VOC-induced Changes in Surface Properties of Carbonaceous Films Prepared by Radio-frequency Sputtering of Gelatin

Iwao Sugimoto,a,† Yoriko Suda,a Hiroshi Muramatsu,b Kazuhiko Takahashi c

a School of Computer Science, Tokyo University of Technology, 1404-1 Katakuragai, Hachioji, Tokyo 192-0982, Japan
b School of Bioscience and Biotechnology, Tokyo University of Technology, 1404-1 Katakuragai, Hachioji, Tokyo 192-0982, Japan
c Department of Systems Design, Faculty of Science and Engineering, Doshisha University, 1-3 Miyakodani Tatara, Kyotanabe, Kyoto 610-0321, Japan

† Corresponding author: sugimoto@stf.teu.ac.jp

Received: 13 September, 2018; Accepted: 9 April, 2019; Published: 25 April, 2019

Carbonaceous films, adsorptive for a range of volatile organic compounds (VOCs), were prepared by radio-frequency (rf) sputtering of biomedical-grade polypeptide gelatin crystals. The film was composed of densely packed nitrogen-rich microcolumns, resulting in a groove-poor structure. The gelatin-sputtered quartz crystal resonator was characterized by a high capability to adsorb VOCs, especially for the small, dielectric molecules of ethanol and water. Using the sorption capacities of 17 kinds of 500 ppm VOCs, we modeled the linear solvation energy relationship, which was substantially governed by electrostatic intermolecular interactions. Kelvin force microscopy (KFM) revealed that surface charging of the gelatin-sputtered film increased with the exposure time of the VOCs. Moreover, the dynamic force mode (DFM) in scanning probe microscopy (SPM) was used to elucidate the interaction force between the tip and the sample surface. The retarding phase shift increased with the exposure time of the VOCs. Deviation of the interaction force, induced by adsorption of the VOCs, was higher for hexane than for ethanol. The polar VOCs and the non-polar VOCs were roughly separated by the principal component analysis using the KFM and DFM data.

Keywords Scanning probe microscopy; Gas-solid interface; Sputter deposition; Carbonaceous film; Gelatin

I. INTRODUCTION

Gas-sensing films deposited on sensitive transducers show subtle changes in surface properties by adsorbates (analytes). These changes typically affect electrical, optical, and mechanical properties, which are mainly determined by the physicochemical characteristics of the adsorbate VOCs. Chemical stimulation by adsorbed VOCs can change the surface properties of a sensing film (adsorbent). Firstly, the adsorbates migrate in the vicinity of the film surface and, then, diffuse into the bulk of the adsorbent film. Among the numerous surface interactions, electrostatic interactions are detectable using several well-established sensitive instruments. Scanning probe microscopy (SPM) is a promising methodology for its capability to obtain information on surface properties and interaction forces with high spatial resolution. Concerning the gas-surface interactions, there have been reports on the chemical doping of graphene oxides [1, 2] and the effects of surface water on SPM measurements [3, 4].

We have already reported in previous works about carbonaceous films comprising densely packed microcolumns separated by narrow grooves prepared using radio-frequency (rf) sputtering of polysaccharide pectin [5] and Japanese calligraphy solid ink disc (sumi) [6]. The “sumi” is composed of a complicated mixture of the lampblack carbon soot and the crude gelatin used as a binder. 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. However,
it remains unknown how sorptive for VOCs the carbonaceous films are when they are prepared by rf-sputtering of the purified gelatin. To our best knowledge, this is the first study on investigating the organic gas-sorption characteristics of the rf-sputtered films of polypeptides, from a surface science point of view.

Gelatin is one of the most utilizable polypeptides for its availability and is also implemented as glue in the field of traditional craftwork and photo-printing. Recently, gelatin films have been widely investigated as a biocompatible and edible platform, whose functionalities are enhanced by impregnating it with physiologically active substances, such as antioxidants [7], antibacterial agents [8], and essential oils [9]. It is indisputable that gelatin-coated dishes are very widely utilized in biological laboratories in order to culture many different types of cells.

In this paper, we report the film characteristics regarding VOC-sorption, surface interactions, and the surface potential of the carbonaceous films prepared by rf sputtering of the purified gelatin crystals. These characteristics were compared with those of the carbonaceous films of the sputtered polysaccharide pectin [10].

