# Effect of Microwave Plasma Surface Treatment for Improved Adhesion Strength of Direct Copper Plating on Polyterafluoroethylene (PTFE)

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**Abstract**
The purpose of this study is to investigate the effect of plasma surface modification to improve adhesion strength between polytetrafluoroethylene (PTFE) and electroless copper plating. PTFE is widely used in many industries because of its unique electrical, thermal, and mechanical characteristics. However, because of its low surface energy, it is difficult to acquire enough adhesion strength between PTFE and other substances without surface modification. Plasma is well known as one of the surface modification techniques that improve adhesion strength.

In this study, high-electron density microwave plasma with nitrogen and hydrogen gas was applied. Nitrogen and hydrogen microwave plasma can modify the surface of PTFE with surface defluoration and the nitrogen functional group. Surface modification techniques with the nitrogen functional group are frequently applied to surface activation for medical devices.

In this experiment, so as to understand the effect of nitrogen functional groups for the plating on PTFE, microwave plasma treatment was conducted under various conditions in terms of treatment pressure. In all conditions, before nitrogen and hydrogen microwave plasma treatment, pre-plasma treatment was conducted with argon gas in order to activate the surface of the PTFE. In this experiment, surface energy of the PTFE after plasma treatment was calculated from the contact angle of water and diiodomethane. The results of surface energy measurement showed that nitrogen and hydrogen microwave plasma treatment was preferable for activating the surface of PTFE. In addition, x-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM) measurements were conducted after the microwave plasma treatment to characterize the modified PTFE surfaces both physically and chemically. The result of XPS measurement showed the nitrogen functional group was generated on the surface of PTFE after plasma treatment. The intensity of the nitrogen functional group was a function of treatment pressure.

AFM measurements showed that there was no marked physical difference between before and after short time plasma treatment. After those measurements, electroless copper plating was conducted on the surface of modified PTFE. After the plating, adhesion strength was observed in order to understand correlation between adhesion strength and the results of chemical and physical measurements. The results showed that the PTFE surface modified by microwave plasma under specific treatment conditions of nitrogen and hydrogen gas could improve the adhesion strength between the PTFE and electroless copper plating.

## Introduction

Polytetrafluoroethylene (PTFE) is widely used for manufacturing various products in many industrial fields because of its several excellent properties, such as high stability against heat, chemical and electric resistance, a low frictional coefficient and a low dielectric constant [1, 2]. The number of properties of PTFE is also preferable for microelectronics applications as a base material of package [3]. However, these properties of PTFE hamper the applications in many cases because of hydrophobic and low adhesion surface property with other materials due to low surface free energy. In microelectronics packaging with PTFE as a base material, adhesion strength between the PTFE and electroless copper plating is important since the base material of the PTFE requires excellent electrical conductivity and resistivity [4, 5].

For these reasons, there is a strong demand to improve adhesion strength between PTFE and electroless copper plating. In order to improve adhesion strength of PTFE, a variety of surface modification techniques including chemical treatment and plasma treatment have been applied [6-11]. These surface modification techniques for PTFE are usually aimed to introduce specific chemical functional groups on to the surface. Chemical treatment with sodium liquid ammonia and sodium naphthalide are well known surface modification techniques in production for improved adhesion strength of PTFE.

However, those chemical treatments are of concern because of their high cost, pollution effects, and changing bulk properties of the PTFE [12]. To make matters worse, large roughness is formed on the surface after the chemical treatment. It is well known that the forming surface roughness helps electroless copper plating increase adhesion strength. However, the forming surface roughness connects to a new concern for micro-scale packaging fabrication. In the future, thickness of copper plating for microelectronics packaging on the polymer would become thinner and thinner because thickness of the copper needs to reach a satisfactory level to respond to micro strip lines formed by etching processes.

Surface roughness of the PTFE would become an obstacle for micro fabrication which requires narrow and thin line patterning. In order to improve adhesion strength between electroless copper plating and PTFE without any difficulty for micro fabrication for packaging, the PTFE surface should be modified without changing bulk properties and forming surface roughness.

The technique of surface modification with low pressure plasmas is an attractive way to modify the surface of the PTFE. Low pressure plasma treatment can modify only a thin surface layer of the PTFE without changing bulk properties. The plasma treatment can be carried out by using chemically reactive or/and inert gases. The plasma treatment for the PTFE with reactive gases leads to introduction of chemical functional groups on the surface of the PTFE. On the other hand, during the plasma treatment for the PTFE with inert gases, ion bombardment occurs on the surface [13, 14].

Excessive ion bombardment is connected to degradation of the PTFE. When surface of the PTFE is irradiated by plasma excessively, polymer chains are decomposed by collision of electrically accelerated ions and electrons [15, 16]. In order to perform effective modification of the PTFE, one of the important things is to positively accelerate the introduction chemical reaction with less ion bombardment.

Some researchers have mentioned about low pressure microwave plasma treatment for polymer surface modification [17]. One of the features of low pressure microwave plasma is that microwaves can generate the plasma without electrodes. Generating plasma without electrodes connects to the situation that there are no electrically accelerated ions and electrons in the plasma. Therefore, microwave plasma can realize polymer surface treatment with small ion bombardment effects. In addition, microwave power sources can generate much higher electron density plasma compared to the radio frequency power source. These features of the low pressure microwave plasma realizes shorter time plasma surface modification processes with small ion bombardment effects [18].

It is often required for low pressure plasma treatment by introducing the nitrogen functional group onto surface of the PTFE. For biological applications, the chemical functionalities of nitrogen groups are known to be effective in covalent coupling of proteins and signal molecules [19-21]. The same as for the biological applications, ammonia or mixture gas of nitrogen and hydrogen plasma can be applied for microelectronics to create a sufficient concentration of the nitrogen group on the polymer surface. Low pressure plasma treatment with nitrogen and hydrogen gases on the PTFE leads to a partial loss of fluorine and incorporation of the nitrogen functional groups.

Partial loss of fluorine and generating the nitrogen functional group could increase the surface free energy on PTFE and improve adhesion strength [22]. Consequently, one of the preferable methods of improving adhesion strength between the PTFE and electroless copper plating is creating the nitrogen functional group efficiently without surface roughness on the PTFE by high density microwave plasma.

The purpose of this study is to investigate the effect of low pressure microwave plasma processing for the PTFE surface modification in order to increase adhesion strength between the PTFE and electroless copper plating. In this study, high electron density 2450MHz microwave plasma system was applied for the PTFE surface treatment. A mixture gas of nitrogen and hydrogen was used for the processing gas. In order to understand the surface physical and chemical properties, several measurement techniques were conducted before and after the plasma treatment. Plasma processing was conducted under various treatment pressures to investigate the effect for surface properties. The PTFE surface free energy after the plasma treatments was measured and calculated from contact angles of water and diiodomethane. To characterize the treated PTFE surfaces, x-ray photoelectron spectroscopy (XPS) measurement was conducted. Surface condition and roughness were measured by atomic force microscope (AFM). Finally, the adhesion strength of electroless copper plating on the plasma treated PTFE was measured using the T-peel test. There was investigation of the correlation to the surface properties and results of the adhesion strength.

**Experiment**

A commercially available thickness of 3mm flat sheet of the PTFE was applied for the experiment. The sheets were cut into 60mm x 130mm pieces. The sheets were cleaned with methanol and acetone in an ultrasonic water bath for 10minutes, and then the sheets were dried at ambient temperature. Before all nitrogen functional group generating treatment, pre-treatment with 30seconds argon gas plasma was performed for the PTFE in order to activate the surface.

Figure 1 shows the schematic diagram of the microwave plasma apparatus used for the surface treatment of the PTFE in this study. In the case of microwave plasma, the plasma was generated by 2450MHz microwave power source. Microwave was led to the vacuum chamber through the wave guide and the quartz window as a dielectric material set on the top of the chamber.

The microwave which was led inside the chamber excited molecules, and then, plasma was generated on the surface of the quartz window on the vacuumed side.

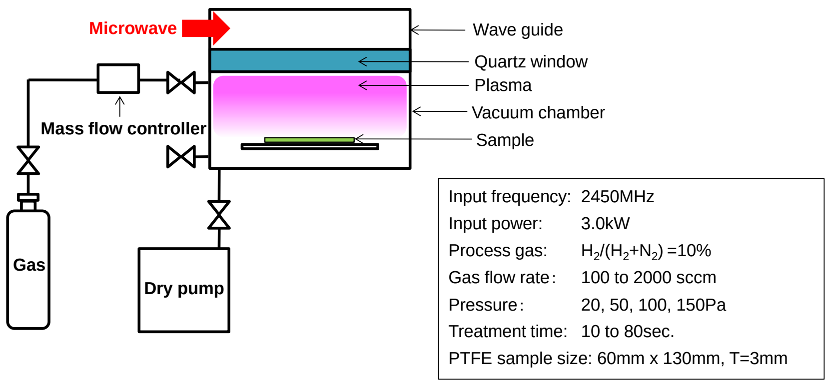


**Fig. 1. Schematic diagram of microwave plasma system**

This type of the plasma is generally called surface wave plasma because the plasma was generated just on the surface on the quartz window by propagating microwaves on the surface of the dielectric. Excited atoms and molecules generated by the surface wave plasma diffused downward toward the surface of the PTFE without impressed electromotive force, so that they simply fell downstream and initiated chemical reaction on the surface of the PTFE without physical impact.

