

Hydrophilization treatment of polyimide using Ar-O₂ mixture gas surface wave plasma

Oxygen radical density and plasma parameter dependence

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The hydrophilization treatment of polyimide is important in various applications. This paper has described the experimental research findings which explore what the parameter with large effect in the plasma treatment of polyimide is. The low pressure surface wave plasma of the argon oxygen mixed gas which can expect large homogeneity spatially was used for the experiment. The plasma state was measured by the electrostatic probe. The oxygen radical expected to be active species important for surface treatment was measured by the catalyst probe. It turned out that it depends for the water contact angle on the surface of polyimide by which plasma treatment was carried out in an oxygen radical density strongly.

Keywords-Surface wave plasma; Surface modification; Polyimide; O radical; Electron temperature; Electron density

1. INTRODUCTION

Flexible printed circuit board (FPC) is well known for wiring of electric devices, such as a cell phone and a personal computer. FPC consists of metal layer and polyimide. Polyimide has superior characteristics. So Polyimide is broadly used as base material of FPC or insulating material for electrical devices.^{1,2} Process of making up FPC includes forming conductive layer on surface of polyimide. Before forming conductive layer, preliminary treatment is necessary so that give hydrophilic property to surface of polyimide.³ As of today, chemical processing has generally used. But chemical processing has some issues including influence to environment or forming rough surface. Therefore plasma processing attracts attention.^{4,5,6} Plasma processing has some advantages. First, it has no influence to environment. Second, it takes short time. Third, it doesn't roughen the surface of polyimide. The mechanism of increasing hydrophilic property caused by plasma treatment seems that functioning group including O is formed on surface of substance. So it seems that O radical in plasma contributes considerably to increasing hydrophilic property. There are many researches of the surface modification of plastic material using plasma. However there is almost no research of surface modification using surface wave plasma. Therefore we decide to conduct research using surface wave plasma. Surface wave plasma has wide processing area. But plasma parameter varies rapidly with distance from plate.

From the above, the purpose is that we investigate fundamental characteristics and look for optimum condition in surface modification of polyimide using surface wave plasma. In addition, we pay attention to plasma parameter and O radical density.

2. EXPERIMENTAL SETUP

2.1 Surface Wave Plasma Apparatus

Apparatus of generating plasma consists mainly of wave guide, microwave source and vacuum chamber. Vacuum chamber is 200mm in inner diameter and 220mm in height. Vacuum chamber has four ports for gas inflow and exhausting and pressure measurement. Pressure in chamber is evacuated with vacuum-pump. Since microwave is supplied to slot antenna on bottom of the chamber, surface wave plasma is generated.

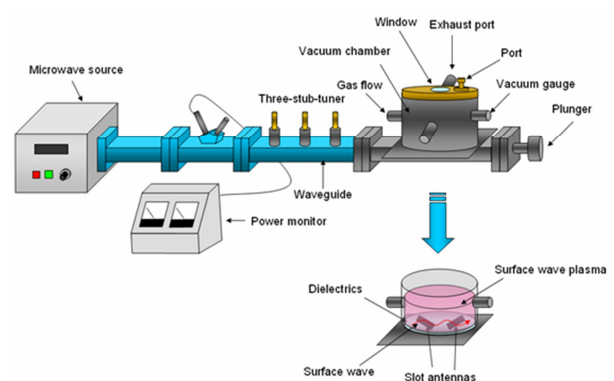


Fig.1 Surface wave plasma apparatus

2.2 Langmuir Probe Method^{7,8,9}

We conducted plasma parameter measurement using Langmuir probe. Electron temperature, electron density and electron energy distribution function is derived from current-voltage characteristics. Figure 2 shows schematic diagram of Langmuir probe measurement circuit.

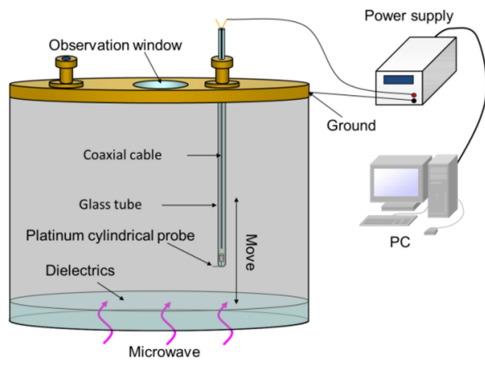


Fig.2 Langmuir probe measurement setup

2.3 Contact Angle Measurement

Hydrophilic property given by plasma treatment is evaluated with contact angle measurement. Figure3 shows an example of reduction of contact angel .

