Pd-doped SnO_2-based oxide semiconductor thick-film gas sensors prepared by three different catalyst-addition processes

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Abstract—Three different procedures for adding Pd compounds to SnO_2 particles have been investigated. These processes are: (1) coprecipitation; (2) dried powder impregnation; and (3) calcined powder impregnation. The microstructures of SnO_2 particles have been analyzed by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). In the coprecipitaion method, the process does not restrain the growth of SnO_2 particles and it forms huge agglomerates. In the dried powder impregnation method, the process restrains the growth of SnO_2 particles and the surfaces of the agglomerates have many minute pores. In the calcined powder impregnation method, the process restrains the growth of SnO_2 particles further and the agglomerates have a lot more minute pores. The sensitivity ($S = R_{air}/R_{gas}$) of the SnO_2 gas sensor made by the calcined powder impregnation process shows the highest value ($S = 21.5$ at 5350 ppm of C_3H_8) and the sensor also indicates the lowest operating temperature of around 410°C. It is believed that the best result is caused by the plenty of minute pores at the surface of the microstructure and by the catalyst Pd that is dispersed at the surface rather than the inside of the agglomerate. Schematic models of Pd distribution in and on the three different SnO_2 particles are presented.

Index Terms—Gas sensor, Catalyst, Palladium, Tin oxide, Coprecipitation, Dried powder impregnation, Calcined powder impregnation

I. INTRODUCTION

The chemical reaction between adsorbed oxygen at the surface of SnO_2 and reduced gas in air requires high thermal energy. Most of the gas sensors, therefore, need a heater in the device and obtain necessary operating temperature using the heater [1-2]. A number of different adding methods of a small amount of catalyst have been proposed in order to increase the chemical reaction and decrease the power consumption of the sensor [1-3].

The important parameters of the catalyst-addition process are the fineness in size and the uniform distribution of catalyst on the SnO_2 surface. An excessive amount of catalyst showed non-uniform distribution of fine particles and formed a big cluster, thus these caused the improper electronic sensitization and created the inappropriate catalysis [4-5].

In general, every time metal and semiconductor make contact, the energy band bending of semiconductor takes place by electron exchange due to the work function difference [6]. When Pd and SnO_2 make contact, the Fermi level (E_F) of SnO_2 is decreased and fixed to the E_F of Pd [5]. If the Pd is converted to PdO by oxidation in air, the energy band of SnO_2 is bending so as to make the electronic balance and the electron depletion region is formed on the surface. Under the deoxidation ambient, on the other hand, the E_F of SnO_2 is increased and fixed to the work function of Pd and this leads to nearly flat band. Yamazoe et al. [5] reported that the variation of E_F and the variation of binding energy of Sn were well agreed in case of Ag that has the same catalytic mechanism as Pd.

The purpose of this study was to determine the optimum process conditions for Pd-doped SnO_2 gas sensor and the appropriate catalyst dispersion models of SnO_2 particles by examining the microstructures of the SnO_2 and chemical state variations of Sn, O and Pd prepared by three different catalyst-addition processes.

II. EXPERIMENTAL

Three different procedures for adding Pd compounds to SnO_2 particles have been examined. These processes are: (1) coprecipitation; (2) dried powder impregnation; and (3) calcined powder impregnation. These activated SnO_2 powders were used to fabricate and characterize the Pd-doped SnO_2-based oxide semiconductor thick-film gas sensors.

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In the coprecipitation method, 2.5N aqueous solution of $SnCl_4$ (Aldrich Chemical Co, USA) and $PdCl_2$ (Aldrich Chemical Co, USA), and 2.5N aqueous solution of NH_4OH (Duksan Chemicals Co, Korea) were prepared. The precipitates were obtained by gradual adding of the solutions into buffer solution to maintain PH 9. The buffer solution contained the mixture of 0.1M $(NH_4)_2CO_3$ and aqueous solution of HCl was used for the stability of PH during the precipitation reaction and for the uniform nuclear generation during the precipitation process [7-8]. Since the precipitated colloidal $Sn(OH_4)$ powders have large specific surface area and adsorb Cl^- ions, the powders were washed by deionized (DI) water and filtered sufficiently. The existence of the Cl^- ions was checked with the generation of silver glass reaction by adding 0.1M $AgNO_3$ aqueous solution to the filtered solution. Another test of the existence of the Cl^- ions was also done by the comparison between the measured resistance of initial cleaning solution and the filtered solution. The cleaned precipitates were dried at 100°C for 24 hours in laboratory atmosphere and then pulverized by agate mortar. The final precipitated powders were obtained by performing the calcination process at 600°C for 1 hour.

