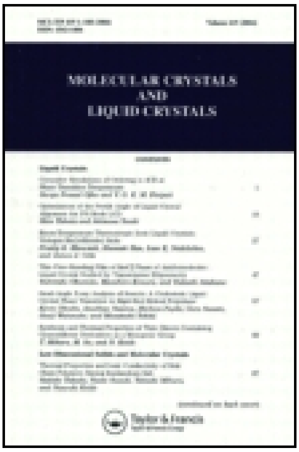

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Hydrophilic Surface Modification and Metallization of Poly(tetrafluoroethylene) Film by Excimer Laser Processing

Hiroyuki Niino [a], Toshinori Murao [b], Sowjun Matsumura [b] & Akira Yabe [a]
[a] National Institute of Materials and Chemical Research (NIMC), Higashi, Tsukuba, Ibaraki, 305, JAPAN
[b] C. Uyemura & Co. Ltd., Deguchi, Hirakata, Osaka, 573, JAPAN

Version of record first published: 24 Sep 2006.

To cite this article: Hiroyuki Niino , Toshinori Murao , Sowjun Matsumura & Akira Yabe (1995): Hydrophilic Surface Modification and Metallization of Poly(tetrafluoroethylene) Film by Excimer Laser Processing, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 365-374

To link to this article: http://dx.doi.org/10.1080/10587259508034017

Mol. Cryst. Liq, Cryst. 1995, Vol. 267, pp. 365–374
Reprints available directly from the publisher
Photocopying permitted by license only

HYDROPHILIC SURFACE MODIFICATION AND METALLIZATION OF POLY(TETRAFLUOROETHYLENE) FILM BY EXCIMER LASER PROCESSING

HIROYUKI NIINO[1], TOSHINORI MURAO[2], SOWJUN MATSUMURA[2], AND AKIRA YABE[1]
[1] National Institute of Materials and Chemical Research (NIMC),
Higashi, Tsukuba, Ibaraki 305, JAPAN
[2] C.Uyemura & Co. Ltd., Deguchi, Hirakata, Osaka 573 JAPAN

Abstract The chemical surface modification of poly(tetrafluoroethylene) (PTFE) film was carried out in hydrazine gas photolyzed with ArF excimer laser irradiation. Hydrophilic surface appeared on PTFE film after the laser treatment. The surface was analyzed with a measurement of water contact angle, X-ray photoelectron spectroscopy, and FTIR spectroscopy (attenuated total reflection). In addition, on the basis of the hydrophilic behavior, we succeeded in the area-selective electroless plating of nickel and copper metal on the chemically modified surface.

INTRODUCTION

Poly(tetrafluoroethylene) (PTFE) is one of the most interesting polymers in the field of electronic materials because of its low dielectric property ($\varepsilon = 2.1$), chemical resistance, and heat stability. It is widely known that PTFE is suitable for a substrate of electronic devices in the microwave region. However, the adhesive strength between a native PTFE surface and metals is negligibly small because of a low surface energy of PTFE, so that the surface modification of PTFE has been widely studied from the viewpoint of industrial applications in the last several decades. Among these studies, chemical etching with sodium naphthalide solution[1] and radio frequency plasma processing with oxygen[2] were employed for the increase of adhesive strength on the surface. The former, however, is not area-selective enough to make fine pattern because of a treating in solution phase, and the latter lacks the durability of modified layer. Recently, the laser-induced modification of fluorocarbon polymer films was reported by Murahara and his coworkers. According to their technique, PTFE surface becomes lipophilic and hydrophilic after the surface reaction with trimethylborane[3] and ammonia/diborane[4], respectively, upon the irradiation of ArF excimer laser ($\lambda = 193$ nm).

We have previously reported a novel hydrophilic modification for PTFE and poly(tetrafluoroethylene-*co*-hexafluoro propylene) (FEP) films using hydrazine (N_2H_4) vapor photolyzed upon the irradiation with ArF excimer laser.[5] The laser processing showed the advantage of area-selective modification that hydrophilic property was observed only on the laser irradiated regions, but not on un-irradiated area. In this paper, we describe an extended investigation of the surface properties of PTFE film concerning radiation conditions and a change with the passage of time after the treatment. On the basis of the hydrophilic surface modification of the PTFE film, we have investigated the area-selective electroless plating (chemical plating) of copper and nickel on PTFE film.

