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Adsorption and Desorption Rate of Multicomponent Organic Species on Silicon Wafer Surface

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The time-dependent change in concentrations of organic species on a silicon wafer surface, the fruit basket phenomenon, is studied using a rate theory for a multicomponent system consisting of a large number of organic species. The theoretical model and the rate parameters evaluated in this study are shown to be effective for predicting the trend and the abundance of nine organic species on the silicon wafer surface in a clean room, because the trend in organic species are classified using the desorption rate constant and because their concentrations in a steady state have a clear relationship with the ratio of the adsorption rate to the desorption rate constant.
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The presence of organic hydrocarbon molecules adsorbed on a silicon wafer surface is widely known to cause a serious problem[1-7] of airborne molecular contamination in the advanced electronic device fabrication process. In order to achieve a sufficiently clean silicon wafer surface, two kinds of studies are needed. The first is for clarification of behavior and the influence[8-12] of the organic species existing on the silicon wafer surface. The second is for measuring and controlling the concentration of the organic species in the clean room air, since these organic species are considered to be mainly adsorbed from the clean room air[8,11,12] onto the silicon wafer surface.

Various organic species currently known to exist on the silicon wafer surface[8-11] show a time-dependent change in their concentrations on the silicon wafer surface, which is called the fruit basket phenomenon.[8,11,13-16] Some organic species rapidly show a peak in their surface concentration on the silicon wafer surface; it decreases later, indicating gradual replacement by the other organic species. Therefore, organic species seem to compete for the adsorption sites on the silicon wafer surface. The fruit basket phenomenon has been discussed from various viewpoints, such as the condition of the silicon wafer surface,[8] the heat of adsorption and vaporization,[8] the boiling point of the organic contaminant,[16] the polarity of the silicon surface,[16] the sticking probability, and the sticking coefficient.[11,17,18] However, an appropriate model for the fruit basket phenomenon has not been developed, due to the lack of desorption concepts.

In order to describe the decrease in a manner similar to the increase in the concentration of the organic species on the silicon wafer surface, the rate of the desorption and the adsorption should be simultaneously taken into account. Therefore, in our previous study,[19] the mechanism of the fruit basket phenomenon has been discussed using the model of multicomponent organic species adsorption-induced contamination (MOSAIC), which is an application of rate theory accounting for the adsorption and the desorption of organic species on the silicon wafer surface. The influence of the condition of the silicon wafer surface was also evaluated using the MOSAIC model.

Since our previous study[19] discussed the fruit basket phenomenon limited for a small system composed of the three organic species, such as propionic acid ester, siloxane (D9), and di(2-ethylhexyl)phthalate (DOP), an additional study is expected to use a larger multicomponent system. This is because the fruit basket phenomenon is considered to occur due to a great number of organic species. Additionally, as predicted in our previous study,[10] the rate parameters in the MOSAIC model should have a relationship with the behavior of the increase and the decrease in the surface concentration of the organic species. Here, it is fortunately noted that Sakamoto *et al.*[20] recently reported the time-dependent behavior of nine airborne organic molecular contaminants on the silicon wafer surface exposed in a clean room air. The MOSAIC model should express their measurements.

Therefore, in this study, the fruit basket phenomenon in a large multicomponent organic species system is studied using the MOSAIC model to clarify the airborne molecular contamination. For this purpose, the time-dependent behavior of nine organic species reported by Sakamoto *et al.*[20] is evaluated using the MOSAIC model. The entire time-dependent behavior of the surface concentration of organic species is shown to have a relationship with the rate parameters in the MOSAIC model. This study shows the applicability of the MOSAIC model to the large multicomponent system, as an important step for validating this model and for achieving a contamination-free silicon surface in the future.

MOSAIC Model

The MOSAIC model used in this study follows our previous report.[19] The MOSAIC model takes into account the following five assumptions for describing the fruit basket phenomenon of various organic species on the silicon wafer surface.

1. There is no interaction between any organic molecule in the gas phase and on the silicon wafer surface, such as a chemical reaction, adduct-formation, an aggregation and condensation, under the environment which has a very small concentration of organic species.

2. The organic molecules are adsorbed on the silicon wafer surface due to the forces[21,22] between the organic molecules and the silicon wafer surface, such as the van der Waals interaction and the electrostatic charges.

