

Structures and VOC-Sensing Performance of High-Sensitivity Plasma-Polymer Films Coated on Quartz Crystal Resonator

Iwao Sugimoto*, Masayuki Nakamura and Mamoru Mizunuma

NTT Lifestyle and Environmental Technology Laboratories
Midori-cho, Musashino-shi, Tokyo 180-8585, Japan

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Radio-frequency sputtering of amino acids, adenine and polyolefins can provide a variety of chemical-sensing films with high sensitivities at low ppb level. The molecular structures of phenylalanine and tyrosine films preserve the basic structures of amino acids. A quartz crystal resonator plate coated with these plasma-polymer films can be used as a mass transducer. That is, transducers with amino acid films showed no softening or damping in the presence of saturated polar and non-polar organic vapors. Co-sorption measurements of water and volatile organic compound (VOC) vapors revealed that the polyethylene film is effective for use in a practical environment due to its high affinity for VOCs and relatively low affinity for water vapor. Phenylalanine and tyrosine films can detect polar VOCs, even though they have already absorbed water vapor considerably, due to their high sorption capacities.

1. Introduction

A multi-sensor array in combination with chemometric data processing enables the realization of a number of gas identification systems, commonly known as the electronic nose. Improving their accuracy and reliability for determining the presence of volatile organic compounds (VOCs) will, however, be a never-ending task.

Among several piezoelectric mass transducers, the thickness-shear-mode quartz crystal resonator (QCR) is superior in terms of signal-to-noise (S/N) ratio and its simple paramet-

ric structure,⁽¹⁾ but inferior in terms of sensitivity. To prepare a practical device, one reasonable approach is to develop sensitive and reliable overlayers for a QCR.

Plasma-polymer films (PPFs), which are produced by vacuum processing under high-energy irradiation, have structural advantages in terms of their chemical-sensing layers: (i) contaminant-free networks with high atomic density, (ii) high restructuring reversibility in response to sorption/desorption of VOCs, and (iii) high adhesiveness to the transducing substrate. These characteristics are attributed to their unique interactive components, such as radical sites, multiple bonds, and crosslinks, and inspire us to try and exploit PPF-based mass-sensitive overlayers for a QCR.

The sorption capacity [corresponding to partition coefficient (K)] of solvent polymeric films for VOCs can be assessed from intermolecular interactions between solute and solvent molecules. Linear solvation energy relationships (LSERs)⁽²⁻⁴⁾ have been widely used as a quantitative description of sorption behavior, and are described by

$$\log K = C_0 + r(R_2) + s(\pi_2) + a(\beta_2) + b(\alpha_2) + l(\log L_{16}),$$

where C_0 is a regression constant; r is the polarizability of the solvent polymer and R_2 is that of solute VOC; s is the polarity of the solvent polymer and π_2 is that of solute VOC; a is the hydrogen-bonding acidity of the solvent polymer and β_2 is the hydrogen-bonding basicity of solute VOC; b is the hydrogen-bonding basicity of the solvent polymer and α_2 is the hydrogen-bonding acidity of solute VOC; l and $\log L_{16}$ are the dispersion/cavity factors of the solvent polymer and solute VOC, respectively. Conversely, if a variety of solutes are used as molecular probes, LSERs can offer structural information on the solvent films.

Complete control of the molecular structure of PPFs is generally difficult. However, we can produce films, such as amino acid films,⁽⁵⁾ which contain the basic structure of raw materials by means of low-power plasma processing. Therefore, we can easily predict the sorption characteristics of probing films, which depend on the nature of raw materials that can be selected from a wide range of organic compounds.

However, the validity and reliability of these LSERs are reduced for solvent films that have complicated polymeric structures that are well represented by highly crosslinked networks of plasma polymers. We must try to extract additional factors from the complicated structures. These factors can simplify the guidelines for explaining the gas-sorption behavior of the PPFs.

Aside from a highly crosslinked structure, we have focused on the fact that plasma-polymeric networks contain unsaturated carbons (radical sites and multiple bonds) that can interact with solute molecules by specific spin-related interaction⁽⁶⁾ and π -electron-derived interactions: π - π interaction,⁽⁷⁾ cation- π interaction,⁽⁸⁾ C-H- π interaction,⁽⁹⁾ and Cl- π interaction.⁽¹⁰⁾

Unsaturated carbons were revealed in our recent study in which polarizability was indicated to be a critical factor affecting vapor-sorption behaviors of sputtered fluoropolymer films.⁽¹¹⁾ We have previously reported that the formation of polarizable unsaturated moieties, such as multiple bonds and radical sites, is promoted by the irradiation effects of ultraviolet light during fluoropolymer sputtering⁽¹²⁾ and that the polarizability-driven gas-sorption capacities of the sputtered films are enhanced by this photo-assisted sputtering.⁽¹¹⁾

To reduce their interfacial energy as much as possible, the structure of PPFs changes reversibly in response to surrounding chemical impulses.^(13,14) This accounts for the reversible sorption-desorption behavior of the PPFs.