FIGURE 1 Chemical structures of PTFE and hydrazine.

EXPERIMENTAL

The radiation apparatus used for the experiments was an ArF excimer laser with the pulse duration of 14 ns (Japan Storage Battery Co., Ltd.; EXL-300). PTFE film was 100 μm and 2 mm in thickness (Figure 1). Hydrazine anhydrous (Tokyo Kasei Kogyo Co., Ltd.) was used without further purification. A reaction vessel having a quartz window was filled with hydrazine vapor under its saturation vapor pressure at room temperature. The pressure of the vessel was monitored with a Pirani gauge having a platinum filament. Laser irradiation to the films was conducted at 10 Hz with 500 - 3000 shots. The fluence (intensity) of laser beam at the window was adjusted to 20 - 50 $mJ \cdot cm^{-2} \cdot pulse^{-1}$. The laser beam was incident perpendicularly onto the films under the hydrazine atmosphere at room temperature. The distance between the sample and the window was *ca.* 1 mm (Figure 2).

Together with the measurement of water contact angle, the treated films were analyzed using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS; VG Scientific Ltd., ESCA LAB Mark2, detection angle θ=90°) using Mg-Kα radiation, and Fourier transform infrared spectrophotometry with attenuated total reflection (FTIR-ATR; Shimadzu, FTIR-8500, prism: KRS-5, detection angle θ=45°).

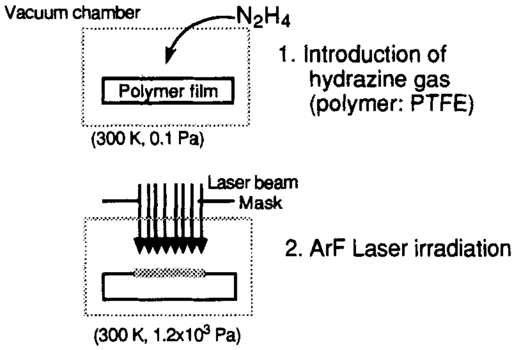

FIGURE 2 Schematic diagram on hydrophilic modification of PTFE film.

RESULTS AND DISCUSSION

Hydrophilic modification by photolyzed hydrazine

When the irradiation of ArF excimer laser to a PTFE film was conducted under a hydrazine atmosphere, a hydrophilic surface was observed on the film. The water contact angle of PTFE surfaces decreased from 130° to 28° upon the laser irradiation at a fluence of 27 mJ•cm^{-2} with 3000 shots. The contact angle decreased gradually with the increase in the number of laser shots (Table I), indicating that hydrophilic groups were introduced onto the PTFE surface upon the laser irradiation. As shown in Figure 3, these hydrophilic properties were preserved for several weeks in ambient air after the laser treatment. In addition, SEM observation indicates that morphological damages appeared on the hydrophilic PTFE surface when the irradiation was carried out with 3000 shots, suggesting that etching gradually occurred in the surface reaction (Figure 4).

TABLE I Contact angle of PTFE film with water upon irradiation with ArF excimer laser [a] under a hydrazine atmosphere [b].

Irradiated shots	Contact angle
Before irradiation	130°
500	60°
1000	34°
3000	28°

[a] fluence: 27 mJ•cm^{-2}, repetition rate: 10 Hz.
[b] saturated vapor pressure at room temperature.

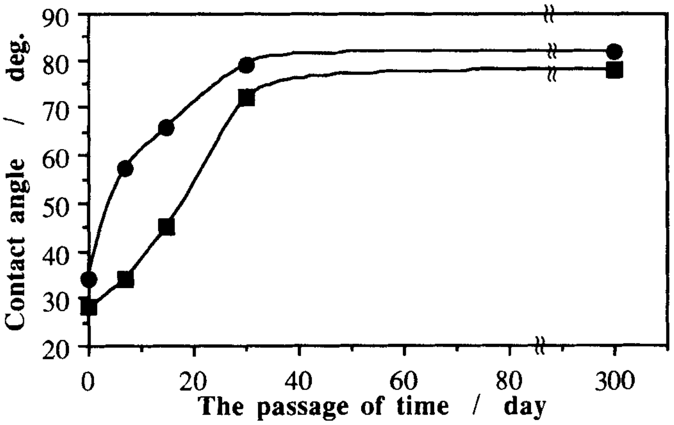

FIGURE 3 Dependence of water contact angle of PTFE film on the passage of time after the laser-treatment, (●): 1000 shots' irradiation, (■):3000 shots' irradiation.