3. The adsorption rate of the organic molecule of species i is proportional to its concentration in the gas phase and is also proportional to the difference between the surface concentration of the total adsorbed organic species and its larger limit. When the silicon wafer surface is sufficiently covered with organic molecules, no additional organic molecule can be adsorbed.

4. The desorption rate of the organic molecules of species i is proportional to its concentration on the silicon wafer surface.

5. The amount of each organic species and that of the larger limit of the total organic species on the silicon wafer surface are evaluated using the weight concentration.

Assumptions 1 and 2 indicate that the adsorption rate of the organic molecules on the organic molecules already adsorbed on the silicon wafer surface is negligible.

From these, the time-dependent behavior of the concentration of organic species i on the silicon wafer surface, S_i (kg m^{-2}), is expressed by Eq. 1

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$$\frac{\partial S_i}{\partial t} = (S_{max} - S)k_{ad,i}C_i - k_{de,i}S_i \quad [1]$$

where t is time (s), C_i is the concentration of the organic species i in the gas phase above the silicon wafer surface (kg m^{-3}), $k_{ad,i}$ is the adsorption rate constant of the organic species i to the silicon wafer surface (m^3 kg^{-1} s^{-1}), $k_{de,i}$ is the desorption rate constant of the organic species i from the silicon wafer surface (s^{-1}), S is the concentration of the total organic species adsorbed on the silicon wafer surface (kg m^{-2}), and S_{max} is the larger limit of the concentration of the total organic species adsorbed on the silicon wafer surface (kg m^{-2}). The existence of S_{max} is considered to be acceptable, since Takahagi *et al.*[2] reported that the organic film on the silicon wafer surface has a constant thickness.

Although the measurement of the concentrations of all the organic species on the silicon wafer surface and in the gas phase is the current goal[23] to be achieved, the influence of any unidentified organic species must be taken into account in Eq. 1. Therefore, the amount of adsorbed organic species, which is not clarified in the present calculation, is taken into account as the background concentration, S_{bg} (kg m^{-2}), as described by Eq. 2

$$S = \sum_j S_j + S_{bg} \quad [2]$$

S_i and S_j ($j \neq i$) can influence each other via S in Eq. 1 and 2. S_{bg} is considered to include two kinds of the organic species, that is, (*i*) the organic species remaining after the silicon wafer surface cleaning performed prior to the exposure of the silicon wafer surface to the clean room air, and (*ii*) the organic species, which is not measured, adsorbed from the clean room air during the exposure of the silicon wafer surface to the clean room air. Future development of the perfect cleaning technique of the silicon wafer surface and the measurement technique, which can clarify every surface concentration of organic species, will allow S_{bg} to be eliminated.

Using S_{bg}, S_{max} is written as follows

$$S_{max} = S_e + S_{bg} \quad [3]$$

where S_e (kg m^{-2}) is the effective larger limit of the concentration of the organic species adsorbed on the silicon wafer surface which is taken into account in this study. Therefore, the equation for the calculation in this study is described as follows

$$\frac{\partial S_i}{\partial t} = \left(S_e - \sum_j S_j\right)k_{ad,i}C_i - k_{de,i}S_i \quad [4]$$

Throughout these calculations, the value of C_i can be assumed to be constant for each organic species, since most of the fabrication process of silicon devices is considered to be performed under steady concentrations of the organic species, which are transported onto the silicon wafer surface following the forced air flow and diffusion in the clean room. Therefore, this study evaluates the values of the product, $k_{ad,i}C_i$ (s^{-1}), which allows a discussion of the adsorption rate even when C_i is unknown. The separation of $k_{ad,i}$ from $k_{ad,i}C_i$ will be discussed in our future study.[24]

In general, surface phenomena, such as chemical reactions[25,26] or contamination, must be studied by taking into account the transport phenomena. Since this study does not evaluate the transport phenomena in the gas phase, the rate of adsorption and desorption should be considered as their overall rates which consist of the transport phenomena and the surface process. The overall behavior of adsorption and the desorption in the clean room, obtained in this study, is considered to be effective in discussing the contamination in a closed wafer box.