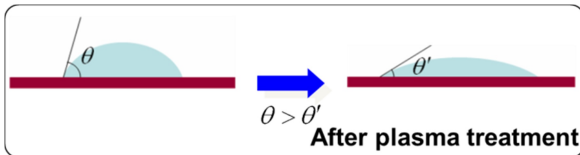


Fig.3 Solid surface and contact angle

2.4 O Radical Density Measurement Using Platinum Catalytic Probe¹⁰

It seems that O radical in the plasma contributes considerably to increasing hydrophilic property. When platinum is immersed in the plasma, O₂ is adsorbed on surface of platinum by dissociative adsorption. And then O radical recombines with O atom on the surface and desorbs. When it recombines to form oxygen molecule, they supplies 5.12eV to platinum. This catalytic reaction occurs considerably when temperature of platinum surface is from 800K to 900K. Figure4 shows principle of O radical density measurement of electric current heating catalytic probe.

It turns on electricity to a thin platinum wire, and heats to the temperature (800-900K) from which a catalytic reaction occurs actively. Let supply energy by turning on electricity is Energy A. Excess energy will be given to platinum if oxygen radical recombines on the platinum surface. Here, let energy which platinum was given is Energy C. The supply energy of the power source is adjusted so that the temperature of the platinum wire may become constant. The difference of the supply energy from the power source by the existence of oxygen radical is the supply energy of oxygen radical. If it thinks that oxygen radical reaches a platinum wire by thermal motion, oxygen radical density can be estimated.

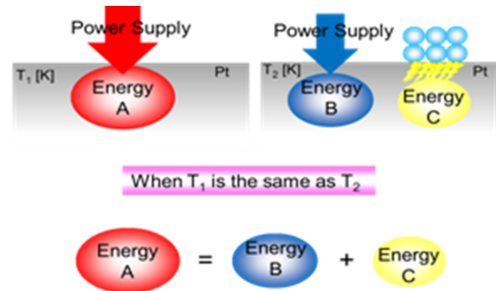
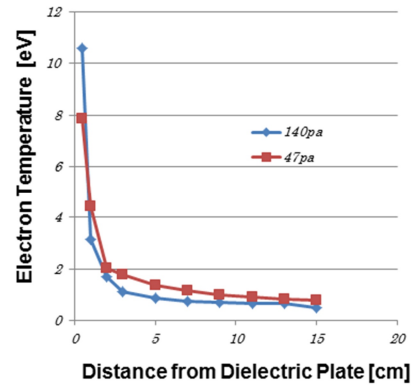


Figure.4 Principle of oxygen radical density measurement

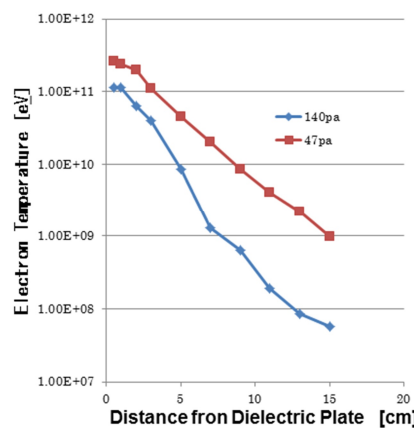
3. RESULTS AND DISCUSSION

3.1 Plasma Parameter

Figure5 shows results of electron temperature Te and electron density Ne measurement. Experimental condition is that flow rate of Ar is 100ml/min, flow rate of O₂ is 10ml/min, power is 300W, pressures are 47Pa and 140Pa. From fig.5, it found that excitation caused by surface wave occurs in a distance up to 2cm. In the position distant from the dielectrics plate, the value of the electron density in 47Pa is the value of this about 10 times in 140Pa. Figure 6 shows electron energy distribution function. Figure 6 shows that the electron with larger energy than 5.12eV exists in a range with a distance of less than 2cm.



(a)



(b)

Fig.5 Variation of electron temperature (a) and electron density (b)

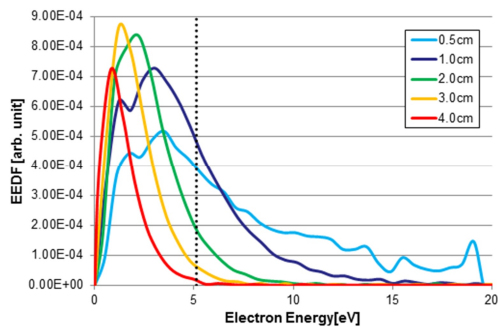


Fig.6 Electron energy distribution function

3.2 O Radical Density

Figure 7 shows results of O radical density measurement. Although it seems that an oxygen radical is generated only near the dielectric plate, it turns out that the oxygen radical is diffused to a distant place as shown in fig.7. That is, the spatial distribution of the plasma differs from radical spatial distribution greatly. On condition of this experiment, the oxygen radical density in which the result of 140Pa of the result of 47Pa is also almost the same is shown.

