

DECOMPOSITION OF HIGHER ORGANIC COMPOUND IN AN ATMOSPHERIC PRESSURE NON-EQUILIBRIUM PLASMA

Kazutoshi KIYOKAWA, Akihito ITOU, and Kazuo SUGIYAMA*

*Department of Applied Chemistry, Faculty of Engineering, Saitama University,
Shimookubo 255, Urawa. 336. JAPAN*

ABSTRACT

Previously, in trying to prepare perovskite type oxide powders by microwave heating, we found out a non-equilibrium argon plasma is generated around the powders and discharge continues stable at atmospheric pressure. In this study, we tried the plasma decomposition of heat-stable higher organic compound such as palmitic acid which is the principal constituent of the finger fats. It was proved that suitable amount of coexistence of oxygen radicals into the argon flow accelerates the decomposition of palmitic acid. The argon-oxygen mixed gas plasma was able to perform a complete elimination of higher organic compound.

INTRODUCTION

A non-equilibrium plasma, or a cold plasma, is used for the processes of film formations, surface reformings, surface etchings, etc. These processes are generally carried out in vacuum in order to make the stable and uniform plasma. However, from the viewpoint of the industry, as the costs of the vacuum systems and their maintenance are expensive, it is preferred to develop the process of the cold plasma without the vacuum system, that is, an atmospheric pressure cold plasma process.

Recently, several processes of an atmospheric pressure glow plasma have been successively developed using a pair of plate electrodes^[1]. By the way, in trying to prepare perovskite type oxide powders by microwave heating, we found out that an atmospheric pressure argon cold plasma is generated

around the powders and glows in the direction of downstream, and the plasma is kept stable. We have studied this atmospheric pressure cold plasma processes with the aim of the industrial application and have previously reported some instances^[2]. In this study, the plasma decomposition of higher organic compound such as palmitic acid on a glass substrate was examined. The coated glass samples were treated with the atmospheric pressure cold plasma, and OES(Optical Emission Spectrometer), FTIR (Fourier Transform Infrared Spectrophotometer) and AFM (Atomic Force Microscope) were used to evaluate the radicals in the plasma or the plasma cleaning effect.

EXPERIMENTAL

The apparatus used for the decomposition of palmitic acid is shown in Fig. 1. Descripti

ons of each unit were reported in detail previously^[3]. This apparatus consists of a microwave generator, an impedance adjustment unit and an applicator. In the applicator, or the plasma generation unit, a quartz tube (18mm O.D.) was used as the plasma generator. For compare an atmospheric pressure plasma with a vacuum plasma in the same apparatus, the vacuum system could be connected to this apparatus. After one gram of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ powder and the substrate were placed in the generator tube respectively. Ar gas was introduced to the tube. The output power of the microwave was varied within the range of 100–400W. The impedance was adapted in order to increase the efficiency of plasma generation. The three stub tuner was adjusted to minimize the power of reflected wave. When the tuner was adjusted, the periphery of the power attained to the plasma state and the plasma expand to the substrate.

Palmitic acid which has a high heat resisting property was used as an inspection material and it was coated on the glass substrate. For the plasma treatment, Ar, Ar+H₂ and Ar+O₂ gases were used and the mixture ratios were varied. The optical emission of the plasma was measured using the multi-channel type spectrometer, in order to evaluate the existence of radicals in plasma. To

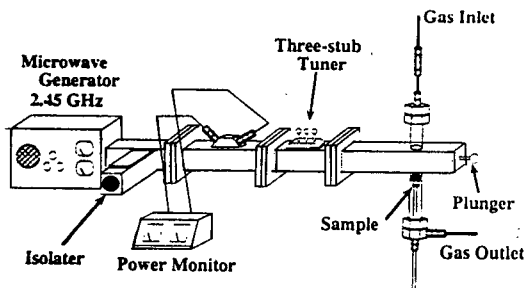


Fig. 1 apparatus

judge the plasma cleaning effect, the substrate was observed with an FTIR spectrometer and the contact angle was measured before and after the plasma treatment. The morphology of the substrate was observed with an AFM, to confirm the cleaning effect.

