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SAW 디바이스를 이용한 냄새물질 측정 및 냄새센서 시스템의 연구

논 문
8-1-8

Detection of Odorants and Study on the Odorant Sensor System by Using SAW Device.

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Abstract

A surface acoustic wave (SAW) sensor for the detection of odorants has been constructed by depositing various phospholipids and fatty acids onto the surface of the SAW device. The characteristics of a SAW device operating at 310 MHz deposited with silicon monoxide were analyzed. Menthone, amylacetate, acetoin, and other organic gases show different affinities to the coated lipids. An explanation is given for different odorant affinities based on the monolayer properties of phospholipids. The identification of odorants depending on the týpe of lipid used for coating is discussed in terms of the similarity of their normalized resonant frequency shift patterns. Using a number of different lipid-coated SAW devices, odorants can be identified by a computerized pattern recognition algorithm.

Key Words(중요용어) : Vapor Sensor(가스센서), SAW Device(SAW디바이스), Piezoelectric Crystal(압전소자), Lipid(지질), Odorant Sensor(냄새센서), LB Membrane(LB막), Olfactory Mechanism(후각 메카니즘).

1. Introduction

Since Sauerbrey[1] developed the empirical equation for the relationship between the frequency shift of a quartz resonator and the mass of substance deposited on its surface, much attention has been paid to piezoelectric crystal detectors as simple, sensitive and reliable detectors.[2-4]

Piezoelectric crystal resonators have been applied to both gas and liquid phase analysis. After King's proposal(1964) that the coated piezoelectric crystal can be used for vapour detection, extensive studies on gas sensors using piezoelectric crystals have been performed[5].

The first study related to the use of SAW devices as gas sensors was reported in 1979[6]. Their operating principles and properties were reported in more detail by Wohltjen[7,8]. They derived an emprical equation for the relationship between the resonant frequency shift of a SAW device and the mass per unit area on the surface of SAW device.

$$\Delta F = (k_1 + k_2) \times F^2 \times \Delta m A^{-1} = K \times F^2 \times \Delta m A^{-1} \quad (1)$$

where ΔF is the change in frequency(Hz) due to the deposited mass, F is the resonant frequency of the SAW device(MHz), k_1, k_2 and K are material constants for the piezoelectric substrate, m is the mass of the substance deposited on the surface(g) and A is the area coated(cm^2).

This equation is the same as that of the quartz crystal resonator.

The sensitivity of piezoelectric detectors and SAW devices is directly proportional to the

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square of the resonant frequency, and is inversely proportional to the surface area. Therefore, a SAW device is considered to be an excellent transducer for a chemical vapour sensor, because the resonant frequency of a SAW device can be two or three orders of magnitude higher than that of an AT-cut quartz crystal resonator. In addition, the lithographic fabrication capability easily permits a complex circuit to be formed on the same crystal surface[9].

The first study related to the effects of odorants on the planar lipid membrane was reported in 1970[10]. Kurihara group emphasized the importance of lipids in olfactory cells for odorant detection[11,12]. They summarized and concluded the pattern recognition mechanism of odour discrimination from their results.

Refered to these result, Okahata[13] reported reception of odorants and specific adsorption of bitter substances on synthetic lipid bilayer coated AT-cut crystal. We have also reported on the application of a lipid coated AT-cut crystal and SAW device for the determination of odorants[14,15].

In this paper, we report the properties of a SAW device as a transducer of an odorant sensor. SAW resonators coated with four lipids are examined as chemical vapour sensors. The identification of odorants is discussed by comparing the behavior of the normalized resonant frequency shift pattern depending on the phospholipid coated.

2. Experimental

2-1. SAW device configuration

The SAW resonator used in this study, which was fabricated on Y-cut(cut angle = 36 degree), X propagating quartz by using standard photo-lithographic techniques, was obtained from Toshiba Co. The SAW device is a two-port resonator (Fig. 1). The electrodes are metallized using aluminium. The interdigital transducer (IDT) consist of 55 pairs with a half wavelength finger space of 5.1㎛. The grating reflector(GR) consist of 230 grooves with a half wavelength finger spacing. The distance between IDTs is 65 ㎛, because the insertion loss is minimum at this distance. The resonant frequency of the SAW device is 310 MHz.