In this experiment, the microwave plasma reactor consists of a cylindrical shape with a diameter of 400mm. The PTFE was placed on a glass plate at a distance of 100mm from the plasma reactor. Microwaves were generated by the constant magnetron output power of 3kW. The mixture gas of nitrogen and hydrogen was applied as the processing gas. Mixture rate of hydrogen/ (hydrogen+nitrogen) was 10% with processing time at a constant 60 seconds.

In order to understand the tendency of the PTFE surface condition forward plasma treatment pressure, the experiment with the microwave plasma took place under various processing pressures of 20, 50, 100, and 150Pa respectively. During the experiment, flow rate was controlled by the mass flow controllers.

The static contact angle between water droplets and the PTFE surface was measured by a contact angle meter. The water droplets made of 2.0μl deionized water were dropped at five different sites on each sheets and averaged. In addition, surface free energy was calculated with the results from contact angles of water and diiodomethane. The same as the water droplets measurement, contact angle of the diiodomethane measurement was conducted five times and results were averaged. The x-ray photoelectron spectroscopy (XPS) measurements were made using an Al k$\alpha$ x-ray source with pass energy of 187.85eV. The x-ray power was set at 400W. The pressure in the chamber was maintained at $1.0\times10^{-8}$Pa. The take-off angle was 45degrees with respect to the sample surface. To understand the surface properties of PTFE, surface roughness were measured before and after the plasma treatment by AFM in the specific conditions. Surface tomography was evaluated for areas of 1μm x 1μm, and 20μm x 20μm with resonance frequencies about 100kHz in a tapping mode. Surface roughness was evaluated using calculated average roughness, Ra.

After the plasma treatments and the investigations of the surface of the PTFE, electroless plating of copper of 0.3μm was carried out in order to investigate the adhesion strength of the electroless copper plating on the treated PTFE. The adhesion strength of electroless copper on PTFE were determined by 90degree T-peel adhesion strength measurement. In order to measure the adhesion strength, electrolytic copper plating of 20μm were implemented on the surface of electroless copper of 0.3μm.

**Result and Discussion**

Hydrophilicity of the PTFE before and after the plasma treatment was identified by contact angle measurement. Figure 2 shows the comparison of the water contact angle measurements of the PTFE as a function of plasma processing pressure.
The untreated PTFE sheets had water contact angle of 104.3 degrees. The contact angle of the treated PTFE decreased in all treatment conditions to about 70 to 90 degrees. These observations indicate that water contact angle of the treated PTFE was lower than that of the untreated PTFE which means that the hydrophilicity of the PTFE was improved by the hydrogen and nitrogen plasma treatment. The contact angle was the lowest under the treatment pressure of 20Pa. The result shows that the contact angles of the PTFE decreased to the lowest value, 69.2 degree and linearly increased with the increased processing pressure, 89.7 degree at 150Pa.

The changes of surface free energy after the plasma treatments were also investigated through the hydrophilic properties of the PTFE surface by carrying out water and diiodomethane contact angle measurements.

The surface free energy ($\gamma$) could be separated into a dispersing parameter ($\gamma^d$, dispersive components) and a polar parameter ($\gamma^p$, polar components). The surface energy could be calculated by Harmonic mean equations as follows:

$(1+\cos\theta_1)\gamma_1=4((\gamma_1^d\gamma_s^d/\gamma_1^d+\gamma_s^d)+\gamma_1^p\gamma_s^p/(\gamma_1^p+\gamma_s^p))$,

$(1+\cos\theta_2)\gamma_2=4((\gamma_2^d\gamma_s^d/\gamma_2^d+\gamma_s^d)+\gamma_2^p\gamma_s^p/(\gamma_2^p+\gamma_s^p))$,

$\theta_1$, $\theta_2$ denote the contact angle of water and diiodomethane. For water, $\gamma_1$=72.8mJ/m$^2$, $\gamma_1^d$=22.1mJ/m$^2$, $\gamma_1^p$=50.7mJ/m$^2$.

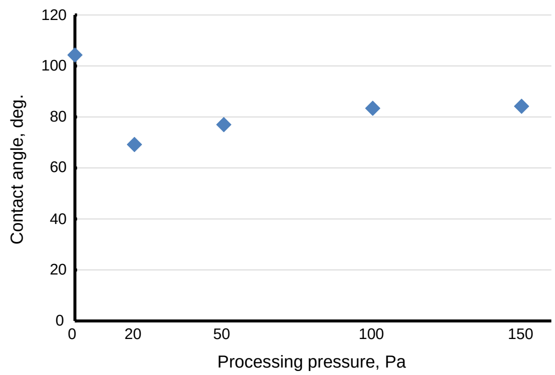


**Fig. 2. Water contact under various treatment pressure**

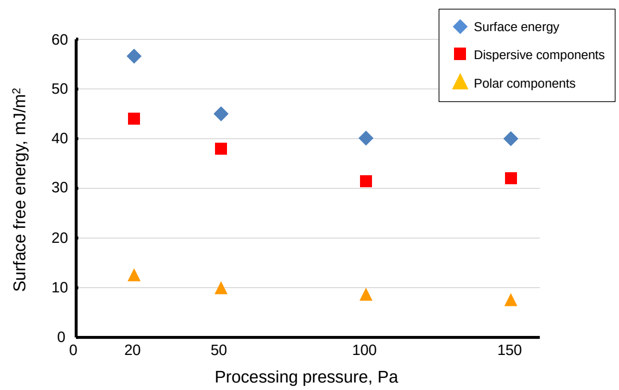


**Fig. 3. Surface free energy under various treatment pressure**

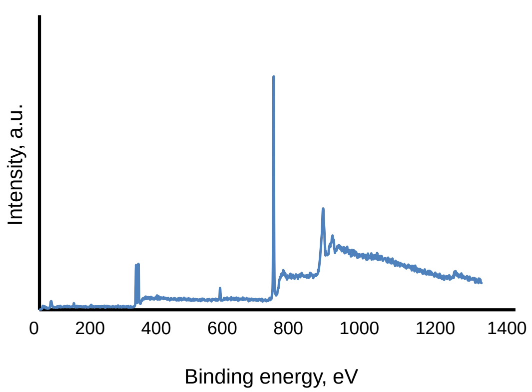


**Fig. 4(a). Wide-range spectra of the untreated PTFE**

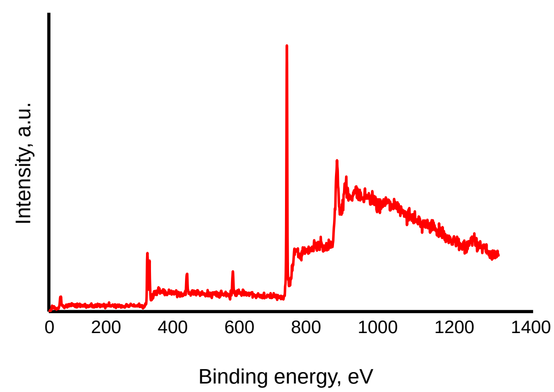


**Fig. 4(b). Wide-range spectra of the treated PTFE**

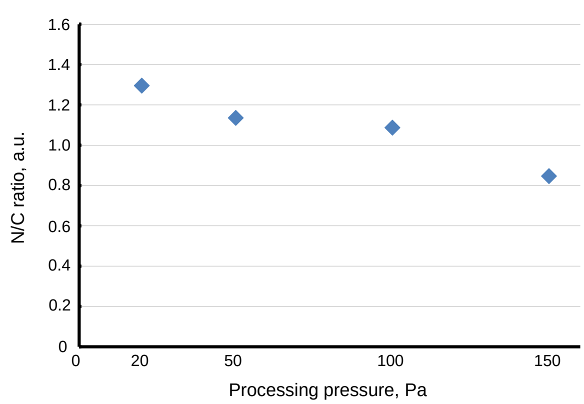


**Fig. 5. N/C ratio under various treatment pressure**

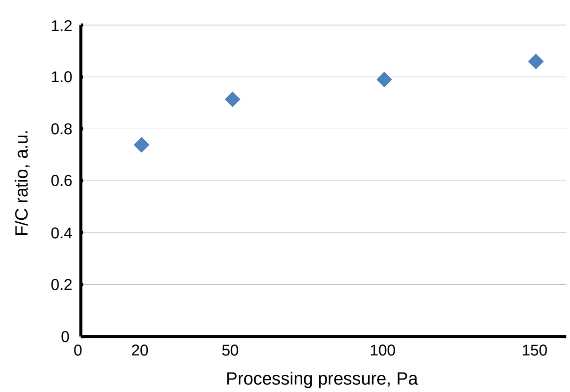


**Fig. 6. F/C ratio under various treatment pressure**

For diiodomethane, $\gamma_2$=50.8mJ/m$^2$, $\gamma_2^d$=44.1mJ/m$^2$, $\gamma_2^p$=6.7mJ/m$^2$.