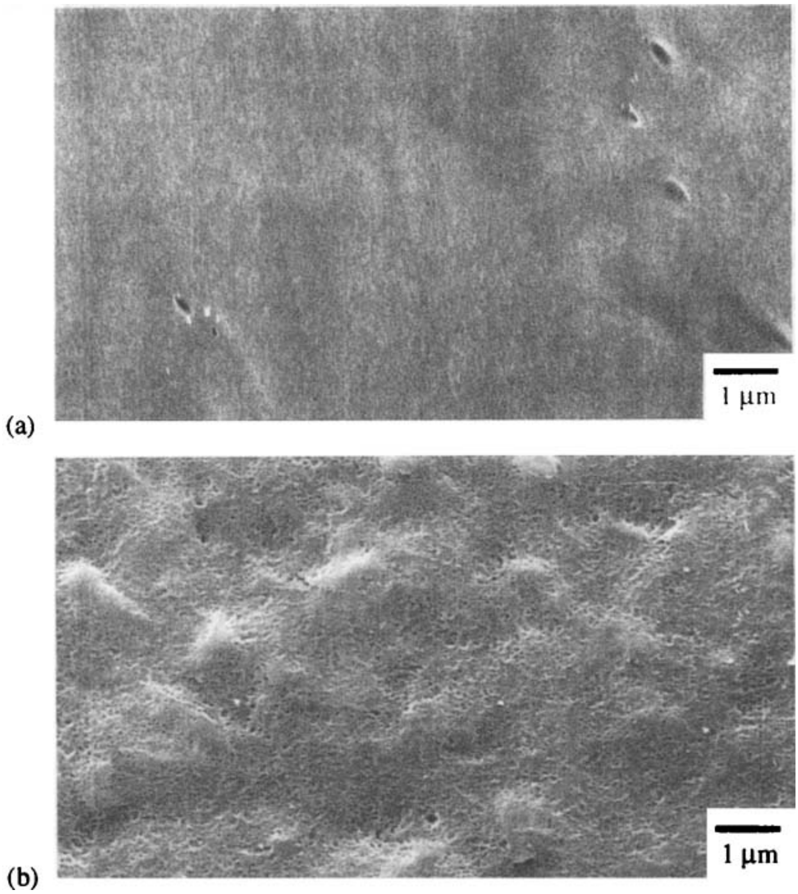

FIGURE 4 SEM pictures on PTFE films after the laser treatment (22mJ•cm^{-2}), (a) before laser irradiation, (b) after laser irradiation with 3000 shots.

Figure 5 shows the XPS spectra of PTFE surfaces before and after laser irradiation. After the irradiation, it was found that an N_{1s} peak appeared on the XPS spectrum while the intensity of the F_{1s} peak decreased in comparison with that of the C_{1s} peak (Figure 5 (b)). The biding energy of the C_{1s} peak was shifted to the low energy side because an electron donating group of hydrogen and amino moieties were substituted for the electron withdrawing group of fluorine by the reaction. After the irradiation with 500 shots, the C_{1s} peak was split to two peaks due to the chemical shift of mixture of substituent.

The atomic ratio of carbon(C): fluorine(F): nitrogen(N): oxygen(O) in Figure 5(b) was estimated to be 1.0: 0.016: 0.19: 0.033 from the calculation of their peak areas using atomic sensitivity factors (C_{1s}: F_{1s}: N_{1s}: O_{1s} = 0.296: 1.00: 0.477: 0.711).[6] Table II shows the atomic ratio of the PTFE film before and after the laser treatment with 500, 1000, 3000 shots. The ratio of F/C on PTFE surface drastically decreases as the number of laser shot increased up to 3000 shots. It is assumed that the irradiated PTFE surface included the substituent of hydrogen atom and the unsaturated bonds of carbon. After the immersion of the hydrophilic film into a CCl_4 solution of bromine (Br_2), new Br_{3d} and Br_{3p} peaks appeared in the XPS spectrum of the film by addition of bromine to an unsaturated carbon bond. Since the atomic ratio of Br/C on PTFE film after the irradiation with 1000 shots was 0.16: 1.0, the substitution by hydrogen atom was presumed to be 65 % .