Silicon monoxide is deposited on the surface of SAW device with vacuum deposition apparatus

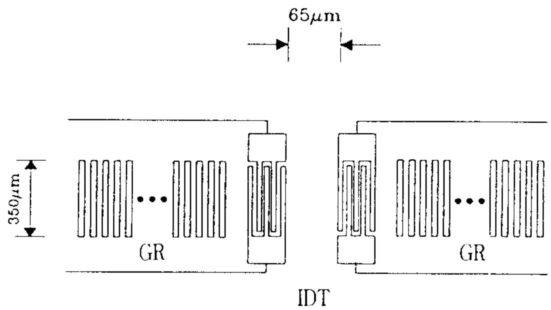

Fig. 1. Two port SAW resonator device, 55 pairs and 230 grooves with 5.1 ㎛ pitch. (GR: Grating Reflector, IDT: Inter Digital Transducer)

(ULVAC EBH-6) and the changes of characteristics of SAW device are analyzed.

In this study, different lipids are used as sensitive films. The coating material is diluted with chloroform(0.2 mg ml^{-1}) and subsequently a thin film is formed by solvent evaporation. The entire surface is covered with the film.

2-2. Apparatus

The schematic diagram of the experimental set-up is shown in Fig. 2. The oscillator circuit is self made. The resonant frequency of the device is determined using a Network/Spectrum analyzer (Anritsu MS620) on line with a micro-computer(NEC 9800). The time interval for the measurement of the resonant frequency is 30 seconds. The SAW device is fixed on top of a small vessel which has two valves for nitrogen gas inlet and outlet. The volume of the vessel is $430cm^3$.

Asolectin, phosphatidylethanolamine(PE), lecithin(from egg) and cholesterol are used as sensitive films. The odorants such as, amylacetate, citral, β-ionone and menthone as well as methanol, ethanol, propanol and butanol are measured. All of them were obtained from Wako Pure Chemical Industries Ltd. PE was obtained from Sigma Chemical Company. All other chemicals used in this study are of analytical grade.

The film is formed by casting of the chloroform solution. The coated film leads to a frequency shift of about 230kHz. The device is placed into clean, dry air for about 3 hours prior to measurement. After positioning the SAW resonator, nitrogen gas was flowed into the vessel. The flow is stopped after the resonant frequency reaches a steady state. Then the valves of the vessel are closed and odorant is injected by microsyringe. The odorant is vaporized in the vessel by heating. The concentration of the odorant is calculated from the vaporized solution volume and the vessel volume(vol vol^{-1}). Amylacetate, citral β ionone and menthone are diluted in methanol mixture is injected, which corresponds to ca. 0.3% (vol vol^{-1}) of methanol in the vessel. The frequency shift by odorant adsorption is calculated by subtracting the frequency change produced by methanol from that caused by the methanol mixture.

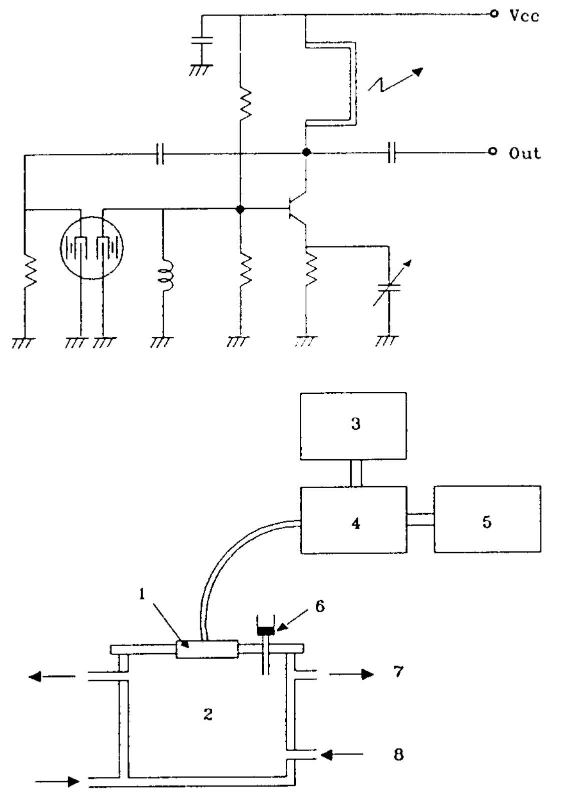

Fig. 2. Schematic diagram of apparatus.
(a) Oscillation system
(b) Experimental system
(1:SAW Device, 2:Thermostated Vessel, 3:Computer, 4:Analyzer, 5:Printer, 6:Septum, 7:Water, 8:Nitrogen)

When the resonant frequency response reaches the steady state again, nitrogen gas is flowed into the vessel to eliminate the odorant. When the resonant frequency showes stable value, the next measurement is performed.