In this paper, focusing on amino acid and polyethylene films, we report the basic mass transduction properties of PPF-coated QCR devices. These properties can be characterized by the structures of PPFs. We also cover the fundamental issues of VOC-sensing: aging characteristics in steam conditions, responses to humidified VOCs, and high sensitivities for VOCs at low ppb level.

2. Experimental

2.1 Sensor device preparation

We prepared piezoelectric mass transducers consisting of a 9-MHz AT-cut QCR (NIPPON DENPA KOGYO) coated with PPFs by diode-type capacitively coupled radio-frequency (rf) sputtering. The sputtering materials were amino acids, adenine, and polyolefins [polychlorotrifluoroethylene (PCTFE) and polyethylene (PE)]. We used DL-histidine and D-isomers of α -amino acids: phenylalanine, tyrosine, alanine, and glutamic acid.

Sputtering was performed in a sputter-up configuration. We used helium as the sputtering gas for the amino acids and the power density was kept at 0.42 W/cm². A detailed description of the deposition methods has been reported previously.⁽⁵⁾ For PCTFE film deposition, we used argon for the sputtering gas and the power density was kept at 2.2 W/cm². The plasma species were monitored by a quadrupole mass filter (ANELVA, AQA-200) that was conditioned by a differential vacuum system. The film deposited on each side of the QCR plate was 0.4 to 0.7 μ m thick.

2.2 Gas sorption measurement

We used a flow system for sorption measurements of pure VOCs, the detailed schematics of which have been shown previously.⁽¹¹⁾ Six QCR sensors were placed in a 30-ml aluminum cell, that was housed in a constant-temperature chamber thermostated at 25 \pm 0.1°C. The VOCs were generated by passing synthetic air (99.9999%) through a diffusion tube containing liquid organic solvents, and the tube cell was immersed in a water bath. The synthetic air was used as a diluting gas as well as a cleaning gas. The typical flow rate of the air was 0.2 l/min. The concentrations of VOCs were determined by dividing their volumes by the volume of synthetic air. A VOC was introduced into the sensor cell after a baseline fluctuation below 1 Hz for 10 min was established by cleaning. Switching between cleaning (background) and measuring modes was done quickly using a four-way valve, which produced a step response; it kept the gas pressure constant by suppressing the experimental deviations. The sorption capacity of each film was determined as the maximum solubility of the VOCs over three h.

Figure 1 shows the gas flow system for sorption measurement of a mixture of water vapor and VOC. This system is basically composed of a VOC feeding system in combination with a water vapor generation line. Water vapor is generated by bubbling deionized water, and the humidity is controlled by the flow rates for bubbling and for