The last part of this section describes the detail in the calculation in this study. Equation 4 in the finite difference form is solved numerically for each organic species, following the procedure shown in Fig. 1. By means of giving the various values for the rate parameters of $k_{ad,i}C_i$, $k_{de,i}$, and S_e as indicated in Fig. 1, various sets of calculated S_1 values are obtained. The rate parameters of $k_{ad,i}C_i$, $k_{de,i}$, and S_e are determined to give the minimum E, defined as follows

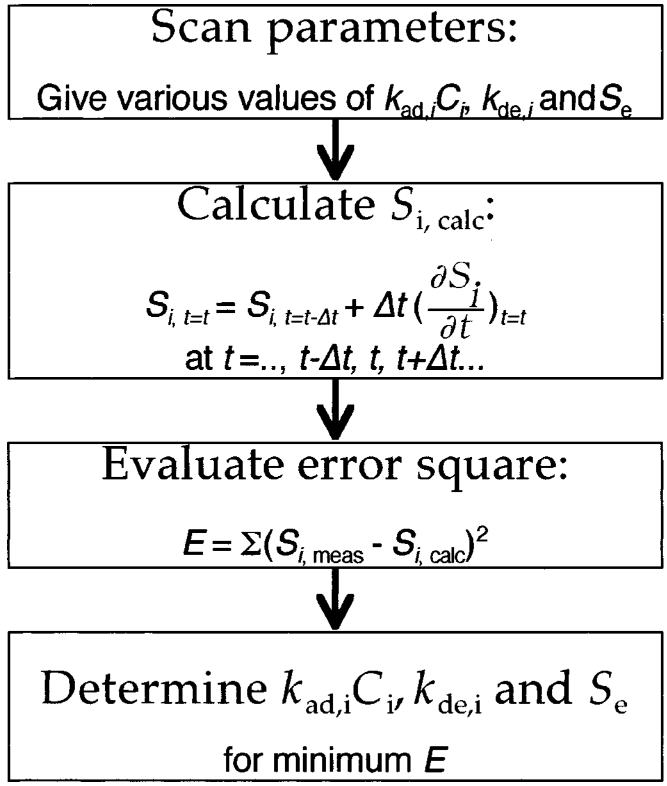

Figure 1. Calculation procedure for obtaining the rate parameters, $k_{ad,i}C_i$, $k_{de,i}$, and S_e. Δt is 1 s in this study.

$$E = \sum_{i,t} [S_{i,meas}(t) - S_{i,calc}(t)]^2 \quad [5]$$

where $S_{i,meas}(t)$ and $S_{i,calc}(t)$ are the S_i measured and calculated, respectively, at time t. Time required for the calculation following the procedure in Fig. 1 increases significantly with the number of the organic species. Therefore, in order to achieve an effectively fast and low cost calculation, the major organic species having the larger concentrations on the silicon wafer surface are performed prior to the determination of the minor organic species with smaller concentrations.

Experimental

The MOSAIC model written above is used to describe the fruit basket phenomenon. The measured time-dependent change in the surface concentrations of nine organic species, recently reported by Sakamoto *et al.*,[20] is used in this study.

The silicon wafer was cleaned by baking in helium gas ambient at 823 K. Then, the cleaned surface of the silicon wafers was exposed to the forced downflow air stream in the clean room for 0-172800 s. After the exposure, the silicon wafer was baked at 673 K for 37 min in helium gas flow in order to desorb the organic species on its surface. These organic species were collected using a solid adsorbent. Then, the concentrations of the organic species on the solid adsorbent were quantitatively measured using thermal desorption gas chromatography mass spectrometry (TD-GC-MS).

Sakamoto *et al.* reported the concentrations of the organic species of bis(2-ethylhexyl)phthalate (DOP), dibutylphthalate (DBP),

