Electroless Copper Plating on PZT Ceramic

By T. Fujinami & H. Honma

A PZT [Pb(Zr,Ti)O_3] ceramic has been used in electronic devices such as pressure sensors, resonators and capacitors, because it holds piezoelectricity. Conductive paste is generally applied for the construction of circuits or electrodes on the PZT ceramic. In small electronic devices, however, its application to micro-circuits or electrodes is not easy. Accordingly, applicability of electroless copper plating on the ceramic was evaluated. Etching with a mineral acid is generally applied for obtaining good adhesion of deposited copper on the ceramic. This may cause deterioration of the electronic properties of the ceramic, however, and for this reason, electroless copper plating without etching becomes important. In this study, the use of the optimum pretreatment process and bath composition under best plating conditions allowed us to obtain electroless copper of sufficient adhesion strength, with no blisters.

Generally, a PZT ceramic is metallized by the application of conductive paste or a vacuum coating. Conductive paste is not applicable to miniaturized electronic devices, however, and film formation rate by vacuum coating is lower than that by electroless plating.[1-7] We concentrated, therefore, on metallization of the ceramic by electroless copper plating. While etching of the ceramic surface is necessary to assure good adhesion strength of the copper to the ceramic, it may change the surface morphologies and composition of the device; moreover, the ceramic is adversely affected by etching. Accordingly, an etching step should be eliminated from the plating process. In this study, pretreatment and plating conditions were investigated that allowed deposition of copper having sufficient adhesion strength and that was blister-free on the ceramic.

Table
Bath Composition & Operating Conditions

$CuSO_4 \cdot 5H_2O$	0.015 M
EDTA·4H	0.24 M
HCHO	0.20 M
2,2´-bipyridine	10 ppm
PEG-1000	100 ppm
pH	12.5
Temp	60 °C
Agitation	Air
Volume	100 mL

Experimental Procedure

Electroless Copper Plating Process

PZT ceramic test samples (32 x 7 mm) were used as a substrate. After ultrasonic cleaning of the surface, sensitizing it with stannous chloride solution, and activating it with a palladium chloride solution, electroless copper was plated on the samples. After activation with palladium ions and immediately before electroless copper plating, the samples were immersed in various reducing agents to examine the acceleration effect on the plating. The basic bath compositions and operating conditions are shown in the table. The thickness of the copper deposit on the PZT was obtained based on the difference before and after plating.

Evaluation Method

Approximately 3-µm-thick electroless copper film was formed on the test samples. Blisters on the film were observed using an optical microscope. The percentage-blistered area of the sample was calculated. The surface morphologies of the copper deposit were examined using a scanning electron microscope (SEM). The adhesion strength of the copper deposit on the PZT substrate was measured by first bonding a rivet on the deposit with epoxy resin, then pulling it off to cause separation of the deposit. The composition of the separated area was then analyzed by energy dispersion X-ray analysis.

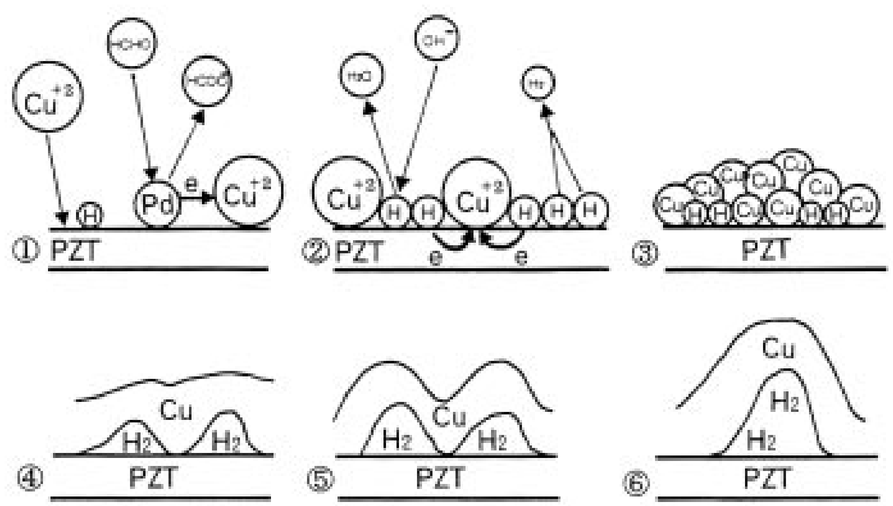

Fig. 1—Schematic diagram of blister generation.