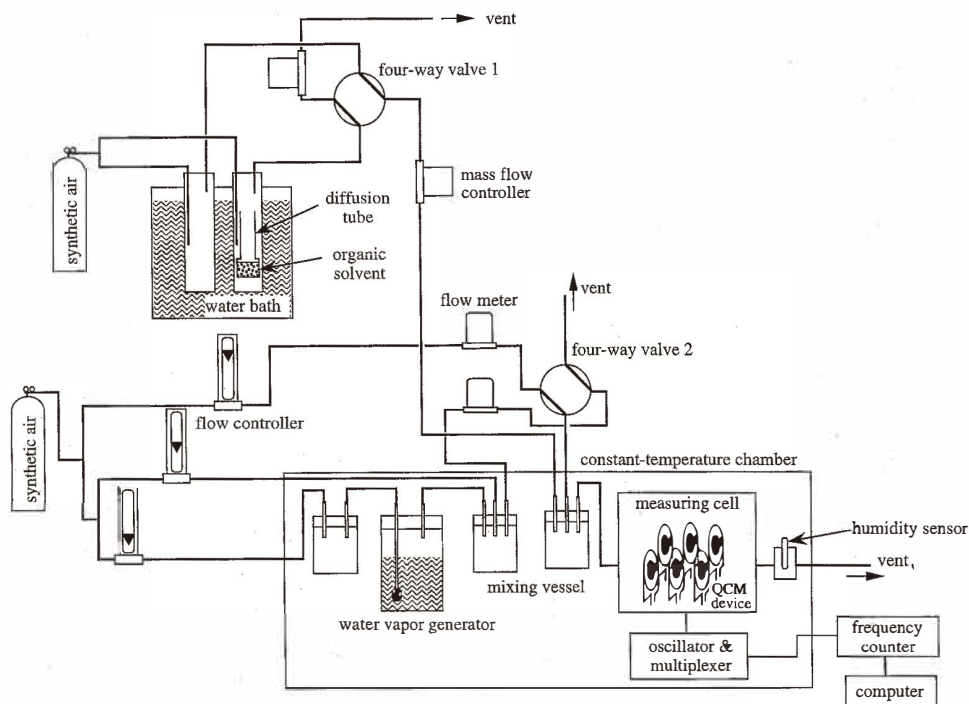


Fig. 1. Gas sorption measurement system for volatile organic compounds.

diluting synthetic air. The relative humidity was determined by a dielectric-type humidity sensor (ROTRONIC, I-155C). Using this system, we can control the concentration of water vapor and VOC vapor independently and feed pure water vapor, pure VOC vapor, or their mixtures to the measuring cell while suppressing the changes in pressure, concentration, and flow rate.

The sorption capacities were determined by measuring the frequency changes after three h of sorption measurements. The frequency of each sensor was measured by a frequency counter (ADVANTEST, R5361A) whose accuracy was 0.1 Hz. We use Sauerbrey's equation⁽¹⁵⁾ to translate the frequency change (ΔF) into mass loading (Δm):

$$\Delta m = -[A(\rho_q \mu_q)^{1/2} / 2F_0^2] \Delta F,$$

where F_0 is the fundamental frequency of the unloaded QCR (9 MHz), A is the electrode area (0.13 cm²), ρ_q is the density of quartz (2.65 g/cm³), and μ_q is the shear modulus of quartz (2.897×10^{11} dyn/cm²). With these constants, we obtain

$$\Delta m \text{ (ng)} = -1.05 \Delta F \text{ (Hz)}.$$

2.3 Film characterization

2.3.1 X-ray photoelectron spectroscopy (XPS)

XPS (VG, MicroLab-MK2) was carried out using low-power (100 W) Mg-K α radiation as the excitation source. The PPF samples were stored in a vacuum chamber at < 10 Pa to prevent aging and contamination. The chamber pressure during analysis was kept below 4.6×10^{-8} Pa. The incident angle of the X-ray beam and the photoelectron take-off angle with respect to the film surface were 90°. The raw materials for the amino acids were analyzed by using pressed pellets. Each binding energy was calibrated to compensate for charging by setting the strongest C_{1s} peak to 284.6 eV, which is representative of CH_x moieties.

2.3.2 Electron spin resonance (ESR) analysis

ESR analysis under Ar atmosphere (at 20°C) was carried out using a BRUKER ESP-350E. The samples were held, perpendicular to the magnetic field, in a TM₁₁₀ cylindrical cavity. The external magnetic field (ranging from 313 to 363 mT) was modulated by 0.5 mT at a frequency of 100 kHz, and the microwave power was 0.4 mW. The reflected signals were detected by a microwave bridge and a digital phase-sensitive detector, and the microwaves were monitored with a frequency counter (HEWLETT PACKARD, HP-5351B).

3. Results and Discussion

First, we report the results of structural characterization of amino acid films. During sputtering, we monitored the plasma species using a quadrupole mass spectrometer. Figure 2 shows the mass spectrum of the plasma species in phenylalanine sputtering. This spectrum exhibits the characteristic fragmentation pattern of phenylalanine, and suggests that sputtering vaporizes the amino acid. The amino acid molecules are likely to form polymeric films on the film substrate through complicated plasma reactions such as condensation and disproportionation. Under the most destructive conditions, elimination induced by bond cleavage produces a number of radical sites that may be quenched by forming bonds with each other, resulting in carbonaceous crosslinked networks.

We previously clarified the preservation of the basic structure of amino acids and the formation of peptide bonds in PPFs by XPS and static secondary ion mass spectroscopy.⁽⁵⁾ The atomic ratios of PPFs evaluated by XPS are listed in Table 1. Aside from the alanine film, the concentrations of carbon and nitrogen in the sputtered films are higher than those in the unsputtered raw materials. That is, the oxygen concentrations of the sputtered films are lower than those of unsputtered ones. It is noteworthy that the atomic ratio of unsputtered raw alanine differs considerably from the stoichiometric value. Oxygen ratios in the sputtered films tend to be reduced by plasma reactions that are likely to cause decarboxylation and dehydration. However, the differences in concentrations of carbon, nitrogen, and oxygen among the unsputtered raw material, the stoichiometry, and the sputtered film for the amino acids that have a benzene ring (benzenoids) are considered negligible. This suggests that benzenoids in plasmas will remain intact and durable due to

