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Odor Sensor Utilizing Surface Plasmon Resonance

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An odor sensor based on surface plasmon resonance (SPR) has been studied for the detection of harmful gases such as ammonia and amines. The sensor was prepared by depositing a molecular recognition membrane on a substrate coated with Au thin film using plasma chemical vapour deposition (CVD). The SPR sensor with acrylic acid thin film as the molecular recognition membrane exhibited excellent selectivity and high sensitivity for ammonia and amines.

1. Introduction

Surface plasmon resonance (SPR) is an optical phenomenon in which incident light excites a charge-density wave at the interface between a highly conductive metal and a dielectric material. The conditions for excitation are determined by the permittivity of the metal and the dielectric material. SPR transduction is widely used as an analytical tool for measuring small changes in the refractive index of a thin region adjacent to a metal surface. The optical excitation of surface plasmon on a thin metallic film has, therefore, been recognized as a promising technique for sensitive detection of chemical species.[1] Several methods have been employed to monitor the excitation of SPR by measuring the light reflected from sensor interface. These include analysis of angle modulation,[2] wavelength modulation,[3] intensity modulation[4] and phase modulation.[5]

It may be possible to apply SPR to a high sensitive odor sensor. Odors, fragrances and aromas have been identified using arrays of gas sensors, such as quartz resonators or oxide semiconductors, in conjunction with associated pattern recognition analysis.[6–13] Recently, we have reported that a novel aroma-sensing method, which uses principle component analysis and neural network pattern recognition of transient responses measured using synthetic-polymer-film-coated quartz resonator gas sensors, is useful in distinguishing the aromas of various kinds of coffee, wines and alcohol.[9,12,13]

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In this paper, we propose that harmful gases such as ammonia, trimethylamine and triethylamine can be detected by measuring SPR using angle modulation. The technique of using a synthetic polymer film as molecular recognition membrane is applied to a SPR sensor.

2. Experimental

Optical SPR sensors are sensitive to change in the refractive index of a sample near a sensor surface. The SPR was measured using the Kretschmann configuration (Toa DKK: PR-40), illustrated in Fig. 1, with a prism and a thin, highly conductive gold metal layer deposited on the prism base. An LED emitting 660 nm light was used as light source in order to excite the SPR. The SPR reflection spectrum (reflected light intensity versus angle of incidence with respect to the normal of the metal/dielectric interface) is measured by coupling transverse magnetically polarized monochromatic light into the prism and measuring the reflected light intensity of the ray exciting the prism versus the angle of incidence. The reflected light was measured using a CCD camera attached to a personal computer. The coupling of energy occurs between the incident light and the surface plasmon waves at the resonance angle, which gives the minimum intensity of the reflected light. The relationship between the resonance angle θ and the wave number of the surface plasmon K_{SP} is given by

$$K_P \sin\theta = K_{SP} \tag{1}$$

and

$$K_{SP} = \frac{\omega}{c}\sqrt{\frac{\varepsilon n^2}{\varepsilon + n^2}}. \tag{2}$$

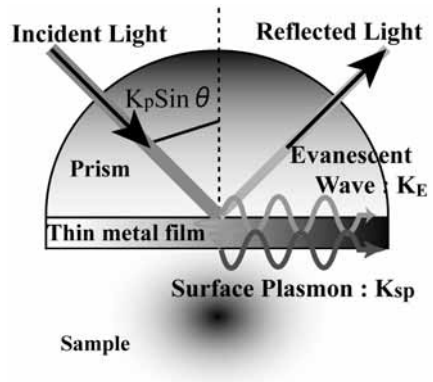

Fig. 1. Kretschmann configuration for generating surface plasmon waves.

where K_P, *K*sp, c, ε and *n* are the wave number of the incident light, the angular frequency of the incident light, the speed of light in vacuum, the permittivity of the thin metal film and the refractive index of a sample near the sensor surface, respectively. Thus, an increase in resonance angle corresponds to an increase in refractive index of a sample near the sensor surface in the SPR reflection spectrum. The schematic configuration of the SPR system is shown in Fig. 2.

In order to utilize this system as a novel odor sensor, a very thin film of acrylic acid as a molecular recognition membrane was deposited on the gold metal thin film using plasma chemical vapor deposition (CVD). The schematic of the plasma CVD system is shown in Fig. 3. A vaporized monomer was introduced into the chamber evacuated at the base pressure of 10 Pa together with Ar as carrier gas. The partial pressures of the monomer vapor and Ar gas were set to be approximately 20 and 80 Pa, respectively. The Ar based plasma was produced by the radio frequency (RF) discharge between two electrodes with a supplied power of 100 W, and activated monomers polymerized on the surface of the thin gold film. Two kinds of monomers, acrylic acid with a carboxyl group and styrene with a phenyl group were used as materials for the molecular recognition membrane. Both monomers have carbon-carbon double bond and are polymerized easily. A typical deposited thickness on the gold film was several tens of nm, which was monitored using quartz resonator.