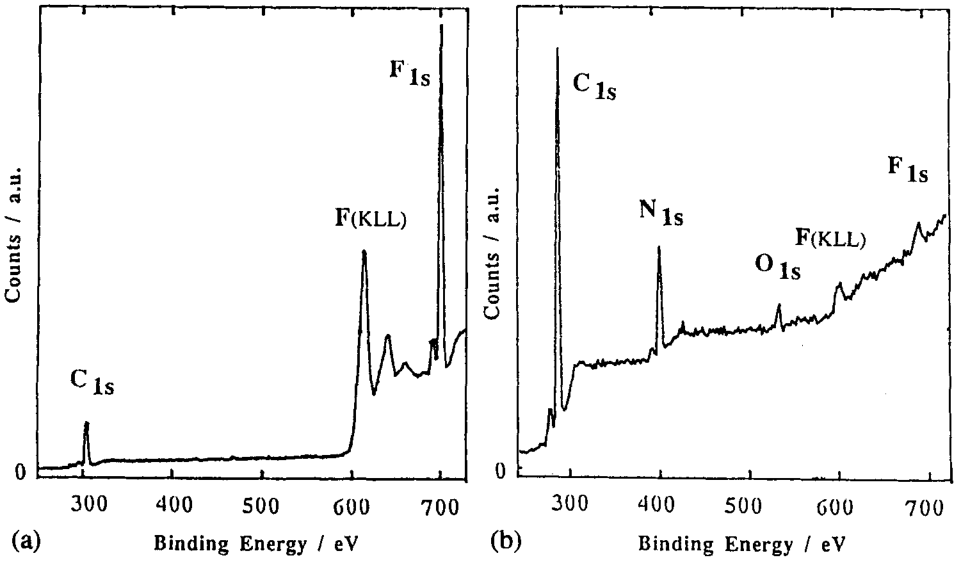

FIGURE 5 XPS spectra of PTFE film before and after irradiation with ArF excimer laser under hydrazine atmosphere; (a) before irradiation, (b) after irradiation (ArF laser: 27 mJ•cm^{-2}, 3000 shots, 10 Hz).

TABLE II Atomic ratio of carbon(C): fluorine(F): nitrogen(N): oxygen(O) on the PTFE surface after laser treatment (fluence: 27 mJ•cm^{-2}, repetition rate: 10 Hz).

Irradiated shots	carbon(C)	fluorine(F)	nitrogen(N)	oxygen(O)
Before irradiation	1.0	2.1	——[a]	——[a]
500	1.0	0.34	0.27	0.033
1000	1.0	0.21	0.28	0.029
3000	1.0	0.016	0.19	0.033

[a] No detection

TABLE III Dependence of the atomic ratio of a hydrophilic PTFE surface on the passage of time after the treatment (ArF laser; fluence: 27 mJ•cm^{-2}, 1000 shots).

Time passage after irradiation	carbon(C)	fluorine(F)	nitrogen(N)	oxygen(O)
Immediately	1.0	0.21	0.28	0.029
70 days	1.0	0.28	0.19	0.083
110 days	1.0	0.36	0.22	0.13
220 days	1.0	0.24	0.21	0.28

Because the oxygen ratio is negligibly small,[7] hydrophilic property is mainly ascribed to nitrogen-containing groups such as amino moieties. The atomic ratios of F/C and N/C were almost the same on standing after the laser treatment (Table III). However, the O/C ratio increased after hundreds' days because the sample was stored in a desiccator with the dry air. From the results of the XPS and contact angle measurement, it is difficult to explain a change in hydrophilicity of PTFE surface with the passage of time

After the laser irradiation at the fluence of 27 mJ•cm^{-2} with 3000 shots, a new absorption peak was not observed on FTIR-ATR spectrum while the intensity ratio at the peak of 507 cm^{-1} / 1203 cm^{-1}, whose mode was ascribed to the stretching and bending vibration of CF_2, increased twice in comparison with that of the fresh film (Figure 6).[8] Since the analytical depth (d) at 500 cm^{-1} (d_1=3.10 μm) of FTIR-ATR was 2.4 times larger than that at 1200 cm^{-1} (d_2=1.29 μm),[9] these results indicated that the surface layer modified by the laser treatment was estimated to be sub-micron deep.