Since peptide bonds are more stable than glycosidic bonds in polysaccharides [11], we have chosen the polypeptide gelatin as a rf-sputtering target to exploit its durability against serious carbonization. The main objective of the present study is to clarify the surface characteristics of the polypeptide gelatin-sputtered films in comparison with the polysaccharide pectin-sputtered films [10], from a viewpoint of VOC sensing. The VOC-induced changes in potentials and interactions are revealed by two variants of SPM and by surface characterization techniques. We have also utilized the multivariate statistical technique for explaining the experimental results quantitatively and qualitatively.

II. EXPERIMENTAL

A. Preparation and characterization of gelatin-sputtered film

The biomedical-graded gelatin, which was originated in pork skin (type A) and was manufactured by MP Biomedicals Inc., was used as a sputtering target material without any further purification. This type A gelatin is composed of almost the same amount of α-helix collagen and double helix collagen [12]. A polyethylene (PE) disc was entirely covered with the gelatin dispersed in hot ethanol and subsequently dried enough under a flow of N₂, as reported previously [13].

The gelatin-coated PE disk was placed at the bottom of an electrode, which was connected to the rf power supply in a diode-type sputtering apparatus with a sputter-up configuration. Helium, used as a plasma gas, flowed at a rate of 40 mL min⁻¹. The pressure during sputtering was 24 Pa, and the rf power density was 3.52 × 10⁻⁴ W m⁻². The deposition was carried out using rf sputtering.

The gelatin-sputtered films were deposited on a polished silicon chip and a 9-MHz AT-Cut QCR (Quartz Crystal Resonator) with Au-electrodes, which were placed on the top grounded electrode. Based on Sauerbrey’s equation [14], the loaded mass (Δm) on the QCR can be correlated with the shift of resonant frequency (Δf) as follows:

\[ \Delta m \ [\text{ng}] = -1.05 \Delta f \ [\text{Hz}] . \]  

Assuming that the carbonaceous materials are uniformly deposited on the QCR and their density is 1.0 g cm⁻³, the film thickness (t) correlates with Δf as follows:

\[ t \ [\text{nm}] = -54 \Delta f \ [\text{kHz}] . \]

The sputtered films deposited on the Au-electrodes of the QCR were analyzed using a Fourier transform infrared spectrometer (DIGILAB FTS300) equipped with a microscope (DIGILAB UMA600, ×150). The measurements were carried out by the Hg-Cd-Te detector with a wavenumber resolution of 4 cm⁻¹, using the reflection method.

An elemental analysis was performed with an X-ray photoelectron spectrometer (JEOL JPS-9200) using Mg Kα radiation as an excitation source. To suppress the structural changes induced by X-ray radiation, the X-ray power was reduced to 100 W and ion etching was not carried out. The atomic ratios were evaluated comparing the peak area multiplied by the relative photoionization cross section [15].

Scanning electron microscopy (SEM) images were obtained using a field emission scanning electron microscope (JEOL, JSM-7700F). The acceleration voltage and the current of the primary electron beam were 5 kV and 5 μA, respectively.

The contact angle of a sessile droplet of water was evaluated using the θ/2 method [16] and recorded with a contact angle meter (Drop Master 300, Kyowa, Japan). The measurements were carried out with an angular resolution of 0.1°, using a CCD camera to image the 1-μL water droplet. The measurements were carried out at ambient condition (28°C, RH 40%).

B. Surface characterization by scanning probe microscopy

The surface potential and the retarding phase shift was evaluated by KFM and DFM measurements, using the SPA-400 measuring unit with the SPI-4000 controller (Hitachi High Technology, Japan). Using the SPI Win software, the surface potential and the retarding phase shift was determined by averaging the values in 1 × 1 μm² images.

The gelatin-sputtered film deposited on a polished silicon chip was fixed on a Ni-coated metal disk by a conductive carbon tape. For KFM and DFM measurements, the central zone of the sample was typically scanned over a 1 × 1 μm² area using the mode-dedicated cantilevers. The spring constant of the cantilever used for DFM (SII DF-20) was 13 N m⁻¹, and its resonant frequency was 123 kHz (Q value = 404). On the other hand, the spring constant of the cantilever used for KFM (SII DF3-R) was 2 N m⁻¹ and its resonant frequency was 25 kHz (Q value = 145).

DFM was conducted using the common amplitude modu-
lation tapping mode [5]. The retarding phase shifts between output and input signals due to vibration of the cantilever reflect 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 shows distribution of changes in the interaction forces on the sample. Under the present experimental conditions, a variation of several nanonewtons in the adhesion force can produce a phase shift of about 2° [17].