In the dried powder impregnation method, Pd-added dried $Sn(OH)_4$ powders were obtained by mixing 0.05M of $PdCl_2$ alcoholic solution made by addition of $PdCl_2$ to the ethanol contained 5% HCl and pure $Sn(OH)_4$ dried powders made by precipitation from $SnCl_4$. The powders were then eventually obtained by calcination at 600°C for 1 hour.

In the calcined powder impregnation method, pure $Sn(OH)_4$ dried powders made by precipitation from $SnCl_4$ were calcined at 600°C for 1 hour and distributed to the ethanol. Alcoholic solution of $PdCl_2$ was then added and this was heated on the hot plate for the volatilization of the solvent, and after one more calcination at 600°C for 1 hour, the Pd-SnO_2 powders were finally obtained. A flow chart of the above-mentioned processes is presented in Fig. 1.

The surface state variations of the gas sensing layers and the chemical state and chemical shift of SnO_2 particles according to the catalyst-addition processes were observed by SEM and XPS, respectively.

Pastes suitable for screen printing were obtained from the activated powders by mixing the organic vehicle (powders : organic vehicle = 7 : 3). Screen printed heater and electrodes were made on the cleaned Al_2O_3 substrate (3.5 x 3.5 x 0.25 mm^3) by using the Pt paste (Haraeus, German) and then annealed at 1200°C for 1 hour after 30 minute drying at 100°C. Gas sensing layers were ultimately screen printed onto the electrodes by the produced pastes and annealed at 600°C for 30 minutes. The detailed thick-film gas sensor structure and the fabrication processes have been described elsewhere [9].

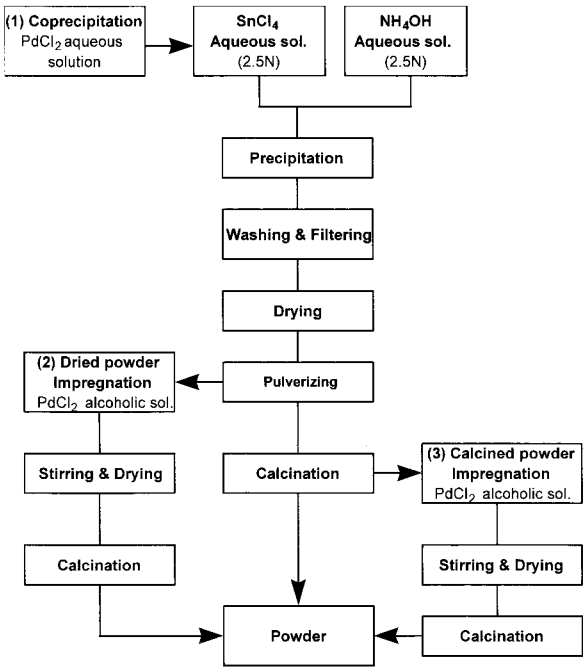

Fig. 1. Flow chart of the fabrication proceses of three different SnO_2 powders.

Gas sensing characteristics according to the catalyst adding methods and adding amount were measured for the various operating temperatures (200~600°C) to 5350 ppm C_3H_8. The operating temperatures were controlled by changing the voltages of the heater of the fabricated sensor and the actual temperatures were measured by the infra-red thermometer. Gas sensitivity of the sensor is expressed by the ratio $S = R_{air}/R_{gas}$, where R_{air} and R_{gas} are the resistances of the gas sensing layer at the working temperature in air and in test gas, respectively.

III. RESULTS AND DISCUSSION

Fig. 2 shows the sensitivity result as a function of operating temperature for various Pd contents made by the calcined powder impregnation method to 5350 ppm C_3H_8.

A gas sensor made by pure SnO_2 powders showed the sensitivity of about 15 at around 560°C. In case of the catalyst Pd of 1wt%, however, the temperature of the maximum sensitivity was lowered to around 410°C and the sensitivity was increased to 21.5, which showed the best sensitivity. When the added catalyst Pd was 2wt%, the sensitivity was decreased presumably

because the excessive amount of catalyst Pd formed the cluster on the SnO_2 surface and that made the improper electronic sensitization and inappropriate catalysis.

