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Surface Selective Metallization of PTFE Substrate through Atmospheric Pressure Plasma Liquid Deposition Approach

大気圧プラズマ化学液相堆積法によるフッ素ポリマー表面への
高密着性金属配線パターン作製

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We have demonstrated surface modification of fluoropolymer for adhesion enhancement of PTFE/electroless copper layer by a combination of an atmospheric pressure plasma treatment with liquid phase self-assembly, which we named atmospheric pressure plasma liquid deposition. This process allows one to make high adhesion interface without altering the surface roughness through a graft copolymerization of P4VP monolayer as a metal-ion trapping layer on a PTFE substrate. The adhesion strength of the functionalized PTFE sheet binding to an electroless copper layer reached ca. 1.0N/mm. In this work, we demonstrate the fabrication of patterned copper layer on PTFE substrate.

1. Introduction

Demand for high-frequency and high-speed transmission have been increased. Fluoropolymer have attracted a great deal of interest in such devices, because of low dielectric and low dielectric loss factor. Poly(tetrafluoroethylene)(PTFE) has dielectric constant of 2.1 and dielectric loss factor of 0.0002@2GHz in wide temperature range of -40℃ to 250℃ and wide frequency range of 5Hz to 10GHz. Due to its surface inertness, however, pristine PTFE surface fails to satisfy the adhesive strength against to various metals that many of the industries require. Prior surface treatment before the metallization for making high adhesive PTFE/metal layer interface has been required. Another important requirement is the direct metallization without seeding PTFE surface with $SnCl_2$ and Pd(0) catalytic cluster. It has known that $SnCl_2$ did not work as a catalyst for electroless plating and inhibited copper deposition. Therefore, various researches about Pd/Sn catalyst-free surface metallization process have demonstrated. In the previous work, we have demonstrated surface modification of fluoropolymer for adhesion enhancement of PTFE/electroless copper layer by a combination of an atmospheric pressure plasma treatment with liquid phase self-assembly, which we named atmospheric pressure plasma liquid deposition (APPLD) approach. This process allows one to make high adhesion interface without roughening the surface through a graft copolymerization of poly(4-vinylpyridine)(P4VP) monolayer as a metal-ion trapping layer on a PTFE substrate [1-4]. The adhesion strength of the functionalized PTFE sheet binding to an electroless copper (Cu) layer reached ca. 1.0N/mm.

In this work, we focused on micro-contact printing (μCP) to transfer patterned poly(dimethylsiloxane) (PDMS) stamps to the surface of a PTFE substrate. As compared with other site-selective methods, μCP has several apparent advantages, such as the convenience of reduplication, simple procedure, low cost and high speed patterning on a large substrate area. We demonstrated the fabrication of micropatterned copper layer on PTFE substrate by APPLD approach.

2. Experimental section

Catalyst-free electroless Cu deposition onto modified PTFE sheet process composes of following five steps: (1) implantation of peroxy radicals on the PTFE substrate by atmospheric pressure helium (He) plasma treatment; (2) graft copolymerization of P4VP from the modified PTFE surface; (3) deposition of copper acetate (CuAc) thin film onto the P4VP-gtafted-PTFE surface; (4) simultaneous reduction of Cu^{2+} ion to Cu(0) and spontaneous formation of copper nanoparticles using atmospheric pressure He plasma; (5) autocatalytic electroless deposition of copper on the PTFE surface seeded with copper nanoparticles.