KFM used a dual-pass vibration mode for the resonances of the tip. One vibration mode resonated mechanically in order to obtain topographic images. The other was an alternating current (AC) superimposed on the direct current (DC) offset voltage for vibrations induced by electrostatic force. The AC was kept at zero, using the feedback regulation of the DC offset voltage. The latter was regarded as the surface potential between the Fermi level and the vacuum level of the sample [18, 19].

C. Instrumentation of VOC flow

Using N$_2$ as a carrier gas, a vapor (adsorbate) flow of VOCs and water was generated by the standard gas generator (PB-1B, Gastec, Japan) based on the diffusion-tube method [20, 21]. The organic vapor concentration was kept at 500 ppm by controlling the temperature of the diffusion tube (308–313 K) and the flow rate, which was kept in a range from 300 mL min$^{-1}$ to 400 mL min$^{-1}$ by a mass flow controller. The VOC-sorption measurement was carried out by smoothly changing the vapor flow in the QCR chamber from pure N$_2$ to 500 ppm VOCs by using a four-way valve [6].

The experimental setup for the SPM measurements is depicted in Figure 1. For measuring the surface characteristics using SPM, the 1000-ppm vapor of adsorbate was fed into the 18-L sound-proof environmental chamber (SPA 400, SII, Japan), containing a SPM unit and a temperature-humidity sensor (RH-02, Pico Tech. U.K.) [10]. The 1000-ppm vapor flow of adsorbates was also generated by the standard gas generator. Humidity of this environmental chamber was kept below RH 13% using silica gel cassettes.

The elemental ratios in a vicinity of the gelatin-sputtered film surface was determined to be C : O : N = 71 : 12 : 17 by X-ray photoelectron spectroscopy. This elemental ratio is comparable with the one found in collagen-sputtered films [6]. Compared to pristine gelatin (C : O : N = 55 : 27 : 18 [24]), the sputtered gelatin has been carbonized through se-

III. RESULTS AND DISCUSSION

Scanning electron microscope (SEM) images of the gelatin-sputtered film are shown in Figure 2. The film is composed of densely packed microcolumns (ca. 1 μm long, 100 nm in diameter), which makes up the fissile bundles separated by narrow grooves. The heads of the microcolumns seem to be fused cohesively, making the top layer with rugged surface. The cohesion has been considerably developed, resulting in the poorer groove (crevasse) than the sumi-sputtered film which was composed of the thinner microcolumns [6].

The formation of this columnar structure is attributable to the plasma-induced carbonization of polypeptides. The growing mechanism of the microcolumns can be explained by the ballistic self-shadowing effect [22, 23], and the formation of narrow grooves (crevasses) is plausibly explained by the relaxation of the compression stress residing in the microcolumnar structure.

The elemental ratios in a vicinity of the gelatin-sputtered film surface was determined to be C : O : N = 71 : 12 : 17 by X-ray photoelectron spectroscopy. This elemental ratio is comparable with the one found in collagen-sputtered films [6]. Compared to pristine gelatin (C : O : N = 55 : 27 : 18 [24]), the sputtered gelatin has been carbonized through se-

![Figure 1: Schematics of the setup for the SPM measurements.](image)

![Figure 2: SEM images of the gelatin-sputtered film; a top surface image (a), and an oblique image of the cross section (b).](image)

![Figure 3: Infrared spectra of the sputtered films of gelatin and sumi, respectively.](image)
lective elimination of oxygen, reconstructing the complicated carbon frameworks in the gelatin-sputtered film. In comparison to the gelatin-sputtered film, the analogous carbonaceous sumi-sputtered film (C : O : N = 80 : 15 : 5) contains higher amounts of carbon and lower amounts of nitrogen. The thinner columns and the thinner top surface of the sumi-sputtered film is probably due to the proceeded carbonization of the complexed mixture of sumi by rf sputtering.

Infrared spectra suggest that the sputtered carbonaceous films contain carboxy, hydroxy, imino, and amino groups, which can significantly affect the surface properties of the film due to their polar characteristics [5], as shown in Figure 3. The O−H and N−H stretching bands ranging above 3000 cm⁻¹ are weaker and their peak shifts to lower wavenumbers for the gelatin-sputtered film than for the sumi-sputtered film. This change in the gelatin-sputtered film suggests that the hydrogen bonding networks has developed enough to suppress free motion of the stretching vibration of the O−H and N−H bonds.

