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Perspective of industrial application of high pressure and low temperature plasma.

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Abstract

An out line of the material process with using the atmospheric pressure glow plasma is described as follows; (1) TiO powder coating with SiO₂ (2) Surface treatment of Fluorinated polymers and (3) Surface cleaning of electronic circuit board with using splay type.

1. Introduction

We previously reported that surface treatment and thin film deposition could be carried out with the atmospheric pressure glow plasma (APG) process. M. Kogoma and coworkers have developed the APG process since 1987^{1, 2)}. This approach can reduce apparatus costs and can also be applied to high vapor pressure substances such as gum, powders and bio-materials³⁾. A stable glow discharge at atmospheric pressure requires: (i) The use of helium or argon for dilution of carrier gas; (ii) The insertion of a dielectric insulator between the electrodes in the discharge gap; (iii) The use of a high frequency, at least higher than 1kHz. Normally the processing rate is dependent on the applied frequency because the discharge current should have one or two pulses per half cycle in low frequency APG discharge^{2, 4, 5)}. However, the temperature rise inside the discharge

zone due to the increase of the discharge frequency restricts the maximum applied frequency.

In the symposium, we will present some applications to the industry as shown in bellow.

1. 1 Powder coating

Some kinds of pigments that are used for cosmetics give rise to a skin irritation problem when they contact the skin directly. To solve this problem, it is more desirable to deposit a silica thin film, which has chemical stability and doesn't spoil the tones of the pigment owing to its colorless transparency. Some previous studies reported powder treatment with glow plasma at a low pressure. However, since handling of powders is difficult, we consider that treatment of powders with low-pressure glow plasma is impractical. So we tried to use atmospheric pressure glow plasma for powder treatment⁴⁾. In this study, we used two kinds of powder samples; TiO for black pigments

of cosmetics. The powder is deteriorating easily by heating or attack of active species such as oxygen radicals in the plasma. Therefore, it needs a low temperature (less than 100 °C) treatment and some ways to protect them from active species or oxidation in the plasma. Then, we investigated and developed silica and TiO₂ deposition methods for each pigment.

1.1.1 Experimental

The diameter of powder particles is few hundred nm. The powders were pre-treated with TEOS (tetraethoxysilan) - ethanol mixture aerosol to adsorb TEOS on the surface of particles. After drying the ethanol, the powder is oxidized in the plasma reactor. The schematics of discharge reactor have shown in the recent report⁴⁾.

The powder is supplied on the top of ultra sonic vibrating horn, and then spattered to the plasma zone with gas flow. The aggregated particles are going to the single particles with the ultra sonic vibration. After treating in the plasma, the powder is accumulated in the powder pool and recycled in the plasma system to have desired deposition. The discharge conditions is as follows: discharge frequency : 13.56MHz, power : 300W, treatment time : 15min, O₂/He gas flow rate : 10ml/3000ml

1.1.2. Results and discussion

1) TiO powder treatment with TEOS in the O₂/He plasma

Figure 1 shows the ESCA spectrum of treated TiO particles oxidized in the O₂/He plasma. In the figure, we can find Si⁴⁺ peak, which is assigned as SiO₂.

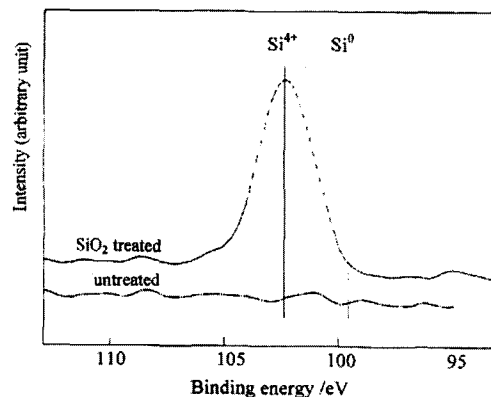


Fig. 1 shows the ESCA spectrum of treated TiO particles oxidized in the O₂/He plasma. In the figure, we can find Si⁴⁺ peak, which is assigned as SiO₂.

Figure 2 shows Si and Ti elemental concentration ratios measured by ESCA as a function of SiO₂ concentration measured by XRF. In the figure, Si/Ti is directly proportional to the SiO₂ concentration. Normally, XRF signal intensity is in proportion to the total concentration of deposited material. On the other hand, ESCA peak heights only show the surface concentration of the elements. So, in this case, SiO₂ is deposited on the particle surfaces with good homogeneity. The amount of deposited SiO₂ can be controlled by the concentration of TEOS in the solvent ethanol at the adsorbing process.