A test gas at a concentration of 1000 ppm was injected into the 500 ml sensing cell at 20 s after the beginning of the measurement under temperature of 20°C and humidity of 55%. The response of SPR sensor was then monitored for 5 min. Eleven harmful gases, ammonia, acetaldehyde, propionaldehyde, xylene, toluene, trimethylamine, triethylamine, dimethyamine, hormaldehyde, acetic acid and butyl acetate, were used as test gases.

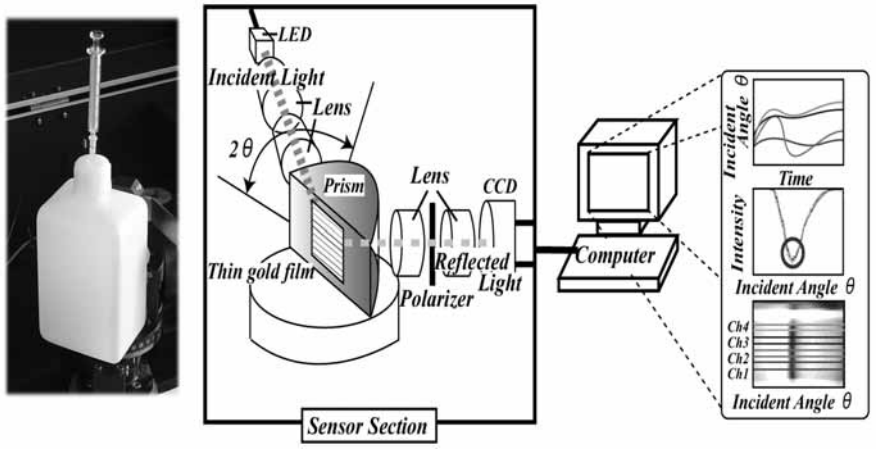

Fig. 2. Schematic diagram of SPR sensor system.

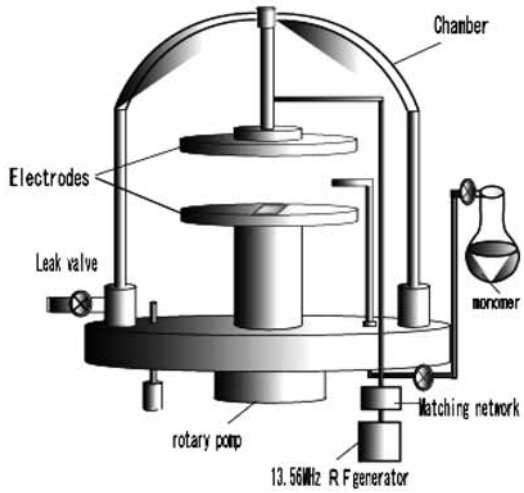

Fig. 3. Schematic of the plasma CVD system.

3. Results and Discussion

Figures 4 and 5 show typical responses of SPR sensors with acrylic acid (46 nm) and styrene membrane (a few tens of nm) to exposure to each test gas, respectively. The SPR sensor using the acrylic acid membrane responded to only the basicitic gases, i.e. ammonia, trimethylamine and triethylamine, with a change in SPR angle on the order of 1°. An adsorption reaction might occur because of the acidity of the acrylic acid membrane and the basicity of these gases, which induced the high response. On the other hand, the SPR sensor using the styrene membrane responded to ammonia, toluene, dimethyamine and butyl acetate with a change in SPR angle on the order of 0.001°, which is equal to the angle resolution of this system. This result suggests that an SPR sensor coated with an acrylic acid membrane exhibits good selectivity for ammonia and amines. The sensitivity of the acrylic acid membrane was 200 times higher than that of the styrene membrane.

The SPR sensor responses of the acrylic acid membrane to various concentrations of ammonia are shown in Fig. 6. An acrylic acid membrane, 46 nm thick was used. The rise time to reach a saturation value for the angle change tended to decrease with increasing ammonia concentration. In addition, each saturation value increased with increasing ammonia concentration, as shown in Fig. 7. The ammonia molecules adsorbed on the membrane surface may equilibrate with ammonia molecules in the gas phase at each equilibrium pressure for various concentrations of ammonia, which causes the coverage of ammonia molecule to be less than unity because change in angle may saturate and become constant for various concentration of ammonia for coverage less than unity. Thus, the SPR sensor is also applicable in high concentration regions. Therefore, this dependence indicates the possibility of quantitatively measurement using the SPR sensor with a molecular recognition membrane. At present, the limiting sensitivity of an SPR sensor