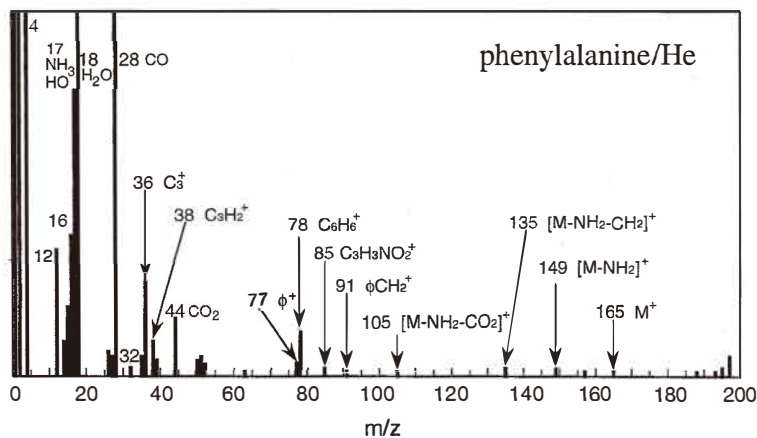


Fig. 2. Mass spectrum of the plasma species in phenylalanine sputtering.

Table 1
Atomic ratios of amino acid films.

| α -amino acid: $\begin{pmatrix} \text{HOOC-CH-NH}_2 \\ \\ \text{R} \\ \\ \text{R}' \end{pmatrix}$ | C (%) | N (%) | O (%) | | |
|--|---------------------------------------|-------------------------|-------------------------|-------------------------|---|
| Glycine | H | 45 (45) 53 | 20 (20) 31 | 35 (35) 16 | unspattered (stoichiometry) sputtered film |
| Alanine | CH ₃ | 71 (50) 57 | 12 (17) 22 | 17 (33) 21 | |
| Glutamic acid | (CH ₂) ₂ -COOH | 56 (62) 64 | 10 (13) 17 | 34 (25) 19 | |
| Histidine | | 55 (55) 64 | 27 (27) 21 | 18 (18) 15 | |
| Tyrosine | CH ₂ - | 70 (69) 76 | 8 (8) 8 | 22 (23) 16 | |
| D-Phenylalanine | CH ₂ - | 76 (75) 78 | 8 (8) 9 | 16 (17) 13 | |

the stability of β -carbons, which cannot become allyl carbons because of their direct bonding to the benzene ring.⁽¹⁶⁾

ESR spectra of all of the sputtered films show featureless broad curves, which are typical of PPFs. The characteristic ESR information is summarized in Table 2. We regard the g values and line widths as being identical for amino acid films. The spin densities of these amino acid films are considerably lower than that of the PCTFE film by one order of magnitude. Corresponding to the low spin densities, the line widths of the amino acid films are smaller than that of PCTFE film. The low spin densities of the amino acid films are probably due to the more stable atomic bonds of amino acids than those of PCTFE that consists of halogenated carbons that are likely to be cleaved by the high electron affinities of halogens.

We investigated the basic performance of the mass transducers in the PPF-coated QCR devices. We used impedance analysis with a network analyzer (HEWLETT PACKARD, HP-4195A) to examine the damping loss of the film. A film-coated QCR was placed in a sealed 100-ml flask filled with saturated VOC vapor, with the highest concentration of VOC at 25°C. Figure 3 shows the frequency shifts and conductance changes of PCTFE and phenylalanine films exposed to the head-space of six organic solvents for ten h. These severe high-concentration conditions (ca. 10%) induce no significant changes in the conductance of phenylalanine film, and this finding is concomitant with quite large frequency shifts. These results show that the phenylalanine-coated QCR is a durable and reliable mass transducers. In contrast, the PCTFE film showed large conductance changes when exposed to polar vapor. These large conductance changes suggest that the mechanical properties of the PCTFE film may be changed by swelling and softening (damping effects)⁽¹⁷⁻²²⁾ caused by the saturated sorption of polar VOCs. However, this damping phenomenon does not occur in saturated non-polar vapors.

The changes in the response of a PCTFE-coated QCR device to 1000-ppm VOCs (3000-ppm acetone) with aging in an environmental chamber (60°C, 85% RH) suggest that it has long-term durability (Fig. 4). Relative ratios of conductance to the initial value tend to decrease for non-polar VOCs and increase for polar VOCs. Bond formation after aging was indicated by the signals for C-H, C=O, and O-H stretching bands that appeared in the infrared spectra of the PCTFE film kept in an environmental chamber for six months. This structural change can explain the enhanced affinities of PCTFE film for polar VOCs.