RESULTS AND DISCUSSION

Figure 2 shows the optical emission spectrum of Ar plasma generated in an atmospheric pressure. This spectrum originated from 4s–4p transition of Ar atom^[4]. In a word, the spectrum of the atmospheric pressure plasma were almost identical to those of the vacuum plasma. Hence, the atmospheric pressure plasma generated by a aforementioned method is a non-equilibrium plasma, or a cold plasma. The optical emission spectra of an Ar+H₂ plasma (Ar:H₂=80:20) are shown in Fig. 3, comparing the atmospheric pressure plasma. Although the peaks of Ar were dominant for vacuum plasma, an H_α (656nm)^[5] peak was much stronger than the

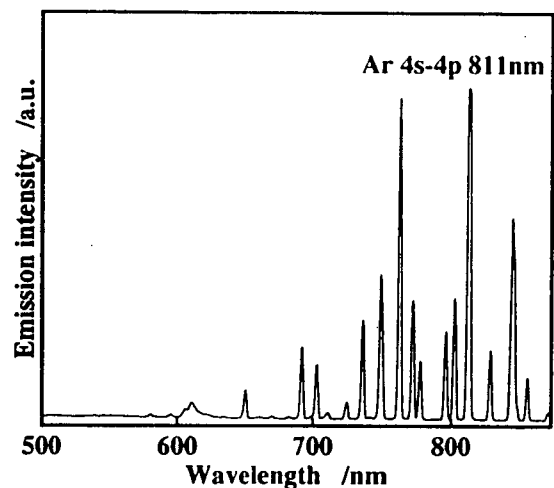


Fig. 2 Emission spectrum of Ar plasma at atmospheric pressure.

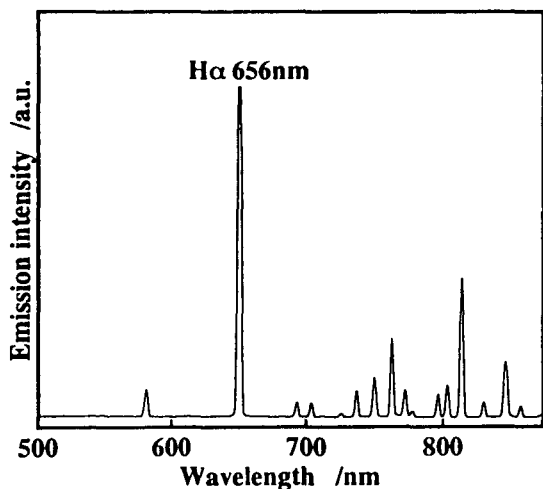


Fig. 3 Emission spectrum of H_2/Ar plasma at atmospheric pressure ; $\text{H}_2/\text{Ar}=20/80\text{vol}\%$.

Ar peak in atmospheric pressure plasma. Figure 4 shows the optical emission spectrum of an $\text{Ar}+\text{O}_2$ plasma ($\text{Ar}:\text{O}_2=80:20$). For the vacuum plasma, the peaks arising from Ar and $\text{O}(777\text{nm})^{[6]}$ were observed. But, for the atmospheric pressure plasma, the peaks of Ar become weak and the peak of O stood out distinctly. These established facts indicate that the excitation efficiency of additive gases in the atmospheric pressure plasma is very high. This phenomenon is not observed very much in the conventional plasma process in vacuum and is peculiar to an atmospheric pressure cold plasma. It is considered that these excitation of additive gases in the atmospheric pressure cold plasma is the resonance one that is caused by an interaction with excited argon atoms.