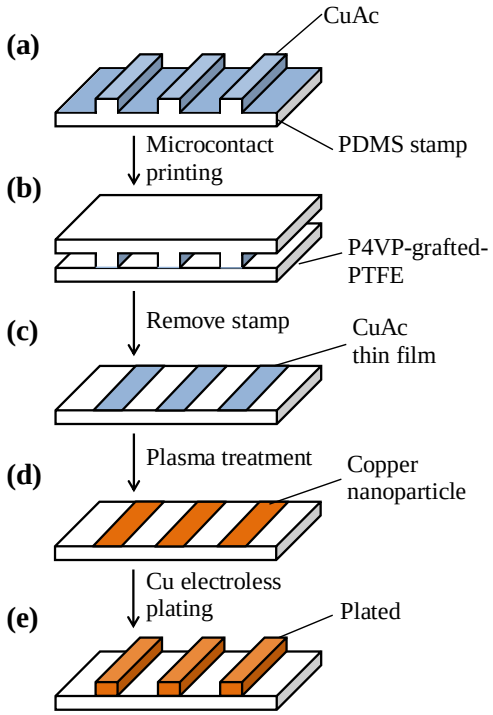

Fig. 1. Schematic of the process steps used to fabricate patterned copper films on P4VP-grafted-PTFE

The PDMS stamp was fabricated by mixing PDMS with curative agent by the ratio of 10:1 to various patterned master silicon substrate and heating to 60℃ for 2h to harden PDMS. Fig. 1 outlines our approach to the selective copper metallization of PTFE substrate: (a) Inking a PDMS stamp with CuAc forms a film of CuAc on the surface of the stamp. (b) μCP brings the film of CuAc in contact with the surface of P4VP-grafted-PTFE. (c) PDMS stamp is removed and transfers a patterned film of CuAc to the PTFE surface. (d) Atmospheric pressure He plasma assists to form copper nanoparticles spontaneously. (e) Immersion in an electroless copper plating bath deposits copper selectively over the CuAc transferred regions of the PTFE substrate.

3. Results and discussion

Fig. 2 shows the change in Cu2p XPS spectra of P4VP-grafted-PTFE sheet before and after CuAc transcription. By stamping CuAc thin film on the P4VP-grafted-PTFE surface Cu2p1/2 and Cu2p3/2 peak were observed at 952eV and 932eV, respectively, and transcription of CuAc thin film to P4VP-grafted-PTFE surface was confirmed. We conducted the exposure to atmospheric pressure He plasma and the immersion in an electroless copper plating bath for the PTFE substrate after transferring CuAc. Fig. 3 shows a photograph image of patterned copper layer on PTFE substrate. The formation of the electroless copper film was

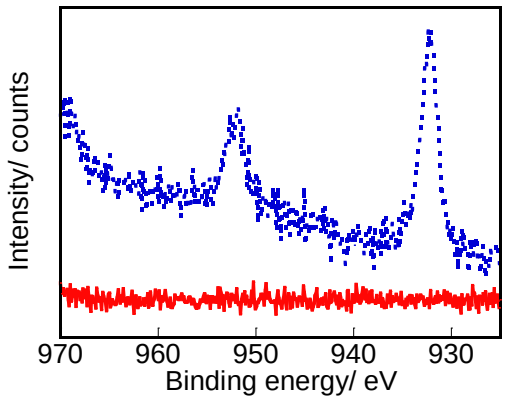

Fig. 2. The change in Cu2p XPS spectra of P4VP-grafted-PTFE sheet before (solid line) and after stamping CuAc (broken line)

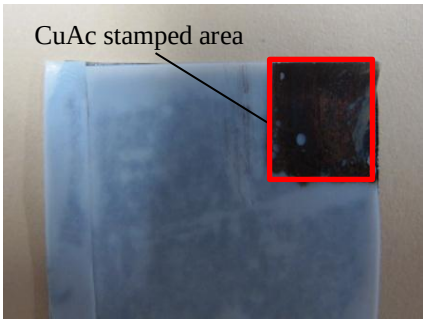

Fig. 3. A image of patterned copper layer on PTFE substrate. Scale bar is 10 mm

confirmed in the CuAc stamped area. From this result, it is suggested that selective metallization of PTFE substrate is possible by patterning of CuAc.

4. Conclusion

We demonstrated the fabrication of patterned copper layer on PTFE substrate by APPLD approach. In our process, the formation of the electroless copper film was confirmed in the CuAc stamped area. In the future, we will evaluate the property of patterning, such as line width and PTFE/Cu adhesion strength.

Acknowledgments

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