The results of the surface free energy measurements are shown in Figure 3 under different treatment pressures. The figure also shows the surface energy of dispersive and polar components of the PTFE.

It shows that surface free energy of the PTFE is increased after modification. The surface free energy of polar component increases from 2.1mJ/m$^2$ to 12.6mJ/m$^2$ and dispersion components increased from 25.4mJ/m$^2$ to 44.0mJ/m$^2$ at the plasma treatment pressure of 20Pa. The maximum total surface energy increased 27.4mJ/m$^2$ to 56.6mJ/m$^2$. The result shows that hydrogen and nitrogen plasma can improve the hydrophilicity and surface energy of the PTFE. The surface free energy was the highest after plasma treatment at 20Pa. The surface free energy was decreased as processing pressure increased, 40.1mJ/m$^2$ at 150Pa. This result is the same as the result of water contact angle measurement.

In order to understand the change in the chemical binding states and atomic concentration of the PTFE surface after the plasma treatment, XPS measurements were conducted. The XPS survey spectra of samples before and after plasma treatment at 20Pa is shown in Figures 4(a) and (b). In the wide-range XPS spectra of the untreated PTFE sample, it can be clearly distinguish two peaks due to carbon and fluorine around 290eV and 690eV.

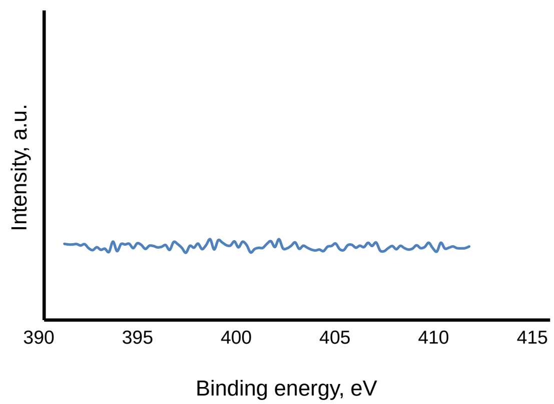


**Fig. 7(a). N 1s spectra of the untreated PTFE**

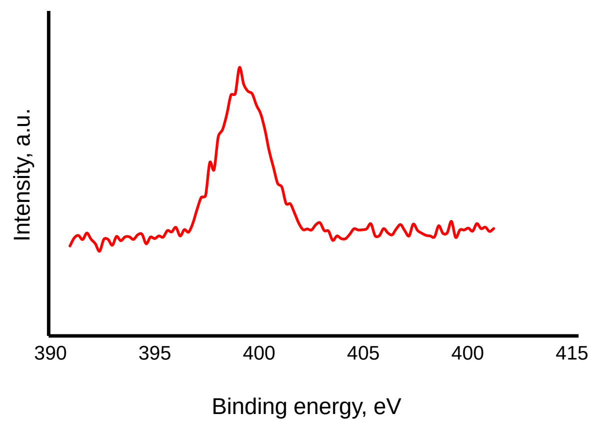


**Fig. 7(b). N1 s spectra of the treated PTFE**

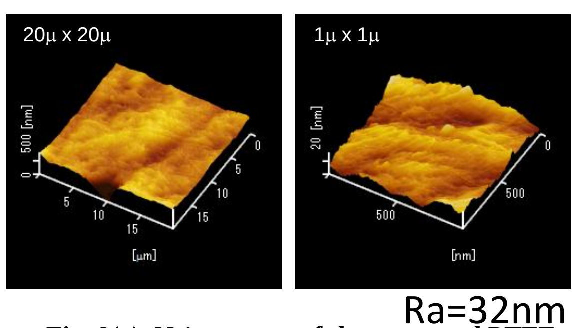


**Fig. 8(a). N 1s spectra of the untreated PTFE**

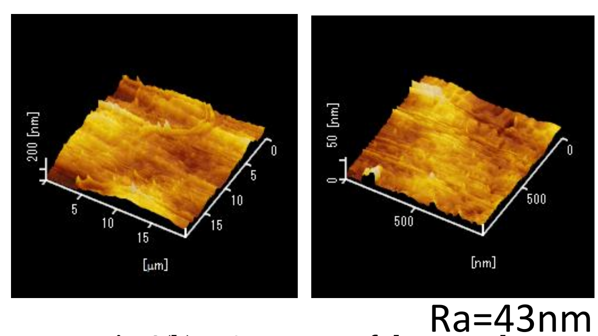


**Fig. 8(b). N1 s spectra of the treated PTFE**

In the spectra of the nitrogen and hydrogen plasma treated PTFE sample, the peak due to nitrogen was easily distinguished at around 400eV. Figure 5, and Figure 6 show N/C, and F/C ratios under different treatment pressure calculated from atomic concentrations of XPS data. The binding energies were referenced to the carbon (C 1s) peak at 285.0eV to compensate for changing effects.

It was found that the N/C ratio was increased as treatment pressure is lower. N/C ratio of treatment pressure 20Pa is 1.3, while the ratio of treatment pressure 150Pa is 0.8. This shows that the nitrogen functional group was introduced effectively on the PTFE surface under low treatment pressure. This could be from atomic or molecular nitrogen attached to the surface as well as absorbed to the surface at low pressure treatment condition.

After plasma treatment, the atomic ratio of F/C decreased to 0.73 at a treatment pressure 20Pa. The result shows that the lower the treatment pressure, the smaller the ratio of F/C. This indicates that plasma treatment introduced defluoration of the PTFE surface at low pressure treatment conditions. These results show that hydrogen and nitrogen plasma treatment could conduct the introduction of nitrogen and substantial surface defluoration as a function of plasma treatment pressure.

N/C was decreased as processing pressure was increased, while F/C was increased as processing pressure was increased. The wide-range XPS spectra shows that the lower processing pressure, the higher the surface modification effect. This phenomenon has correlation with the result of surface free energy measurement. In Figure 7, the results of the N 1s spectra of the before (a) and after (b) treatments are shown. Nitrogen concentration on the treated PTFE surface was observed. However, it is difficult to distinguish NH and $NH_2$ moieties due to the close positions of the energies.

This result means that nitrogen containing groups, such as $NH_2$, might be incorporated into the PTFE surface.

AFM measurement was conducted in order to examine the changes of surface morphology before and after the plasma treatment. Considering the result of surface free energy and XPS measurements, the PTFE treated at 20Pa and the untreated PTFE were selected as samples for AFM measurement. Figures 8(a), and (b) show images of AFM measurements from the untreated and treated PTFE surface. Ra of the untreated PTFE surface was 32nm, while Ra of the treated PTFE was 43nm. There are no major differences between the surface of the untreated and treated PTFE in the AFM measurements. Even though surface roughness was increased, the number of Ra is much smaller than that of chemical surface treatment. The result shows that the microwave plasma treatment with nitrogen and hydrogen gases does not generate surface roughness which could be an obstacle for fabricating micro strip lines.

To investigate the effect of nitrogen and hydrogen plasma treatment for the adhesion strength of electroless copper plating on the PTFE, the T-peel test was carried out after the plasma treatment of 20Pa.

**Table. 1. Peel strength of the untreated and treated PTFE**

| Sample condition | Untreated | Treated |
|---|---|---|
| Peel strength, N/cm | ≦1 | **3.4** |

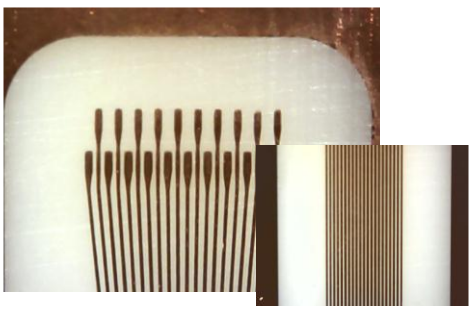

**Fig. 9. Image of pattern on the PTFE by CCD camera**

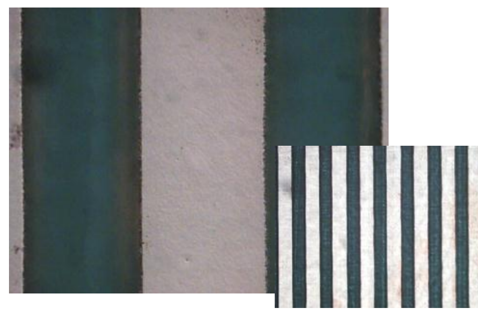

**Fig. 10. Image of pattern on the PTFE by microscope**

In order to carry out the adhesion strength measurement test, electrolytic copper plating of 20μm was implemented on the surface of electroless copper of 0.3μm. Table 1 shows the results of T-peel strength measurement after plasma treatment. Peel strength of electroless copper plating and the treated PTFE of 20Pa is 3.4N/cm. The peel strengths of PTFE without plasma treatment could not be measured for adhesion strength because the adhesion peel strengths were less than 1N/cm which was below the value of measurement limits. The result shows that the adhesion strength between electroless copper plating and PTFE was improved by plasma treatment of mixture gas of nitrogen and hydrogen without large surface roughness. Figures 9 and 10 are the examples of copper lines on the modified PTFE with nitrogen and hydrogen microwave plasma (line/space=50μm/50μm).