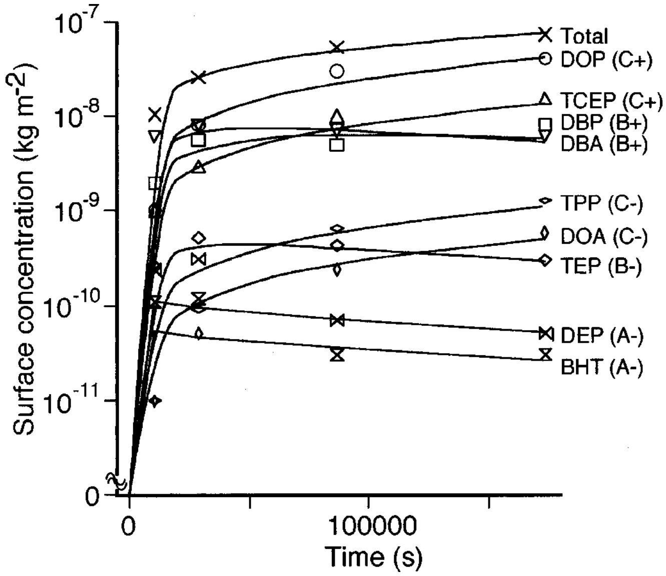

Figure 2. The measured and calculated concentrations of the organic species of bis(2-ethylhexyl)phthalate (DOP), dibutylphthalate (DBP), diethylphthalate (DEP), tris(2-chloroethyl)phosphate (TCEP), triphenylphophate (TPP), triethylphosphate (TEP), bis(2-ethylhexyl)adipate (DOA), dibutyladipate (DBA), and 2,6-di-*tert*-butyl-*p*-cresol (BHT) and their total amounts on the surface of the mirror-polished silicon wafers which had a native oxide film. The calculation is shown using the solid lines. Group A indicates the species whose concentrations increase rapidly and then decrease. Group B indicates the species whose concentrations increase rapidly and remain constant near its peak. Group C indicates the species whose concentrations gradually and continuously increase. Symbols + and − show the species with major and minor surface concentrations, respectively.

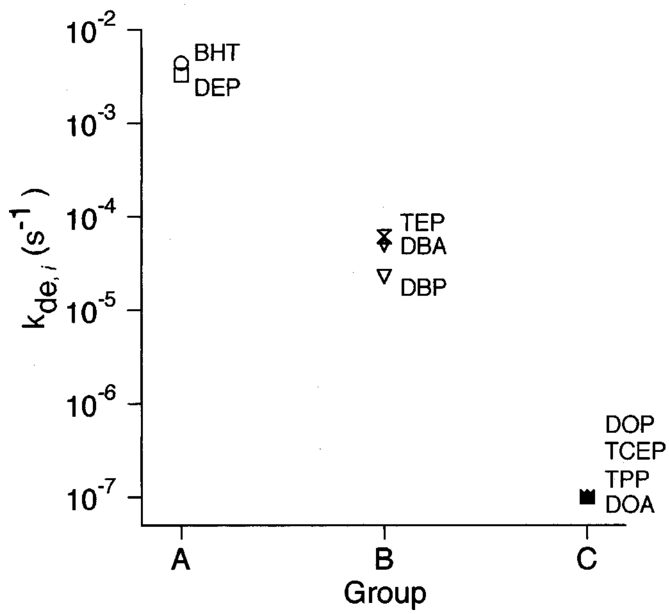

Figure 3. Group classification of time-dependent change in the surface concentration of organic species using $k_{de,i}$. The definition of groups A, B, and C is the same as that in Fig. 2.

diethylphthalate (DEP), tris(2-chloroethyl)phosphate (TCEP), triphenylphophate (TPP), triethylphosphate (TEP), bis(2-ethylhexyl)adipate (DOA), dibutyladipate (DBA), and 2,6-di-*tert*-butyl-*p*-cresol (BHT) on the surface of the mirror-polished silicon wafers which had a native oxide film.

Results and Discussion

The behavior of the nine organic species on the silicon wafer surface are discussed in detail along with determining the rate parameters of $k_{ad,i}C_i$, $k_{de,i}$, and S_e.

Behavior of the organic species.—The measured behavior of the nine organic species[20] is reviewed here using Fig. 2 before performing the calculation using Eq. 4. Figure 2 shows the increase and the decrease in the concentrations of the nine organic species and their total amount on the silicon wafer surface. The behavior of the nine organic species can be classified into three groups. Group A composed of DEP and BHT rapidly increases at the initial stage and decreases to a smaller concentration than its peak value. Group B of DBA, DBP, and TEP also rapidly increases at the initial stage but maintains its concentration near its peak value. The rest of the organic species are classified in Group C, in which the surface concentration gradually and continuously increases.