Results and Discussion

Mechanism of Blister Development

The deposition reaction of the electroless copper, using formaldehyde as a reducing agent, occurs initially at the adsorbed palladium site on the substrate. Subsequently, copper

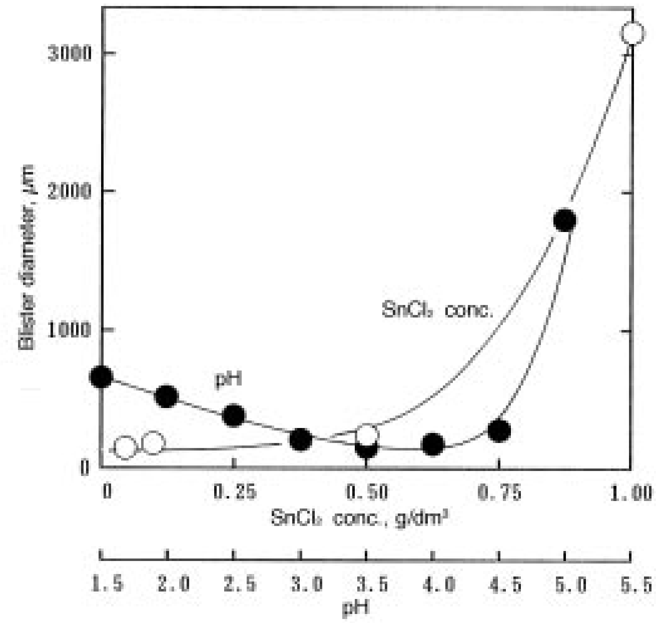

Fig. 2—Relation between sensitizing bath conditions and blisters.

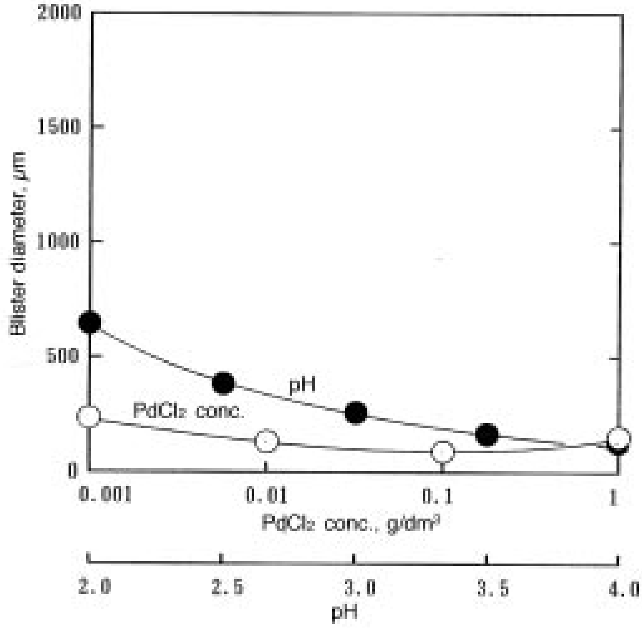

Fig. 3—Relation between activating bath conditions and blisters.

deposition continues auto-catalytically. A large amount of atomic hydrogen is generated by the oxidation of formaldehyde. Subsequently, these hydrogen atoms recombine into hydrogen molecules and hydrogen gas is released from the reaction interface.

$$2H_{ads} \rightarrow H_2 \qquad (1)$$

In this way, hydrogen molecules accumulate at the copper-ceramic interface, resulting in blisters. This blister generation mode is shown in Fig. 1.

Influence of the Catalyst

The catalyst step of electroless copper plating may cause the development of blisters. The influence of the sensitizing treatment on the development of copper blisters is shown in Fig. 2. The sensitizing step greatly influenced the development of blisters. The number of blisters on the copper deposit increased remarkably with an increase in the stannous chloride concentration. The number was particularly increased when the concentration was above one g/L. A layer of loosely adhered stannous ions on the ceramics will be formed and will result in blister formation. When the pH of the sensitizing solution was either less than 3.0, or more than 4.5, the number of blisters increased. Blisters developed vigorously when the pH was adjusted to be greater than 5.