**Conclusions**

In this study, the surface modification of polytetrafluoroethylene (PTFE) technique with nitrogen and hydrogen plasma processing for adhesion strength improvement between electroless copper plating and treated PTFE was investigated. Microwave plasma was applied for surface treatment in order to avoid generating surface roughness by ion bombardment.

In order to understand the effect of processing pressure, plasma treatment was conducted under various pressures. Surface energy calculated from contact angle of water and diiodomethane was maximized at a processing pressure 20Pa was 44.0mJ/$m^2$. The result shows the lower pressure treatment, the higher the surface energy. Chemical characteristics of the PTFE surface before and after plasma treatment were investigated by surface free energy and x-ray photo electron spectroscopy (XPS). The result of XPS measurement shows that nitrogen and hydrogen plasma treatment could conduct the introduction of nitrogen and substantial surface defluoration as a function of plasma treatment pressure.

N/C was decreased as processing pressure was increased, while F/C was increased as processing pressure was increased. The results show that the lower the processing pressure, the higher the surface modification effect. Physical surface property of the treated PTFE under a processing pressure of 20Pa was investigated by atomic force microprobe (AFM). The results of the AFM measurements show that the PTFE surface treated by plasma was almost unchanged even as Ra increased slightly. Adhesion strength was measured by using the T-peel experiment after plasma treatment of 20Pa. Peel strength of electroless copper plating and the treated PTFE of 20Pa is 3.4N/cm.

**References**


[1] K. -M. Baumgärtnear, J. Schneider, A. Schulz, J. Feichtinger, M. Walker: Surf. Coat. Technol. 142-144 (2001) 501.
[2] C. Wan, J. -R. Chen, Appl. Surf. Sci. 253 (2007) 4599
[3] J. Z. Wu, E.T. Kang, K.G. Neoh, C.Q. Cui, T. B. Lim, Int. J. Adhesion. Adhesive. 20 (2000) 467
[4] M. A. Mohammed, V. Rossbach, J. Appl. Polym. Sci. 50 (1993) 929
[5] M. K. Shi, B. Lamontagne, L. Martinu, A. Selmani, K. Appl. Phys. 74 (1993) 1744
[6] S. L. Kaplan, E.S. Lopata, J. Smith, Surf. Interface. Anal. 20 (1993) 331
[7] C. Y. Huang, W.Y. Chiang, Angew. Makromol. Chemie. 209 (1993) 9
[8] V. Boittiaux, F. Boucetta, C. Combellas, F. Kanoufi, A. Thiebault, M. Delamar, P. Bertrand, Polymer. 40 (1999) 2011
[9] Y. Momose, Y. Tamura, M. Ogino, S. Okazaki, M. Hirayama, J. Vacuum Sci. Technol. 10 (1994) 229
[10] N. Inagaki, S. Tasaka, T. Umehara, J. Appl. Polym. Sci. 71 (1999) 2191
[11] N. Inakgaki, S. Tasaka, Y. Goto, J. Appl. Polym. Sci. 66 (1997) 77
[12] H. Xu, Z. Hu, S. Wu, Y. Chen, Mater. Chem. Phys. 80 (2003) 278
[13] T. Hirotsu, S. Ohnishi, J. Adhesion 11 (1980) 57
[14] X. Xie, T. R. Gengenbach, H. J. Griessner, J. Adhesion Sci. Technol. 6 (1992) 1411
[15] N. Inagaki, S. Tasaka, S. Shimada, J. Appl. Polym. Sci. 79 (2001) 808
[16] N. Inagaki, K. Narushima, S. K. Lim, J. Appl. Polym. Sci. 89 (2003) 96
[17] Y. Takagi, Y. Gunjo, H. Toyoda, H. Sugai, Vacuum. 83 (2009) 501
[18] A.A. Meyer-Plath, K. Schröder, B Finke, A. Ohl, Vacuum. 71 (2003) 391
[19] Y. Wan, J. Yang, J. Yang, J. Bei, S. Wang, Biomaterials. 24 (2003) 3757
[20] C. S.arra-Bournet, S. Turgeon, D. Mantovani, G. Laroche, Appl. Phys. 39 (2006) 3461
[21] F. R. Pu, R. L. Williams, T.K. Markkula, J. A. Hunt, Biomaterials, 23 (2002) 2411
[22] J. P. Badey, E. Espuche, Y. Jugnet, B. Chabert, T. M. Duc, Int. J. Adhesion. Adhesives. 16 (1996) 173

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# Effect of Microwave Plasma Surface Treatment for Improved Adhesion Strength of Direct Cooper Plating on Polyterafluoroethylene (PTFE)

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**Hyogo Pref., Japan**

# Background

## Current condition of PTFE

- Excellent properties Ex. high stability against heat, electrical conductivity, and resistivity
- Widely used in many industrial fields Ex. biomedical, aero space, microelectronics
- Adhesion strength for Cu plating is important for microelectronics applications

## Problem of using PTFE

- Hydrophobic surface property and low adhesion surface with other materials

## Solutions

- Chemical treatment with sodium liquid ammonia and sodium naphthalide
  →Changing bulk properties, high cost, bad effect for pollution, formed surface roughness
- **Low-pressure plasma treatment** by generating amino functional group

  *Merits*

  →Changing properties only thin surface layer

  *Demerits*

  →Generate weak layer with degradation by ion bombardment

# Purpose

## Ideal PTFE surface treatment for improve adhesion

- High speed plasma surface modification without degradation

## Purpose

- Investigate plasma surface modification technique for PTFE in order to improve adhesion strength of cupper plating without degradation

## Evaluation

Plasma treatment for PTFE

Surface wettability and free energy measurements

Chemical composition measurement

→ Surface roughness investigation

Electroless Cu plating on PTFE

↓

Adhesion strength measurement

*Surface wettability, free energy measurement*
→**contact angle of water and diiodomeathane**

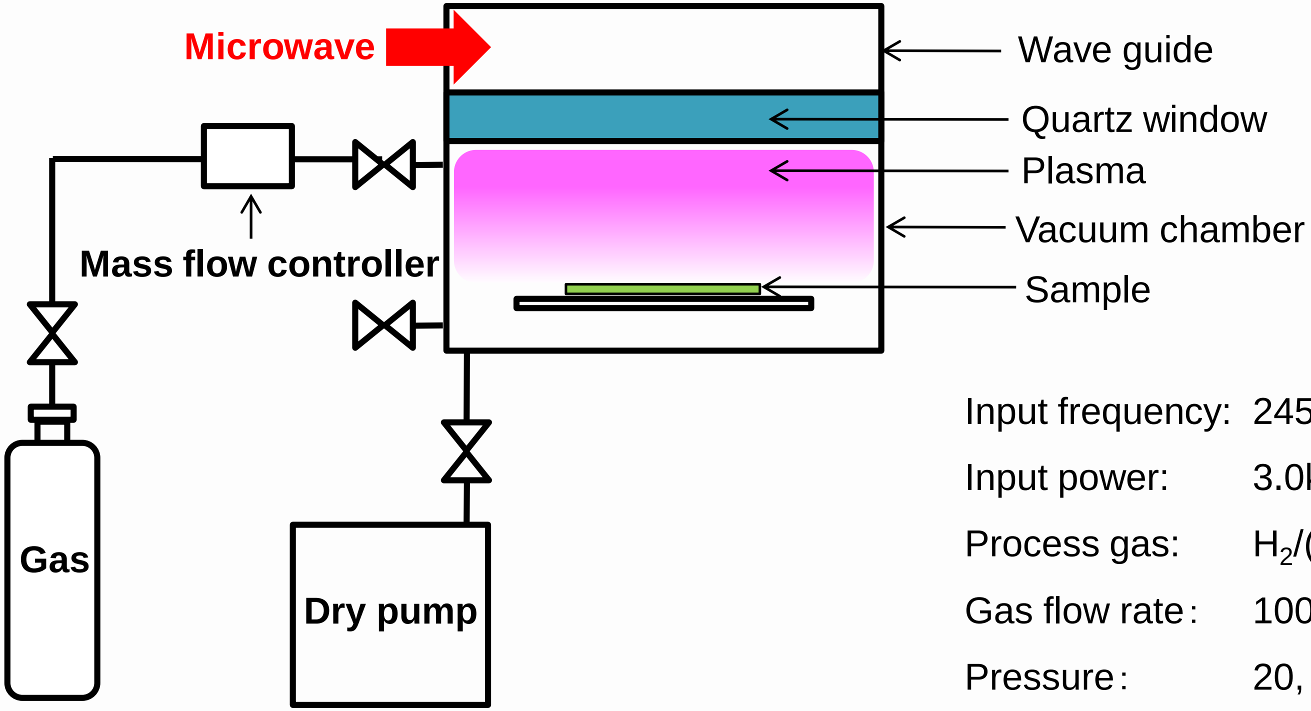
*Chemical composition measurement*
→**XPS**