3. Results and Disscussion

Figure 3 shows that the typical frequency responses depend on the amount of deposited silicon monoxide. The insertion loss at the resonant frequency, and the frequency shift increases with the amount of deposited silicon monoxide.

The results shows a linear relationship in the range of 600Å of silicone monoxide(Fig. 4). From these results, it is known that this SAW device can be used as a transducer of gas sensor.

Figure 5 shows the effect of temperature on resonant frequency. From this result, it is shown that the Rayleigh wave velocity of the bare SAW resonator exhibits a low temperature coefficient arround room temperature.

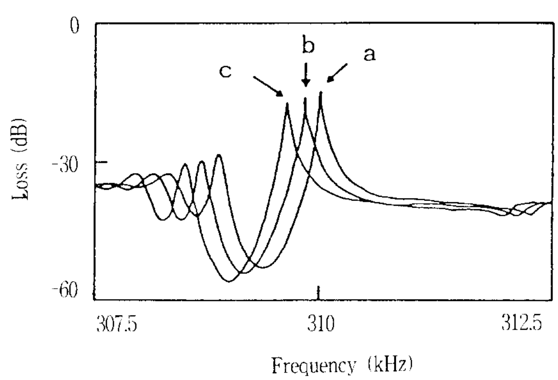

Fig. 3. Typical insertion loss versus frequency for two-port SAW resonator with silicon monoxide deposition.
(a: 0Å, b:100Å, c:200A silicon monoxide deposition)

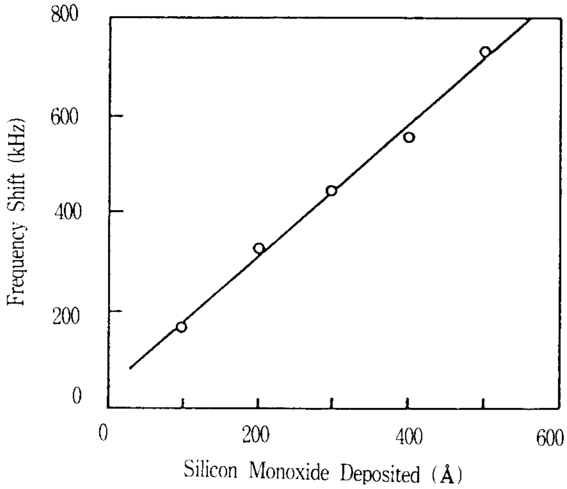

Fig. 4. The correlation between frequency shift and silicon monoxide deposition on the SAW resonator.

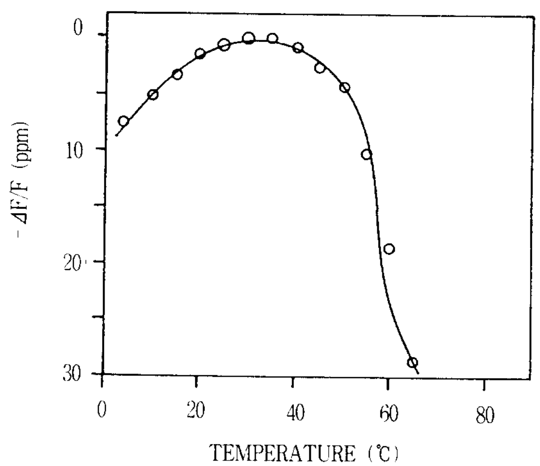

Fig. 5. Typical fractional frequency change versus temperature for two-port SAW resonator as illustrated in Fig. 2.