To this point, the features of the atmospheric pressure cold plasma were mentioned. Practical treatment results are described as under. Table 1 shows the relation between a variety of gas (Ar , $\text{Ar}+\text{H}_2$, $\text{Ar}+\text{O}_2$) and contact angle of the treated substrates. In the ex-

periment, the flux of gases, the microwave power, and the treatment time were fixed at $600\text{ml}/\text{min}$, 300 W and 20 min , respectively.

Table 1 Values of contact angle of the substrates treated with various plasma gases.

In using Ar gas plasma, there was no difference between the contact angles before and after the treatment. In short, the atmospheric pressure cold plasma of Ar had no ability to treat the substrate that had been coated palmitic acid on its surface. When $\text{Ar}+\text{H}_2$ gas was used, the contact angle increased by the treatment. On the other hand, on the case of $\text{Ar}+\text{O}_2$ gas, the contact angle decreased with the treatment. In brief, it was found that the surface contact angle of the substrate can be controlled by means of the atmospheric pressure cold plasma treatment. The IR absorption spectra of the substrates are shown in Fig. 5. Although the absorption resulting from palmitic acid was observed before the plasma treatment, the decomposed with the shape of the spectrum were changed

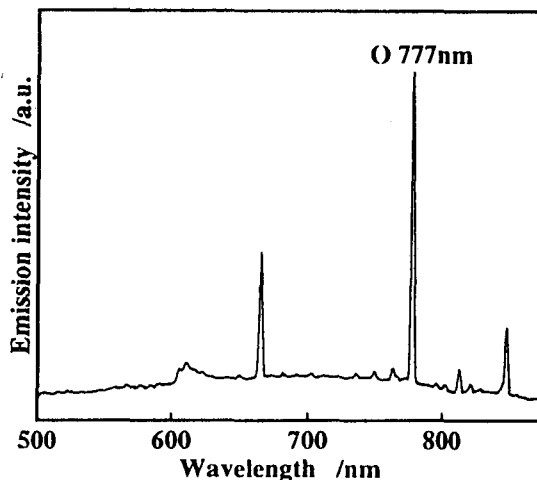


Fig. 4 Emission spectrum of O_2/Ar plasma at atmospheric pressure ; $\text{O}_2/\text{Ar}=20/80\text{ vol}\%$.

Table 1 Values of contact angle of the substrates treated with various plasma gases.

plasma gas	contact angle(degrees)
Ar	60-70
H ₂ /Ar	70-90
O ₂ /Ar	<5
before treatment	60-70

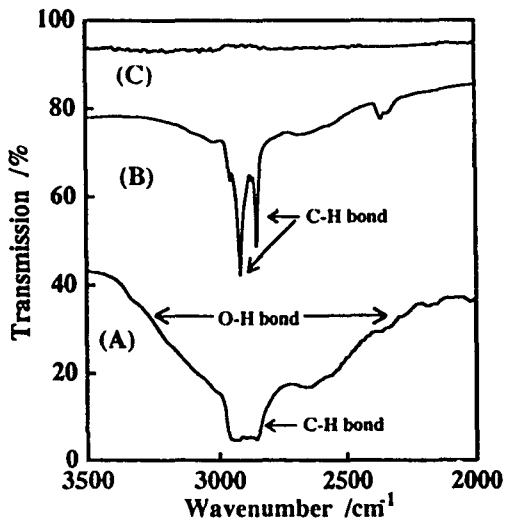


Fig. 5 Refracted IR spectra of palmitic acid coated on the glass substrate
 A : palmitic acid coating substrate
 B : H₂-Ar plasma treated substrate
 C : O₂-Ar plasma treated substrate

after the treatment. With the Ar+H₂ plasma treatment, the broad absorption arising from O-H vanished. Considering the IR absorption spectrum, OES and contact angle measurement results, O-H was Ar+H₂ plasma treatment. Moreover, after the Ar+O₂ plasma treatment, no absorption was observed. The reappearance of this result was confirmed by many experiments. This result demonstrates that the atmospheric pressure cold plasma in Ar+O₂ flow have the high decomposing ability of palmitic acid on glass substrates.