*Surface roughness measurement*
→**AFM**

*Adhesion strength measurement*
→ **90deg. T-peel test**

# Experimental Apparatus

## Microwave plasma equipment




Input frequency: 2450MHz

Input power: 3.0kW

Process gas: $H_2/(H_2+N_2)$ =10%

Gas flow rate : 100 to 2000 sccm

Pressure : 20, 50, 100, 150Pa

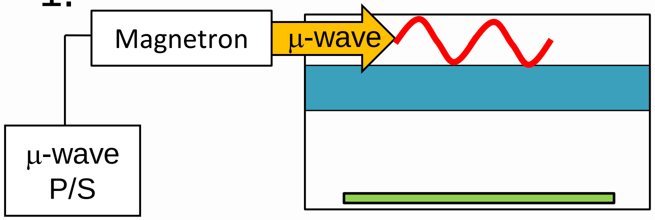
Treatment time: 10 to 80sec.

PTFE sample size: 60mm x 130mm, T=3mm

# Features of Microwave Plasma

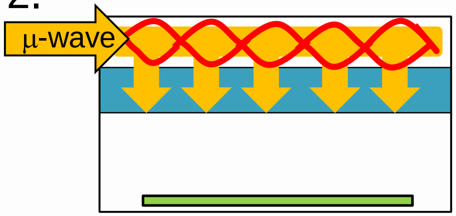
## Surface wave plasma (SWP)

1.



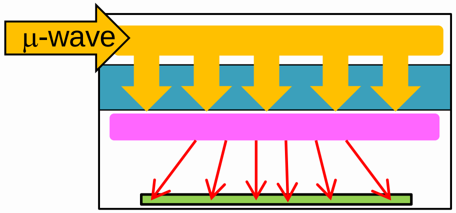

μ-wave generated by magnetron is led into the wave guide

2.




μ-wave leaks and propagates into the chamber through the quartz window

3.




Plasma is generated on the surface of quartz window

## Electron density

Electron density of microwave plasma is much higher than that of RF plasma

- Electron density of microwave plasma : **$10^{12}/cm^{-3}$~**
- Electron density of RF plasma : **$10^{8}/cm^{-3}$ ~**

## Process mechanism

Excited atoms and molecules generated in microwave plasma are diffused and fall to the sample

- Microwave plasma process: **No physical impact , only chemical reaction occurred**
- RF plasma process: **Physical impact of ion bombardment assists chemical reaction**

# Experimental Overview

## Types of Plasma for PTFE surface treatment

・Microwave plasma (SWP)

## Processing conditions

| | |
|---|---|
| Pre-treatment | : Methanol and asetone in an ultrasonic water bath for 10min.<br>Argon plasma for 30sec. |
| Plasma treatment | : $H_2$+$N_2$ plasma treatment for 60sec. |
| Input power | : 3kW |
| $H_2$+($H_2$+$N_2$) | : 10% |
| Pressure | : 20, 50, 100, 150Pa |

## Evaluation methods

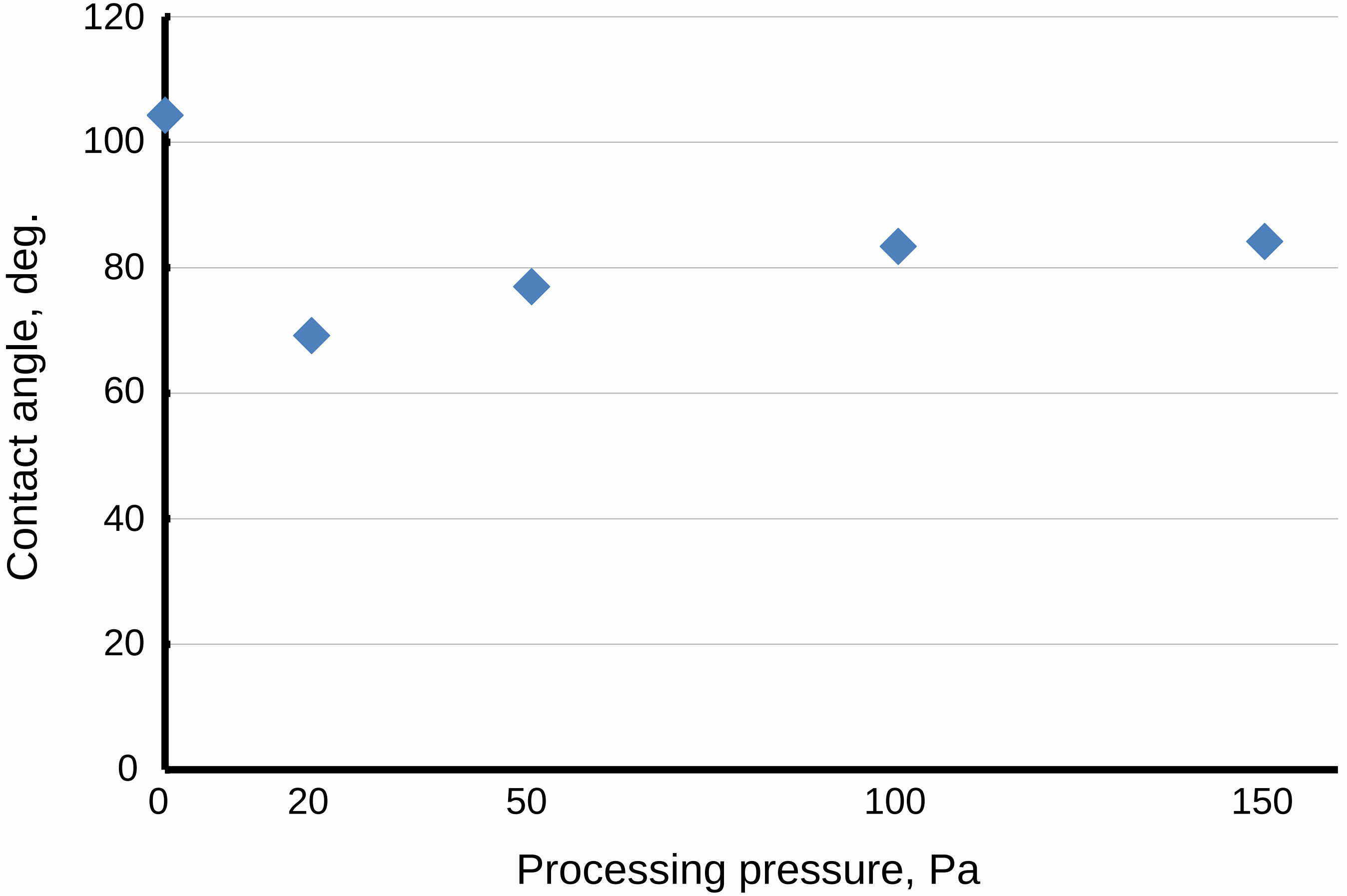
*Surface wettability, free energy measurement*
→**Contact angle of water and diiodomeathane**