The effect of thicknes of coated sensitive film is investigated by changing the amount of coated lipid as shown in Fig. 6. If the frequency change due to the coated lipid (ΔF_{film}) is between 180 kHz, the frequency shift by gas adsorption (ΔF_{gas}) is almost the same. It is known that the surface of SAW device was coated with lipid sufficiently when ΔF_{film} is above 180 kHz. However, the S/N ratio became extremely low above 100ng of coated lipid, which led ΔF_{film} to

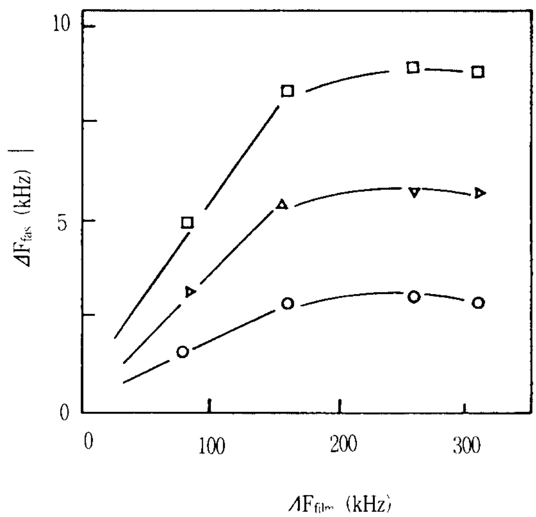

Fig. 6. The correlation of frequency shifts due to PE coating and frequency shifts due to adsorption of butanol gas. (□:5700ppm, △:3800ppm, ○:1900ppm)

ca. 230 kHz, because of faster increased insertion loss and the resultant low Q value (the degree of slope of wave). Hence we coat about 100ng (dry weight) of lipid on the surface of device.

Figure 7, 8 shows response profiles obtained from two consecutive on-off exposures and consecutive exposures to 1.9m*l*/*l*(by volume) of butanol, respectively. The response changes linearly with the consecutive exposures to butanol.

Figure 9 shows the correlation between resonant frequency shift and odorant concentration for an asolectin coated SAW resonator. The concentration is represented by using logarithms for comparison. The results demonstrate that the lowest concentration required to give a measurable frequency change is different among individual odorants. The sensitivity represents the slope obtained from a linear least squares fit of replicate data set of responses. The sensitivities are about 45 Hz/ppm for β-ionone, 35 Hz/ ppm for citral, 12 Hz/ppm for menthone and 2.6 Hz/ppm for amyl acetate, respectively. These results correspond with the changes of olfactory threshold value in biological cells obtained by Nomura et al.[11,12] at least qualitatively. They measured the changes in the surface pressure of

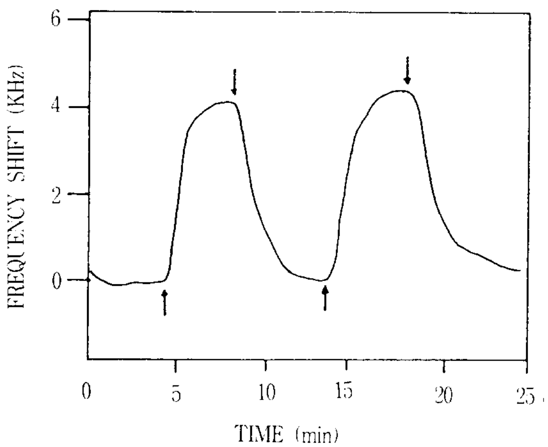

Fig. 7. Typical response of PE coated SAW resonator repeatedly exposed to 1900 ppm of butanol.
(↑:Butanol input, ↓:Nitrogen input)

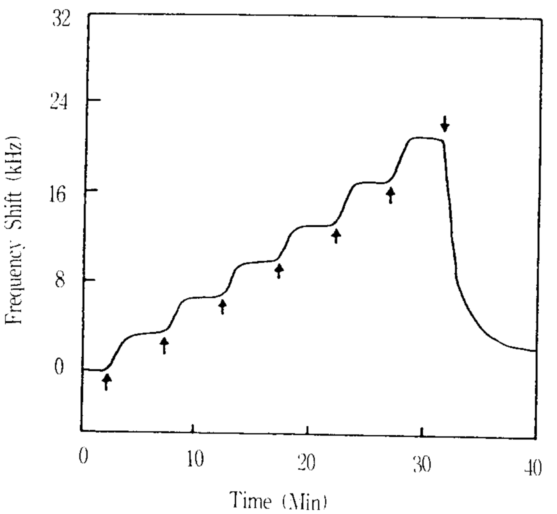

Fig. 8. Typical response of PE coated SAW resonator upon continuous exposure to 1900ppm of butanol.
(↑:Butanol input, ↓:Nitrogen input)