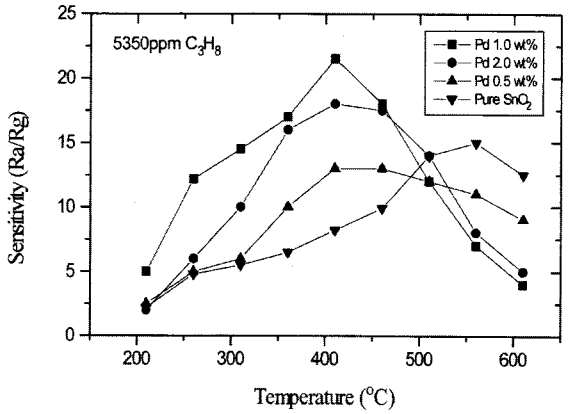

Fig. 2. Sensitivity as a function of operating temperature for various Pd contents made by the calcined powder impregnation method to 5350 ppm C_3H_8.

Fig. 3(a) exhibits the XRD patterns of the powders made by pure SnO_2, coprecipitaion, dried powder impregnation and calcined powder impregnation methods. Fig. 3(b) describes the specific surface area variation with the four different Pd-addition processes measured by BET method. As shown in the figures, the peak intensity and the specific surface area, respectively, had little characteristic difference among the four catalyst-addition methods, and it was revealed that the various Pd-loading processes had no significant influence on the crystallization or the particle size of the SnO_2.

Fig. 4 shows the sensitivity result as a function of operating temperature for the different Pd-addition processes to 5350 ppm C_3H_8 when the 1wt% of catalyst Pd is loaded. The sensitivity of the gas sensor with the pure SnO_2 powders was about 15 at around 560°C. The sensitivity of the gas sensors was increased and the operating temperature was decreased in the order named pure SnO_2, coprecipitation, dried powder impregnation and calcined powder impregnation. The gas sensor made by the calcined powder impregnation method had the maximum sensitivity of 21.5 at near 410°C. It is believed, from the result of the calcined powder impregnation method, that the gas sensitivity was enhanced because the large area of the sensing layer was reacted with the adsorbed oxygen and the target gas probably due to the improvement of interaction of the gas and SnO_2 by the catalyst-addition process.

Fig. 5 indicates the variation of the microstructure of the SnO_2 by SEM according to the different catalyst Pd-addition processes. In the coprecipitation method, the formation of huge agglomerates of several μm in size by the close gathering of the first particles of 10~20 nm in size was observed. It can be seen that there were plenty of large pores between the agglomerates, but there were few minute pores inside the agglomerates. This inclination was similar to the microstructure of the pure SnO_2. Almost all of the added Pd was formed inside the SnO_2 agglomerates. It is considered that the catalyst effect of response promotion with the test gas was insignificant because the amount of Pd exposed to the air at the surface of the agglomerate was quite small.

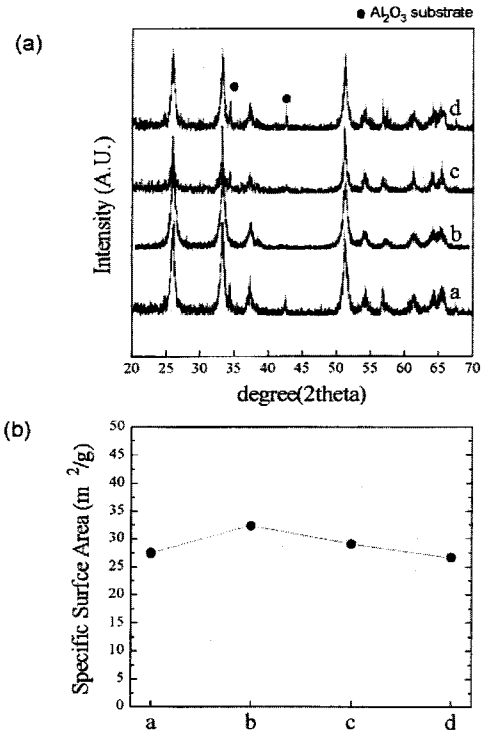

Fig. 3. (a) XRD spectra of Pd-added SnO_2 powders with the different Pd-addition processes. (b) Specific surface area variation with the different Pd-loading methods. [a: Pure SnO_2, b: Coprecipitation, c: Dried powder impregnation, d: Calcined powder impregnation. (a: Pure SnO_2, b, c, d: SnO_2-1wt% Pd)]