Tin oxide or tin hydroxide may be formed on the ceramic with increasing pH of the sensitizing solution. Palladium chloride concentration as an activator may cause blisters, and the experimental result is shown in Fig. 3. The blisters became very few in number and small in size when the palladium chloride concentration was maintained at around 0.1 g/L at pH 4. The number of blisters increased, however, upon lowering the pH of the activating solution. Many spotty and undeposited areas were observed when the pH of the activation solution was raised above 4.

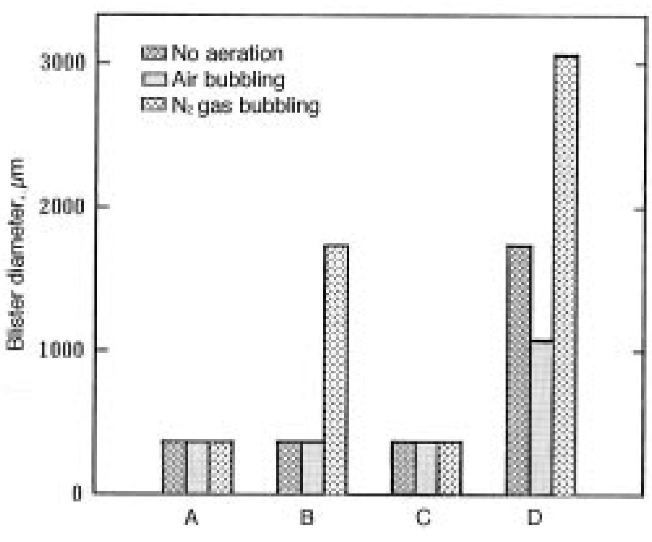

Fig. 4—Relation between various accelerators and blisters: (A) without acceleration; (B) hypophosphite solution; (C) hydrazine sulfate solution; (D) DMAB solution.

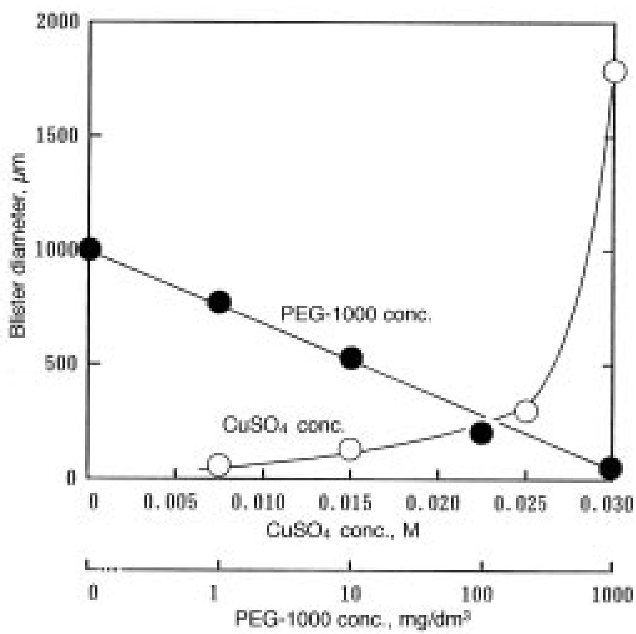

Fig. 5—Relation between electroless copper bath composition and blisters.

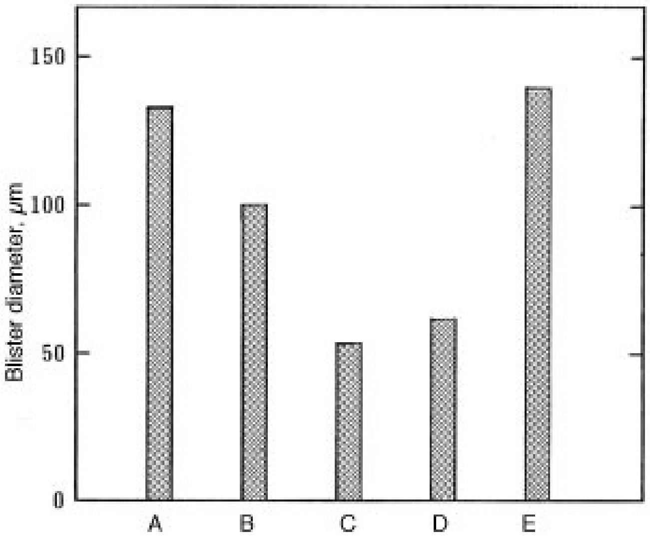

Fig. 6—Relation between types of aeration and blisters: (A) air bubbling; (B) air bubbling before plating; (C) no aeration; (D) N_2 gas bubbling before plating; (E) N_2 gas bubbling.

