Metal-Organic Chemical Vapor Deposition of $Pb(Zr_xTi_{1-x})O_3$ Thin Films for High-Density Ferroelectric Random Access Memory Application

June Key Lee, June-Mo Ku, Chung-Rae Cho, Yong Kyun Lee, Sangmin Shin, and Youngsoo Park

Abstract— **The growth characteristics of metal-organic chemical vapor deposition (MOCVD) $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films were investigated for the application of high-density ferroelectric random access memories (FRAM) devices beyond 64Mbit density. The supply control of Pb precursor plays the most critical role in order to achieve a reliable process for PZT thin film deposition. We have monitored the changes in the microstructure and electrical properties of films on increasing the Pb precursor supply into the reaction chamber. Under optimized conditions, Ir/IrO_2/PZT(100nm)/Ir capacitor shows well-saturated hysteresis loops with a remanent polarization (Pr) of ~28μC/cm^2 and coercive voltage of 0.8V at 2.5V. Other issues such as step coverage, compositional uniformity and low temperature deposition was discussed in viewpoint of actual device application.**

Index Terms — **PZT, MOCVD, Ir, FeRAM, ferroelectric, thin film, capacitor, COB, hysteresis loop, liquid delivery**

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I. INTRODUCTION

Intensive investigation has been focused on ferroelectric thin film technology since 1960s because of the promising properties of ferroelectric materials for the application of nonvolatile memory devices. Due to the development of thin film deposition technology, and introduction of ferroelectric materials such as $PbZr_xT_{1-x}O_3$ (PZT), $SrBi_2Ti_2O_9$ (SBT), and $Bi_{4-x}La_xTi_3O_{12}$ (BLT), intensive studies on ferroelectric random access memories (FeRAM) have been conducted again during the last decade.[1-6] Currently, mega-bit density FeRAMs have been successfully fabricated on the research level, and low density (below 256 Kbit) FeRAMs has been developed for introduction into the market.[3,6,7]

Chemical solution deposition (CSD) has been one of the primarily used thin film deposition techniques to date. However the CSD method has a critical drawback in that it can not be utilized for high density memory devices because the substrate must undergo the planarization process in order to spin-coat ferroelectric films with CSD technique. A stack or three-dimensional structure should be employed in order to increase capacitor charge in a defined cell area. Ferroelectric capacitor formation cannot be implemented onto a three-dimensional structured electrode by the CSD method, and can be achieved only by the metal-organic chemical vapor deposition (MOCVD) method. According to international technology roadmap for semiconductor (ITRS), the semiconductor industry believes that

MOCVD technique should be utilized for the integration of 128 Mbit FeRAM and beyond.[8]

MOCVD of ferroelectric thin films, especially PZT, has also been investigated extensively over the last decade. Unlike conventional CVD, PZT MOCVD has a fundamental problem in that stable delivery of precursors is hard to achieve with conventional bubbler technology.[9-12] Volatility of precursors can be enhanced by elevating the temperature of the delivery system to about 200℃. However precursors tend to degrade gradually at an elevated temperature for extended periods, rendering them nonvolatile. Furthermore vapor pressure in the bubbler varies with time, and therefore constant delivery is hard to achieve.[13] In order to overcome the limitation of precursors, liquid delivery was suggested and exhibited promising results, although it still requires reproducibility for the mass production.[14-16] In order to realize a reliable PZT film deposition process, the effects of major process parameters were investigated in this study. We especially focused on the Pb precursor supply. General issues, such as precursor degradation and electrode structure, are also discussed practically.

II. Experimental

Film deposition was carried out in a Nexcap 2000 CVD reactor (Sunic System Ltd.). The MOCVD apparatus was designed for uniform deposition of a 6-inch wafer using the showerhead technique, and a liquid delivery system was utilized to control the input amount of the precursor solutions within ±1% accuracy.[17] Tmhd-based organometallic compounds, such as $Pb(tmhd)_2$, $Zr(tmhd)_2(O^iPr)_2$ and $Ti(tmhd)_2(O^iPr)_2$, were used for metal-organic precursors, dissolved in octane solvent with a concentration of 0.05M, and reserved separately in each ampoule. The precursor solution was changed into the vapor state in the vaporizer heated at 235℃, and then delivered into the reaction chamber. PZT films were grown on an Ir/Ti (150/10nm) electrode, which was sputter-deposited at 200℃ on a 200 nm oxidized Si(100) wafer. The growth rate was 5.5~6.0 nm/min within the Pb source supply ranges, resulting in a PZT film thickness of about 100 nm after the deposition of 18 min.