From the viewpoint of the abundance on the silicon wafer surface, DOP, TCEP, DBA, and DBP can be recognized to be major species. The others, TPP, TEP, DOA, DEP, and BHT, are considered to be minor species, because their surface concentrations are smaller than 10% of those of the major species. In Fig. 2, the major and the minor species are indicated using the symbols + and −, respectively.

The rate parameters of $k_{ad,i}C_i$, $k_{de,i}$, and S_e for the nine organic species are evaluated using Eq. 4 based on the MOSAIC model by means of fitting the measured values shown in Fig. 2. The solid lines in Fig. 2 show the surface concentrations of the organic species on the silicon wafer surfaces calculated using the rate parameters obtained in this study. The calculation following the procedure in Fig. 1 determined the value of S_e in this study to be 1×10^{-7} kg m^{-2}.

Figure 2 shows that the trend in the calculated surface concentrations of the organic species of groups A, B, and C agree well with those measured. Therefore, the first conclusion in this study is that the MOSAIC model can be used to discuss the adsorption and the desorption in the multicomponent system composed of a great number of organic species.

Rate parameters and surface concentration.—This section evaluates the influence of the rate parameters obtained in this study on the trend in the organic species, and further discusses the prediction theoretically performed in our previous study[19] where the behavior of the nine virtual species with various combinations of adsorption rates and desorption rates have been predicted using Eq. 1.

In order to discuss the relationship between the rate parameters in Eq. 4 and the trends of groups A, B, and C, the value of $k_{de,i}$ is plotted in Fig. 3. This figure shows that the organic species having a large $k_{de,i}$ larger than 10^{-4} s^{-1}, are classified as group A, in which the surface concentrations rapidly increase and then decrease. The surface concentrations of the organic species, group B, with $k_{de,i}$ between 10^{-6} and 10^{-4} s^{-1} rapidly increases and tend to maintain their value near its peak. The organic species with $k_{de,i}$ smaller than 10^{-6} s^{-1} belong to group C in which the surface concentrations gradually and continuously increase. The relationship between $k_{de,i}$ and groups A, B, and C coincides with those predicted in our previous study.[19] Therefore, it is concluded that the trend in the time-dependent change in the surface concentration of the organic species are predicted based on the value of $k_{de,i}$.

Since the prediction of the surface concentration amount of the organic species is also effective for the systematic study of the fruit basket phenomenon, $k_{ad,i}C_i$ is evaluated next. In Fig. 4, $k_{ad,i}C_i$ for various organic species are plotted as a function of the surface concentration of organic species obtained at 172,800 s, the last measurement point in Fig. 2. As predicted in our previous study,[19] the surface concentration of the organic species after a very long time from the initiation of the adsorption shows no relationship with $k_{ad,i}C_i$.

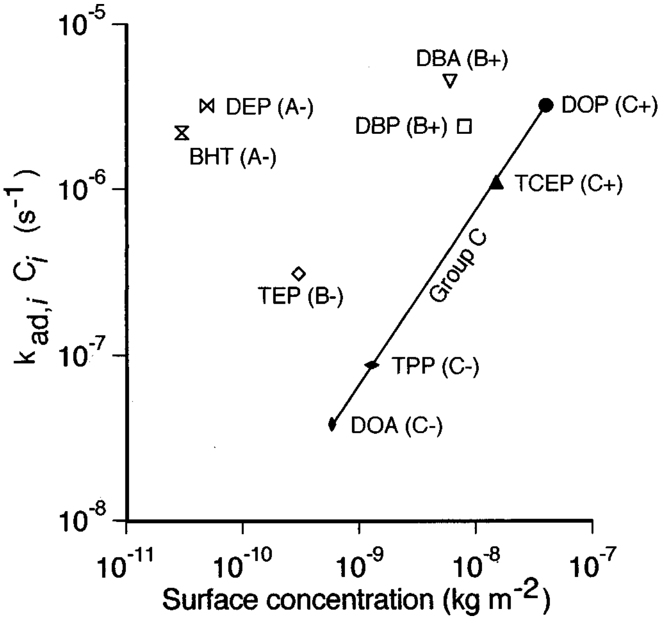

Figure 4. Relationship between $k_{ad,i}C_i$ and the surface concentration of organic species obtained at the last measurement point in Fig. 2.

