Theoretical Calculation and Experimental Verification of the Hf/Al Concentration Ratio in Nano-mixed $Hf_xAl_yO_z$ Films Prepared by Atomic Layer Deposition

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***Abstract*—We have proposed a characteristic method to estimate real composition when multi component oxide films are deposited by ALD. Final atomic concentration ratio was theoretically calculated from the film densities and growth rates for HfO_2 and Al_2O_3 using ALD processed $Hf_xAl_yO_z$ films. We have transformed initial source feeding ratio during deposition to final atomic ratio in $Hf_xAl_yO_z$ films through thickness factors (R_{HfO_2} and $R_{Al_2O_3}$) and concentration factor(C) defined in our experiments. Initial source feeding ratio could be transformed into the thickness ratio by each thickness factor. Final atomic ratio was calculated from thickness ratio by concentration factor. It has been successfully confirmed that the predicted atomic ratio was in good agreement with the actual measured value by ICP-MS analysis.**

***Index Terms*—Atomic Layer Deposition, HfO_2, Al_2O_3**

I. INTRODUCTION

Atomic layer deposition (ALD) has been considered to be the most promising thin film deposition technology due to excellent step coverage and precise control for thickness and concentration.[1,2] Therefore, ALD process has been adapted for many thin films such as Al_2O_3[3], Ta_2O_5[4], HfO_2[5], ZrO_2[6], $HfSiO_x$[7], $Hf_xAl_yO_z$[8], $SrTiO_3$[9], and $AlZrO_x$[10] and so on. Among them, multi component thin films like $HfSiO_x$, $HfAlO_x$ have been intensively tried for the purpose of enhancement of electrical and physical properties. For example, our group has reported that thermal endurance can be enhanced by incorporating of aluminum into HfO_2.[8] We also reported that the electrical properties such as leakage current and capacitance can be changed with atomic concentration ratio. In this kind of multi component oxides, therefore, concentration control is very vital to the physical and electrical properties which are significantly affected by their composition. Moreover, in case of thin films with well defined stoichiometry such as $SrTiO_3$, composition should be controlled much more precisely than other simple multi component films like $HfAlO_x$. It is of course that optimum properties can be accomplished by trial and error changing feeding ratio. However, it is also true that the real composition can not be known until actual composition analysis will be done.

In ALD process, multi component thin films are generally formed by repeating unit cycle like $[S_A/P/R/P]_m[S_B/P/R/P]_n$ in which S_A means the feeding for precursor A and P means purge and R means reactant gas respectively. Dr. Kang et al. refer to the above overall cycle as super cycle and each component cycle like $[S_A/P/R/P]$ or $[S_B/P/R/P]$ is called as sub cycle.[11] In this kind of ALD process, entire film concentration is supposed to be changed by changing the ratio of sub cycle (m : n). So far, some research groups including us have shown that overall concentration of thus prepared multi component thin films can be changed well as the original intention. However, it does not seem like that the relationship connecting initial feeding ratio (m: n) to final atomic concentration ratio are well understood with good explanation.

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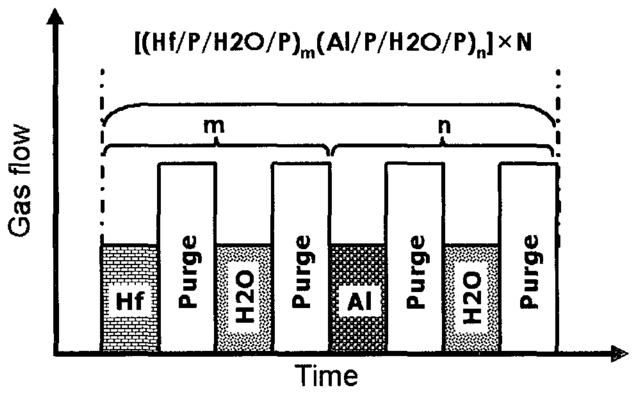


Fig. 1. Schematic diagram for gas feeding sequence for ALD process of $Hf_xAl_yO_z$ thin films