For the measurement of electrical properties, a top Ir/IrO_2 (70/30 nm) electrode was sputter-deposited, and etched off to pattern the capacitors with the size of 100x100 μm^2. The etching process was accomplished by the inductively coupled plasma-reactive ion etcher (ICP-RIE). The compositional analysis of PZT film was performed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and X-ray fluorescence (XRF). Structural properties were analyzed by X-ray diffraction (XRD) and secondary electron microscopy (SEM). Electrical properties were measured using the Radiant Technologies RT66A system.

III. Results and Discussion

As for the bottom electrode, Iridium (Ir) should be utilized because platinum (Pt), a typical bottom electrode for CSD, cannot sustain the electrode stack in the COB structure. If a Pt electrode is used for the electrode, an oxide layer (generally IrO_2) should be inserted between Pt and the oxygen barrier layer in order to prevent the fatigue problem. Unlike the CSD process, we have found serious delamination at the Pt/IrO_2 interface, which conceivably originates from the hydrogen-induced damage during the MOCVD process.[18] The selection of a proper precursor system is the first step for the MOCVD process. The precursor system should be harmonized with a delivery system in order to obtain a stable precursor supply into the reaction chamber. We have monitored our delivery system, especially the vaporizer, by checking the pressure gauge attached to the vaporizer. It displayed very stable pressure values for more than 6 months. Chemical stability of three precursors was also evaluated using the proton-nuclear magnetic resonance (H-NMR) technique after keeping the precursor solution for 2 months in an SS-316L ampoule. H-NMR analysis indicated that the $Pb(tmhd)_2$ and $Zr(tmhd)_2(O^iPr)_2$ solutions were very stable. On the other hand, $Ti(tmhd)_2(O^iPr)_2$ solutions were degraded by about 8%. Interestingly, in spite of the precursor degradation, we could not observe any difference in the deposition process. It is thought that precursors were degraded during sample treatment for H-NMR analysis, or the effect of the degraded precursor is negligible.

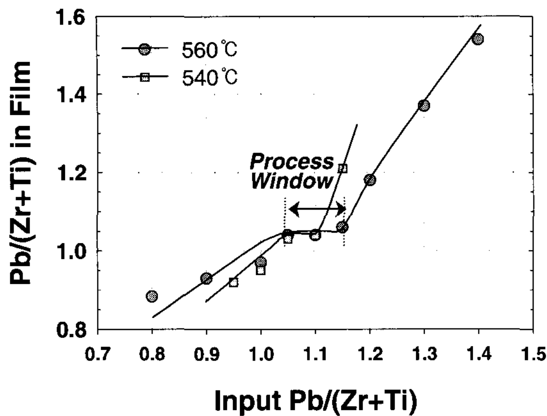

Fig. 1. Pb/(Zr+Ti) values in deposited films as a function of input Pb/(Zr+Ti). Process window doubled in size when the films were deposited at 560℃ compared to those of 540℃. Input Zr/Ti is fixed at 40/60, and Zr/Ti ratios in films were always around 30/70.

There are so many process parameters in the PZT MOCVD that we fixed minor parameters at roughly optimized conditions in order to focus on the major parameters. As a consequence of the preliminary work, we determined that the following four parameters are very critical to achieve a reliable process. Vaporizer temperature is a decisive factor for obtaining the stable liquid precursor supply, because decomposed residue or nonvolatile precursors are left in the vaporizer if the temperature is either too high or too low. It is optimized to 235℃ in this work. The flow rate of oxygen gas is also crucial because precursor, especially Pb precursor, is highly dependant on the oxygen partial pressure when Pb atoms participate in the formation of a perovskite structure.[19,20,21] Generally the decomposition of the Pb precursor mainly depends on the amount of oxidation gas. In order to remove this oxygen partial pressure dependence, oxygen was supplied in excessive amount. Substrate temperature is a fundamental factor that can be used to regulate the width of the process window directly. In general, higher temperature deposition yields a wider process window.[22] As shown in Fig.1, the width of the process window is almost doubled when the deposition temperature is increased from 540℃ to 560℃ in our experimental system. In this study, deposition was