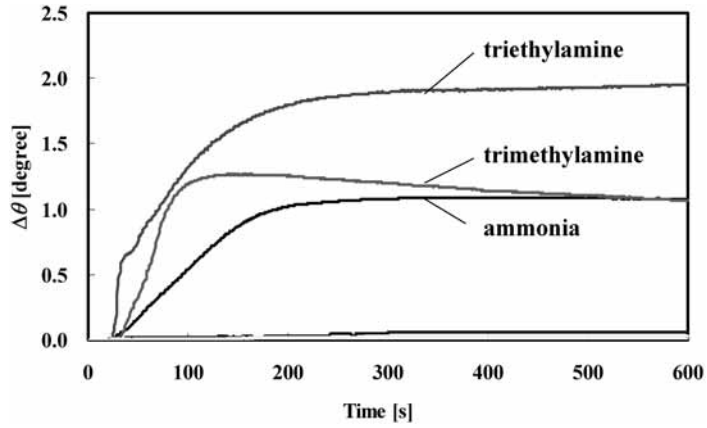

Fig. 4. Responses of an SPR sensor coated with acrylic acid to various gases, where $\Delta\theta$ is change in resonance angle.

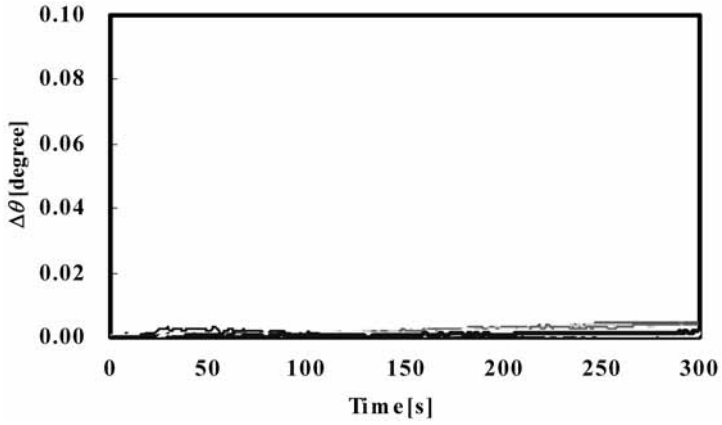

Fig. 5. Responses of an SPR sensor coated with styrene to various gases, where $\Delta\theta$ is change in resonance angle.

coated with acrylic acid thin film for ammonia and amines can be estimated to be several ppm, because the accuracy of the SPR angle change is about 0.001°. The SPR sensor response for various thicknesses of acrylic acid membrane for ammonia is shown in Fig. 8. The concentration of ammonia was 200 ppm and the thicknesses of the membranes were 31, 40 and 46 nm. Since rise times of a few second were obtained for each thickness, the adsorption for each thickness might occur though the same process for the range of the conditions evaluated. Each saturation value increased as the thickness of the acrylic acid membrane increased, which is shown in Fig. 9. The sensor did not respond if the membrane were over 50 nm thick because the distance of approach of the evanescent wave of incident light to the interface between the Au film and the membrane is expected to be

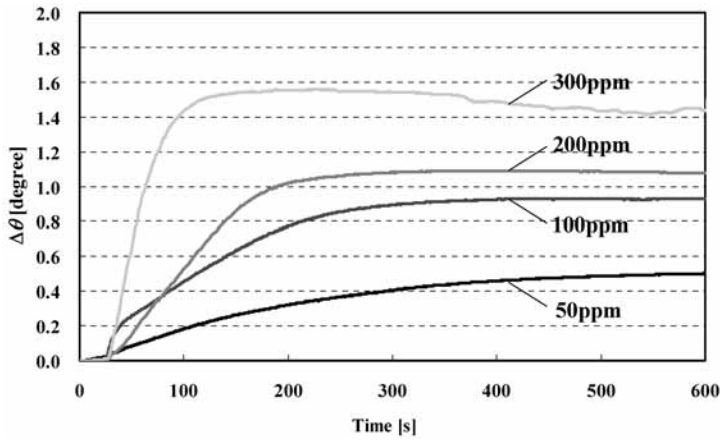

Fig. 6. Responses of an SPR sensor coated with acrylic acid for various concentration of ammonia, where $\Delta\theta$ is change in resonance angle.