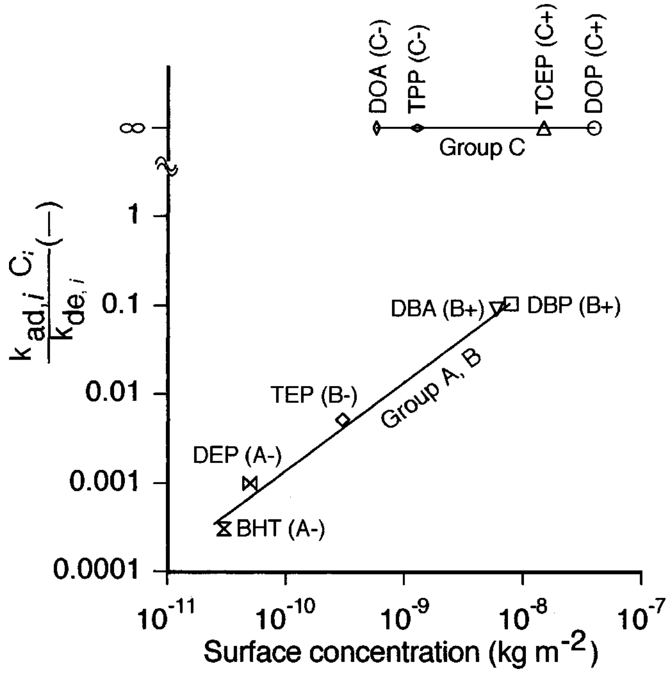

Figure 5. Relationship between the ratio, $k_{ad,i}C_i/k_{de,i}$, and the surface concentration of organic species obtained at the last measurement point in Fig. 2.

For further study, it should be noted here that the surface concentration of the organic species is influenced by both the adsorption and the desorption. In a steady state

$$\frac{\partial S_i}{\partial t} = 0 \qquad [6]$$

where the surface concentration of the organic species i is described using Eq. 4 as follows

$$S_i = \frac{k_{ad,i}C_i}{k_{de,i}}\left(S_e - \sum_j S_j\right) \qquad [7]$$

Therefore, the surface concentration of the organic species after a very long time, sufficient to achieve a steady state, is expected to be dominated by the ratio of $k_{ad,i}C_i$ to $k_{de,i}$. In order to investigate the relationship obtained in Eq. 7, the ratio of $k_{ad,i}C_i$ to $k_{de,i}$ is evaluated and plotted in Fig. 5 as a function of the surface concentration of the organic species for the last measurement point in Fig. 2, which is assumed to be nearly in a steady state. Since the surface concentration of the organic species at the last measurement point has a very clear relationship with the ratio of $k_{ad,i}C_i$ to $k_{de,i}$, this ratio is considered to be an important factor for predicting the final condition of an airborne molecular contamination on the silicon wafer surface.

For group C, for which $k_{de,i}$ is near 0 s^{-1}, the ratio of $k_{ad,i}C_i$ to $k_{de,i}$ becomes infinite. However, taking into account the fact that the organic species of group C has a relationship between $k_{ad,i}C_i$ and the surface concentrations at the last measurement point, as shown in Fig. 4, the behavior of group C is considered to be predicted by using $k_{ad,i}C_i$.

Additionally, Eq. 7 is consistent with the conclusion in our previous study[19] that the organic species having the largest adsorption rate and the smallest desorption rate results in their greatest abundance on the silicon wafer surface. For studying further, the physical and chemical properties of each organic species should be studied from the viewpoint of the interaction between the organic molecule and the surface of silicon and silicon oxide.

Conclusions

The model of multicomponent organic species adsorption induced contamination (MOSAIC) is validated by using it to describe the fruit basket phenomenon for a silicon wafer surface exposed to clean room air. The increase and the decrease in the measured concentration of the nine organic species are reproduced by accounting simply for their adsorption and desorption. The trend in the organic species is classified using the desorption rate constant. Their concentrations after the exposure to clean room air for very long time have a clear relationship with the ratio of the production of the adsorption rate constant and the organic species concentration in the gas phase to the desorption rate constant. Since the rate parameters, $k_{ad,i}C_i$ and $k_{de,i}$, are shown to have a clear relationship with the actual trend in the various organic species, the MOSAIC model is considered to be effective for describing the adsorption and the desorption and thus predicting the fruit basket phenomenon.

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