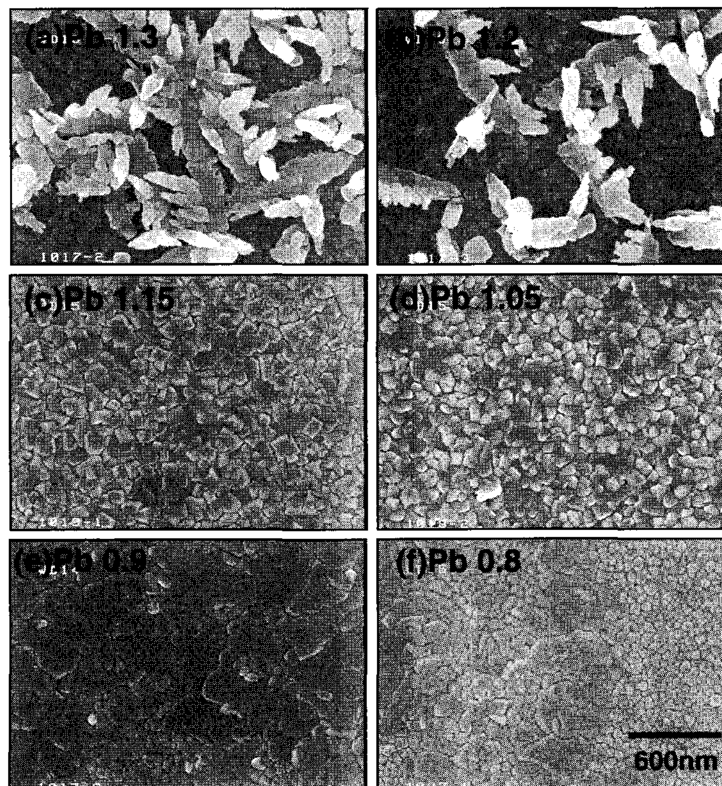

Fig. 2. SEM images of deposited films as a function of input Pb/(Zr+Ti).

