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Removal of Static Electricity on Polyimide Film Surface by O_2 or Ar Cold Plasma Etching

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Abstract: Cold plasma of O_2 or Ar was irradiated on hydrophobic Kapton surface to attenuate or remove the electrostatic potential. A measurement on charge dissipation speed clarifies the obscure effect of plasma. These consequences reveal that O_2 plasma etching is more effective than Ar plasma. After 30 days, the dissipation speed of accumulated charge on initially etched sample has not changed under summer season.

Keywords: Kapton, O_2 plasma, Ar plasma, Charge dissipation speed

Introduction

It is well known that plasma treatment can modify polymer surface easily without using wet chemicals. Plasma surface modification is involved in surface properties from plasma-substrate interactions; functionalization, etching, chain scission and cross-linking. Functionalization can change surface chemical properties to be hydrophilicity or hydrophobicity. Etching is closely related to physical property such as surface morphology and friction properties. It has been reported that atmospheric pressure plasma treatment did not deteriorate bulk properties of substrate [1,2], while tensile strength of fibers and fabrics were reduced in the intensive low-pressure plasma conditions [2-6].

Etching process of glow discharge plasma with inert argon and reactive oxygen gas causes distinct weight decrease of polymer by volatility and removal of bombarded molecular to variability of gas pressure.

Thus, it accelerates the anchoring effect which is composed of micro crater or micro pore, to say another word, irregular roughness.

This morphological phenomenon might be a cause of excellent adhesion between polymer interface. Simultaneously, this etching bombardment produces radicals and the other hydrophilic functional groups on fragmented molecular chain.

Recently, the necessity for anti-static property of organic polymer surface is an important issue.

Polyimide has significant advantages over ceramic insulators as follows. It offers the property of stress relief and elasticity and it also give ability to design molecule corresponding to specifically required shape and gives further chemical resistance and thermal resistance [7-9].

Most of all, their excellencies led it to launch into very large scale integration(VLSI) chip not to mention of flexible print circuit board(FPCB) [3]. Hence, polyimide has predominated in the advanced stream that can be represented as missile, aircraft, the shape of other matrix composited materials [10-12].

Another application of aerospace field is anti-therm tile adhesives for space shuttle and solar cell for satellite.

Also, it can be applied to a field of electronic materials as FPCB or passivation of intergrated circuit(IC) and VLSI semiconductor process [3]. Especially, in chip making process, two functions can be summarized as following. One is surface protection and the other is insulation at interlayer. Former can be further subdivided into junction coating, passivation, and α-ray shielding [7-9].

Thus, for many years, Dupont's Kapton has been accepted as standard of polypyromellitimide. Kapton has played a major role in FPCB technology as shape of thin film. Because thermal expansion coefficient of Kapton is nearly equal to that of copper and it has superior relaxation ability for load applied on the film [7-9,13].

But significant electrostatic potential is caused by properties of non-polarity, high dielectric constant (3.5) and low surface tension, etc.

Especially, the static electricity give rise to spark mark of static charge on surface. Also, serious contamination on ultra-purity demanded FPCB surface is caused by attraction of impurities or dust, resulting in the decline of adhesion force between flexible film and metal wire [14-16].

Therefore the necessity of surface cleaning and purity sustainment is critical in FPCB processes [17,18].

Electrostatic phenomenon causes several problems such as breakage of semiconductor chip, purity deterioration, and reduction of adhesion. Namely, when they can be divided into three kinds of troubles occurred by static charge potential, at first they can be resulted from electrical troubles such as dust absorption by attraction force;

$$F = 4.4 \times 10^{10}\, V^2 A/D^2 \text{ (dyne)} \qquad (1)$$

where F: attraction force, A: area, V: difference of charge potential, D: distance.

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Hence, adhesion fails by repulsion force or nerves shock happen by electrical impulse.

Secondly it can be cited that any discharge troubles can occur through electrical troubles.

Discharge energy E was calculated as E=1/2 CV^2, where C is capacitance.

The last is human body troubles such as saccharine and pH increase in blood or calcium increase in urine [14].

Therefore blending of additives has been developed for some Kapton film which modified in several ways to remove the disadvantages mentioned above.