lipid monolayers, or the membrane potential changes of liposome by the addition of various odorants in a liquid phase. The structure of odorants is extremely diverse and it is difficult to find a molecular recognition mechanism by lipid layers on the chemical structure level. However,

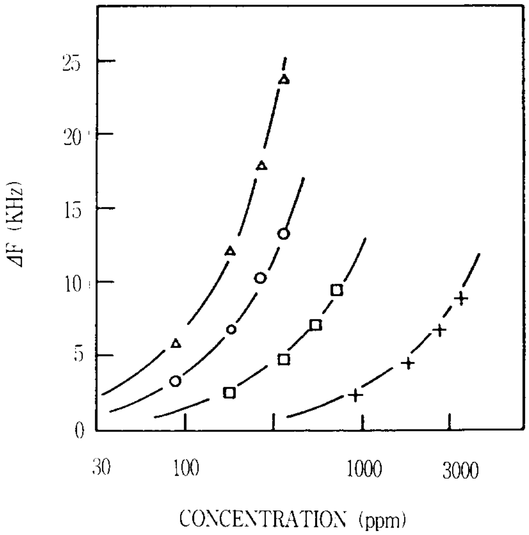

Fig. 9. The correlation between concentration of odorants and resonant frequency shifts for asolectin coated SAW resonator.
(+:Amylacetate, □:Menthone, ○:Citral, △:β-ionone)

they hypothesized in their reports that the changes were induced by odorant adsorption on the hydrophobic region of the membrane and the resulting conformational changes led to variations in the surface charge environment. It is considered that these results reflected the equilibrium between the lipid membrane and the liquid phase.

The correlation between resonant frequency shift and concentration of alcohols for the asolectin coated SAW device is also examined (Fig. 10). The lowest concentration required to give a measureable frequency change is in decreasing order: methanol, ethanol, propanol, and butanol. This result is in agreement with the data obtained by Nomura and Kurihara. They found that the lowest concentration required to give a measurable membrane potential change decreased linearly when the length of hydrocarbon chain of alcohol was increased. Dielectric constant considerations allow this behavior to be predicted, at least qualitatively. Lipid compounds like asolectin are quite hydrophobic and are not likely to accomodate very much polar solvent in the lipids layers. Present results also show the same

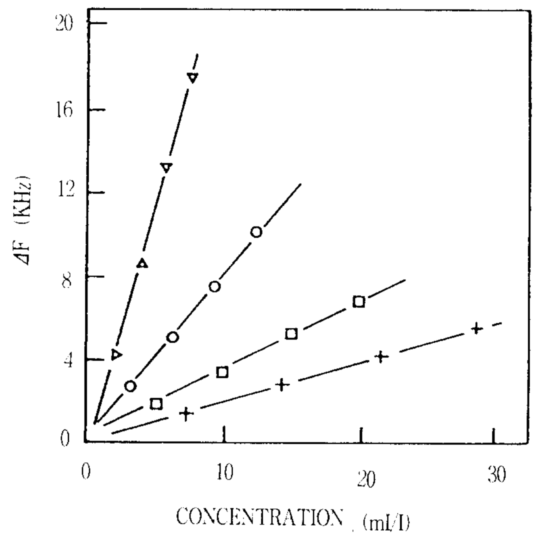

Fig. 10. The correlation between concentration of alcohols and resonant frequency shifts for asolectin coated SAW resonator.
(+;Methanol, □;Ethanol, ○;Propanol, △;Butanol)