Our group has recently reported that amorphous $Hf_xAl_yO_z$ films can be formed by ALD process by tuning source feeding number (m, n) unlike the laminate film structure in which each component layer is visibly distinguishable. Moreover this nano-mixed $Hf_xAl_yO_z$ films turned out to be applicable to the DRAM capacitor dielectric due to its excellent thermal stability and high manufacturability.[8] Concerning the concentration control in ALD process, we aimed to predict real Hf/Al atomic ratio from the initial source feeding ratio during deposition and finally confirm that by using ICP-MS analysis. Moreover, we tried to understand how the final atomic concentration can be predicted from the initial source feeding ratio.

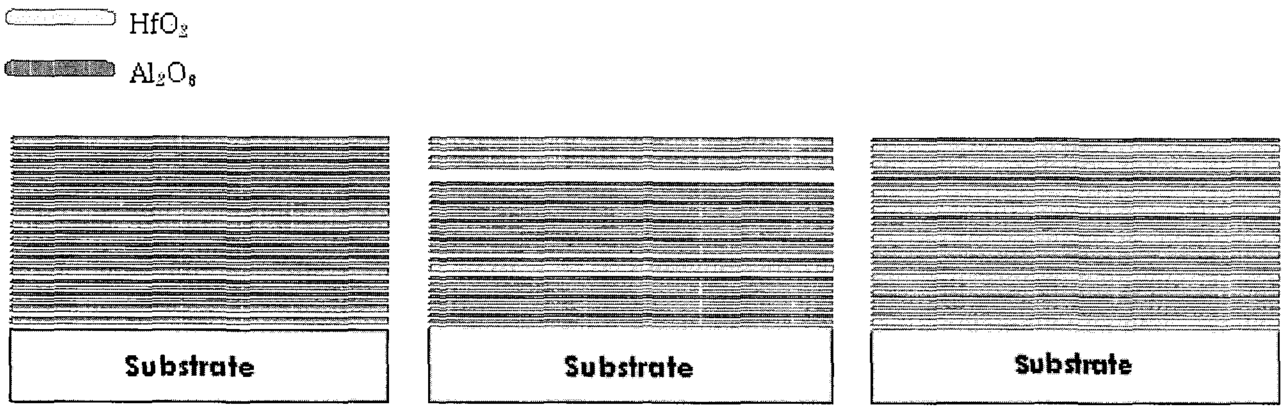
II. EXPERIMENTS

Nano-mixed $Hf_xAl_yO_z$ films were fabricated by ALD process having gas feeding sequence as shown in Fig. 1. $Hf[N(C_2H_5)(CH_3)]_4$ and $Al(CH_3)_3$ were used as chemical precursors for Hf and Al. Water vapor was used as an oxidation source. Argon gas was introduced into the reaction chamber for purging residual source gas or reactant gas. During deposition, substrate temperature was maintained at 300°C in order to avoid the decomposition of Hf precursor. All the $Hf_xAl_yO_z$ films were deposited on bare (100)-Si wafer. Nano-mixed $Hf_xAl_yO_z$ films with different composition have been made by varying the feeding ratio (m : n) from 6:1 to 1: 4. Film densities were measured by X-Ray Reflectivity (XRR) assuming two layers of interfacial layer and main $Hf_xAl_yO_z$ layer. Growth rates were calculated from the film thickness measured by transmission electron microscopy (TEM). Real concentration of $Hf_xAl_yO_z$ films was analyzed by ICP-MS in which films were etched away from Si substrates by HF solution (HF:DI = 4:1). Binding energy of core electrons for component elements in $Hf_xAl_yO_z$ films was analyzed by X-ray photo electron spectroscopy (XPS). XPS analysis was done by angle resolved mode.