In the dried powder impregnation method, there were a small number of the huge agglomerates. But there were a lot more minute pores in comparison with the coprecipitation, and the surface of the agglomerate was very rough. Since the particle growth and cohesion took place with the mixture of 1~3 nm sized amorphous $Sn(OH)_4$ particle and Pd, some portion of the added Pd was distributed between the first particles of SnO_2, and in this case the target gas probably could not penetrate and reach the catalyst. The rest of the added catalyst Pd was distributed at the surfaces of the agglomerates.

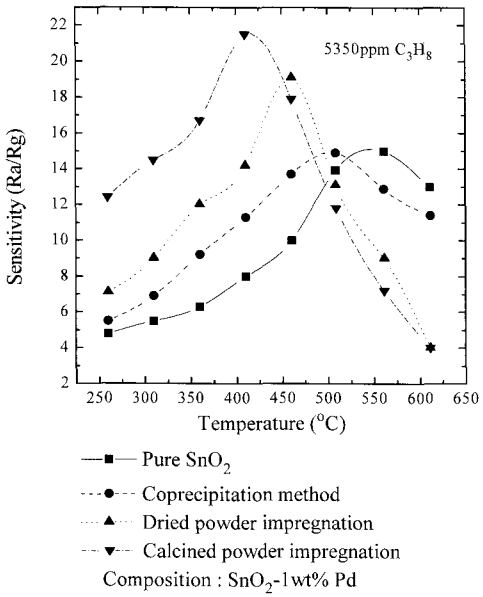

Fig. 4. Sensitivity as a function of operating temperature for the different Pd-addition processes to 5350 ppm C_3H_8.

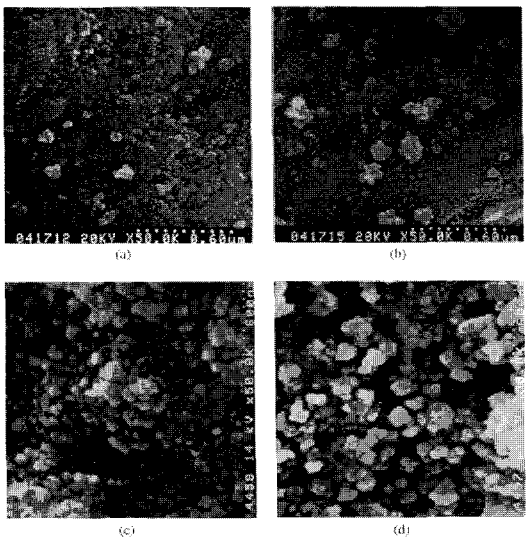

Fig. 5. SEM images of the SnO_2 surfaces: (a) Pure; (b) Coprecipitation; (c) Dried powder impregnation; (d) Calcined powder impregnation.

In the calcined powder impregnation method, plenty of porous large and minute pores were observed. It can be seen that the first particles of 10~20 nm in size were gathered and the second particles of 100~110 nm in size were made and the third huge agglomerates were formed. There were lots of minute pores between the second particles compared to the other catalyst-addition methods. Most of the added Pd was formed at the surface rather than the inside of the agglomerate because the Pd was added to the SnO_2 powders that was already crystallized by the calcination process. It is believed, therefore, that the amount of Pd exposed to the air was much greater than the other Pd-addition processes and the sensitivity showed the highest value.

Fig. 6 shows the binding energies of Sn and O of the pure SnO_2 together with the three different catalyst-addition processes when the 3 wt% of Pd is added. Binding energy moved to the lower value in the order named pure SnO_2, coprecipitation, dried powder impregnation and calcined powder impregnation, and the observed spin-orbit splitting displayed about 8.45eV regardless of the various Pd-loading methods, which demonstrated almost same result in the previous literature [10].

