

# ADSORPTION MODEL OF CONDENSED ORGANIC COMPOUND ON THE SUBSTRATE FACED TO THE CORONA DISCHARGE TYPE AIR IONIZERS

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## ABSTRACT

In recent years, the control of airborne ions has become one of the important research items of indoor environment. Generally, it is quite difficult to get the sample of airborne ions, because their electric charge might be discharged if they touch any surface. The authors considered that it would be possible to evaluate how many of the sampled molecules had existed as ions in air, if the relationship between airborne ion's concentration and its adsorption rate to the surface was clarified. In this research, absorption of condensed organic compound ions on the substrate faced to the corona discharge type ionizers was studied, and the model for the adhesion rate of ions on charged plate surface was proposed. This model consists of the Langmuir-type surface absorption and the molecular sedimentation models, and the model contains electrostatic diffusion and the electrophoresis. The authors also added the influence of the fragmentation of target molecules to this model. As a result, the predictions estimated by this model agreed well with the experiments.

## KEYWORDS

Adsorption model, Ionized substance, condensed organic compound

## 1. INTRODUCTION

The control of airborne ions has been one of the important research items of indoor environments, especially in the semiconductor manufacturing environments. In recent years, fundamental studies on the behavior of airborne ions is becoming more important to study the effect of negative ions on human health, ion's acceleration effect on gas-particle transition, and so on.

Total ion concentration, which exists in the target field, can be measured with the electric current. However, it is difficult to evaluate how many percentage of specific substance exists as airborne ions. Also, we can't judge if sampled airborne substance existed as airborne ions or not, because the electric charge is already discharged when it was sampled.

The authors considered that it would be possible to evaluate how many of the sampled molecules had existed as ions in air, if we clarify the relationship between the airborne ion concentration and the rate, which ions adhere to the surface. In this research, absorption of condensed organic compound ions on the substrate faced to the corona discharge type ionizers was studied, and the advanced model for the adhesion rate of ions on charged plate surface was proposed.

## 2. MODELING OF ION'S SEDIMENTATION AND ADSORPTION

Absorption of condensed organic compound ions on the substrate faced to the corona discharge type ionizers was studied, and the model for the adhesion rate of ions on charged plate surface was

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proposed. Factors, which affect on the ion's adsorption on the charged surface was shown in Figure 1. Electrophoresis  $V_{dE}$  and electrostatic diffusion  $D_E$  act on the airborne ions in the electrostatic field, and also the effect by the molecular and turbulent diffusion ( $D_M$  and  $D_T$ , respectively) should be considered. Assuming the concentration of airborne ions  $n_0$ , ion's sedimentation flux  $J_0$  to the surface is shown in the following formula.

$$J_0 = (D_T + D_M + D_E)dn/dz|_{z=0} + V_{dE} \cdot n_0 \tag{1}$$

$dn/dz|_{z=0}$ : Gradient of ion's concentration on the surface

If the electric force doesn't act on the substance, sedimentation flux is described as following  $J_1$ .

$$J_1 = (D_T + D_M)dn/dz|_{z=0} \tag{2}$$

This model was proposed by Kagi and Fujii (Figure 2), and it showed a good agreement with experiment. The authors added the factors of electrophoresis  $V_{dE}$  and electrostatic diffusion  $D_E$  to the model. These factors are described as follows.

$$D_E = \kappa TB = \kappa TZ / Ne, \quad V_{dE} = NeEB = ZE \tag{3}$$

$\kappa$ : Boltzmann constant,  $T$ : Absolute temperature,  $B$ : Kinetic mobility,  
 $Z$ : Electric mobility,  $N$ : Unit number of charge,  $e$ : Electric charge of electron

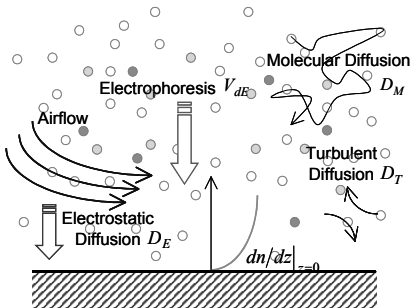
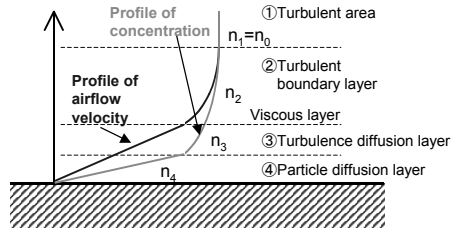
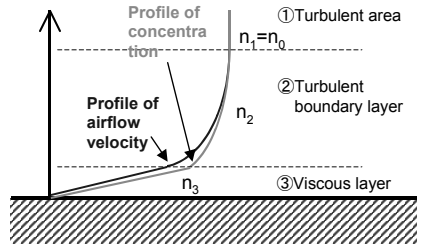


