electroless deposition could be also carried out on polyester and polyimide substrate surfaces after photo-oxidation by VUV-exposure in the same manner.¹⁶ If the QP4VP₃₀ polycation can be adsorbed on a substrate surface by electrostatic interaction, selective metallization by copper will be achievable in the identical fabrication processes consisting of the surface adsorption, the pattern VUV-exposure, and the Cu electroless deposition. In general, surface modification of organic polymer and inorganic oxide substrates suitable for electroless deposition should be investigated every substrate. Time-consuming hard efforts are required to choose a mean among physical and chemical methods of surface medication. Our developed method using the polycation single-layered adsorption film is very simple and available to a variety of substrate surfaces taking a negative charge in solution. Furthermore, the method will be capable of reducing sufficiently harmful industrial waste in the manufacture of wiring circuit boards.

PROPOSAL OF RECYCLING A POLYMER SUBSTRATE OF A WIRING CIRCUIT BOARD

Wiring circuit boards after use are crushed in a powder state. Powdered wiring boards are separated into resin powder and metal powder by specific grav-

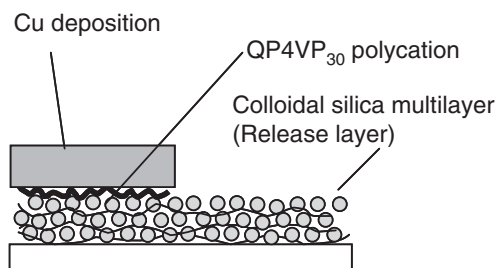


Figure 10. Schematic representation of a substrate-recyclable wiring circuit board containing a release layer consisting of a silica nanoparticle and polycation multilayer prepared by layer-by-layer deposition.

ity. The metal powder is refined to pure metal by electrochemical means. The resin powder is often disposed of by landfill or in burning it. The author thinks fit to recycle the insulating polymer substrate used in the wiring circuit boards from the industrial standpoint aiming at achieving green sustainable chemistry. Taking into account the fact that the polycation adsorption film was available to a variety of negatively charged substrate surfaces, we demonstrated a method for recycling a polymer substrate used in wiring circuit boards. For the purpose, a release layer was designed between a substrate polymer layer and a wiring metal layer as shown in Figure 10.¹⁹ A colloidal silica multilayer was used as the release layer. The multilayer was prepared by layer-by-layer deposition from a silica nanoparticle of 200 nm in average diameter and a polycation of poly(diallyldimethylammonium chloride) according to the literature reported by Ariga and coworkers.²⁰ When a colloidal silica layer was the outermost surface of the multilayer, the substrate surface took a negative charge and adsorbed the QP4VP₃₀ polycation designed for the Cu electroless deposition. The outermost layer of the QP4VP₃₀ adsorption film was micropatterned by 172 nm light through a photomask and plated using the acidic PdCl₂ aqueous solution and the Cu electroless plating bath in the same way. We could prepared Cu wiring on the polymer substrate with the release layer. When the wiring circuit board was immersed in an alkaline NaOH aqueous solution, silica nanoparticles in the release layer were dissolved so that the metal wiring part and the polymer substrate could be separated without crushing. The polymer substrate was available again at least three times.

CONCLUSION

In this review, our recent study of single-layered adsorption films formed by cationic molecules and polymers on a negatively charged substrate surface was described, aiming at achieving site-selective poly-