Amino acid films, which consist of polar oxygen and/or nitrogen moieties, are expected to exhibit high sorption capacities for polar vapors on the basis of their hydrophilic

Table 2
Summary of ESR analysis.

| Film | Spin density (spin/cm ³) | g value | Line width (G) |
|---------------|--------------------------------------|-----------|----------------|
| phenylalanine | 8.8×10^{18} | 2.0032 | 12 |
| alanine | 4.8×10^{18} | 2.0042 | 12 |
| glutamic acid | 6.8×10^{18} | 2.0040 | 13 |
| PCTFE | 7.8×10^{19} | 2.0037 | 47 |

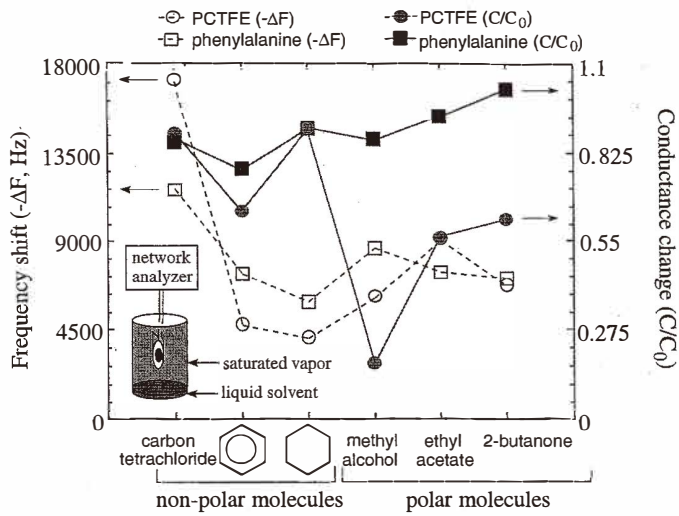


Fig. 3. Frequency shift and conductance change (C_0 : conductance before gas sorption; C : conductance when exposed to saturated vapors) of PPF-coated QCR devices.

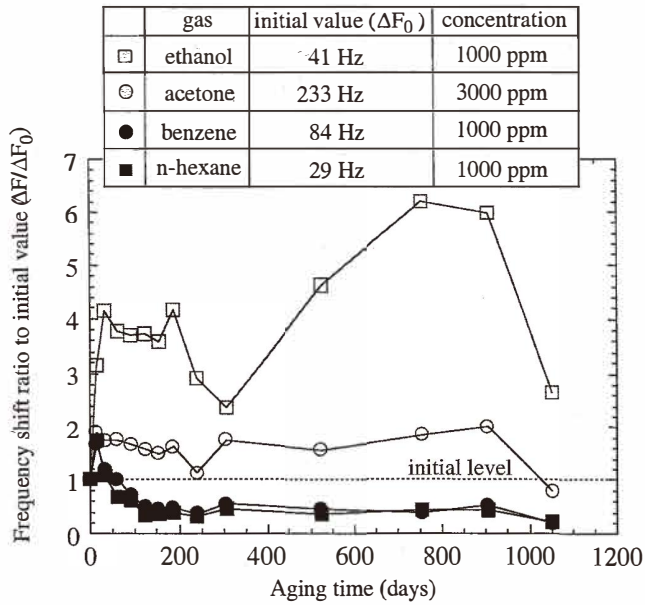


Fig. 4. Response changes of the aged PCTFE-coated QCR device.

molecular structure. Figure 5 shows the isothermal sorption capacities of amino acid films for low concentration vapors of acetaldehyde and formic acid at 25°C. These results suggest that the detection limit is at the sub-ppm level. Also, the almost proportional increase in sorption capacity with increasing vapor concentration suggests that these sorption characteristics basically obey Henry's law.

We could generate an extremely low concentration vapor stream using nerolidol ($C_{15}H_{26}O$), which is classified as a woody flavor source in the Flavors & Fragrance catalog (Aldrich Chemical Co., Inc.). High sensitivities and a variety of step responses of PPF-coated QCR devices are seen for 50-ppb nerolidol flow at 2 l/min (Fig. 6). It can be observed that the QCR devices coated with PE, phenylalanine, and tyrosine films have extremely high sensitivities for detecting long-chained alcohol vapors at low ppb levels. In contrast, the PCTFE film exhibits a negligible change in frequency of no more than 3 Hz, but it can have a specific affinity for nonpolar species having high polarizabilities, such as benzene derivatives and fully chlorinated carbons (CCl_4 and C_2Cl_4).⁽¹¹⁾