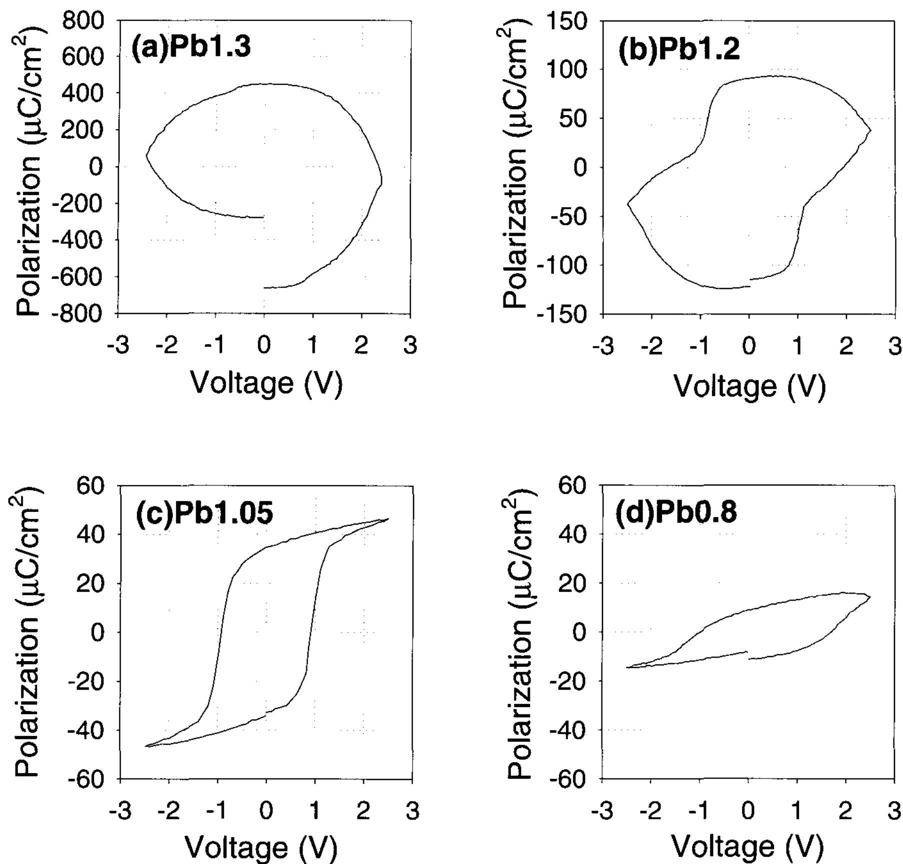

Fig. 3. Hysteresis loops of PZT capacitors prepared with various input Pb/(Zr+Ti) values.

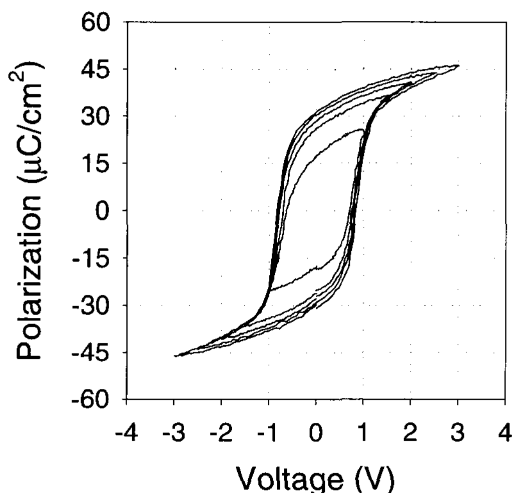

Fig. 4. Family hysteresis loops of optimized PZT capacitor. Input Pb/(Zr+Ti)=1.05. Loop is almost saturated at 1.5V. Deposition temperature is 560.

ainly performed at 560℃, because it is the highest temperature at which the bottom electrode contact ($Ir/CoSi_2$) could be maintained in our COB structure. Additionally, this temperature belongs to the diffusion-limited regime that is helpful for achieving a reliable deposition process compared to the surface reaction-limited regime. The molar ratio of the input Pb precursor, Pb/(Zr+Ti), appears to be the most important process parameter based on the present results. Surface morphology (Fig. 2) of deposited films manifest the effect of Pb precursor input. When the Pb input is deficient, a pyrochlore phase is mixed with the perovskite phase. As the Pb precursor input increases, the pyrochlore phase begins to disappear and only the perovskite phase is observed for a while, which is the process window. If excessive Pb is added, PbO is formed on the PZT film surface. Films have very high surface roughness due to the existence of PbO, and we can identify whether the film contains excessive Pb or not even with the naked eye. As shown in Fig. 3, hysteresis loops are also seriously influenced by the Pb content. When Pb is deficient, films behave like paraelectrics

with a small amount of ferroelectric property. Leakage currents are so high in Pb-excess PZT films that ferroelectric switching currents are buried under the leakage currents.

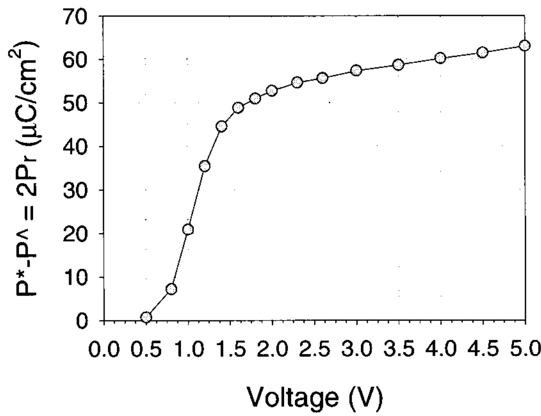

Fig. 5. Remanent polarization vs applied voltage characteristic of optimized PZT capacitor. Input Pb/(Zr+Ti)=1.05.

Table 1. Atomic proportion of PZT film deposited on patterned Ir electrode. Analysis was carried out using STEM-EDAX.