Additives can be used such as alumina, carbon, fluorine, and mica. For instance, several types of Kapton are available as following; conductive carbon filled Kapton type XC ($10^{12}\ \Omega\cdot$cm), fluorine filled Kapton F, mica filled Kapton X-M, and non filled Kapton type H. Particularly, alumina-filled Kapton known as type XT commercially.

It is thermally and electrically conductive film that has been concurrently served as an insulating layer of radiant heat [7-9,19]. However, comparing with these methods, glow discharge plasma is an advanced ultra-surface modification and smart cleaning technology [10,11,17,18,20-23].

It is not yet known what kind of influences is exerted on the transient electromagnetic field generated by spark discharge between charged metals. Matsushita *et al.* [24] also have reported methods of electrostatic separation of plastics by mixer.

When mixture was charged by friction in a mixer with rotary blades, it falls through a horizontal electric field of 4 kV/cm into three zones under the field. Proper time of mixing, high speed of spin and low humidity led the purity of the separated pellets to increase. Fujiwara and Kawaguchi [25] studied on the electromagnetic field from spark numerically analyzed by finite-difference time-domain(FDTD) method. It was found that the presence of the metallic bodies can increase the field level depending on their size.

Koo *et al.* [26] also acquired similar results for several plastics by sputter etching and Ar cold plasma treatment. Also, the study worked on the etching process as a pre-treatment technique for graft polymerization.

First of all, the final goals of this study are summarized and emphasized as follows; to decrease static charge potential and to establish surface roughness. Hence, we also aim to accomplish surface purification or cleaning in order to protect on dust attraction and to remove on any residual organics (oligomer), residual metallic contaminants and native oxides simultaneously. It has been known that contaminants are formed on the surface of Kapton and they can be cleaned out by means of inert argon or reactive oxygen cold plasma treatment.

Experimental

Plasma Treatment

The plasma treatment of the Kapton films was carried out under 0.1~1 torr pressure for 0.5~10 min in a plasma deposition system at 50~200 watt power.

Measurement of Anti-static Property

An electrostatic measuring apparatus was investigated to test anti-static property of plasma etched Kapton film. This system includes a mode of compulsory application on corona discharge. Corona discharge is carried out through needle electrode under atmospheric pressure.

Charge dissipation velocity can be indicated as value of half decay time. Setting up test condition is as follows. The distance between electrode and plate marks was 150 mm, plate spine velocity was 1500 rpm, corona discharge voltage was ±7 kV, application time was 30 second, and temperature was fixed in the range of 20 ± 5 °C.

Particularly, this test has been executed either summer or winter. Where the humidity and temperature conditions of season are 60 ± 2 % RH and 30 ± 3 °C for summer and 20 ± 2 % RH and 20 ± 3 °C for winter. Also, experiment has been carried out under the condition of 30 ± 2 % RH and 25 °C for spring. Measurement of saturate voltage on static potential was ignored, because of heterogeneous accumulation of current in corona discharge field.

Results and Discussion

Considering the removal of electrostatic potential buildup the cold plasma etching can be an effective technology among various discharge method.

Figure 1 represents the relationship between treating time and half decay time of Kapton film treated with oxygen or Ar plasma.

Measurement of static charge potential was carried out in 5 minutes after O_2 plasma in the atmosphere of summer season. This plot shows rapid decline of half decay time

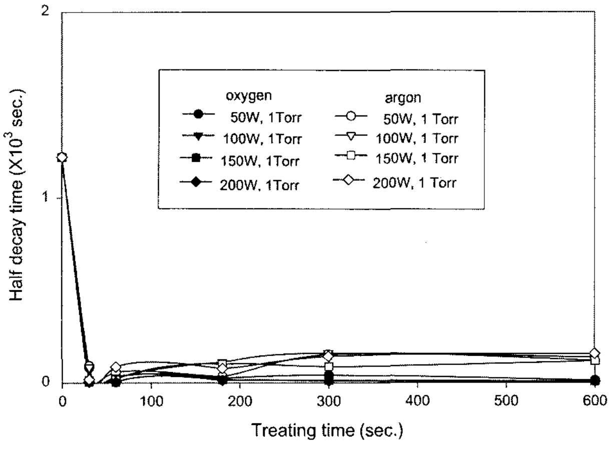

Figure 1. Relationship between treating time and half decay time of Kapton film treated with plasma of argon and oxygen in summer season.