Fig.1 Behavior of ions near the surface



a) Model for particle sedimentation  
 Fujii, Xie and Kim (1989)



b) Model for molecular sedimentation  
 Kagi and Fujii (2000)

- surface molecules are already adsorbed : 100% reflected
- surface nothing are adsorbed : to be adsorbed with coefficient S
- already adsorbed molecules : to be desorpted with coefficient K

Fig.3 Adsorption and desorption based on Langmuir's model

Fig2. Previous models for particulate and molecular sedimentation

Here, the authors simply assumed that airborne ions were consisting of macromolecules such as condensed organic compounds with negative or positive charge. We considered the behavior of ions reached to the surface should be same with that of uncharged organic compounds. Physical or chemical absorption of organic compounds on the surface is described using the Langmuir-type model (Figure 3). Adsorbed molecular concentration  $n_s(t)$  on the surface was modeled using the sticking-probability  $s$ , leaving-probability  $k$ , and saturated concentration  $n_a$  of molecules, and it was described as the function of exposure time.

$$n_s(t) = \frac{sJ_1(t)}{\frac{sJ_1(t)}{n_a} + k} \left[ 1 - \exp\left\{-\left(\frac{sJ_1(t)}{n_a} + k\right)t\right\}\right], \quad J_1(t) = sn_0V_d - \left(\frac{sn_0V_d}{n_a} + k\right)n_s(t) \quad (4)$$

### 3. CALCULATION OF ABSORPTION RATE OF IONS TO THE SURFACE

When the surface of substrate was charged in a high voltage, such as more than 100V, the term of  $V_{dE}$  becomes the most significant factor in formula (1). Therefore, largest absorption rate is obtained when the surface is charged at opposite voltage to the target ions.

Figure 4 shows the prediction of absorption rate obtained using formula (1) and (4). Adsorption rate was compared in different charging voltages and in different concentrations of airborne ions.

In the beginning of exposure, concentration of adsorbed substance on the surface showed the tendency, which increased exponential to the time. After some exposure time, surface concentration was saturated, and it became to show less dependency on the voltage or concentration of airborne ions. The time to reach to the saturation became shorter according to increase in the charging voltage or in the concentration of airborne ions.

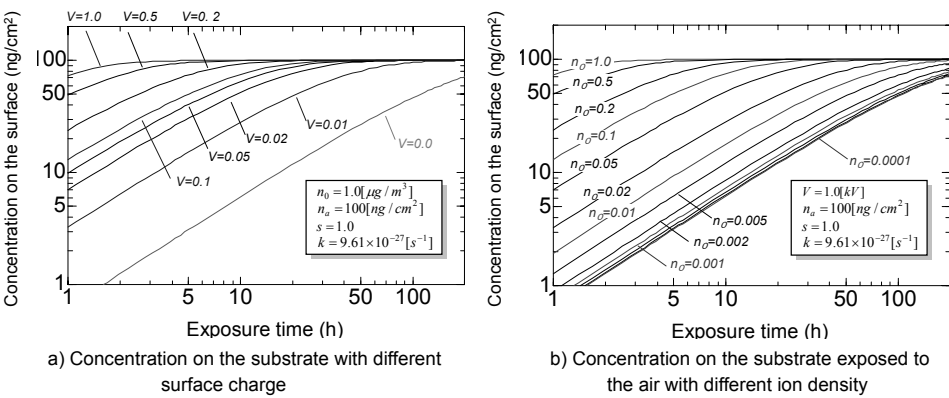


Fig.4 Simulated concentration of adsorbed condensed organic compound on the surface

## 4. COMPARISON WITH THE EXPERIMENTS

Experiments were performed using TCEP (Tris (2-chloroethyl) phosphate) ions. Negative or positive ion's flux to the surface was increased monotonously according to the voltage of the surface, and concentration of TCEP on the surface was grown in a same tendency when the absolute value of voltage was relatively small. Result of present model well agreed with experiment.

However, concentration on the surface was decreased contrary to the surface voltage, if the absolute value of voltage exceeded 10kV. This means that the electric current was not transported by TCEP, but it was transported by another substance.

Figure 5 shows the result of API-MS analysis on a gas compound with TCEP, before and after the gas was exposed to high voltage. We found that a wide range of fragment would be generated during the gas was exposed to high voltage. We thought that airborne TCEP ions around the substrate were split into the fragment because of high voltage, and that it affected to the absorption rate of TCEP on the surface. We thought that airborne TCEP ions around the substrate were split into the fragment because of the high voltage surface, and that it affected to the TCEP's concentration on the surface.