*Chemical composition measurement*
→**XPS**

*Surface roughness measurement*
→**AFM**

*Adhesion strength measurement*
→ **90deg. T-peel test**

# Contact Angle ($H_2O$)




Plasma conditions

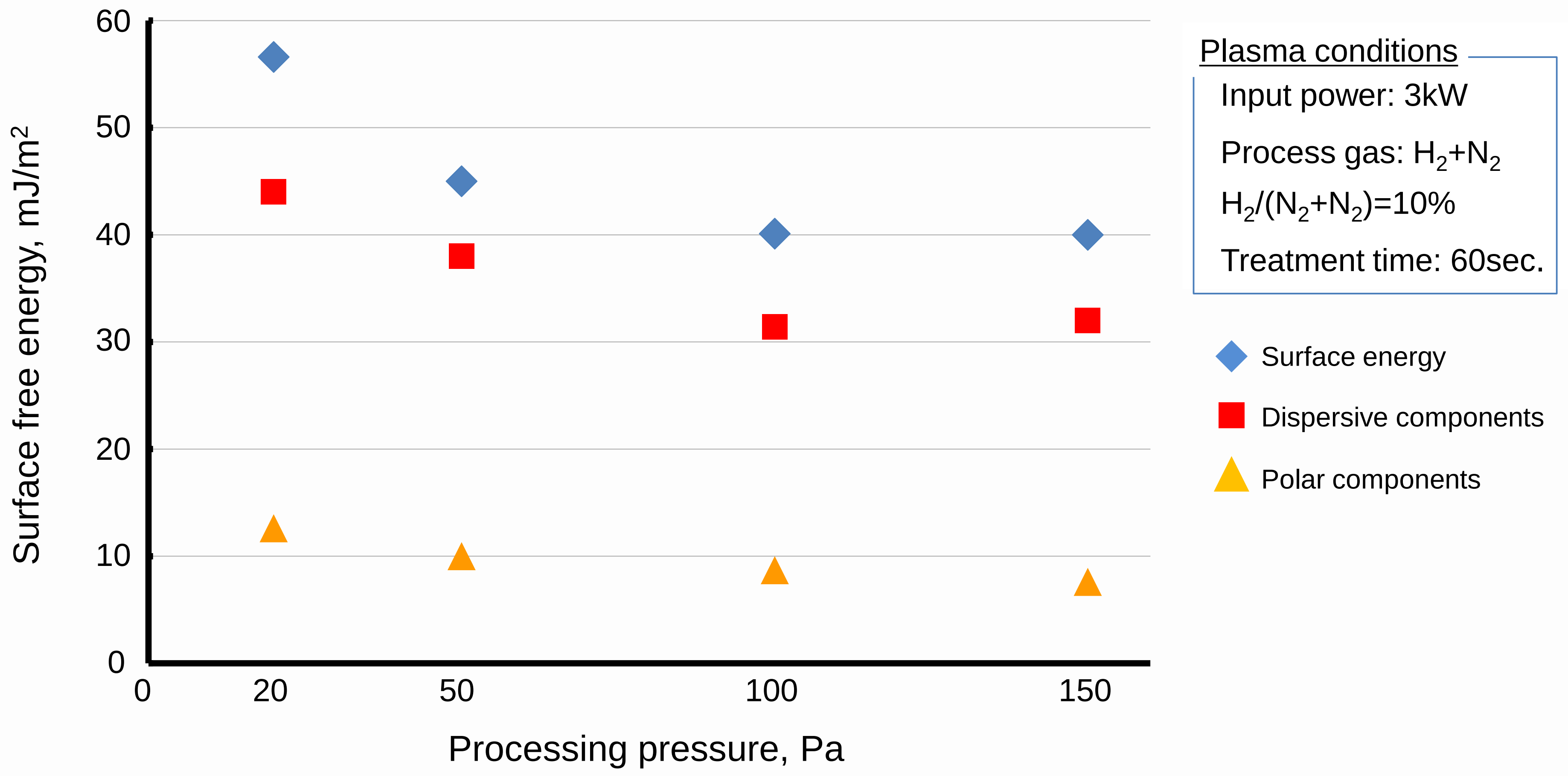
Input power: 3kW

Process gas: $H_2$+$N_2$

$H_2$/($N_2$+$N_2$)=10%

Treatment time: 60sec.

# Surface Free Energy

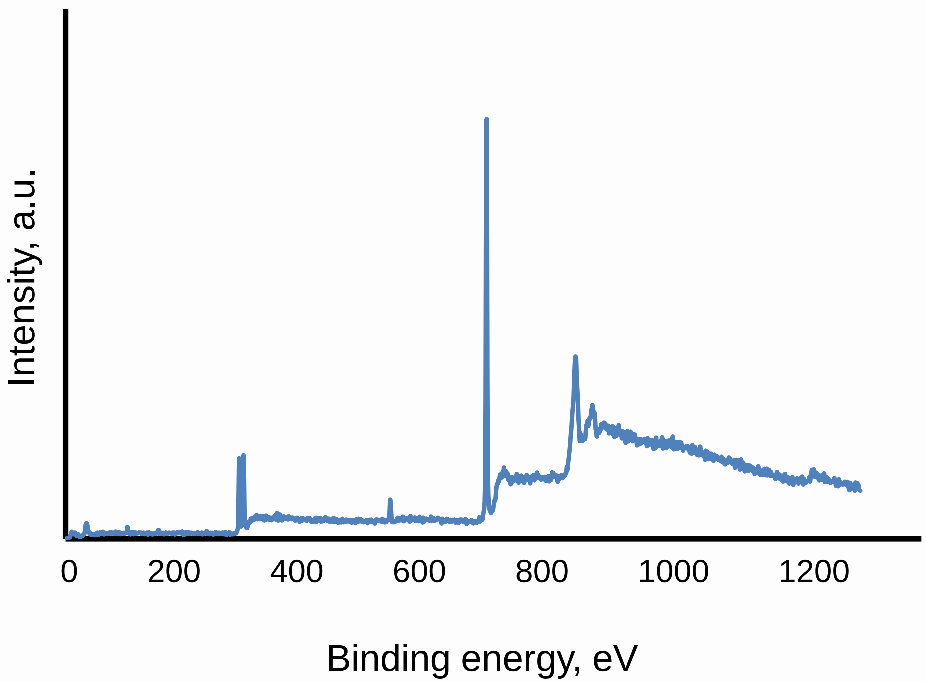


# XPS Wide-range Spectra

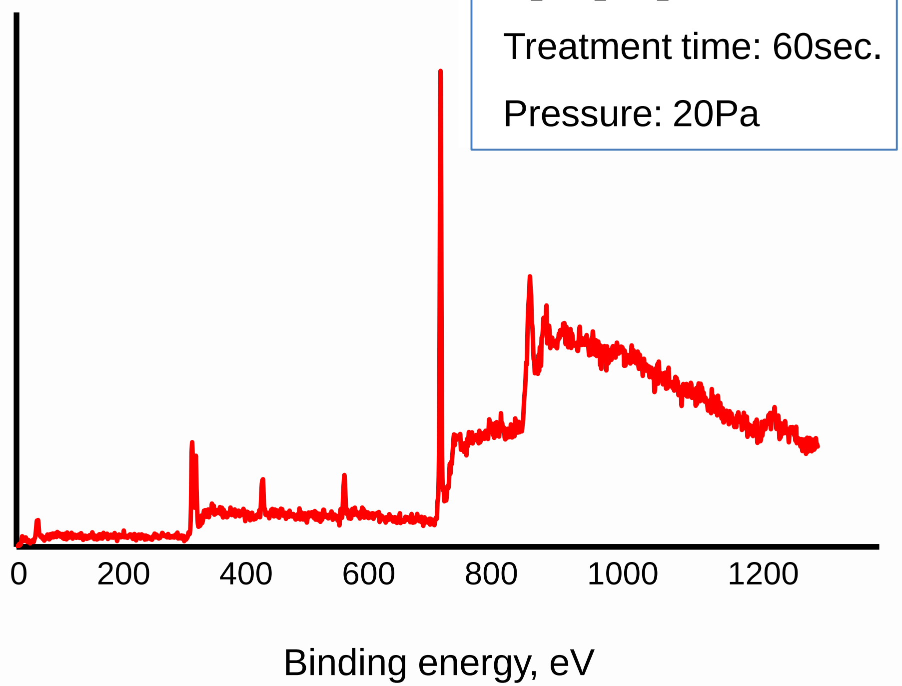
Plasma conditions

- Input power: 3kW
- Process gas: $H_2+N_2$
- $H_2/(N_2+N_2)=10\%$
- Treatment time: 60sec.
- Pressure: 20Pa