At the dispersibility test in water, because of the particle surface charging, untreated TiO powder sunk immediately in to the de-ionized water. But, treated TiO powder did not sink until longer than few ten hours. For the application, when the stain process is carried out on a substrate, the dispersibility of fine powder in water is very important factor. It seemed that after covered with SiO₂, ξ potential of the particle surfaces are changed from that of TiO (0 volt at pH 6) to SiO₂

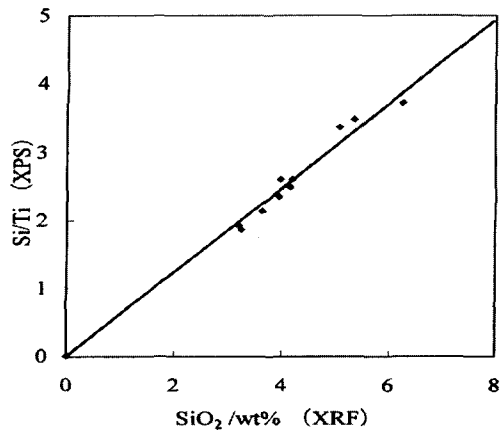


Fig. 2 shows Si and Ti elemental concentration ratios measured by ESCA as a function of SiO_2 concentration measured by XRF.

(0 volt at pH 3). So, the SiO_2 coated particles dispersed in neutral water (pH 7).

In the pigments for cosmetics, which is coated with TEOS, uncompleted dissociation residue give bad smell and also irritate the human skin. In figure 3, surface residual carbon concentration of treated TiO is decreased with plasma oxidation.

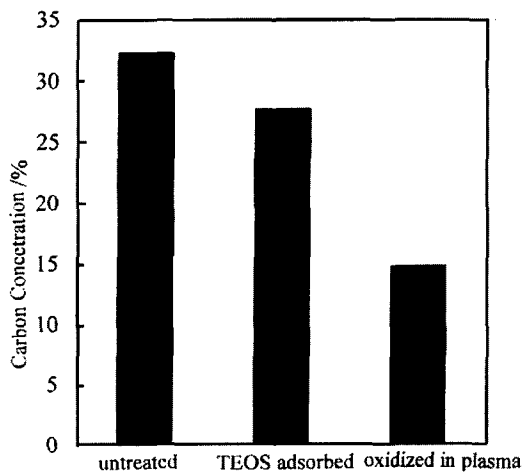


Fig. 3 In figure 3, surface residual carbon concentration of treated TiO is decreased with plasma oxidation.

Figure 4 shows the ESCA spectrum of unheated and heated ($450\text{ }^\circ\text{C}$) TiO. In comparison of both spectrums, the peak of Ti^{2+} is lost in heated spectrum. The naked TiO powder will be easily oxidized in the high temperature stain process on the substrate of electronic display panel and change the color from black to white. After coated with silica, the powder did not change the color by heating in $450\text{ }^\circ\text{C}$, 30 min.

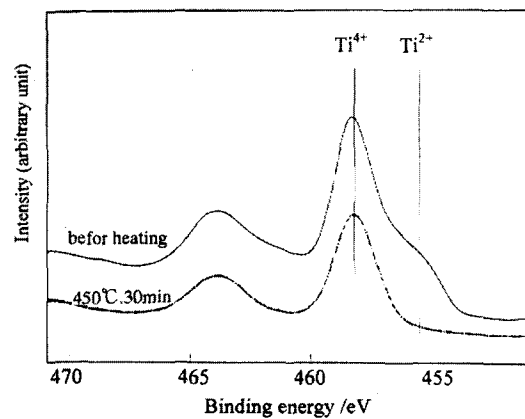


Fig. 4 Figure 4 shows the ESCA spectrum of unheated and heated ($450\text{ }^\circ\text{C}$) TiO.

1. 2 Surface treatment of Fluorinated polymers⁴⁾

Fluorinated polymers, such as polytetrafluoroethylene (PTFE), have been used as typical inert materials for many situations, such as packaging materials. They, however, have a big problem: the difficulty of the adhesion. Some agents, which contain metallic sodium, are often used for surface treatment of these polymers to improve the adhesion. However, this treatment needs a large amount of cleaning water and the disposal of much waste fluid. Moreover, their surfaces become blackish through the wet treatment. So a new

dry process instead of the wet treatments has been desired.