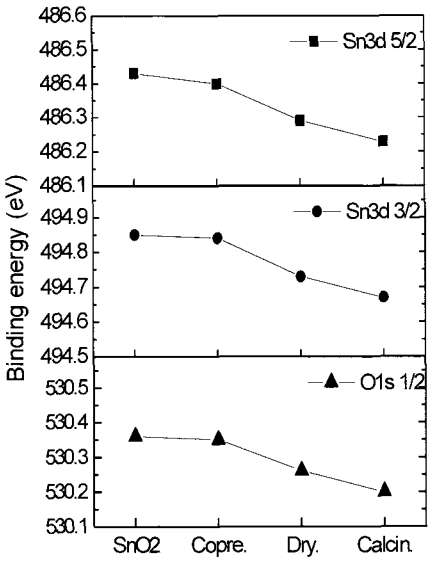

Fig. 6. Binding energy of Sn3d and O1s core levels with various Pd addition-processes. (Pd content: 3wt%)

Fig. 7 indicates the XPS of the catalyst Pd dispersed on the SnO_2 surface with the three different Pd-addition processes. There was no peak for the coprecipitaion method and there were Pd peaks for both the dried powder impregnation and the calcined powder impregnation methods. The binding energy of $Pd3d_{5/2}$ by the dried powder impregnation and the calcined powder impregnation was 336.00eV and 336.07eV, respectively, thus they showed PdO states (336.1eV) rather than metal state (334.9eV). Spin-orbit splitting was 5.29eV and it was almost same as the formerly reported value (5.35eV) [10].

If there is no change in oxidation state of Sn after the addition of Pd, binding energy change can be explained by the Fermi energy change because the terms of energy changes by partial atomic charge and relaxation energy are negligible. Accordingly, in case

the dispersed, fine PdO particles contact the surface of the SnO_2, the E_F of SnO_2 decreases and eventually the binding energy decreases because of the work function difference between SnO_2 and PdO. This type of decrease regarding the binding energy of Sn can be more specifically explained as follows.

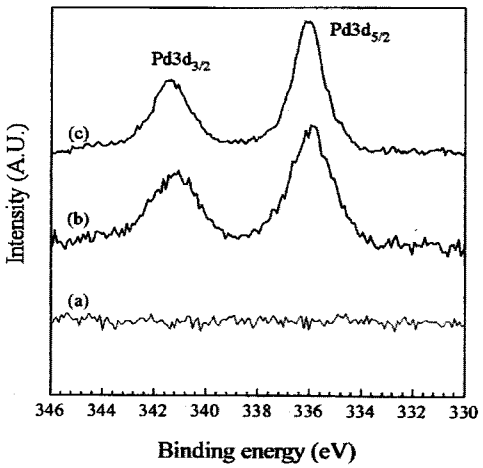

Fig. 7. XPS of 3d core levels of Pd dispersed on the SnO_2 surface with three different Pd-addition processes (SnO_2-3wt% Pd): (a) Coprecipitation; (b) Dried powder impregnation; (c) Calcined powder impregnation.

In the coprecipitation method, as mentioned earlier, almost all of the Pd was formed inside the agglomerates rather than the surface of the SnO_2. The amount of Pd under the state of oxide on the SnO_2 surface could be negligible. Hence, it is considered that PdO could not be detected by XPS analysis. In the both impregnation methods, on the other hand, Pd was formed on the surface of SnO_2 rather than the inside of the agglomerates, and that made the XPS possible. There were a great deal of PdO particles on the SnO_2 surface and that made the E_F of SnO_2 and the binding energy of Sn decrease as well by the contact of the SnO_2 and PdO. The calcined powder impregnation process showed greater decrease of biding energy of Sn compared to the dried powder impregnation method, and this is mainly because the Pd was added to already-grown SnO_2 particles by the calcination process. There was, therefore, little Pd inside the agglomerates and most of the catalyst was formed on the surface of the SnO_2, and this made even more decrease of the E_F of SnO_2 possible.

Since the XPS analyzes the thickness of several decades of Å on the particle surface, in case of the coprecipitation, the decrease of biding energy of Sn by the catalyst Pd that was formed inside of the agglomerates could not be found. In the cases of two impregnation methods, on the contrary, there were a large amount of Pd particles on the SnO_2 surfaces, thus it was easy to find the Pd peaks and the decreases of the binding energy of Sn. As a result, it can be said that when the same amount of Pd is impregnated, a greater decrease of the biding energy of Sn means that there are a larger amount of Pd particles on the surface.