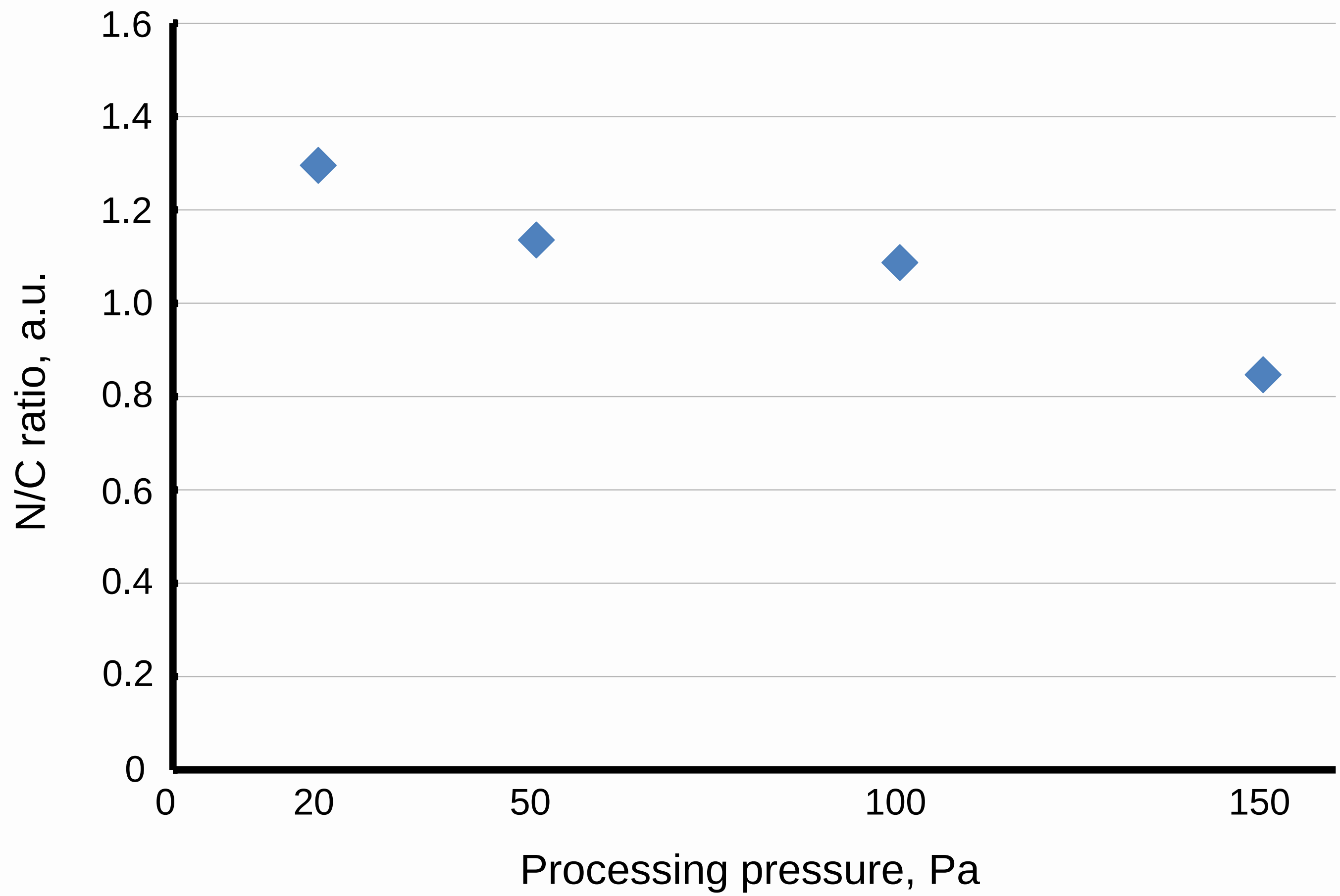
Untreated




Treated



# Nitrogen Containing




Plasma conditions

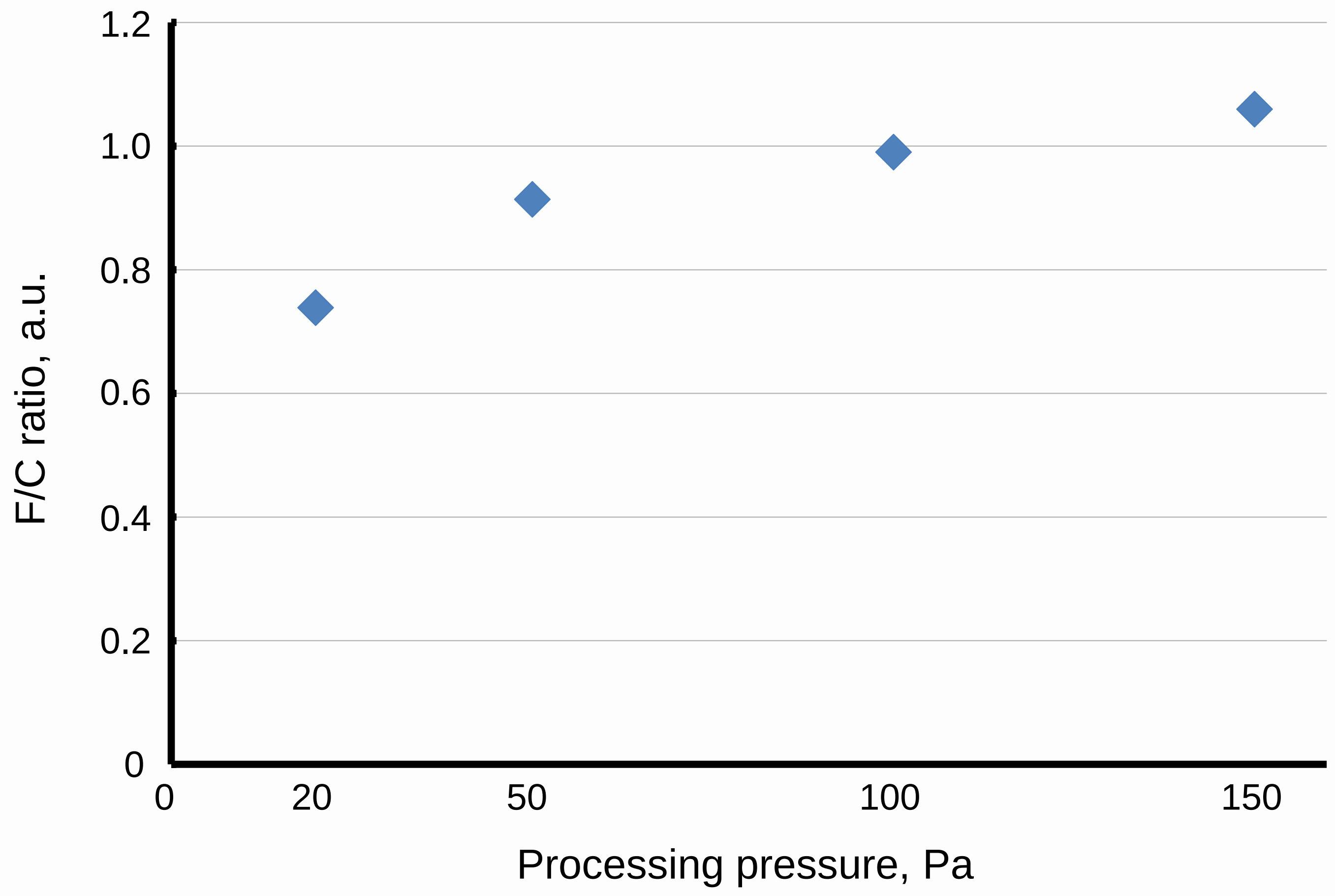
Input power: 3kW

Process gas: $H_2+N_2$

$H_2/(N_2+N_2)=10\%$

Treatment time: 60sec.

# Fluorine Containing




Plasma conditions

Input power: 3kW

Process gas: $H_2+N_2$

$H_2/(N_2+N_2)=10\%$

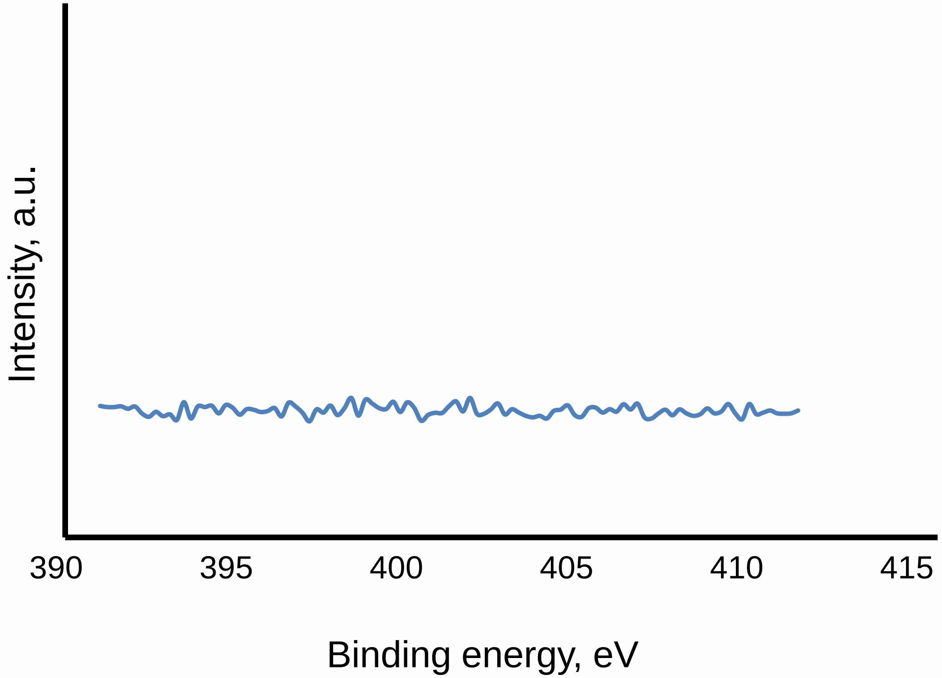
Treatment time: 60sec.