III. RESULTS AND DISCUSSIONS

It has been recently reported that single alloyed films in which HfO_2 and Al_2O_3 are fully mixed in nano scale, could be formed by maintaining feeding number (m , n) 10 or less. In that report, we have referred to that as Nano-mixed film, which means component films like HfO_2 and Al_2O_3 are mixed in nano-scale. If feeding numbers are higher than 10 or higher, entire film reveals itself as laminate film composed of some distinguishable layers. This phenomenon is actually from the fact that HfO_2 layers or Al_2O_3 layers are not formed as a continuous layer, that is, requires a certain cycle to form a continuous layer. During deposition of single layers, each molecule is supposed to be landed over the same layers throughout the entire deposition period only except for the initial transient period such as initial feeding cycle or incubation cycle. On the other hand, in case of nano-mixed films, landing molecules are always experiencing both Al_2O_3 and HfO_2 previously formed over the substrate, which means that deposition environments are remarkably different from those of single oxide films. This can also means that the way of depositing nano-mixed $Hf_xAl_yO_z$ films should be understood very differently from single HfO_2 and Al_2O_3 films. Therefore, we need to know exactly how individual source feedings contribute to the film formation in terms of film thickness especially in the nano-mix regime ($m, n<10$) in which component layers are not distinguishable and homogeneously mixed.

In order to predict final atomic concentration in multi component films like $Hf_xAl_yO_z$ under this situation, we presumed that two points should be accurately understood. The first one is how the individual source feedings



(a) Hf : Al = 1:1 (b) Hf : Al = 2:1 (c) Hf : Al = 6:1

Fig. 2. Design of film structures for the evaluation of growth rate for each component layers

contribute to the entire film formation in terms of films thickness. And then, the second one is how many atoms are involved during the operation of one sub cycle like ($Hf/Ar/H_2O/Ar$) or ($Al/Ar/H_2O/Ar$). We conceptually thought that initial source feeding ratio could be transformed into the final atomic concentration ratio through the above two steps.

For the sake of reflecting the different deposition circumstances in nano-mixed films, we designed some experiments as described in Fig.2. The purpose of this experiment is to evaluate the degree of contribution of each component layer in terms of film thickness by changing the number for HfO_2 at a fixed Al_2O_3. From this experiment, it could be considered that the increment in thickness of HfO_2 could be projected. In this experiment, we changed Hf/Al feeding ratio (m/n) from 6/1 to 1/4. The region of higher Hf portion is for the evaluation of HfO_2 and the higher Al part is for the evaluation of Al_2O_3. Fig.3 shows the growth rates of $Hf_xAl_yO_z$ films having different Hf/Al feeding ratio. Growth rates were calculated from thickness of $Hf_xAl_yO_z$ films measured by transmission electron microscopy (TEM). We can see that there are the two different linear regimes having well defined slopes in which left one reflects the behavior of HfO_2 and right one reflects the behavior of Al_2O_3 especially in nano-mix regime (m, n < 10). In this figure, the slope can be also understood as an increase in the growth rate per each feeding cycle. In our experiments, the growth rates for HfO_2 and Al_2O_3 were 0.82 and 1.13 respectively. These values are a little bit different from those (1.15 for Al_2O_3 and 0.78 for HfO_2) acquired from thickness variation for single films as a function of cycle. It was thought that this difference came from the difference of substrate layer on which source molecules are adsorbed. It is considered that the growth rates from Fig.3 well reflect the real situation during deposition comparing to that in single oxide film. Thus obtained values are considered to be very intrinsic depending on the nature of precursor and reactant. For example, when we changed the oxidant from water vapor to ozone, we found that growth rates in nano-mixing regime were 1.14 and 0.80 for HfO_2 and Al_2O_3 respectively. These values are very different from the case of water vapor. Therefore, can be thought that that thus extracted growth rates can be considered as a characteristic