1.2.1 Experimental

For the treatment, we used the capacitive coupled plasma chamber shown in Fig. 1. The fluorinated polymer samples used in this study were PTFE (NILACO Co., Ltd., $t=0.125$) and PFA (perfluoro-alkyl group) (NILACO Co., Ltd., $t=0.05$) films, whose sizes were 20 mm \square 40 mm. The plasma was generated with a 100 kHz power supply at 50 W. We tried to use two treatment methods: 1) A sample film was treated with He plasma (50 W) for 10 minutes. Then it was soaked in 5% TMB (trimethoxyborane)/*n*-butanol solution and was dried in air. Lastly, it was treated with 0.5% H₂/He plasma. 2) A sample was treated with 0.13 %TMB/1% H₂/He plasma. TMB was supplied via bubbling of TMB by He gas. Hereafter, we call these methods "Abs-borane" and "TMB/H₂/He plasma", respectively.

1.2.2 Results and discussion

Table 1 shows the plasma treatment conditions. Fluorinated polymers have low adhesive strength because their surfaces are very flat and are covered with fluorine atoms.

Figures 2 (a) - (b) show the variation of the atom number ratios of F/C and O/C observed

Table 1 The plasma treatment conditions.

Discharge frequency	100 kHz
Discharge power	50 W
Distance between the electrodes	5 mm
Treatment time	0.5~10 min
Flow rate of He	2000 cm ³ min ⁻¹
Flow rates of H ₂	10, 20 cm ³ min ⁻¹
Flow rate of He (for bubbling)	20 cm ³ min ⁻¹

from XPS. Though boron atoms were detected by XPS, B/C values were less than 0.1, and the relation between B/C and peel force was not found.

Thus, we neglected boron on the treated sample surface in this study. And although PFA samples ought to contain one oxygen atom in their unit structure, we found only quite small the O_{1s} peak and a slight peak assigned to C-O bond in the C_{1s}. So O/C value of untreated PFA in Fig. 2 (a) is near to zero; this value was approximately same as that of untreated PTFE, which was slight oxidized in the atmosphere. The reason of this result was not clear.

Figures 5 (a) - (b) show the results of peel tests of PFA and PTFE, respectively. The adhesive forces of PFA and PTFE treated by plasma were about 230 and 270 times stronger than the forces of untreated films, whose values were 0.004 and 0.006 kg · 20 mm⁻¹. In addition, the results of PFA showed the higher force values than the controls, while those of PTFE showed lower values. Then we treated PTFE with 0.25% O₂/He plasma, which was the most effective treatment in a previous study⁶⁾. However, the peel force of 0.25 %O₂/He plasma-treated PTFE was lower than

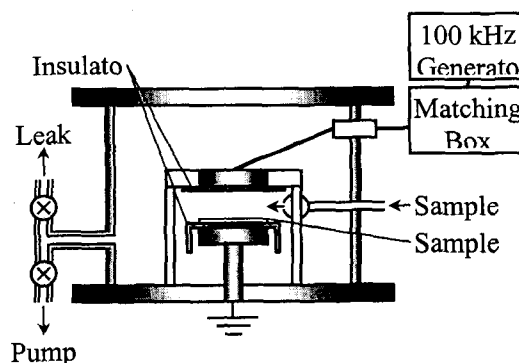


Fig. 5 Schematic diagram of the interior of the capacitive coupled reactor.

that of TMB/H₂/He plasma-treated PTFE. Thus, TMB/H₂/He plasma treatment was the most effective treatment in this study.

1. 3. Surface cleaning of electronic circuit board with using spray type APG reactor⁵⁾

Some organic impurities on the printing wiring surfaces have a bad influence on the metal contacts. The plasma treatment or ashing in a low pressure has very fast treatment to remove such impurities. However to insert this method in to a assembly line in the atmosphere is hardly used. We had already found that Atmospheric Pressure Glow Plasma (APG) had enough ashing rate to remove the organic impurities with using cylindrical spray type discharge reactor to treat small area⁷⁾. Now we propose new type reactor that can treat wider area than that of the recent one.

1. 3. 1 Experimental

The spray-type reactor used in this study, shown in Fig. 1, was a capacitively coupled reactor, comprising two quartz glass plates between the electrodes. The discharge volume could be varied from 3.00 cm³ to 5.25 cm³ by changing the electrode height from 20 mm to 70 mm. The electrode width was 50 mm. We can change the distance between the quartz glass plates from 1.5 mm to 0.5mm. A rectangular slit, of dimensions 0.5 mm × 50 mm, was located at the bottom of the reactor.