# XPS Narrow-range Spectra N 1s

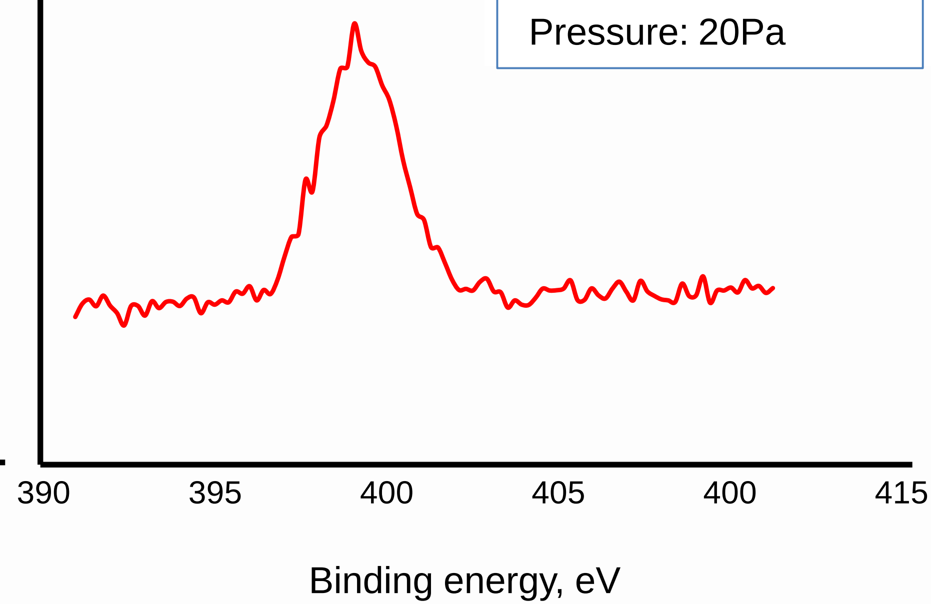
Plasma conditions

- Input power: 3kW
- Process gas: $H_2$+$N_2$
- $H_2$/($N_2$+$N_2$)=10%
- Treatment time: 60sec.
- Pressure: 20Pa

Untreated

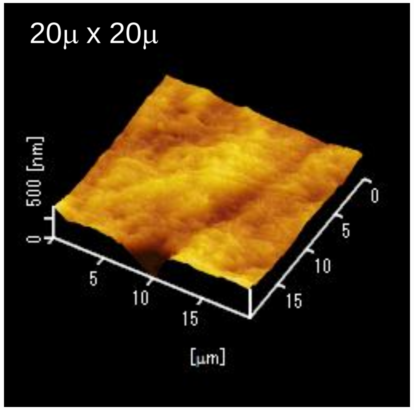


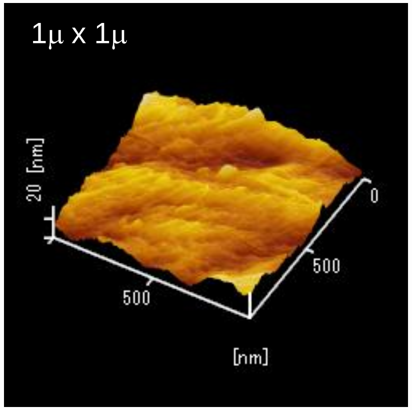

Treated



# AFM images

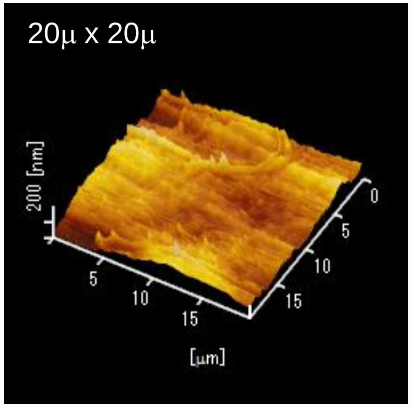
## Untreated

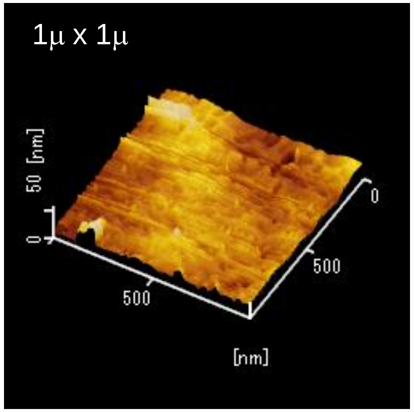



Ra= 32nm

## Treated




Ra= 43nm

**Plasma conditions**

- Input power: 3kW
- Process gas: $H_2$+$N_2$
- $H_2$/($N_2$+$N_2$)=10%
- Treatment time: 60sec.
- Pressure: 20Pa

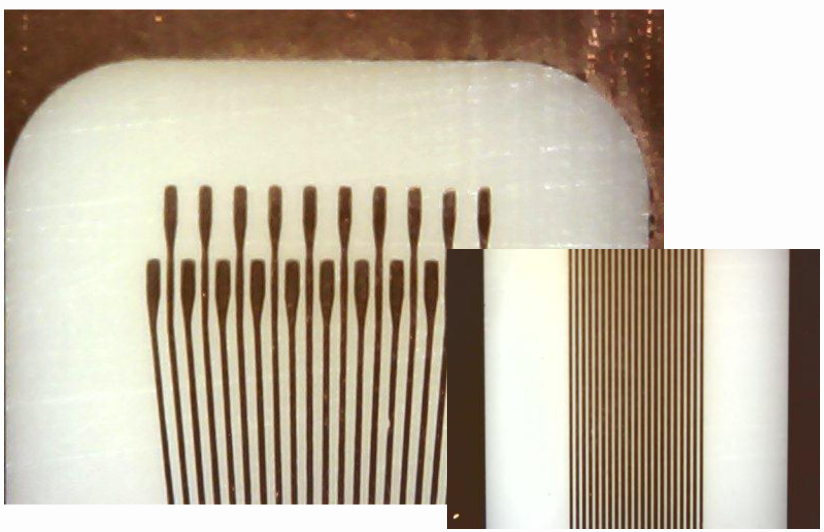
# T- Peel Test

| Sample condition | Untreated | Treated |
|---|---|---|
| Peel strength, N/cm | ≦1 | **3.4** |

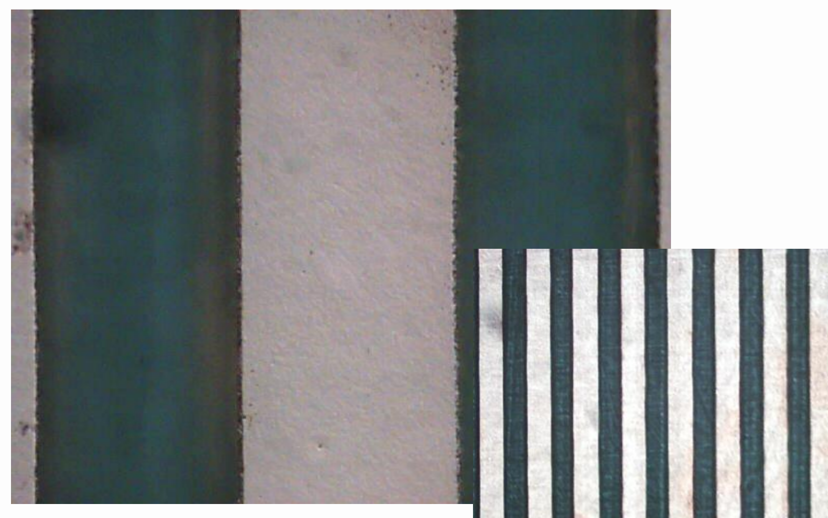
Plasma conditions

- Input power: 3kW
- Process gas: $H_2+N_2$
- $H_2/(N_2+N_2)=10\%$
- Treatment time: 60sec.
- Pressure: 20Pa

**Example of Cu plating on treated PTFE (L/S=50μ/50μ)**



CCD camera images



Microscope images

# Summery

## Purpose

- Investigate plasma surface modification technique for PTFE in order to improve adhesion strength of cupper plating without degradation

## Plasma treatment and evaluation methods

- Microwave plasma treatment with nitrogen and hydrogen for PTFE under various processing pressure
- Evaluate surface of the PTFE by surface free energy, chemical and physical properties
- Evaluate peel strength btw/ the treated PTFE and electroless Cu plating

## Result

The result shows that microwave plasma process can increase adhesion strength between the PTFE and electroless Cu plating without surface roughness formation.

# Thank you for listening