The averaged contact angles of a sessile drop of deionized water were 16.5° and 34.7° for the sumi-sputtered film and for the gelatin-sputtered film, respectively. The higher wettability of the sumi-sputtered film is attributable to higher contents of O−H and N−H groups than for the sumi-sputtered film. This change in the gelatin-sputtered film suggests that the hydrogen bonding networks has developed enough to suppress free motion of the stretching vibration of the O−H and N−H bonds.

The sorption of VOCs was monitored by the resonant frequency decrease of the film-deposited QCR, due to mass loading. According to Sauerbrey’s equation, we can estimate the mass of the adsorbate VOCs on the adsorbent film. Figure 4 summarizes the “sorption capacity”, which is evaluated by the amounts of adsorbates normalized by film thickness for 500-ppm VOCs. Both the amounts of adsorbates and the film thickness have been estimated by the Sauerbrey’s equation, as expressed in Eq. (1) and Eq. (2), respectively. In Figure 4, the adsorbates are ordered by the relative dielectric constants. The sorption capacities for ethanol and water, which have high dielectricity, are extremely higher than for the other species. The sorption capacities of non-polar species such as hydrocarbons are very small. In comparison to the sumi-sputtered film, the gelatin-sputtered film is adsorptive for polar (dielectric) small molecules, whereas its sorption capacities for non-polar molecules are comparable to the sumi-sputtered film. This indicates that the gelatin-sputtered film adsorbs the polar small molecules predominantly, keeping its sorption capacities for other species comparable to the sumi-sputtered film.

We applied a multivariate regression model to the gas-sorption capacities of sputtered films based on the linear solvation energy relationships (LSER) [25, 26], using the physicochemical molecular descriptors listed in Table 1. This table supplementary includes nitrogen as a reference. LSER modeling is one of the benchmarks to investigate the quantitative structure property relationships. Moreover, it is informative for material design in membrane technologies especially from viewpoints of separation, condensation, and transportation.

The LSER model estimates the gas-sorption capacity corresponding to the gas-film partitioning coefficient (K) of the adsorbent sputtered film as:

$$\log K = \log L^16 + C_0,$$

where $C_0$ is a regression constant. The individual terms are
physicochemically identified with particular interactions between adsorbate gas and adsorbent film; the term $Rr$ for interactions by $n$ and $\pi$ electrons (an indication of polarizability); the term $zs$ for dipole-relevant interactions (measures the permanent dipolarity or induced dipolarity); the term $\beta a$ for hydrogen-bonding interactions [basicity-acidity (acceptor-donor) of hydrogen atom]; the term $ab$ for the reverse combination of acidity-basicity (donor-acceptor) of hydrogen atom, and the term $l$ for the dispersion interaction and the thermodynamically entropic effect for cavity formation (i.e., it is a general measure of lipophilicity for hexadecane) [27]. The variables $r$, $s$, $a$, $b$, and $l$ determine the properties of the adsorbent film. The coefficients $R$, $\pi$, $\alpha$, $\beta$, and log $L^{16}$ are parameters of the adsorbate gas. They are shown in Table 1, which additionally indicates the two-phase partitioning coefficients for gas-water ($L_w$) [28, 29] and octanol-water ($P$) [27, 30]. These indices take part in the intermolecular interactions thermodynamically and kinetically. None of these terms is completely independent of the others. For instance, the polarity correlates with hydrogen-bonding and polarizability associated with the dispersion force.

Using the sorption capacities of 17 kinds of adsorbates shown in Figure 4, the LSER equation quantifying the partitioning coefficient ($K$) of the gelatin-sputtered film is written as the following form:

$$\log K = 0.1 R + 0.3 \pi + 0.6 \alpha + 0.2 \beta - 0.5 \log L^{16} - 2.4.$$
It is recognizable that the electrostatic interactions originated in the inhomogeneous distribution of surface charges substantially govern the VOC-sorption characteristics of the gelatin-sputtered film. This is because the corresponding coefficients $r$, $s$, $a$, and $b$ are positive whereas the thermodynamic coefficient $l$ representative of lipophilicity is negative.

