Scanning Probe Microscopy Analysis of the Adsorption of Volatile Organic Compounds on Carbonaceous Films with Microcolumnar Structure*

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Adsorption interactions between adsorbate of volatile organic compound (VOC) and adsorbent film were investigated using Kelvin probe force microscopy and differential force microscopy. An adsorbent film with carbonaceous columnar structures was prepared using radio-frequency sputtering of pectin. The VOCs were identified by their dielectric constants, polarizabilities, and refractive indices. Polar VOCs enhanced the interaction forces and negative surface potentials of the adsorbent films. The negatively charged potential showed thermal drift, which is stronger for polar VOCs. Thermal release of electrons trapped in the surface states by band bending was enhanced by the adsorption of polar species. Activation energy is closely correlated with the negative shift of the surface potential. Quantitative structure property relationship analyses suggest that the local charges of adsorbate VOCs are crucial for these surface properties: surface potential, surface interaction force, and adsorption amount.

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I. INTRODUCTION

Responses of non-specific gas-sensors potentially involve comprehensive information on discriminant analysis of volatile organic compounds (VOCs). Sorption-desorption dynamics at the surface of gas-sensing layer are essential for understanding the sensor’s responses, which are phenomenologically based on physicochemical indices. Chemical stimulation by adsorbate VOCs can change the surface properties of a sensing film (adsorbent). Usually the adsorbates adsorb and migrate on the surface of an adsorbent and subsequently diffuse into the bulk of the film. Among the numerous physicochemical indices, electrostatic interactions are detectable using a number of well-established sensitive instruments. Scanning probe microscopy (SPM) has huge potential in this area because of its capability to precisely measure electronic structure and forces with a high spatial resolution. The effects of chemical doping on charge transport characteristics of graphene oxides and on the work function of graphene electrodes have been reported previously [1, 2]. The effects of surface water on SPM measurements have been also discussed [3, 4].

We have reported that carbonaceous films comprising densely packed microcolumns, that are separated by narrow grooves are prepared through radio-frequency (rf) sputtering of polysaccharide pectin [5]. These nanostructured films have high sorption capacities for a wide range of VOCs, which can be regarded as chemical dopants or surface modifiers of the adsorbent film.

The main objective of this study was to investigate the perturbation effects of adsorbates (VOCs) on the surface characteristics of the adsorbent carbonaceous film using two types of SPM: Dynamic force microscopy (DFM) and Kelvin probe force microscopy (KFM). A key concern was to determine whether shape-oriented specific adsorption would occur at the columnar structure. A carbonaceous dielectric film with a densely packed columnar structure is considered to be a suitable adsorbent for studying electrostatic interactions with VOCs. In a real setting, numerous pre-adsorbed species should be taken into account, such as surface water, which is anticipated to be an actively sensing component for hydrophilic VOCs. The VOC-dissolved surface water would be desorbed due to reducing electrostatic forces. In this study, we have conditioned both the surfaces of the adsorbent film and the probing cantilever of SPM through an overnight flow of N2 to simplify the interaction surfaces. SPM measurements in ideal conditions, i.e. without any surface water, would clarify the subtle changes to surface characteristics of adsorbent films induced by chemical stimulation of adsorbates.

II. COMPUTATIONAL METHODS

A. Preparation of the adsorbent film

Carbonaceous films were deposited on a polished silicon chip and a 9-MHz AT-Cut quartz crystal resonator (QCR) with Au-electrodes, which had been cleaned with UV irradiation and ozone exposure. The deposition was carried...
out using rf sputtering, as reported in our previous paper [5]. Pectin dispersed in hot ethanol was distributed on a polyethylene (PE) disk, and subsequently dried in an N$_2$-flow. This pectin-coated PE disk was placed on an under electrode connecting the rf power supply in a diode-type sputtering apparatus with a sputter-up configuration.

B. DFM and KFM measurements using SPM equipment

The surface potential and the retarding phase shift have been evaluated by the measurements of KFM and DFM, using the SPA-400 measuring unit with the SPI-4000 controller (SII, Japan). Using the SPIWin software (SII, Japan), the surface potential and the retarding phase shift have been determined by the most frequent mode of the single peaked histogram obtained by the images of KFM and DFM.

The pectin-sputtered film deposited on a polished silicon chip (ca. 10 x 10 mm) was fixed on the Ni-coated metal disk by conductive carbon tape. For KFM and DFM measurements, the central area of the identical sample was typically scanned over a 200 x 200 nm using the corresponding cantilevers. The spring constant of a cantilever used for DFM (SII DF-20) was 13 N/m, and its resonant frequency was 123 kHz (Q-value = 404). The spring constant of a cantilever used for KFM (SII DF3-R) was 2 N/m and its resonant frequency was 25 kHz (Q-value = 145).