	Pb		Ti
Top Ir	106.2	27.0	73.0
Side Ir	105.4	28.0	72.0
ILD oxide	172.6	27.6	72.4

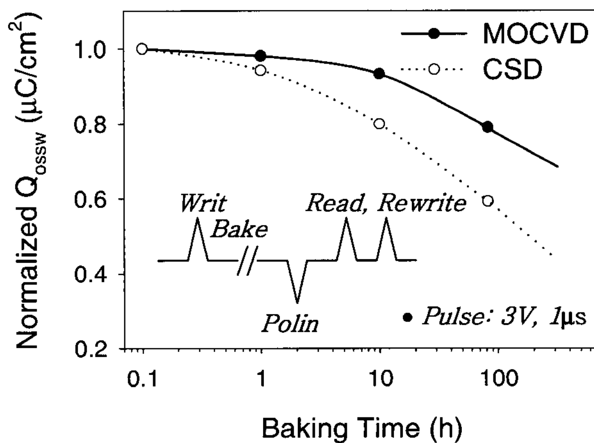

Fig. 6. Retention properties of optimized MOCVD PZT and CSD-derived PZT capacitors. Capacitors were baked at 150℃ and applied pulses are 3 V and 1 μsec.

PZT thin films prepared with optimized parameters exhibit excellent hysteretic properties as shown in Figs. 4 and 5. The hysteresis loop is saturated even at 1.5V, and shows a high remnant polarization value (2Pr) of about 50μC/cm^2 and coercive voltage of 0.75V (75 KV/cm). Leakage current is slightly high, 10^{-4}A/cm^2 at 2.5V which is the operational voltage of 32M FeRAM. MOCVD PZT capacitors have better resistance against the retention test compared to CSD-derived PZT capacitors as shown in Fig. 6. After baking at 100 h at 150℃, MOCVD PZT and CSD-derived PZT thin film capacitors maintain about 80% and 60% of the initial switching charge, respectively.

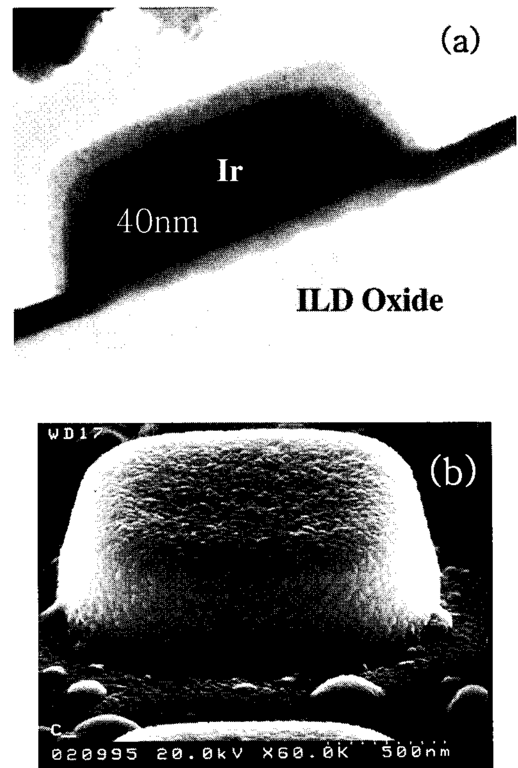

Fig. 7. TEM and SEM images of PZT films deposited on Ir stack electrode (height 400 nm, width 140 nm). Step coverage is about 70%. Films deposited on ILD oxide have a very rough surface topology.

Deposition behavior on the stack electrode was examined using a patterned Ir electrode (height 400 nm and width 1200 nm). Step coverage was very poor, about 70% as shown in Fig. 7(a). This might be attributed to the fact that deposition was carried out at a high temperature, namely in the diffusion-limited regime. As

shown in Fig. 7(b), the perovskite phase was well developed on the Ir stack, but the film grown on an interlayer dielectric (ILD) oxide shows inferior surface morphology. From a stoichiometrical viewpoint, a film on ILD oxide contains very high Pb atoms (Table I). Not only an electrode but also an ILD (interlayer dielectric) oxide which separates electrode stacks should be considered because its deposition behavior is quite different from that of an Ir electrode on an ILD oxide. From a practical point of view, it appears that the current PZT MOCVD technology performed in the diffusion-limited regime, is not suitable for a three-dimensional structure due to poor step coverage. However, it is believed that it can replace CSD-derived PZT film because of its advantages of the retention property and superior ferroelectric property. Moreover, the bottom electrode height can be reduced considerably using this technology.