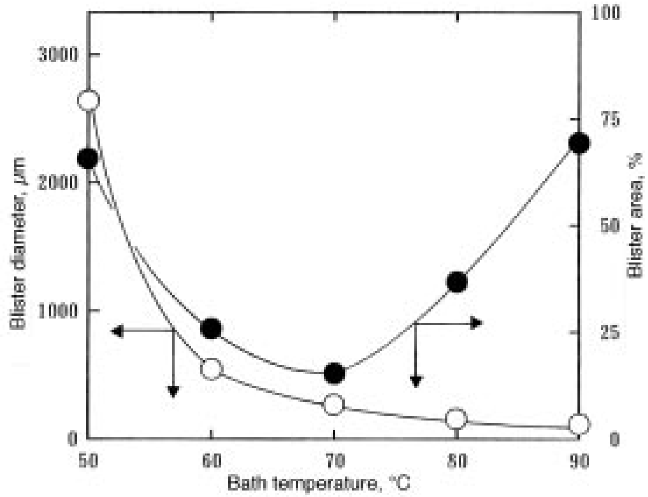

Fig. 7—Relation between bath temperature and blisters.

Influence of Acceleration Process

The catalytic activity of palladium may be increased by the acceleration step. Effects of acceleration on the electroless copper plating were investigated, using hypophosphite, hydrazine sulfate and DMAB as a reducing agent. The effect of the acceleration step on blistering of the copper is shown in Fig. 4. Many blisters were observed when the substrate was treated with DMAB and hypophosphite as an acceleration solution, because the initial electroless plating reaction began very actively and generated large amounts of hydrogen. The dissolved oxygen (DO) concentration in the accelerating solution also influenced the development of blisters. When the DO was decreased by introducing an inert gas, such as nitrogen or argon, into the accelerating solution, the number of blisters increased significantly.

Influence of Bath Composition

The influence of the bath composition on the formation of blisters was studied by changing the concentration of copper and polyethylene glycol. The development of blisters is shown in Fig. 5. The number of blisters increased with an increase in the copper ion concentration. Many blisters were found at a concentration greater than 0.03 mol/L. This is considered to be derived from the stress accumulation on the electroless copper films with increase of the copper concentration and generation of atomic hydrogen. In general, the surfactant in the electroless copper bath is effective in improving the ductility and reducing the stress of the deposited copper.[8,9] The development of blisters decreased linearly with an increase in polyethylene glycol in the plating bath because polyethylene glycol adsorbs at the reaction interface and hydrogen was readily released from the copper deposits. Hydrogen content in the copper deposits decreases with addition of polyethylene glycol.[4] As a result, copper deposits of low stress were obtained and the development of blisters was suppressed.[10-12]

Influence of the Operating Conditions

The influence of aeration in the electroless copper plating bath on blistering was examined, and the result is shown in