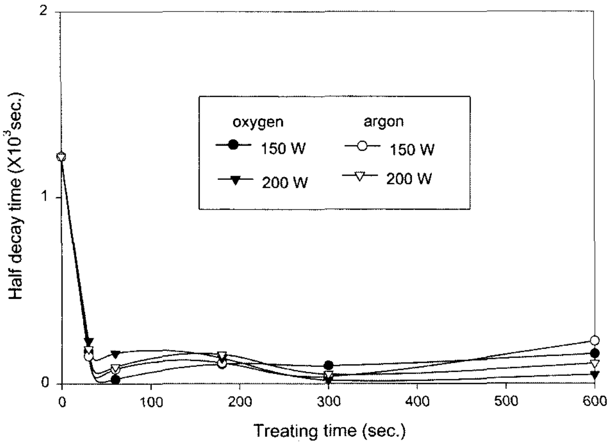

Figure 2. Relationship between treating time and half decay of Kapton after 30 days in summer season.

even at the treatment time of below 1 minute.

The difference of two curves was appeared at about 100 second and all of values showed rapid decrease just under 60 second treatment only. Oxygen plasma is more effective than argon plasma in attenuation of electrostatic potential. This may be due to the induction of hydrophilic functional groups, such as hydroxyl, carbonyl and carboxyl, which cause increase in electrical conductivity against hydrophobic polymer surface. On the contrary, in the case of inert Ar plasma, the formation of free radicals predominates over the interaction of plasma phase before functional group implantation. Therefore, the principles on dissipation of static charge potential can be explained as the generation of several hydrophilic functional groups. Especially, the generation of radical is very important in non-reactive Ar plasma.

Figure 2 represents the changes of half decay time at 30th day after plasma initial irradiation. Static charge measurement was carried out in 30 days after O_2 plasma irradiation in the atmosphere of summer season.

Compared with Figure 1, it showed a little retardation of dissipation speed for static charge accumulation. It means the increase of half decay time for static-charge saturation.

Figure 3 represents half decay time of saturated charge potential on sample when treated with O_2 cold plasma. Static charge potential was measured in 5 minutes after O_2 plasma ignitable irradiation in the atmosphere of winter season.

Value of untreated sample measured in winter season was higher than that of measured in summer season. Half decay time of Kapton film treated with oxygen or Ar plasma showed rapid decrease and reached nearly 0 in summer season, but it dropped until more than 1,000 second in winter season.

Figure 4 showed the relationship between plasma treating time and half decay time of saturated static charge. Static charge dissipation was measured in 5 minutes after Ar plasma irradiation in the atmosphere of winter season.

Comparing these curves with Figure 3 curves, the reactive O_2 plasma is much more effective than Ar plasma in elimination of static charge potential.

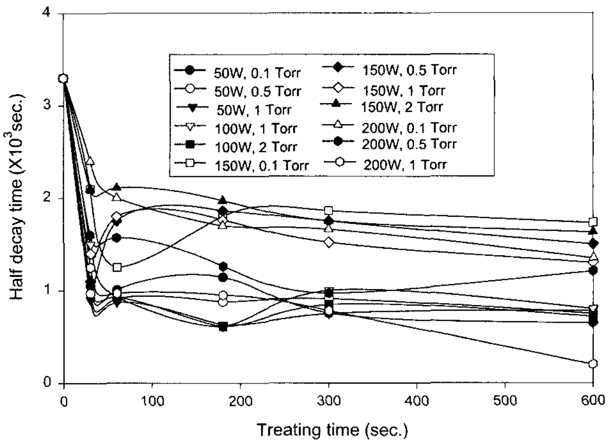

Figure 3. Relationship of treating time versus half decay time of Kapton treated with oxygen plasma in winter season.