In a practical situation, we must consider the existence of water vapor, which should affect the responses of QCR devices via its highly dipolar interaction with QCR overlayers. We have measured sensor responses of PPF-coated QCR sensors exposed to a flow of a gaseous mixture of water and VOC (n-butyl alcohol or toluene). Using the measurement system shown in Fig. 1, we first attempted to attain the background level at which each QCR device was exposed to a flow of pure synthetic air by setting two sets of four-way valves to feed pure synthetic air. After attaining equilibrium, the gas flow into a measuring cell was changed to pure water vapor using four-way valve 2. The response curves of QCR

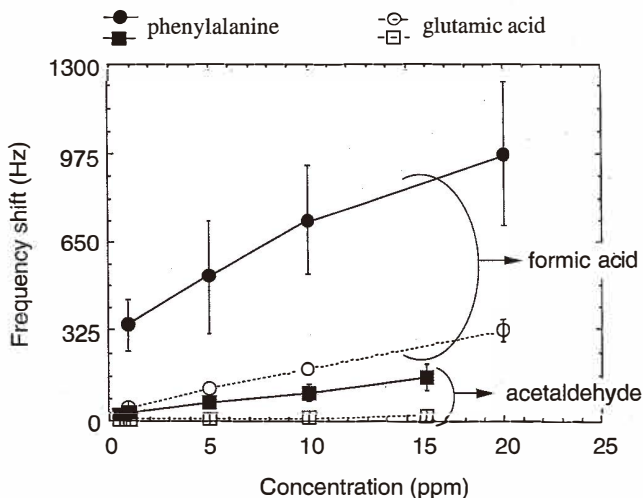


Fig. 5. Change in frequency of QCRs coated with amino acid films with varying concentrations of acetaldehyde and formic acid vapors.

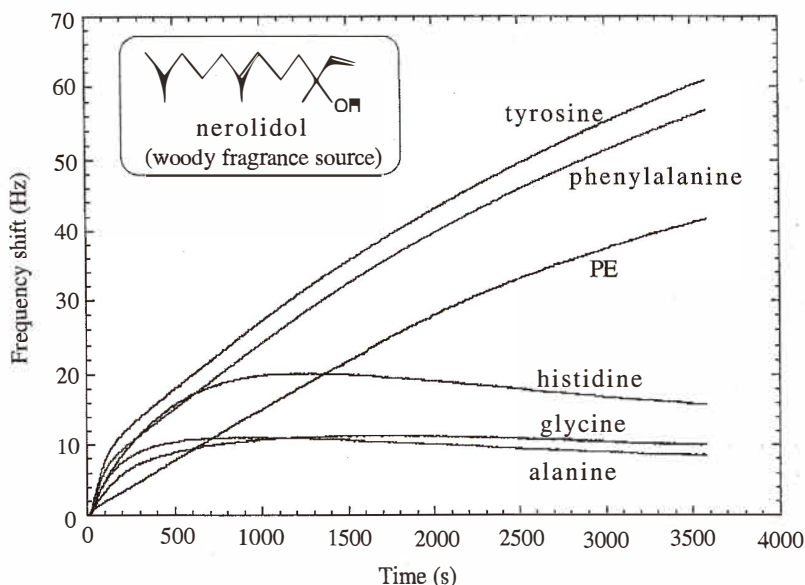


Fig. 6. Step responses of PPF-coated QCR devices to 50-ppb nerolidol vapor.

sensors for sorption of water vapor are depicted in Figs. 7(a) and 8(a). After QCR sensors were exposed to pure water vapor for five h, VOC vapors were added to the gas feeding line by turning four-way valve 1. The sensor response curves are shown in Figs. 7(b) and 8(b), which express the changes from pure water vapor (background) to a mixture of water and VOC vapors.

We first measured the case of *n*-butyl alcohol (Figs. 7(a) and 7(b)) and then measured that of toluene (Figs. 8(a) and 8(b)). Comparing Figs. 7(a) and 8(a), all of the frequency shifts of QCR sensors in Fig. 8(a) have been reduced due to the aging effects induced by iterative sorption/desorption of vapors. Figures 7(a) and 8(a) show that polar amino acid films have high sorption capacities for water vapor and that non-polar PCTFE and PE films have low affinities for water vapor. These results are in accordance with the structures of the PPFs. After sufficient sorption of water vapor, which reached the quasi-equilibrium state, 104-ppm *n*-butyl alcohol vapor was added to the gas feeding line. Figure 7(b) shows an extremely large frequency shift for the PE-coated QCR with a high S/N ratio. Phenylalanine and tyrosine films also responded to additional *n*-butyl alcohol impulses; however, their response curves are inferior to that of the PE film. Histidine, adenine, and PCTFE films showed no detectable changes in their frequency shifts. Except for PE films, PPFs expressed no detectable changes in the presence of 107-ppm toluene vapor (Fig. 8(b)). These measurements of co-sorption of water and VOC vapors revealed that the PE film is effective for use in a practical environment due to its high affinity for VOCs and relatively