The ashing treatments were carried out as follows: O₂ diluted with He (or Ar) was introduced from the top of the reactor and made to pass through the discharge zone, following which it blew over the sample, all at atmospheric pressure. Table 1 shows details of the discharge conditions.

We used a photoresist, OFPR-800 (Novolak Resin, Tokyo Ohka Kogyo), to simulate an organic impurity in this study⁸⁾. The ashing rate was calculated from the resist thicknesses before and after ashing, which were measured with a surface profile measuring system (DEKTAK IIA, Sloan).

2. Results and discussion

First, we examined the relationship between the ashing rate and the gas velocity. The discharge power was adjusted to maintain the power density at values of 100 and 140 Wcm⁻³ for the O₂/He and O₂/Ar mixtures, respectively. Figures 2 (a) and (b) show the variations of the ashing rates as a function of the transit time for different gas flow rates, when using the O₂/He or O₂/Ar mixture, the transit time being calculated from the distance and the gas velocity⁹⁾. Both figures show that the ashing rates decreased exponentially with increasing transit time, and that all the measured data fell on a single straight line plot, even when the gas velocity was changed. This indicates that an increase of the gas velocity merely reduces the transit time. Moreover, the ashing rate at the slit (where the transit time is zero.) was determined by the residence time of gas in the discharge zone and the power density. Therefore, the ashing rate would be raised significantly by increasing only the gas velocity; we thought that the simplest way to achieve this would be by narrowing the slit gap. The slopes of the lines in Figs. 2 (a) and (b) are $-1.1 \times 10^3 \text{ s}^{-1}$ and $-1.3 \times 10^3 \text{ s}^{-1}$, respectively, smaller than those in our previous study, where the respective slopes for He/O₂ and Ar/O₂ mixture were about $-5.0 \times 10^3 \text{ s}^{-1}$ and $-1.9 \times 10^3 \text{ s}^{-1}$ ⁸⁾. Since the drop in the ashing rate

presumably arises from a reduced density of active species, such as oxygen radicals, impinging on the sample surface, this result suggests that processes leading to losses of active species were reduced by changing the reactor structure.

Figure 4 shows a typical spectrum of the O₂/He plasma. Almost all OES peaks can be assigned to helium or oxygen atoms. We have also compared the variations of the emission intensities to those of the ashing rate as a function of the O₂ concentration in the mixture; as shown in Fig. 5, we found that two peaks, assigned to He 3p³P-2s³S (388.8 nm) and O 3d⁵D-3p⁵P (926.5 nm), displayed a variation similar to that of the ashing rate. Although the curves of the emission intensities do not overlap perfectly with that of the ashing rate, the maxima all occur at the same O₂ concentration. Therefore, the optimum ashing rate can be found simply by looking for OES maxima while changing a plasma parameter such as O₂ concentration, a result which confirms the practical value of OES measurements.

3. Conclusion

Atmospheric Pressure Glow (APG) Plasma can treat many kinds of solid materials such as powder, film and fine polymer tube as same situation as in the low pressure plasma. However, the APG

plasma processing is able to use in atmospheric ambience, therefore it has an advantage in the point of view of the industrial application compared with low-pressure plasma.

Referances

1. S. Kanazawa, M. Kogoma, T. Moriwaki and S. Okazaki, *J.Phys. D: Appl. Phys.*, **21**, 838~840 (1988)
2. S. Kanazawa, M. Kogoma, S. Okazaki and T. Moriwaki, *Nuclear Instruments and Methods in Physics Research*, B37/38, 842~845 (1989)
3. Y. Babukutty, R. Prat, K. Endo, M. Kogoma, S. Okazaki and M. Kodama, *Langmuir*, **15**, 7055~7062 (1999)
4. T. Mori, S. Okazaki, T. Inomata, A. Takeda and M. Kogoma, *Proc.9th Symp. Plasma Sci. Mater.* 7(1955)
5. R. Prat, T. Suwa, M. Kogoma and S. Okazaki, *J. Adhesion*, **66**, 163 (1998)
6. K. Tanaka, T. Inomata and M. Kogoma, *Thin Solid Films*, **386**, 217 (2000).
7. K. Taniguchi, K. Tanaka, T. Inomata and M. Kogoma, *J. Photopolymer Sci. Tech.*, **10**, 1, 113 (1997).
8. K. Tanaka, T. Inomata and M. Kogoma, *Plasmas and Polymers* **4**, 4, 269 (1999).