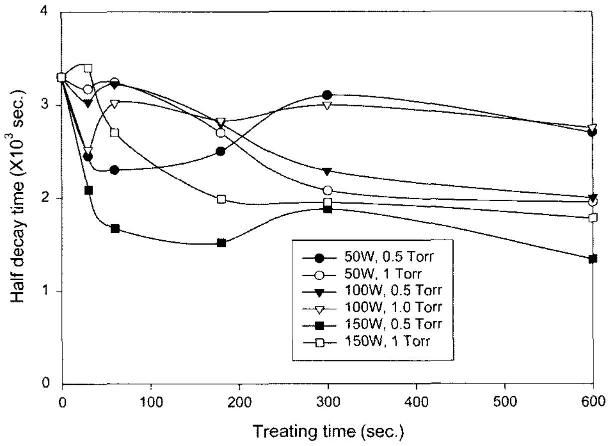

Figure 4. Relationship of treating time versus half decay time of Kapton film treated with argon plasma in winter season.

Nevertheless, remarkable phenomena can be detected in case of Ar plasma treatment. Component of oxygen atoms has grown progressively in spite of nonexistence of O_2 particles under Ar plasma treatment. It can be explained that free radical may interact with atmospheric O_2 gases originated from atmosphere after treatment.

In addition, the O_2 or hydrophilic functional groups cause adsorption of moistures on hydrophobic film surface. This phenomena have previously reported in many articles lately.

Some values of increased electrical conductivity and reduced dielectric ratio on over most surface have been obtained by absorption of moisture as a function of those functional group and residual oxygen.

We can deduce that realization of anti-static effect is caused by radicals and hydrophilic functional groups.

Figure 5 indicates a series of changes for half decay time according to irradiation time. Sample film was treated with

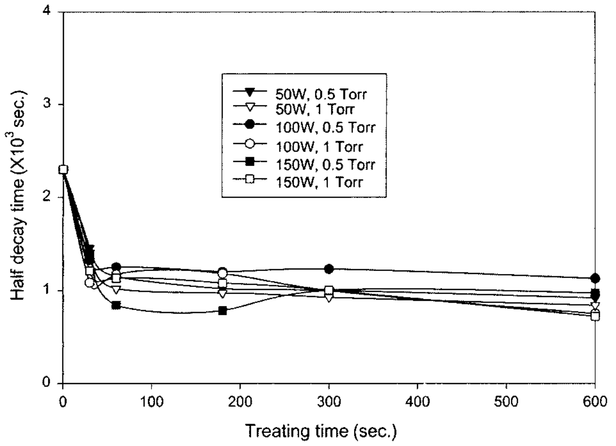

Figure 5. Relationship of treating time versus half decay time of Kapton film treated with argon plasma in spring season.

plasma of Ar. Measuring half decay time of static charge was carried out in 5 minutes after Ar plasma etching in spring season.

Value of untreated sample ranks with 2,300 second but it drops more than 1,000 second rapidly just as prompt plasma treatment. In contrast to the relative humidity of 20 %, these plots represent consistency, showing a distinctive attenuation of decay time on dry winter season.

From this result, damp season is more effective than dry cold season for realization of anti-static effect.

Generally speaking, antistatic effect of plasma etched sample has deteriorated with time. This reduction can be originated from the bond rotation of segments that contain hydrophilic functional groups.

This phenomenon can be reversed depending on external changes. So, it is closely related to continuity of plasma effect.

The hydrophilic functional groups move into core of polymer when they encounter hydrophobic groups. It is often referred to repulsion and rotational motions.

The half decayed time of irradiated sample has not changed significantly even after 30 days.

Conclusion

The O_2 and Ar cold plasma have been irradiated on hydrophobic Kapton film surface to remove electrostatic potential. We obtained remarkable improvement of antistatic property by cold plasma treatment which summarized as follows.

1) The etching technology of O_2 cold plasma is more effective than that of Ar plasma in removing electrostatic potential.

2) Cold plasma treatment executed in damp season removes static charge more efficiently comparing with dry winter season. Also, we can deduce conclusively that the moisture absorption due to hydrophilic group can cause less accumulation of static charge potential, which caused fast dissipation of static electricity on film surface.

The half decayed time of irradiated sample did not show distinctive changes even after 30 days under summer season.

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