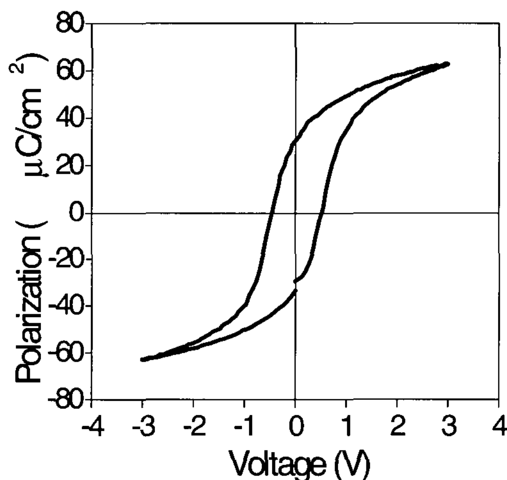

Fig. 8. Hysteresis loop of low temperature deposited PZT capacitor. Deposition temperature is 460℃.

In order to improve the step coverage, film deposition should be implemented at low temperature, that is surface reaction-limited regime. Enhancing PZT nucleation is the key step of low temperature deposition to grow perovskite phases. Therefore we employed seed layer and successive rapid thermal anneal (RTA) at 600℃ was performed to make nucleation sites prior to PZT film growth.[17] As shown in Fig. 8, PZT film capacitor exhibits excellent hysteritic properties, such as high remnant polarization value (~25μC/cm^2) and low coercive voltage (~50KV/cm). At present low temperature deposition is manifestly inferior to high temperature deposition in terms of film quality and process stability. However many research currently shows promising results using new deposition technique such as atomic layer deposition. Low temperature process must be achieved in order to realize high density FRAM devices.

IV. Conclusion

High quality PZT thin films were successfully deposited on an Ir electrode at the deposition temperature of 560℃ by the LS-MOCVD method. The liquid-delivery system was greatly matched with a precursor system [$Pb(tmhd)_2$, $Zr(tmhd)_2(O^iPr)_2$ and $Ti(tmhd)_2(O^iPr)_2$, dissolved in octane]. The control of Pb precursor supply plays the most critical role in realizing a reliable PZT thin film deposition process. As increasing the Pb precursor supply into the reaction chamber, the microstructure changed from pyrochlore phase to perovskite phase, and then the PbO phase begins to appear. The film surface became rougher due to the PbO formation and leakage currents significantly increased. Under optimized conditions (input Pb:Zr:Ti = 1.05:0.4:0.6), PZT capacitors exhibit saturated hysteresis loops with a remanent polarization (2Pr) of ~50 μC/cm^2 and coercive voltage of 0.75 V at 1.5 V. It appears that PZT MOCVD at a high temperature, that is in the diffusion-limited regime, is not suitable for a three-dimensional structure capacitor due to poor step coverage. However, it is believed that it can replace CSD-derived PZT film because of its advantages of retention property and reduced bottom electrode height. In order to improve the step coverage, low temperature deposition was evaluated using seed layer and RTA technique. Compared to the high temperature deposition, we have faced some technical troubles We obtained very promising

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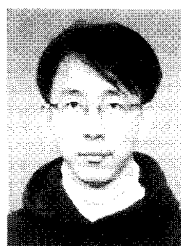

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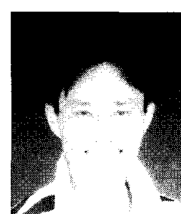

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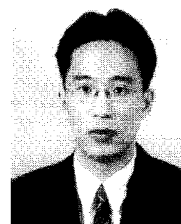

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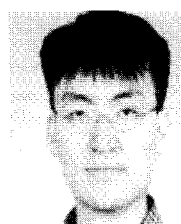

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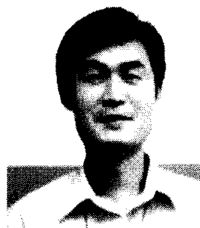

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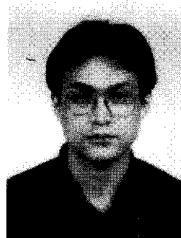

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