Electroless Cu Plating Assisted by Single-Layer Adsorption Films of a Cationic Polymer Electrolyte Containing Pyridyl Groups

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Preparation of tailor-made molecular surfaces to resist or promote surface adsorption of functional materials with a nanometer size is one of important challenges in surface science. We have recently reported that photopatterned monolayers of a cationic adsorbate on a silica surface are successfully available for adsorption templates of charged poly(styrene) spheres through electrostatic attraction and repulsion.[1] In addition, photopatterned single-layer adsorption films of cationic polysilane derivatives[2,3] and poly(1-alkyl-4-vinylpyridinium halide)s[4] have been available for electroless pattern plating of nickel-phosphorus based on selective adsorption of SnO_x colloids as catalyst precursors.

In this study, we designed a novel cationic polymer adsorbate of poly(4-vinylpyridine-*co*-1-dodecyl-4-vinyl- pyridinium bromide), abbreviated as p(py-pym), for electroless Cu plating. Compared with our previous methods, this method using the polymer adsorbate containing pyridyl groups was expected to achieve process reduction, plating resolution improvement, and conductivity upgrade in an effort to fabrication printing-wiring circuit boards in house electric appliances. The adsorbate design was based on the following reasons. Pyridyl groups work as adsorption sites of a Pd^{2+} ion as a catalyst precursor. Pyridinium groups work as multipoint adsorption sites to a silica surface. Hydrophobic dodecyl groups will work as thickness controllers of its adsorption film.

A polymer adsorbate of p(py-pym) with a quaternization percentage of 30% was prepared by the reaction of poly(4-vinylpyridine) with dodecyl bromide. Single-layer adsorption films of p(py-pym) were obtained by immersion of a silica plate in its solutions with different mix proportions of good solvent EtOH to poor solvent H_2O and multiple rinses. Electroless Cu plating was carried out by immersion in a $PdCl_2$ aqueous solution and in a Cu plating bath containing $H_2PO_2^-$ as reductant.

The UV-visible absorption spectroscopy analysis revealed that an average surface density of the pyridyl group in the p(py-pym) adsorption films was increased with an increase of mix proportions of poor solvent H_2O. The surface density in the case of a mixture containing 80 wt.% H_2O was estimated to be 1.7 times as high as that in the case of only good solvent ethanol. Photopatterning of the p(py-pym) adsorption films could be carried out by imagewise irradiation with 172 nm deep-UV light under a reduced pressure. Removal of the adsorption film from a silica surface was confirmed by zeta-potential and contact angle measurements. Using a photopatterned adsorption film of p(py-pym), we investigated electroless Cu deposition behavior on a substrate surface. Cu plating took place only on unexposed surfaces leaving the adsorption film. This suggested clearly that the p(py-pym) adsorption film was capable of assisting electroless deposition of Cu. Coordination of Pd^{2+} ions to pyridyl groups of p(py-pym) was verified by X-ray photoelectron spectra of N(1s) indicating that a peak binding energy of pyridyl moiety shifted from 399.1 eV to 399.9 eV after the $PdCl_2$ treatment.

Figure 1 shows the SEM images of Cu deposition on the photopatterned film prepared from ethanol solutions with a mix proportion of (a) 0 wt.% and (b) 80 wt.% H_2O. Obviously, the surface coverage of Cu deposition was dependent on mix proportion in the film-forming solutions. It was revealed from ICP-AES analysis that the adsorption amount of Pd species in the case of 80 wt.%-H_2O mix proportion was 1.4 times larger than that in the case of 0 wt.%-H_2O, concomitantly with an increase of surface densities of pyridyl groups in the adsorption film.

It was concluded that the photopatterned single-layer adsorption film of p(py-pym) was useful for electroless pattern plating of Cu. Such a cationic polymer adsorbate would have distinctive advantages of compatibility with a milder solvents, a variety of substrates, inexpensive cost and industrial waste reduction in wiring board fabrication, compared with currently used thick polymer photoresists.

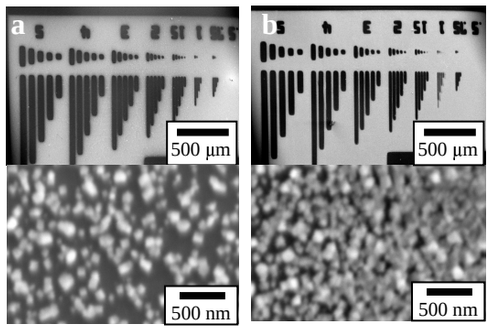

Fig. 1. SEM images of Cu plated silica substrates. A H_2O content in an EtOH/H_2O solution was (a) 0 wt.% and (b) 80 wt.%.

[1] Nakagawa, M. et al. *Langmuir* **2003**, *19*, 8769

[2] Nakagawa. M. et al. **2001**, *JP331770*

[3] Nakagawa, M. et al. *Kobunshi Ronbunshu*, **2003**, *60*, 531

[4] Nakagawa, M. et al. submitted