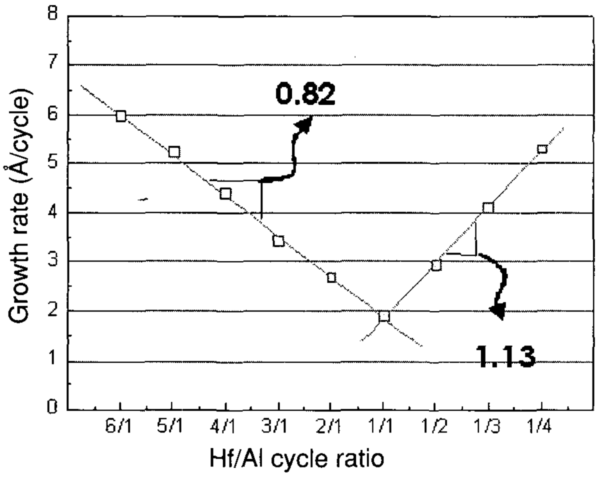


Fig. 3. Variation of growth rates of $Hf_xAl_yO_z$ films as a function of source feeding ratio

Table. 1. Calculation of Hf/Al atomic ratio using thickness factors and concentration factor

No	Hf/Al Feeding Ratio			Hf/Al Thickness Ratio		Hf/Al Concentration Ratio		
				HfOx	AlOx	HfOx	AlOx	Hf/Al
#1	6	1	6.00	4.92	1.13	4.92	1.65	2.98
#2	5	1	5.00	4.10	1.13	4.10	1.65	2.49
#3	4	1	4.00	3.28	1.13	3.28	1.65	1.99
#4	3	1	3.00	2.46	1.13	2.46	1.65	1.49
#5	2	1	2.00	1.64	1.13	1.64	1.65	0.99
#6	1	1	1.00	0.82	1.13	0.82	1.65	0.50
#7	1	2	0.50	0.82	2.27	0.82	3.30	0.25
#8	1	3	0.33	0.82	3.40	0.82	4.95	0.17
#9	1	4	0.25	0.82	4.53	0.82	6.60	0.12

Table. 2. Characteristic values for HfO_2 and Al_2O_3

	HfO_2	Al_2O_3
Growth Rate (Å/cycle)	0.82	1.13
Density(g/cm^3)	9.16	3.23

measure of contribution to the film formation per source feeding in terms of film thickness. This result also means that these characteristic values can be used very usefully getting information about how many atoms are involved during one period of source feeding. So we newly defined these two values as thickness factors (R_{HfO2}, R_{Al2O3}) for each layer. These factors can be extracted from experiments and also used for the transformation initial ratio [m : n] of component sub cycle to thickness ratio by multiplying them by initial ratio. More specifically, [m : n] is transformed into thickness ratio through [m x R_{HfO2} : n × R_{Al2O3}]. After this transformation, entire film can be treated as a simple bi-layer with the same ratio calculated above. Thus calculated thickness ratios can be found in the third column of Table.1.

For the next step, we need to know how many atoms are involved for each layer. For this purpose, we tried to obtain film densities by X-ray reflectivity (XRR). It is well known that XRR technique can give useful information about roughness, thickness as well as film density. It is thought that film density can give the number of molecules within film per unit volume, area or thickness simply dividing by molecular weight. Moreover, we can also think that atomic numbers in HfO_2 and Al_2O_3 film with the same thickness can be estimated. For the convenient use, we adapted a new factor, concentration factor(C).

Overall procedure for the definition of C is as follows.