SPM images of the gelatin-sputtered film surface are shown in Figure 5, in which the surface potential and phase shift corresponded to the topography are exhibited. All of the images were recorded under a pure N$_2$ flow without VOCs. The potential image measured by KFM has an exceedingly low resolution, containing many noisy horizontal lines [Figure 5(b)]. This may be attributed to the low tracking speed for charge modulation. Despite the unclear images, we have determined the averaged surface potential by using computational statistics.

Figure 6(a) shows the time course of changes in surface potential starting at changing a flow from pure N$_2$ to 1000 ppm VOC by turning a four-way valve. These surface potentials are the averaged values of the $1 \times 1$ $\mu$m$^2$ area: Sequential lines (a), regression lines (b), and rates of changes estimated by regression lines (c).

It is recognizable that the electrostatic interactions originated in the inhomogeneous distribution of surface charges substantially govern the VOC-sorption characteristics of the gelatin-sputtered film. This is because the corresponding coefficients $r$, $s$, $a$, and $b$ are positive whereas the thermodynamic coefficient $l$ representative of lipophilicity is negative.

As described in elemental ratios revealed by XPS, the relative content of nitrogen is apparently higher for the gelatin-sputtered film than the polysaccharide pectin-sputtered film (C : O : N = 75.0 : 19.5 : 5.5) [10]. As shown in Figure 3 (FTIR spectrum), the gelatin-sputtered film contains a number of the ammonium ions with hydrogen bonds, inducing the positive charge at surface. On the contrary, the oxygen-rich pectin-sputtered film takes predominately the negative charge due to the ionized carboxyl groups, which are also assigned by FTIR measurement [10]. Comparing the sputtered films originated in the polypeptide gelatin and polysaccharide pectin, it is revealed that the ionic functional groups are likely to govern electrostatic characteristics of the sputtered films.

In the KFM measurement, the drift of the gelatin-sputtered film is in an opposite direction to the pectin-sputtered films. The direction of the drift is governed by the polarity of the initial potential. The potential tends to enhance since the charge increases with time. The gelatin-sputtered film with positive potential shows a gradually increasing drift of the surface potential, whereas the pectin-sputtered film, with negative potential, has a gradually decreasing drift [10].
Figure 7 shows the shifts in surface potential from keeping under pure N₂ for 10 min to introducing the 1000-ppm VOCs by turning a four-way valve. It is worth noting that 1-propanol only shows the negative shift from pure N₂ to 1000 ppm VOCs. This negative shift of 1-propanol is reproducible for three measurements. Contrary to 1-propanol, 2-propanol shows a positive shift like the other VOCs. The entropy effect [31] of the linear carbon chain may be due to this unique negative shift, taking into account their amphiphilic characteristics interactive with surface water, as indicated in Table 1.

In contrast to the KFM images, the DFM images are clear, and especially informative about the boundary of micro-columns [Figure 5(c)]. The increase of charging enhances the interaction force between the probe tip and film surface, as shown by the DFM measurements summarized in Figure 8(a, b). The large retarding phase shifts are indicative of the large interaction with probe tip at the boundary of micro-columns. It is recognizable that the VOC molecules predominantly adsorbed on the boundary (periphery) of micro-columns rather than the head of micro-columns, according to the DFM image. The time-course of shifts of retarding phase shift starting at changing a flow from pure N₂ to 1000 ppm VOC is shown in Figure 8(a). These shifts are also averaged in the 1 × 1 μm² area, like the KFM measurements. Contrary to the surface potential, they show a negative drift, suggesting a gradual increase of surface interaction due to adsorption of the VOCs. The highly polar species generally show higher rates of negative drifts than the poorly polar species, as summarized in Figure 8(b). The polysaccharide pectin-sputtered film generally shows the same tendency of time-course of retarding phase shift in the DFM measurements [10]. This is also due to the gradual increase of surface interaction by enhancement of charging as revealed by KFM measurements [10].

Figure 9 shows the time-dependent standard deviation for ethanol and hexane, which are taken as paradigms for polar and non-polar species. The figure is summarized for four measurements of each VOC. Polar ethanol shows small deviation in comparison with non-polar hexane until 40 min. In the early stage of adsorption, the small fluctuation in polar ethanol is due to stable adsorption by stronger interactions, in comparison with non-polar hexane.