DFM was conducted by the widely used amplitude modulation tapping mode [6]. The retarding phase shifts between the output and input signals for the vibration of cantilever reflects the interaction force between tip and sample. A topographic image can be obtained by plotting the feedback regulation required to keep the vibration amplitude constant. A phase shift image provides the changes in distribution of interaction forces on a sample. Under our experimental conditions, a change of several nN in the adhesion force can produce a phase shift of about 2° [7].

KFM used a dual-pass vibration mode for the resonances of the tip. One resonates mechanically to obtain topographic images. The other is an AC current superimposed on the DC offset voltage for vibrations induced by electrostatic force. The AC current was kept at zero, using feedback regulation of DC offset voltage, which can be regarded as the surface potential between the Fermi level and vacuum level of the sample surface [8, 9].

C. Generation and instrumentation of VOCs

Using N$_2$ as a carrier gas, a vapor flow of VOC and water were generated by the standard gas generator (Gastec PB-1B, Japan) based on a diffusion-tube method [10, 11]. The organic vapor concentration was kept at 1000 ppm by controlling the temperature of the diffusion tube (308-313K) and the flow rate, which was kept constant by a mass flow controller ranging from 300 to 400 mL/min.

The vapor was fed into the 18-L sound-proof environmental chamber (SPA 400, SII, Japan), containing the SPM unit, the temperature-humidity sensor (RH-02, Pico Tech. U.K.), and the pectin-sputtered QCR for sorption monitoring. The schematics of the setup are depicted in Fig. 1. The inner wall of the chamber is covered with insulating resin. The gas flow into the chamber was smoothly changed to either pure N$_2$ or to the N$_2$-based VOC, using a four-way valve. Both of the flow rates were identical using two mass flow controllers (MQV9500, Azbil, Japan). The pure N$_2$ flowing in environmental chamber was kept overnight to condition the surfaces of both the adsorbent film and the cantilever.

Based on Sauerbrey’s equation [12, 13], the amounts of massive changes in QCR can be estimated by the shift in the resonant frequency; the coefficient of proportionality was 1.05 ng/Hz. This relationship was also used to determine the amounts of the film deposited on the QCR substrate by rf sputtering.

D. Chemical and statistical calculations

The intermolecular interaction forces between adsorbate VOCs and adsorbent film were investigated using the chemical calculation method. The final geometric optimization of the adsorbates was performed using a semi-empirical quantum-chemical AM1 parameterization with the AMPAC 8.0 program (SemiChem, Kansas) [14, 15]. The resulting physicochemical molecular descriptors produced by AMPAC were loaded into the CODESSA (Comprehensive descriptors for structural and statistical analysis) program (ver. 2.13, SemiChem, Kansas) [16, 17] along with the results of the measurements by KFM, DFM, and QCR. More than 500 molecular descriptors were calculated using CODESSA for the adsorbate. Regression analysis to determine the best quantitative structure property relationship (QSPR) modeling was basically carried out using the most significant five molecular descriptors.

III. RESULTS AND DISCUSSIONS

A scanning electron microscope (SEM) image of the pectin-sputtered film is shown in Fig. 2(a). The film is composed of the densely packed seamless microcolumns (ca. 1-μm long), which make up bundles separated by narrow grooves. We attribute the formation of this nano-structured film to the self-organized carbonization...
FIG. 2. (a) SEM image of the pectin-sputtered film. (b) SPM images of the pectin-sputtered film under N$_2$ flow: Topographic image (left), Surface potential image (center), and Phase shift image (right).

of polysaccharide frameworks by plasma decomposition. Higher pressure tends to produce a uniform microlamellar structure without grooves. The growing mechanism of the microcolumns and narrow grooves is explained by a ballistic self-shadowing effect [18, 19].

X-ray photoelectron spectroscopy (XPS) was used to determine the elemental ratios in the vicinity of the film surface, ranging from C : O : N = 72 : 21 : 7 to C : N : O = 78 : 18 : 4. The elemental ratio of carbon is inversely proportional to that of oxygen and nitrogen. Compared to pristine pectin, the rf sputtering had enhanced carbonization, which was induced by the elimination of the oxygenated carbon species and a reconstruction of the carbon frameworks. We consider the inclusion of nitrogen in the sputtered molecular frameworks to originate from the residual nitrogen in air. An activated nitrogen species was generated in plasma and reacted with the sputtered species resulting in the film-constituents.