By the reaction of the hydrophilic PTFE surface with trifluoroacetic anhydride ($(CF_3CO)_2O$) gas, a new absorption peak due to a carbonyl group was observed at 1700 cm^{-1} in Figure 6(c) as the results of the formation of an amide moiety (1). It was evidenced that the introduction of amino groups onto the irradiated surface induced the hydrophilicity on the PTFE surface.

$$R\text{-}NH_2 + (CF_3CO)_2O \longrightarrow R\text{-}NHCOCF_3 + CF_3CO_2H \qquad (1)$$

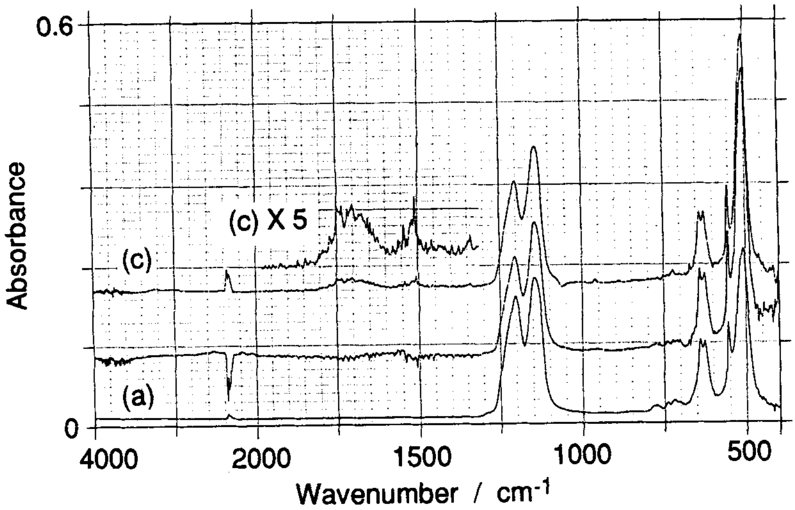

FIGURE 6 FTIR-ATR spectrum of PTFE film, peak intensity is normalized at 1145 cm^{-1}; (a) fresh surface, (b) after hydrophilic processing (ArF laser, 27 mJ• cm^{-2}, 3000 shots), (c) after treatment with trifluoroacetic anhydride gas.

Hydrazine is an indispensable molecule for the formation of the hydrophilic PTFE surface, because the PTFE film, whose absorption coefficient at 193 nm is negligibly small,[13] is not excited with ArF laser irradiation. It has been reported that •N_2H_3, •NH_2, •H radicals, and :NH nitrene are formed by the photolysis of hydrazine gas at 193 nm.[10-12] These reactive intermediates are expected to play a key role in the surface reaction. Further investigation concerning the reaction mechanism to produce hydrophilic surfaces is in progress.

Electroless plating on PTFE film

By the laser treatment, the surface of PTFE films could be changed to hydrophilic and the surface energy increased in comparison with that of a native PTFE. As the results, we intended to extend the hydrophilic modification into electroless plating.[14] The activators for the plating will be deposited only on the hydrophilic region, If the laser irradiation is carried out through a mask by contact a projection method, area-selective metallization will be performed on the surface of PTFE films.

After the hydrophilic treatment upon the the irradiation of an ArF laser beam through a photographic mask, the procedure of nickel metallization consists of four steps (Figure 7). First, the hydrophilic PTFE films were dipped into 0.5 M aqueous H_2SO_4 for 30 s as a pre-dipping, followed by rinsing with de-ionized water at room temperature (RT). Second, the dipped film was immersed into an aqueous solution of palladium(II) sulfate (KAT-450, C.Uyemura Co.) for 2 min at 35 °C in order to produce a catalyst for electroless plating. Third, as a post-dipping, the substrates were dipped into 0.5 M aqueous H_2SO_4 and de-ionized water at RT again. Finally, the catalytic films were immersed in an electroless nickel plating bath (Nimuden®-SX, C.Uyemura Co.) for 3 - 30 minutes at 60 °C.