As the decomposition temperature of palmitic acid determined by DTA measurement was over 400°C, it is difficult to decompose palmitic acid by means of general heating methods. In order to corroborate the ability, or a plasma cleaning effect, the surface morphology of the substrate was observed with an AFM. Fig. 6 shows the changes of the surface morphology. For comparison the glass substrate which had been ultrasonically cleaned in an acetone bath was observed. The surface configuration of the glass substrate was rough. However, the substrate coated palmitic acid had a smooth surface. In other words, the existence of palmitic acid on the substrate could be investigated with an AFM measurement. Then the plasma treated subst-

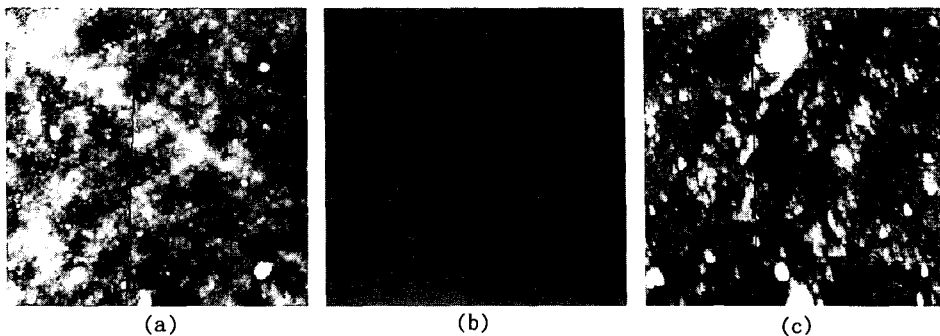


Fig. 6 AFM images and values of surface mean roughness(*Ra*) of the samples
 A : glass substrate, *Ra*=2.21 nm
 B : palmitic acid coating substrate, *Ra*=0.51 nm
 C : O₂-Ar plasma treated substrate, *Ra*=2.44 nm

rate was observed. From this observation, it was found that the surface configuration of the treated substrate with the plasma returned to the same level of the glass substrate's surface. In short, cleaning effect of the atmospheric pressure plasma was ascertained in the view point of the surface observation, too.

Fig. 7 shows the effect of the clearance between the substrate and the plasma source on treatment time. It took 20 minutes for a distance of 30 mm to decompose the palmitic acid completely, and the treatment time increased exponentially with increasing the distance.

Subsequently, the relation between the microwave output power and the treatment time was investigated under the condition of fixed substrate position and varied gas ratio of O_2 and Ar. As the result of this experiment, it was confirmed that the treatment time decreased with increasing the microwave output power. Furthermore, the mixture ratio

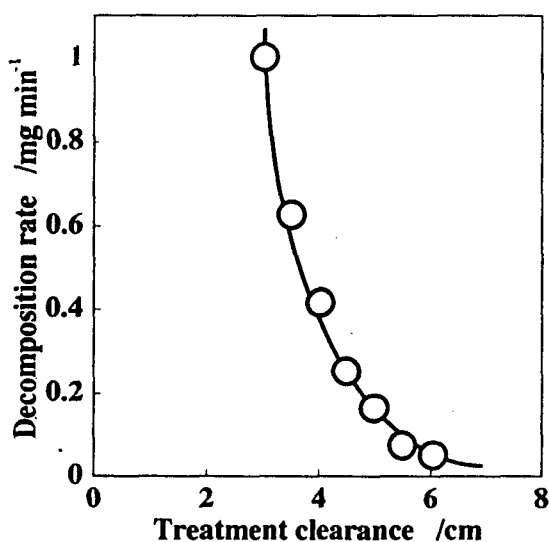


Fig. 7 Relationship between decomposition rate and treatment clearance

had a strong effect on the treatment time. At a microwave output power of 300 W, the treatment time was almost same at any ratios. Below 300 W, the treatment time at high O_2/Ar ratio was shorter than that in low O_2/Ar ratio. But above 300 W, the tendency reversed.