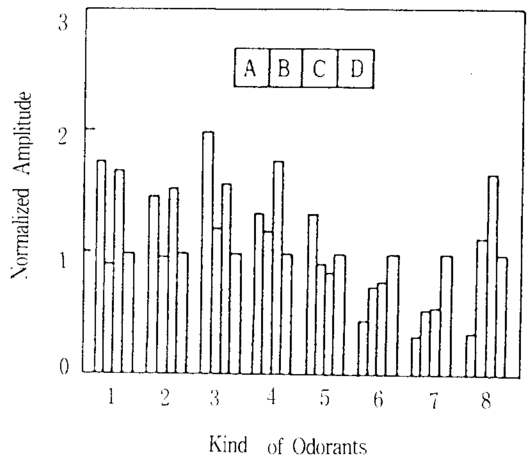

Fig. 11. Normalized pattern of resonant frequency shifts to respective odorants, (1)Methand., (2)Ethanol, (3)Propanol, (4)Butanol, (5)Amyl acetate, (6)Menthone, (7)Citral, (8)β-ionone with the following lipids coated
(A)Phosphatidylethanolamine
(B)Asolectin (C)Lecithin, (D)Cholesterol

phenomena.

Other lipids are also coated on the SAW device and used as odorant sensors. The responses are different for each lipid. Therefore, the frequency shift for each odorant of the different lipids is presented with pattern. The patterns cannot be compared directly with each other due to the different vapor concentration. Normalization is necessary for comparison. Therefore, we normalize the response as follows:

$$P(i,j,k) = \Delta F(i,j) / \Delta F(i,k) \qquad (2)$$

where P is the pattern factor, i is the kind of odorant, j is the kind of lipid and k is the reference lipid.

Cholesterol is used as the reference lipid, because the cholesterol coated SAW device showed the highest response.

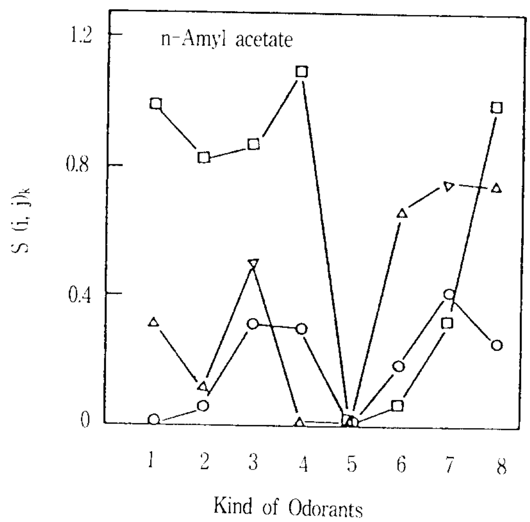

Fig. 12. Calculated similarity of the pattern based on the response of each odorant (1)Methanol, (2)Ethanol, (3)Propanol, (4)Butanol, (5)Amyl acetate, (6)Menthone, (7)Citral, (8)β-ionone with the following lipids coated.
(□)Phospha tidylethanolamine,
(○)Asolectin, (△) Lecithin

The results after normalization procedure are shown in Fig. 11. The normalized pattern can be used for the identification of odorants. The patterns are usually compared by the addition of squares of the difference in the values for each film between two patterns, and the sum is used as reference index. In this study, the natural lipids are used as selective films, and we assume that the recognition of odorants is related to pattern recognition.

Therefore, the relative difference is defined as the degree of similarity and used as index of odorants.

$$S(i,j)r=ABS[P(i,j,k)-P(r,j,k)]/P(r,j,k) \qquad (3)$$

where S is the degree of similarity. The above symbols have the same meaning as in equation (2) and r is a reference odorant.

Figure 12 shows the degree of similarity among eight odorants. The degree of similarity is specific and represents a pronounced pattern for each odorant.

4. Conclusions

The characteristics, such as resonant frequency and insertion loss, of a SAW device are changed proportional to deposited silicon monoxide and it is known that this SAW device can be used as a transducer of odorant sensor.

Organic gases show different affinities to the coated lipids, and an explanation is given for different odorant affinities based on the properties of phospholipids. The identification of odorants depending on the lipid used for coating is discussed in terms of the similarity of their normalized resonant frequency shift. From these results, it follows that a lipid coated SAW device can monitor different odorants. Using a number of different lipid coated SAW devices, odorants can be identified by a computerized pattern recognition algorithm. This approach could open a wide field for the detection of odorants.

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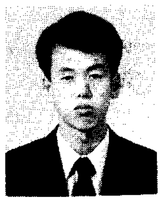

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