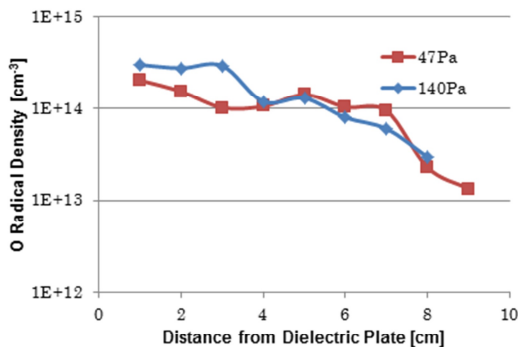


Fig7. Distance dependence of O radical density measurement

3.3 Contact angle measurement

Figure 8 shows results of contact angle measurement. Generally for electroless plating, it is thought that the water contact angle of 30 degree or less is desirable. A less than 10cm region fulfills this condition from the dielectrics plate. As shown in Fig. 5, in the case of 140Pa, and the case of 47Pa, electron density differs greatly. However, both water contact angles show the value almost same as a case. On the other hand, as compared with the measurement result of the oxygen radical shown in Fig. 7, it turns out that it depends for the water angle of contact in oxygen radical density strongly.

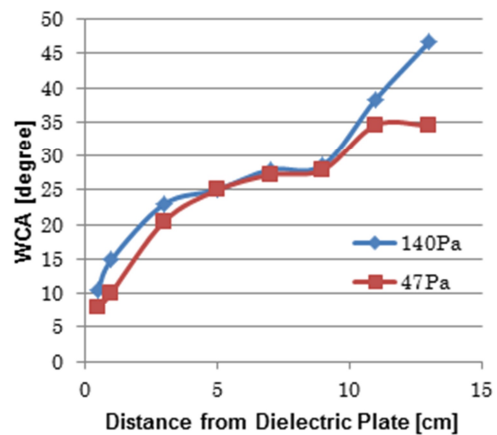


Fig.8 Results of contact angle measurement

4. SUMMARY

In this research, we conducted plasma parameter measurement of Ar-O₂ surface wave plasma, O radical density measurement, and contact angle measurement. We also evaluate hydrophilic property of polyimide surface given by plasma treatment. It found that O₂ dissociation caused by surface wave occurs in a distance up to 2cm. However O radical density distribute to more far area. Rapid lowering of the temperature and the density of the plasma is observed in the location distant from the dielectric plate in the surface wave plasma. However, hydrophilization treatment was enough performed in the considerably distant location. The reason is because the spatial distribution of the oxygen radical is larger than the spatial distribution of the plasma enough. There fact because clear from measurement of the radical density by the catalytic probe.

5. REFERENCES

1. Jiangnan Lai, et al: " Study on hydrophilicity of polymer surfaces improved by plasma treatment " , Applied Surface Science 252 3375-3379 (2006)
2. Akihiro Uemura, Tomoya Tanabe, Satoru Iwamori: " Effect of Sputtering Condition on Thin Films Deposited by r.f. Sputtering with a Polyimide Target " , IEEJ Trans. FM, Vol.130, No.2,2010
3. Syuichi Ogasawara, "material of printed circuits and surface treatment technique" in Japanese, surface technology, Vol46, No.3, p.210-214, 1995
4. Shohei Ikari, Shuichi Ishida, Takashi Matsuoka, Tomoko Hirayama, Kiyotaka Kato : " Effect of Oxygen Plasma Treatment on Adhesion of Copper Plating Film to Polyimide Film for Flexible Printed Circuits " , Journal of the Society of Materials Science, Japan, Vol.59, No9, pp.705-711, Sep.2010
5. Cheng Cheng, Zhang Liye, Ru-Juan Zhan: "Surface modification of polymer fibre by the new atmospheric pressure cold plasma jet", Surface & Coatings Technology 200 6659-6665 (2006)

6. Atsushi Yokotani, "Surface modification technology of the plastic by vacuum ultraviolet rays" in Japanese, Comber tech, No.421, p.110-113, Apr.2008
7. Shinriki Teii, "Plasma fundamental engineering" in Japanese, Uchidarokakuho
8. The Japan Society of Plasma Science and Nuclear Fusion Research, "Generation and diagnosis of plasma" in Japanese, Koronasya
9. Hideo Sugai, "Electron energy distribution function and radical composition" in Japanese, The Japan Society of Plasma Science and Nuclear Fusion Research, Vol.77, No.7,p.660-665
10. Nobuyuki Haraki, Saiensu Nakao, Shigeru Ono, Shinriki Teii: " Oxygen radical density measurement in O2-N2 gas mixture plasma by means of a thin platinum wire ", Electrical Engineering in Japan, Vol.149, No.4, p.14-20 (2004)