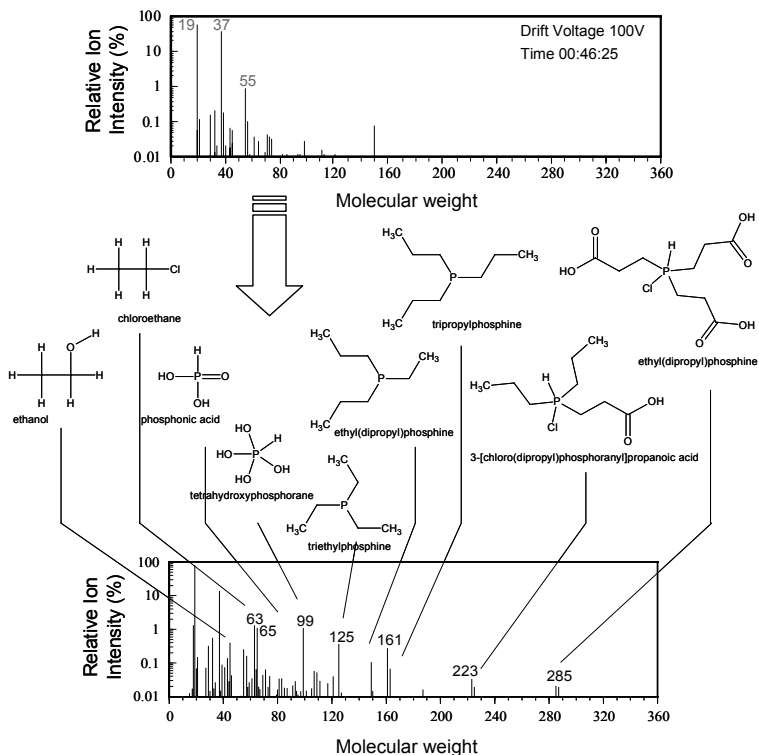


Fig.5 Detected ions before (upper) and after (lower) the gas compound with TCEP was exposed to high voltage -Identified fragment ions are shown in lower graph-

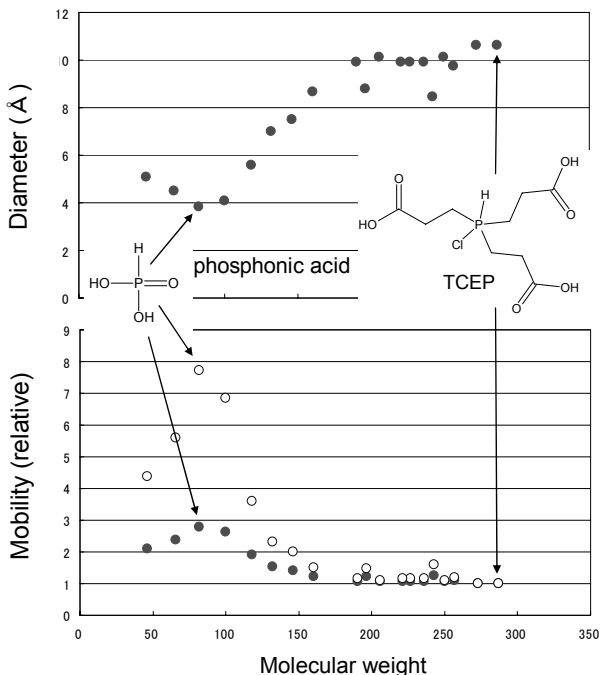


Fig.6 Molecular scale (diameter obtained from MO simulation) and Mobility of fragment ions

## 5. A STUDY ON THE MOBILITY OF FRAGMENT IONS

Material element of each fragment ion was studied. Figure 5 also shows the result. It seems that fragment ions having molecular weight larger than 100 are the wreckage of TCEP ions, and the others seems the parts split from TCEP ions. These fragment ions have larger mobility, because their molecular weight is smaller than original TCEP ions. It is easy to predict that many part of electric current will be transported by these fragment ions. Electrostatic mobility of the ion is described as follows.

$$Z = NeC_c / 3\pi\eta d \quad (5)$$

$C_c$ : Cunningham coefficient,  $\eta$ : Viscosity of field gas,  $d$ : Diameter of the ion

Mobility and diameter of the ion have following relationship.