Regardless of polarity, the gradual enhancement of the surface charging, represented by the shift in KFM, profoundly correlates with the gradual increase of surface interactions, as shown in the DFM measurements. Figure 10 exhibits the score plots of principal component analysis on the VOCs using the 1st principal component (PC1) as the abscissa and the 2nd principal component (PC2) as the ordinate. Principal component analyses were carried out by using the feature values of the shifts at 1, 5, 10, 20, 40, 60, 80, 100, and 120 min in the KFM and DFM measurements for each 1000-ppm VOC, as indicated in Figures 6(a) and 8(a). These nine values are expected to depict the time-course of the shifts in a stepwise manner. It is possible to recognize that the VOCs are roughly divided into two areas, corresponding to highly polar species (alcohols and water) and non-polar species (hydrocarbons), except for hexane. The anomalous situation of hexane, locating in an area of polar species in Figure 10(b), is attributable to its high hydrophobicity [32]. This would eliminate a number of surface water molecules as an effect of the dissolu-
tion-derived decrease of surface tension typical of the amphiphilic species [33]. Moreover, amphiphilic acetate with poorly polar characters is also located in both of the polar and non-polar areas in Figure 10(a).

Factor loadings of the main principal components are summarized in Table 2. These values indicate the correlation coefficients of each explanatory valuable (the time-dependent shift) to the objective valuable (principal component). In both of the KFM and DFM measurements, the shift values at 20, 40, 60, and 80 min are crucial to PC1, which is the most informative component as indicated by the proportion of variance in the parentheses. Then, the VOCs are roughly discriminated by polarity, based on the shift data at several ten minutes after enough exposure of the VOCs. On the other hands, the early shifts at 1, 5, and 10 min and the late shifts at 100 min and 120 min are important for PC2, which is poorly informative.

Table 2: Factor loadings of main principal components.

<table>
<thead>
<tr>
<th></th>
<th>KFM</th>
<th>DFM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PC1</td>
<td>PC2</td>
</tr>
<tr>
<td>1 min</td>
<td>0.872</td>
<td>−0.363</td>
</tr>
<tr>
<td>5 min</td>
<td>0.909</td>
<td>−0.350</td>
</tr>
<tr>
<td>10 min</td>
<td>0.882</td>
<td>−0.357</td>
</tr>
<tr>
<td>20 min</td>
<td>0.924</td>
<td>−0.329</td>
</tr>
<tr>
<td>40 min</td>
<td>0.964</td>
<td>−0.040</td>
</tr>
<tr>
<td>60 min</td>
<td>0.931</td>
<td>0.208</td>
</tr>
<tr>
<td>80 min</td>
<td>0.962</td>
<td>0.254</td>
</tr>
<tr>
<td>100 min</td>
<td>0.873</td>
<td>0.441</td>
</tr>
<tr>
<td>120 min</td>
<td>0.776</td>
<td>0.605</td>
</tr>
</tbody>
</table>

IV. CONCLUSIONS

Nitrogen-rich carbonaceous films were prepared by radio-frequency sputtering of biomedical-graded polypeptide gelatin. These films are composed of densely packed microcolumns, resulting in a groove-poor structure. The quartz crystal resonators (QCRs) coated with these films are adsorptive for a number of volatile organic compounds (VOCs). The QCR with the adsorptive film has specifically pronounced affinity for polar and small VOCs, in comparison to the nitrogen-poor sumi-sputtered film.

The intermolecular interactions by the electrostatic force play a decisive role in the linear solvation energy relationships, which were modeled using the sorption capacities of 17 kinds of VOCs. Kelvin force microscopy (KFM) reveals that surface charging increases with exposure of the VOCs proportionally to the increase in the interaction force as measured with a dynamic force mode (DFM). The direction of the drift during KFM measurements is opposite between the polypeptide gelatin-sputtered film and the polysaccharide pectin-sputtered film. These are basically due to the predominant charging groups in the sputtered films, namely an ammonium group for the gelatin film and a carboxyl group for the pectin film.

The increasing rate of the surface interactions by exposure to the VOCs is higher for the polar species than for the non-polar species. Deviation of the interaction force induced by adsorption of the VOCs is higher for hexane than for ethanol at an early stage of adsorption until 40 min. The scatter plots of the 1st and 2nd principal components can basically discriminate between the polar species and the non-polar species, by using the shifted values at 120 min in the KFM and DFM measurements. This rough discrimination is basically achieved by the 1st principal component,
which is mainly composed of the shifted values between 20 min and 80 min, i.e., long exposure of the VOCs.

Acknowledgments

The authors would like to thank Y. Ishida, H. Kato, and S. Taka-ya for their technical supports.

References