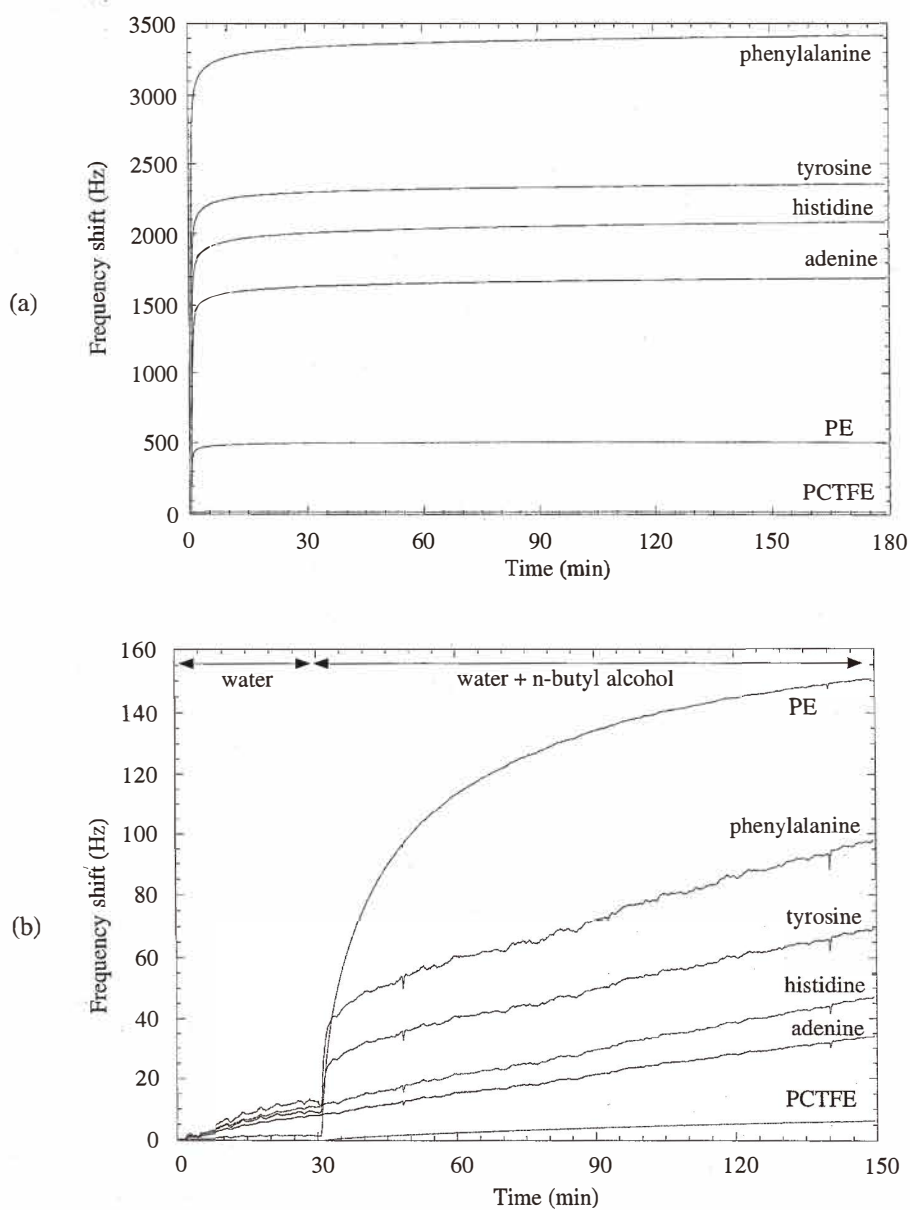


Fig. 7. (a) Step responses of PPF-coated QCR devices to pure water vapor at 14.3% RH. (b) Step responses of PPF-coated QCR devices to 104-ppm n-butyl alcohol (baseline of each sensor is the quasi-equilibrium state attained by sorption of 14.3% RH water vapor for five h).