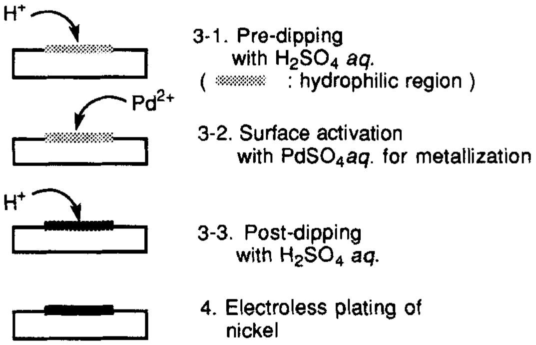

FIGURE 7 Schematic diagram on selective-area electroless plating of nickel metal on the laser-treated PTFE films.

Figure 8 shows the nickel metal plated on the laser irradiated regions but not on surrounding PTFE. The metal image suggested that the surface activator was only deposited on the irradiated regions due to hydrophilicity on the area. The nickel metal on the PTFE film showed metallic luster and could not be peeled off for an adherence test using a conventional tape test (tape: No. 401, Nitto Denko Co.). The adhesive strength between the nickel metal and PTFE film was estimated to be 150 kg•cm^{-2} by a pull-stud test.

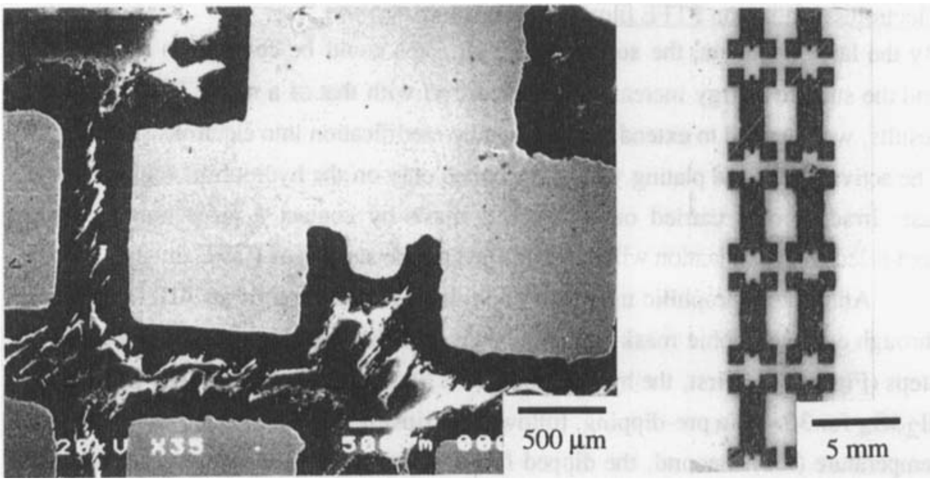

FIGURE 8 The electroless plating of nickel metal deposited on a PTFE film after the area-selective irradiation of an ArF laser beam. Sharp areas are the nickel metal.

For copper metallization, we employed four steps as follows (Figure 9); (i) pre-dipping of 0.5 M aqueous H_2SO_4 for 1 min at RT, (ii) activation with Sn^{2+} - Pd^{2+} ion for 4 min at RT [AT-105, PED-104(promoter)], (iii) acceleration to produce Pd^0 colloid for 2 min at RT (AL-106), (iv) electroless copper plating for 45 min at 60 °C (ELC-SP).

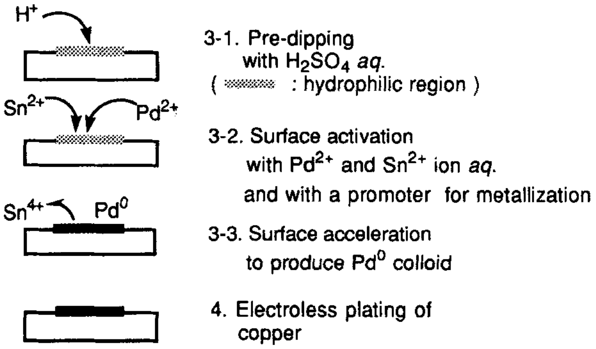

FIGURE 9 Schematic diagram on selective-area electroless plating of copper metal on the laser-treated PTFE films.