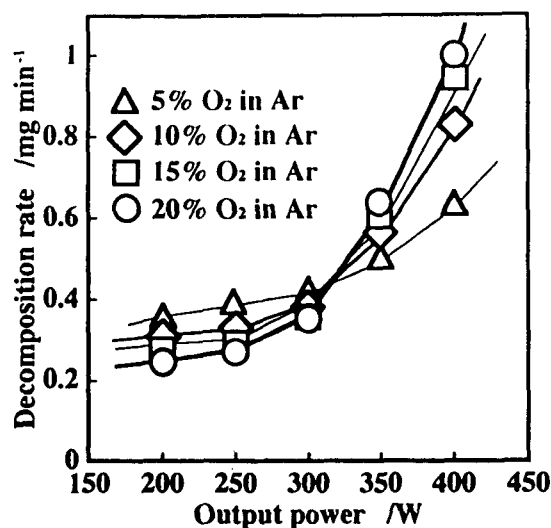


Fig. 8 Relationship between decomposition rate and microwave output power

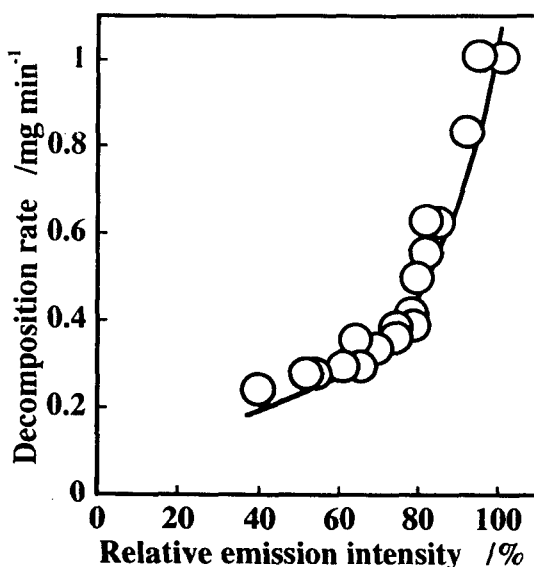


Fig. 9 Relationship between decomposition rate and relative emission intensity

To explain this phenomenon, the axis of abscissas was converted into the optical emission intensity ratio of O and Ar (I_o/I_{Ar}). Consequently, the specific tendency became clear. Figure 9 shows the effect of the optical emission intensity ratio on the treatment time. The treatment time dramatically decreased with increasing the ratio. Hence, it was conjecture that this decomposition was owing to oxygen radicals. It is very important for treatment to excited the additive gas effectively. In short, it was deonstrated that our atmospheric pressure cold plasma is very competent for the treatment of substrates.

CONCLUSION

The findings of the pesent experiments are summarized as follows:

1) By using the atmospheric pressure argon cold plasma which was caused by a microwave irradiation to a perovskite type

oxide powder, the additive gases such as hydrogen or oxygen molecules could be effectively excited.

2) Without damage of glass substrate we succeeded in the complete decomposition of palmitic acid on the substrate by the atmospheric pressure cold plasma under argon and oxygen mixed gas flow.

REFERENCES

1. M. Kogoma, Y. Okazaki, KAGAKU KOGYO, **56**, 232 (1993).
2. K. Sugiyama, OYO BUTURI, **63**, 588 (1994).
3. K. Sugiyama, K. Tsutsumi, T. Matsuda, DENKI KAGAKU, **60**, 1012 (1992).
4. R. W. B. Pearse, "The Identification of Molecular Spectra", P.10, John Wiley & Sons(1976).
5. R. W. B. Pearse, *ibid.*, p.170
6. R. W. B. Pearse, *ibid.*, p.255