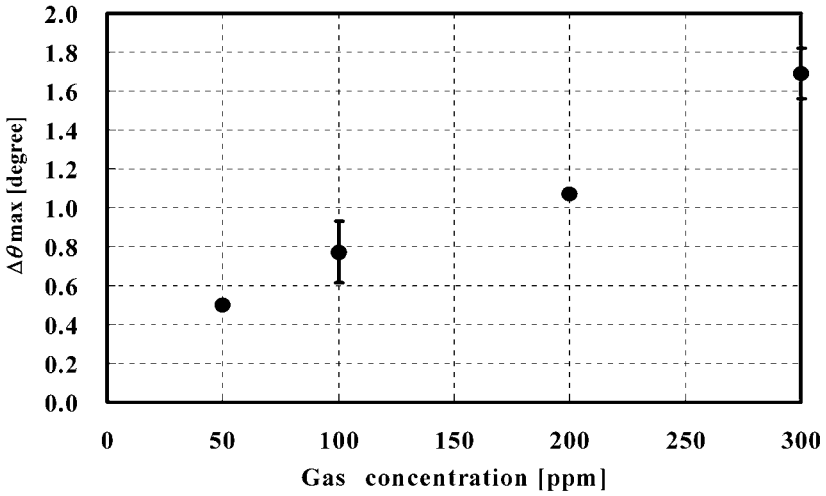

Fig. 7. Dependence of maximum resonance angle change, $\Delta\theta_{max}$, on ammonia concentration of acrylic acid membrane.

several tens nm. If ammonia molecules are adsorbed only on the surface of the membrane, the change of refractive index, namely the change of resonance angle, on the thin Au film may be small.

4. Summary

An odor sensor using the SPR phenomenon has been demonstrated. An SPR sensor with an acrylic acid membrane as a molecular recognition has exhibited excellent selectiv-

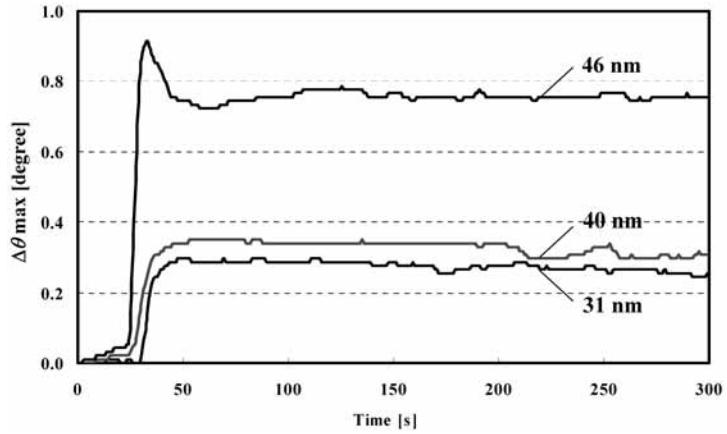

Fig. 8. Responses of an SPR sensor for various thicknesses of acrylic acid membrane, where $\Delta\theta$ is the saturated value of resonance angle change.

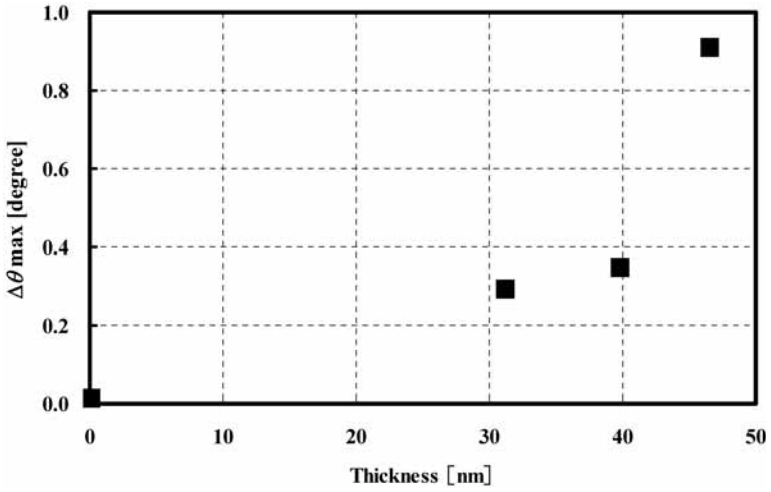

Fig. 9. Dependence of maximum resonance angle change $\Delta\theta_{max}$ on thickness of the acrylic acid membrane based on exposure to ammonia at a concentration of 200 ppm.

ity for ammonia and amines, whereas an SPR sensor with a styrene membrane has little selectivity for gases studied. The output of the SPR sensor increased with increasing ammonia concentration, which indicates the possibility of measuring gas concentration quantitatively with high sensitivity. The detection limit for ammonia is estimated to be several ppm. Moreover, the output of the SPR sensor for ammonia increased as the thickness of the acrylic acid membrane increased. We expect that the sensitivity of SPR sensor can be improved by optimizing the thickness of the molecular recognition membrane.

An SPR sensor with molecular recognition membranes may becomes a useful tool to

identify odors, fragrances and aromas. It is possible to use such a sensor for the detection of the freshness of fish because ammonia and the amines are given off during the deterioration of fish after death.[14]

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