The gas sensor fabricated by the calcined powder impregnation method showed the highest sensitivity and this was simply because there was the greatest decrease of the biding energy of Sn due to the catalyst Pd-addition process. Since the catalyst reaction by Pd is redox reaction and this is reversible, the binding energy recovers the original state again with the reduced gas contact, in other words, by deoxidation of Pd from the PdO of the surface. In consequence, this provides the effective current path due to the thinner depletion layer and helps the sensor resistance to decrease, subsequently makes the gas sensitivity increase.

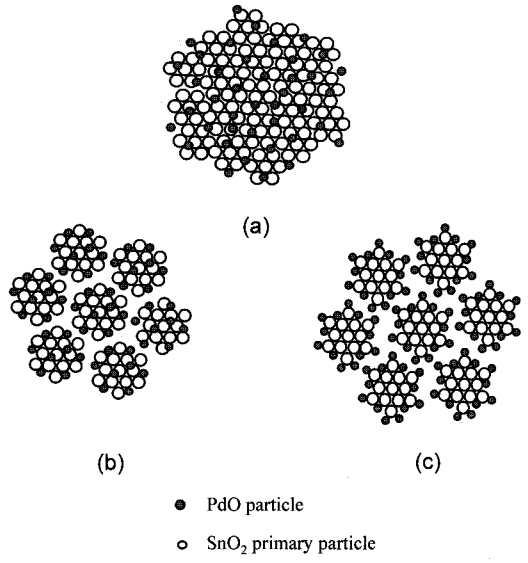

Fig. 8. Schematic models for Pd distribution in and on the SnO_2 particles with three different catalyst-addition processes: (a) Coprecipitation; (b) Dried powder impregnation; (c) Calcined powder impregnation.

Fig. 8 illustrates the schematic models for the Pd distribution in and on the SnO_2 particles with the three different Pd-addition processes according to the above-mentioned experimental results. In the coprecipitation method, most of the catalyst Pd was inside the agglomerate and there was no Pd detected by the XPS analysis, thus the gas could not penetrate and reach the catalyst (Fig. 8(a)). In the dried powder impregnation method, most of the added Pd was on the surface of the agglomerate and the decrease of the binding energy of Sn could be detected by XPS, consequently the gas could diffuse and contact the catalyst Pd (Fig. 8(b)). In the calcined powder impregnation method, almost all of the catalyst Pd was on the surface of the agglomerate

and the greatest decrease of the binding energy of Sn could be detected by XPS, and for this reason, it helped the sensor to have the significant improvement of the gas sensing characteristics (Fig. 8(c)).

IV. CONCLUSIONS

Three different procedures for adding Pd compounds to SnO_2 particles have been studied. These processes are: (1) coprecipitation; (2) dried powder impregnation; and (3) calcined powder impregnation. The microstructures of SnO_2 particles have been analyzed by XRD, BET, SEM and XPS. In the coprecipitaion method, the process does not restrain the growth of SnO_2 particles and it forms huge agglomerates. In the dried powder impregnation method, the process restrains the growth of SnO_2 particles and the surfaces of the agglomerates have many minute pores. In the calcined powder impregnation method, the process restrains the growth of SnO_2 particles further and the agglomerates have a lot more minute pores. Sensitivity tests of the fabricated gas sensors by the three different Pd-addition methods are performed and the SnO_2 gas sensor made by the calcined powder impregnation process shows the best sensing characteristic (S = 21.5 at 5350 ppm of C_3H_8) and it also indicates the lowest operating temperature of around 410°C. Schematic models of Pd distribution in and on the three different SnO_2 particles are presented according to the assorted experimental results in this study. It is believed that the best result is caused by the plenty of minute pores at the surface of the microstructure and by the catalyst Pd that is dispersed at the surface rather than the inside of the agglomerate because the catalyst Pd is added to already-grown SnO_2 particles.

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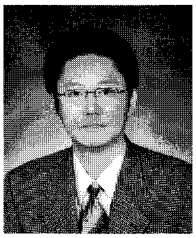

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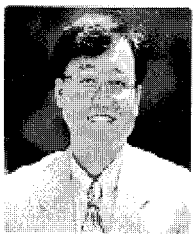

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