$$Z \propto (1 + \lambda/d)/d \propto (1/d + \lambda/d^2) \quad (6)$$

$\lambda$ : Mean free path

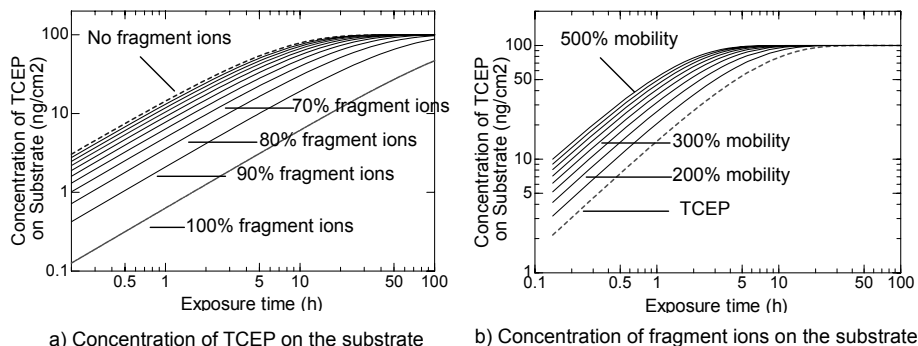


Figure 7 Concentration of TCEP and fragment ions on the substrate, simulated using the model with the effect of fragment ions is considered

Diameters of ions were calculated from MO simulation, and mobility of these fragment ions in electrostatic field were compared with that of original TCEP ions. Figure 6 shows the result. Mobility of fragment ions, especially having smaller molecular weight less than 150, becomes much larger than that of TCEP.

Electric current is transported both by TCEP ions and fragment ions, in the field, which includes both of them. However the percentage of electric current transported by fragment ions will be increased, when the concentration of fragment ions is large or fragment ions have larger mobility.

Absorption rate of TCEP and fragments on charged surface were studied using the proposed model. Absorption rate of TCEP becomes small, when the fragment ions having high concentration, or having a large mobility. Absorption of TCEP on the surface charged higher than 10kV was estimated considering the effect by the fragment ions. The result agreed well with the experimental tendency.

## 6. CONCLUSIONS

Absorption of condensed organic compound ions on the substrate faced to the corona discharge type ionizers was studied, and the advanced model for the adhesion rate of ions on charged plate surface was proposed. This model consists of the Langmuir-type surface absorption and the molecular sedimentation models, and the model contains electrostatic diffusion and the electrophoresis. The authors also added the influence of the fragmentation of target molecules to this model. As a result, the predictions estimated by this model agreed well with the experiments.

## REFERENCES

1. S. Fujii, G. Xie, and K. Y. Kim (1989) "Modelling of aerosol particle deposition in unidirectional flow cleanrooms", J. of Architecture, Planning and Environmental Engineering, No.397, 30-36 (in Japanese).
2. N. Kagi and S. Fujii (2000) "Theoretical study on adsorption mechanisms of gaseous matter from cleanroom air onto silicon wafer surface", J. of Architecture, Planning and Environmental Engineering, No.530, 67-71 (in Japanese).

3. W. C. Hinds (1982) "Aerosol Technology", John Wiley & Sons, Inc.
4. Y. Suwa, S. Fujii, N. Kagi, H. Tamura, et.al. (2005) "Simultaneous counting and sampling method of ionized substances in the air", Proc. of 22th. Annual Meeting of JAAST, 211-212 (in Japanese).
5. Y. Suwa, S. Fujii, N. Kagi, H. Tamura, et.al. (2006) "Adsorption model of ionized condensed organic compounds to the surface of charged plate", Proc. of 24th. Annual Meeting of Contamination Control, JACA, 197-199 (in Japanese).
6. N. Kagi, H. Tamura, T. Taira, et.al. (2006) "TCEP behavior in the air and adsorption on wafer under the corona discharge type air ionizers", Proc. of 23th. Annual Meeting of JAAST, 211-212 (in Japanese).
7. H. Tamura, N. Kagi, S. Fujii, et.al. (2005) "Influence of the ion to the gaseous organic substance in indoor environment (part.1), -Experiment of wafer exposure under the corona discharge type air ionizer-", Proc. of 23th. Annual Meeting of Contamination Control, JACA, 225-227 (in Japanese).
8. H. Tamura, N. Kagi, S. Fujii, et.al. (2006) "Behavior on adsorption of condensed organic compound to the charged wafer", Proc. of 24th. Annual Meeting of Contamination Control, JACA, 5-6 (in Japanese).
9. Y. Suwa, H. Tamura, N. Kagi, S. Fujii, et.al. (2006) "Adsorption of condensed organic compound on the wafer faced to the corona discharge type air ionizer (part 2) -Adsorption model considering the influence of fragment ions and its comparison with the experiment -", Proc. of 23th. Annual Meeting of JAAST, 257-258 (in Japanese).
10. Y. Suwa, H. Tamura, T. Taira, N. Kagi and S. Fujii (2007) "Adsorption model of ionized condensed organic compound to the surface of charged plate (part2)", Proc. of 25th. Annual Meeting of Contamination Control, JACA (in Japanese).
11. G. A. Bird (1994), "Molecular Gas Dynamics and the Direct Simulation of Gas Flows", Oxford Science Pub.