mer microsphere adsorption and metallization by electroless deposition. Polar transition of the substrate surface taking a positive charge to a negative charge by photochemical means was useful for selective surface adsorption of charged colloidal materials by electrostatic attraction and repulsion. The substrate surface having the positively charged region of the cationic adsorption monolayer and the negatively charged regions of the bare substrate was available to adsorption template for microsphere adsorption. It was found that the hydrophobic interaction among long-chain alkyl groups should be considered in addition to the electrostatic attraction. The charge-patterned substrate surface was also available to selective adsorption of colloidal catalyst precursor, which led to selective Ni-P electroless deposition. The polycation adsorbate was designed for Sn-free Cu electroless deposition. The selective metallization using the polycation adsorbate could be carried out on a variety of polymer and oxide substrate surfaces taking a negative charge in the same preparation method involving the surface adsorption, the pattern exposure, and the electroless deposition. The wiring circuit board with the release layer of a colloidal silica multilayer was readily separated into its metal and polymer parts by its immersion in an alkaline aqueous solution dissolving the colloidal silica. Currently used photoresist systems use a thick photoresist layer of sub-micrometers to several tens of micrometers, while our developed single-layered adsorption film has a thickness of several nanometers. If the newly developed system is adapted in the fabrication of metal wiring circuit boards, the amount of industrial waste will be reduced significantly. The author believes that this kind of nano film science and technology will be useful in industrial processes in 21st century.

REFERENCES

1. M. Gulla and P. Sricharoenchaikit, *Eur. Pat. Appl.*, EP483484 (1992).
2. C. S. Dulcey, J. H. Jr. Georger, V. Krauthamer, D. A. Stenger, T. L. Fare, and J. M. Calvert, *Science*, **252**, 551 (1991).
3. W. J. Dressick and J. M. Calvert, *Jpn. J. Appl. Phys.*, **32**, 5829 (1993).
4. C. S. Dulcey, J. H. Jr. Georger, M.-S. Chen, S. W. McElvany, C. E. O'Ferrall, V. I. Benezra, and J. M. Calvert, *Langmuir*, **12**, 1638 (1996).
5. W. J. Dressick, C. S. Dulcey, M.-S. Chen, and J. M. Calvert, *Thin Solid Films*, **284–285**, 568 (1996).
6. S. L. Brandow, T. L. Schull, B. D. Martin, D. C. Guerin, and W. J. Dressick, *Chem. Eur. J.*, **8**, 5363 (2002).
7. H. Sugimura, K. Ushiyama, A. Hozumi, and O. Takai, *Langmuir*, **16**, 885 (2000).
8. H. Sugimura, K. Hayashi, N. Saito, L. Hong, O. Takai, A.

- Hozumi, N. Nakagiri, and M. Okada, *Trans. Mater. Res. Soc. Jpn.*, **27**, 545 (2002).
9. A. Hozumi, H. Sugimura, Y. Yokogawa, T. Kameyama, and O. Takai, *Colloids Surf., A*, **182**, 257 (2001).
 10. M. Fujii, B. Li, K. Fukuda, T. Kato, and T. Seimiya, *Langmuir*, **15**, 3689 (1999).
 11. M. Nakagawa and N. Nawa, *Kobunshi Ronbunshu*, **60**, 531 (2003).
 12. T. W. Ebbesen, K. Tokumaru, M. Sumitani, and K. Yoshihara, *J. Phys. Chem.*, **93**, 5453 (1989).
 13. M. Nakagawa, S.-K. Oh, and K. Ichimura, *Adv. Mater.*, **12**, 403 (2000).
 14. M. Nakagawa, N. Nawa, T. Seki, and T. Iyoda, *Langmuir*, **19**, 8769 (2003).
 15. M. Nakagawa, N. Nawa, and T. Iyoda, *Langmuir*, **20**, 9844 (2004).
 16. M. Nakagawa, Y. Suzuki, N. Nawa, and T. Iyoda, Jpn. Kokai, Tokkyo Koho, 2005, JP2005264256-A2.
 17. Y. Suzuki, M. Komura, M. Nakagawa, and T. Iyoda, *Trans. Mater. Res. Soc. Jpn.*, **30**, 695 (2005).
 18. H. Kind, A. M. Bittner, O. Cavalleri, K. Kern, and T. Greber, *J. Phys. Chem. B*, **102**, 7582 (1998).
 19. M. Nakagawa, Y. Suzuki, N. Nawa, and T. Iyoda, Japanese Pat. Appl., JP2005062184 (2005).
 20. K. Ariga, Y. Lvov, I. Ichinose, and T. Kunitake, *Appl. Clay Sci.*, **15**, 137 (1999).



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