The XPS and Fourier transform infrared spectroscopy (FTIR) suggest that the sputtered film contains carboxy, imino, and amino groups, which can significantly affect the surface properties of the film due to their polar characteristics [5]. The mean contact angle of a sessile drop of de-ionized water on the sputtered film was 16.5 degree. The drop has been soaked into the film within 1-min after the completion of measurements, probably due to a capillary effect of grooves between the hydrophilic columnar bundles.

SPM images of the film surface are shown in Fig. 2(b). All of the images were recorded under a pure N$_2$ flow without any adsorbrates. The potential image shows low resolution horizontal lines, which tend to disappear after a number of scans, when the sample is exposed to an adsorbate, especially water. We attribute these noisy horizontal lines to an attractive force between a scanning tip and a surface of the film. Despite the unclear image, we observe that the head of the column has a slightly more positive potential than that of the groove. The column surface is negatively charged, probably due to surface electrons, accumulated in the peripheral area.

The phase shift at the head of the column is smaller than that at the periphery. The higher amount of negative charge and the higher degree of negative phase shift of the peripheral area suggest that the electrostatic interaction is stronger at the peripheral area than at the head of the column.

The adsorption of adsorbates was monitored by the pectin-sputtered QCR, whose resonant frequency decrease linearly by mass loading of adsorbates. The adsorption rates for some adsorbates, in line with their relative dielectric constants ($\varepsilon_r$), are shown in Fig. 3. The adsorption rate for ethanol and water, with a high $\varepsilon_r$, is higher than for the non-polar species. However, their adsorption rate and $\varepsilon_r$ are inversely ordered. This may be caused by the lower concentration of water vapor, as water tends to be liquefied by condensation effects induced by hydrogen bonding, constructing molecular networks.

Figure 4 shows the time-course of the phase shifts
FIG. 5. Phase shift after 2-h exposure to VOC depended on polarizability ($\alpha$) of VOC parameterized by relative dielectric constant ($\varepsilon_r$).

FIG. 6. Time course of the shift of surface potential starting at changing a flow from pure N$_2$ to 1000-ppm VOC.

changing from pure N$_2$ to a 1000-ppm adsorbate measured using DFM. The non-polar species tend to precede the phase resulting in the positive shifts, whereas the polar species tend to retard the phase inducing negative shifts. The changes of hexane are similar to that of pure N$_2$ without VOC.

The phase shifts after 2-h exposure to VOCs parameterized by a measure of the relative dielectric constant ($\varepsilon_r$) and polarizability ($\alpha$) of adsorbates are shown in Fig. 5. The correlation coefficients of the phase shifts to $\varepsilon_r$ or $\alpha$ suggest that phase shifts profoundly correlate with $\varepsilon_r$ or $\alpha$, which is a measure of the electronic susceptibility to an external field. The polar species enhance the attractive interaction, whereas the non-polar species reduce it. These findings imply that the attractive interaction is based on electrostatic forces, which are enhanced by polar species with high $\varepsilon_r$ values.

The time course of surface potentials measured by KFM shows a negative shift for all of VOCs, as shown in Fig. 6. This shift represented by water in Fig. 7 was closely linked to an increase in temperature, probably induced by the operation of the measurement equipment, an increase in ambient temperature, or a combination of both. After exposure of each carbonaceous film to a different adsorbate flow for 4 h, the negative shift in the surface potential tends to be higher for polar species than for non-polar species, as shown in Fig. 8. These negative shifts profoundly correlate with the polarizability ($\alpha$), in addition to refractive index (n) and relative dielectric constant ($\varepsilon_r$), which are related to the susceptibility in response to the surrounding electric field.

The time-dependent negative shift of the surface potential indicates thermal drift (Fig. 7). The thermal release of electrons trapped in the surface states by band bending [20] can be attributed to the gradual decrease in the surface potential. This mechanism is enhanced by the adsorption of a polar species.

The activation energies of adsorbates have been evaluated by an Arrhenius plot, as shown in Fig. 9. Except for water, the activation energy tends to decrease with increasing the negative shift of surface potential. This tendency may be due to the fact that the higher amounts of negative charge (electrons) reduce the activation energy due to the enhancement of electron mobility. However, water with the largest negative shift deviates from this tendency. This may be caused by the adaptation...
TABLE I. Principal molecular descriptors of adsorbate for modeling the best regression in a QSPR analysis on the shift of surface potential (KFM measurements). $R^2 = 1.0000$ and $s^2 = 0.0012$.