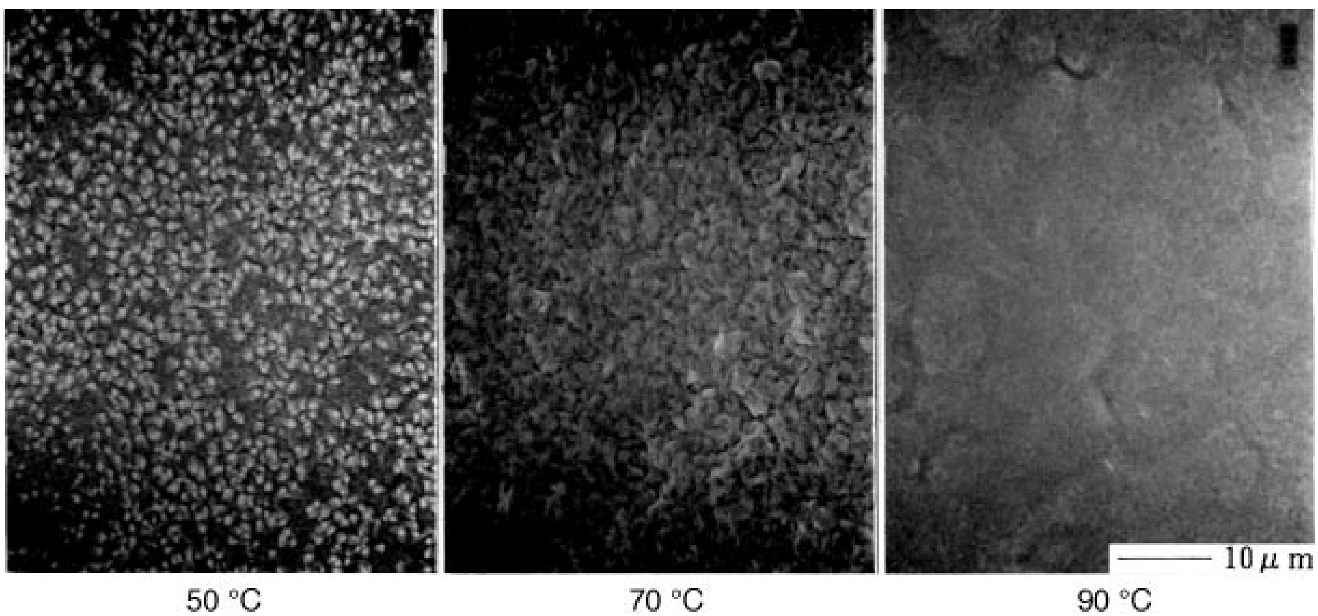

Fig. 8—Effect of temperature on surface morphology of deposits.

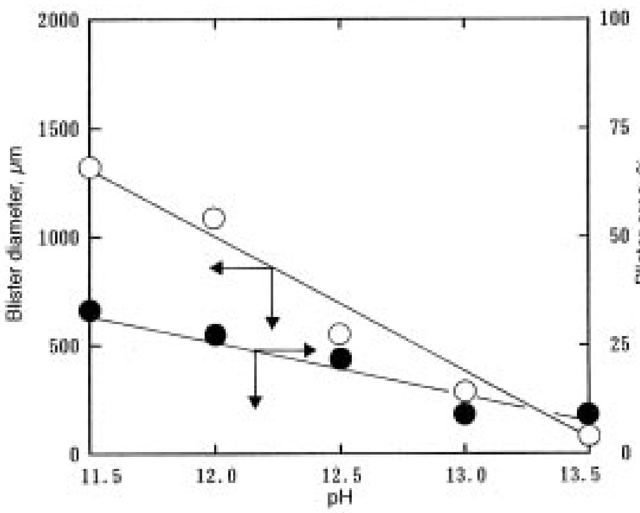

Fig. 9—Relation between bath pH and blisters.

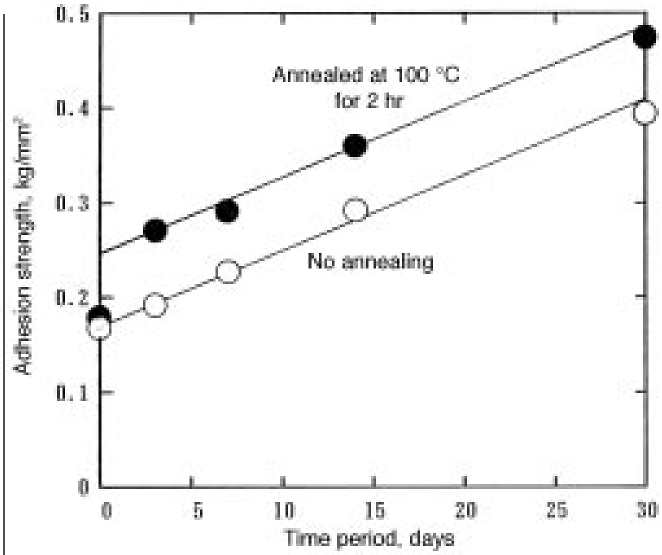

Fig. 10—Adhesion strength as a function of storage time.