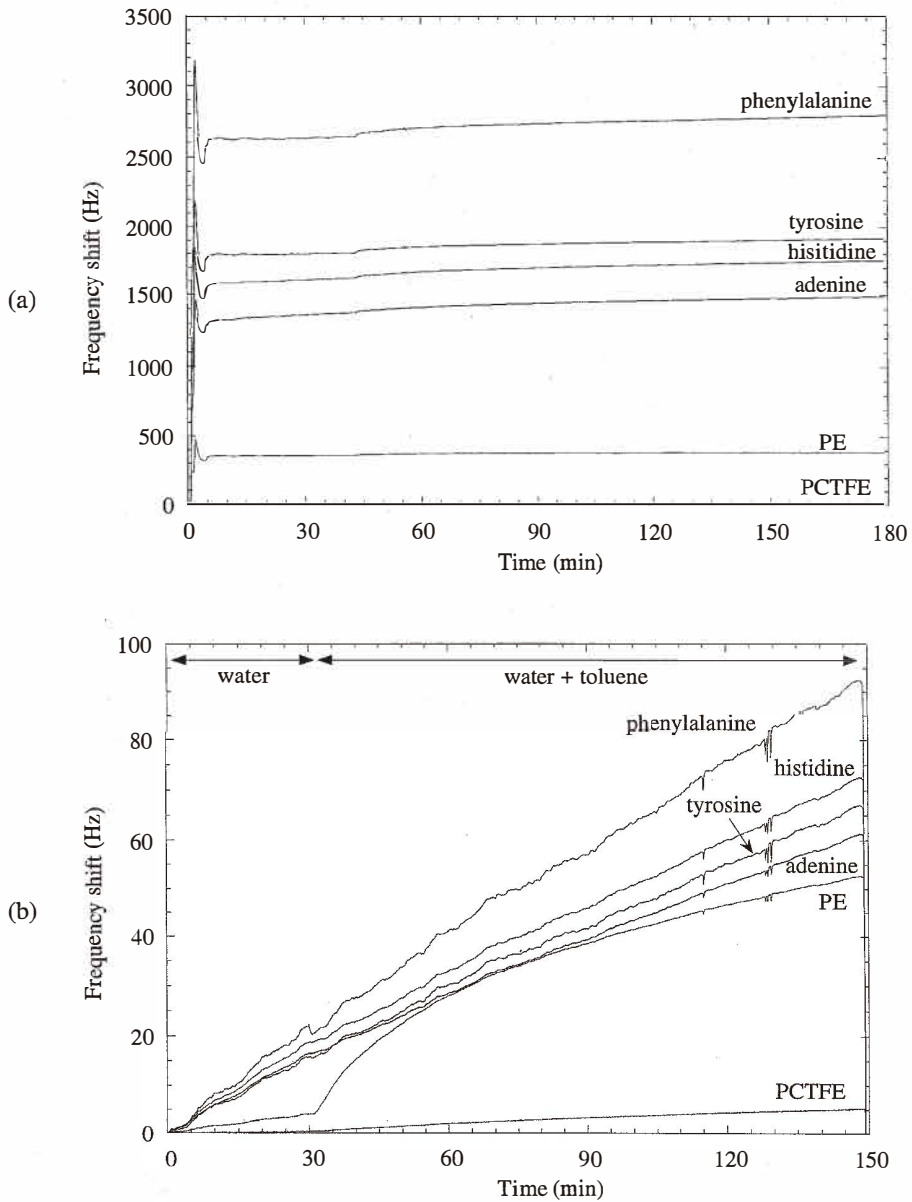


Fig. 8. (a) Step responses of PPF-coated QCR devices to pure water vapor at 19.2% RH. (b) Step responses of PPF-coated QCR devices to 107-ppm toluene (baseline of each sensor is the quasi-equilibrium state attained by sorption of 19.2% RH water vapor for five h).

low affinity for water vapor. Phenylalanine and tyrosine films may be able to detect the polar VOCs, even though they have already absorbed water vapor considerably, due to their high sorption capacities.

4. Conclusion

Radio-frequency sputtering of amino acids, adenine and polyolefins can provide a variety of chemical-sensing films. XPS and ESR analyses suggest that the molecular structures of phenylalanine and tyrosine films preserve the basic structure of the amino acids. A quartz crystal resonator plate coated with these plasma polymer films whose properties can be modified by adjusting their molecular structures, can be used as a mass transducer. That is, transducers using amino acid films showed neither softening nor damping in the presence of saturated vapors of polar and non-polar VOCs; however, a PCTFE film induced damping for polar VOCs.

Amino acids, especially phenylalanine and tyrosine, and polyethylene films have high sensitivities; that is, they respond satisfactorily to 50-ppb nerolidol vapor. Co-sorption measurements of water and VOC vapors revealed that the PE film is effective for use in a practical environment due to its high affinity for VOCs and relatively low affinity for water vapor. Phenylalanine and tyrosine films can detect polar VOCs, even though they have already absorbed water vapor considerably, due to their high sorption capacities.

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