<table>
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<th>Ranking</th>
<th>Regression coefficient</th>
<th>t-test value</th>
<th>Descriptor</th>
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<tr>
<td>0</td>
<td>1.70e+01</td>
<td>83.11</td>
<td>Intercept</td>
</tr>
<tr>
<td>1</td>
<td>-5.16e+02</td>
<td>-947.25</td>
<td>XY shadow / XY rectangle (size and geometrica shape of molecule)</td>
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<tr>
<td>2</td>
<td>-2.47e+02</td>
<td>-727.44</td>
<td>Number of occupied electronic levels / number of atoms</td>
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<td>570.50</td>
<td>HOMO energy</td>
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<tr>
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<td>Bonding information content</td>
</tr>
<tr>
<td>5</td>
<td>1.45e+01</td>
<td>166.32</td>
<td>Max atomic orbital electronic population</td>
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</table>

TABLE II. Principal molecular descriptors of adsorbate for modeling the best regression in a QSPR analysis on the shift of resonant frequency (QCR measurements). $R^2 = 1.0000$ and $s^2 = 0.0009$.

<table>
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<td>187.99</td>
<td>Intercept</td>
</tr>
<tr>
<td>1</td>
<td>8.82e+01</td>
<td>724.28</td>
<td>Average structural information content (topological: atomic connectivity in molecule)</td>
</tr>
<tr>
<td>2</td>
<td>-1.97e-02</td>
<td>-859.57</td>
<td>Difference in charge partial surface areas</td>
</tr>
<tr>
<td>3</td>
<td>-6.94e+01</td>
<td>564.23</td>
<td>Relative negative charge</td>
</tr>
<tr>
<td>4</td>
<td>1.61e+01</td>
<td>371.30</td>
<td>Randic index (the coordination numbers of atoms)</td>
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<tr>
<td>5</td>
<td>2.78e+02</td>
<td>325.19</td>
<td>Maximum partial charge</td>
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</tbody>
</table>

FIG. 9. Shift of surface potential after 4-h exposure to VOC and activation energy evaluated by the temperature-dependence of the shift of surface potential (Arrehenius plot).

arrangement of molecular networks of water, which creates oppositely oriented clusters, reducing the activation energy.

Based on QSPR modeling [21], Table I summarizes the most significant molecular descriptors used for fitting the maximum likelihood linear regression between the predicted and measured values of surface potentials. The QSPR analysis suggests that the KFM evaluation mostly depend on the molecular indices of electrostatics, geometrics, and quantum mechanics. In addition to the polarity parameter, the indices of topological-electronic and molecular mechanics are significant descriptors for the surface potential. These results suggest that the orientation-driven surface potential is closely related to molecular geometrics.

The principal molecular descriptors for the DFM measurements are the weighted partially negative surface area, the atomic charge weighted partially positive surface area, and the minimum electron-electron repulsion for a hydrogen atom. The phase shifts, reflecting the surface interactions, are exclusively depended on partial charge inducing electrostatic forces.

Polarity-related descriptors attributed to local charges of the adsorbates are crucial for surface potential and surface interactions. This is supported by the QSPR analysis for the resonant frequency shift of the QCR, which indicates the amounts of adsorbate on the adsorbent film, as summarized in Table II. In addition to the polarity-related descriptors, the topological descriptors representing the atomic connectivity and coordination in an adsorbate molecule are also essential for the QSPR model on the amounts of adsorbate on the adsorbent film.

IV. CONCLUSIONS

The surface potential and interaction forces of pectin-sputtered carbonaceous films with a columnar structure were evaluated using by KFM and DFM. In the peripheral area, both surface potential and phase shift are more negative than at the head of the columns. These results suggest that the peripheral area shows stronger electrostatic interactions than the head. The exposure to polar VOCs (1000 ppm) enhances the negative charging and surface interactions by dielectric forces. The surface potential shows thermal drifts with fluctuations, which tends to be smaller for polar species. The adsorption of a polar species enhances the thermal release of electrons trapped in the surface states by band bending. Except for water, the activation energy tends to decrease with increasing the

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negative shift of surface potential. There is a close correlation between the sorption amount, surface potential and surface interaction induced by exposure to VOCs. These findings are supported by QSPR analyses, which suggest that the local charges of adsorbate are crucial for these surface properties.

**ACKNOWLEDGMENTS**

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