Fig. 6. Aeration had no effect on the generation of blisters. When aeration was not applied, the number of blisters decreased. In general, the thickness of the diffusion layer at the reaction interface increases without aeration; therefore, the deposition rate of copper decreased, resulting in suppression of blistering. The influence of bath temperature on blistering was also examined, and the result is shown in Fig. 7. The maximum diameter of blisters decreased with an increase in the temperature. The blistered area showed minimum values at 70 °C. On the other hand, morphologies of copper deposits became rough at 50 °C or below, as shown in Fig. 8. Accordingly, hydrogen was easily occluded in the deposits and the number of blisters increased. Figure 9 shows the relationship between the formation of blisters and the pH of the electroless copper bath. The maximum diameter of the blisters and the blistered area decreased with an increase in pH. Morphologies of the copper deposits became rock-like structures with a rise in pH. Under these conditions, ductile copper deposits with low stress can be obtained.

Adhesive Strength of Copper Deposits on the PZT Ceramic

When electroless copper is deposited without any etching process on the PZT ceramic, the adhesion strength becomes the most important consideration. The influence of thermal treatment on the adhesive strength of the deposit was examined, as shown in Fig. 10. The adhesion strength immediately after plating was approximately 0.2 kg/mm^2 and increased to 0.4 kg/mm^2 after 30 days. Adhesion was also increased by thermal treatment at 100 °C for two hr after plating. Such improvement of adhesion is attributed to the removal of the diffusible hydrogen in the copper films.[11] Accordingly, the ductility of the copper may also be improved by thermal treatment.

The surface configuration and composition of the separated side of the copper deposit after adhesion testing was inspected by SEM and EDX (Fig. 11). It was confirmed that the surface configuration of the PZT ceramic was copied exactly to the separated side. All of the constituents of the ceramic were found on the separated films. Accordingly, electroless copper deposits with sufficient adhesion strength may be obtained with optimum compositions of relevant baths.

Findings

Electroless copper plating on the PZT ceramic without etching was examined and the following results were obtained. The development of blisters was greatly affected by the sensitizing process. It was confirmed that blisters increase in number with an increase in the stannous chloride concentration. When the PZT ceramic was treated with 0.01 g/L of stannous chloride and 0.1 g/L of palladium chloride successively, practically acceptable adhesion strength of the copper on the ceramic was obtained without blistering. The blistering was eliminated when the concentration of copper sulfate in the electroless copper bath was maintained at 0.015 mol/L with an addition of 100 mg/L of polyethylene glycol (average molecular weight 1000). In addition, the electroless copper plating should be done at pH 13 and 70 °C. The adhesion strength of the copper on the PZT ceramic was found to be 0.4-0.5 kg/mm^2 after the thermal treatment.

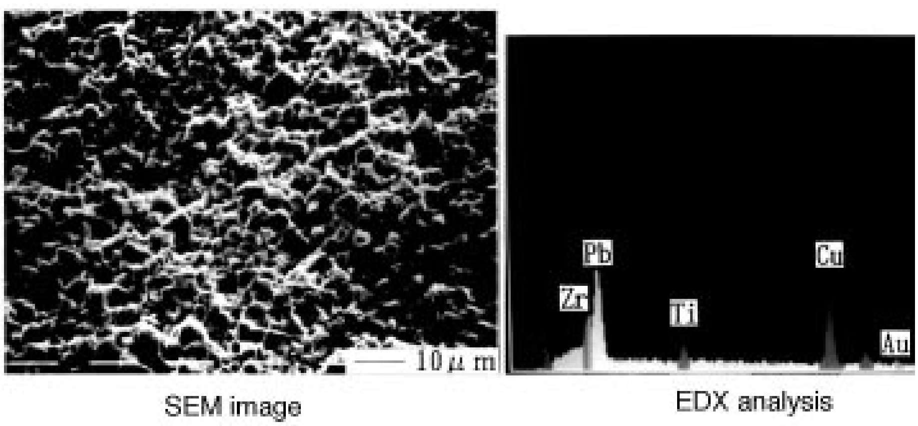

Fig. 11—SEM image and EDX analysis of peeled-off side.

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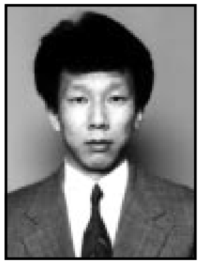

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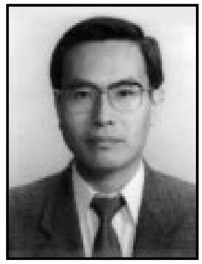

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