The time required for the deposition of copper metal on PTFE film after immersion into the plating bath was dependent on the number of laser shots conducted in the surface modification; when the film was irradiated with 3000, 1000, and 500 shots, it required 3, 6, and 12 s, respectively. In this process, differing from the case of nickel, the copper metal was plated on the entire PTFE surface, indicating that the activators were deposited on the entire surface by the promoter to improve the adhesion of plating metal and substrate. However, the well-defined image of copper metal appeared on the film after the adherence test with the tape, due to a clear difference between irradiated and un-irradiated regions in adhesion. The adhesive strength between the copper metal and PTFE film was estimated to be 80 kg• cm^{-2} by the pull-stud test.

CONCLUSIONS

We have studied in detail the surface modification and metallization of PTFE film. The surface reaction of fluorocarbon polymers with photolyzed hydrazine gas is an effective method to prepare substrates with hydrophilic surfaces. Most of fluorine atoms on the surface layer of PTFE film were replaced by hydrogen atom and amino groups in the reaction. The modified layer had sub-micron ordered thickness.

By the treatment of electroless plating on the hydrophilic PTFE film, area-selective metallization of nickel and copper was performed. The metallized layer had a sufficient adhesive strength, so that the processing was useful for a practical use. Fluorocarbon polymer films are most suitable for substrates of high-density multichip interconnection in electronics industry because of their remarkably low dielectric constants in comparison with that of other conventional polymers.

ACKNOWLEDGMENT

We thank Nitto Denko Co. for supplying PTFE films.

REFERENCES

1. E.R.Nelson, T.J.Kilduff, and A.A.Benderly, *Ind. Eng. Chem.*, **50**, 329(1958).
2. J.R.Hall, C.A.L.Westerdahl, M.J.Bodnar, and D.W.Levi, *J. Appl. Polym. Sci.*, **16**, 1465(1972).
3. M.Okoshi, M.Murahara, and K.Toyoda, *J. Mater. Res.*, **7**, 1912(1992).
4. M.Okoshi, M.Murahara, and K.Toyoda, *Mat. Res. Soc. Symp. Proc.*, **201**, 451(1991).
5. H.Niino and A.Yabe, *Appl. Phys. Lett.*, **63**, 3527(1993).
6. J.Chastain *Ed.*, *"Handbook of X-ray Photoelectron Spectroscopy "*, Perkin-Elmer Co., Minnesota, p.252(1992).
7. Before the analysis of samples with XPS, the samples were exposed to the ambient air after the surface modification.
8. The analytical depth of XPS is a few nanometers, and the analytical depth of FTIR-ATR is a few microns. The chemical composition of the films relative to its depth profile was obtained when a specimen was measured with both the techniques.
9. When a PTFE film (refractive index: $n_2=1.35$) is analyzed using FTIR-ATR with the prism of KRS-5 ($n_1=2.4$) at the detection angle of $\theta=45°$, the analytical depth (d_p) is dependent on the wavelength (λ) of analytical beam;
$$d_p/\lambda = (\lambda/2\pi n_1)[\sin^2\theta - (n_2/n_1)^2]^{-0.5}$$
$$\approx 0.155$$
10. W.G.Hawkins and P.L.Houston, *J. Phys. Chem.*, **86**, 704(1982).
11. P.Lindberg, D.Raybone, J.A.Salthouse, T.M.Watkinson, and J.C.Whitehead, *Mol. Phys.*, **62**, 1297(1987).
12. H.Biehl and F.Stuhl, *J. Photochem. Photobiol. A: Chem.*, **59**, 135(1991).
13. K.Seki, H.Tanaka, T.Ohta, Y.Aoki, A.Imamura, H.Fujimoto, H.Yamamoto, and H.Inokuchi, *Physica Scripta*, **41**, 167(1990).
14. H.Niino and A.Yabe, *Appl. Phys. Lett.*, **60**, 2697(1992).