$$N_{Hf} = \rho_{HfO_2} / M_{HfO_2} \tag{1}$$

$$N_{Al} = 2 \times \rho_{Al_2O_3} / M_{Al_2O_3} \tag{2}$$

$$C = N_{Al} / N_{Hf} \tag{3}$$

N_{Hf} and N_{Al} mean the number of atoms in moles per unit volume and M_{HfO2} and M_{Al2O3} are molecular weight. M_{HfO2} is 210.49g and M_{Al2O3} are 101.96g. ρ_{HfO2} and ρ_{Al2O3} are film densities measured by XRR technique and 9.16g/cm^3 and 3.23g/cm^3 as can be seen in Table. 1. In equation (2), the number "2" is originated from two atoms in one Al_2O_3 molecule unlike HfO_2. We can guess that film density is also dependent on the nature of precursor and reactant and so on like previously defined thickness factors. When using ozone instead of water vapor, it was found that ρ_{HfO2} was 9.8g/cm^3 and ρ_{Al2O3} was 3.6g/cm^3 a little bit higher than that in H_2O case. That is why concentration factor can also be treated as an intrinsic property similarly to the preciously defined thickness factors. From this calculation, N_{Hf} was 0.4352mole/cm^3 and N_{Al} was 0.6336mole/cm^3 and finally the value of 1.4559 was obtained as a concentration factor, which means that Al atoms were involved by 1.4559 times higher than Hf atoms. It can also be interpreted the number of Al atoms for film with the same thickness is larger than Hf just by concentration factor, 1.4559.

This concept leads us to think that we can also transform the preciously calculated thickness ratio to the final relative atomic ratio just by multiplying concentration factor. Thus calculated final atomic ratio can be found in the final column of Table. 1. When we change the initial feeding ratio of Hf/Al from 6:1 to 1:4, the atomic ratio was found to be changed from 2.98 to 0.12. If we get straight on our entire procedure for the transformation, it becomes as follows.

$$m:n \;\Rightarrow\; m \times R_{HfO_2} : n \times R_{Al_2O_3} \;\Rightarrow\; m \times R_{HfO_2} : n \times R_{Al_2O_3} \times C \tag{4}$$

Initial feeding ratio is transformed into thickness ratio through two thickness factors (R_{HfO2}, R_{Al2O3}) and then finally changed into atomic ratio by concentration factor(C).

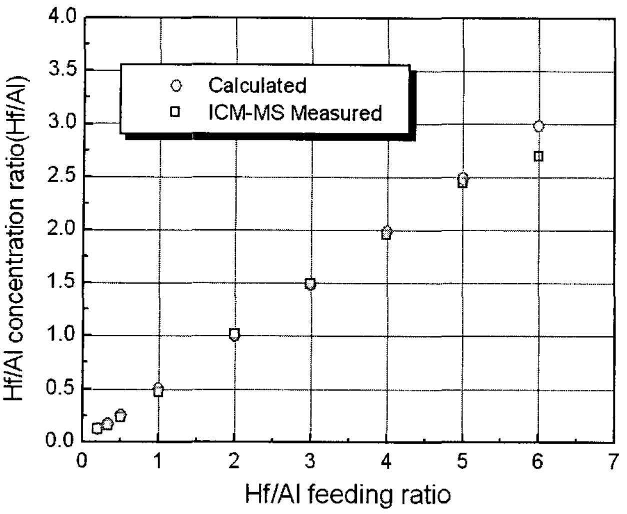


Fig. 4. Comparison of Hf/Al atomic ratio between calculated values and measured one by ICP-MS

Finally, we tried to verify the real atomic ratio in films by inductively coupled plasma mass spectroscopy (ICP-MS). For ICP-MS analysis, nano-mixed $Hf_xAl_yO_z$ films were completely etched away from silicon substrate by using 4:1 HF solution with diluted water. No residual film could be found on substrate, which means that all elements were efficiently exploited for the analysis. We compared calculated values with those analyzed by ICP-MS as shown in Fig.3. As can bee seen in this figure, ICP measured values are in good agreement with our calculated one except only for the case of Hf:Al=6:1. So far, it has been generally believed that the concentration of multi component thin films by ALD can be precisely controlled by changing feeding number. However, there have been few reports on how the real composition could be correlated with initial source feeding ratio. According to the above result, it is certain that our suggestion for composition calculation can be very useful for us to make multi component thin films with fixed certain stoichiometry such as $SrTiO_3$ film without any trial and error.

We finally analyzed the binding states for core electrons of each element by X-ray photoelectron spectroscopy (XPS) as shown in Fig.5. The possibility of erroneous binding energy shift during analysis was minimized by using angle resolved mode in which take-off angle was maintained at 60 degree. From this analysis, it was found that there were two notable points. The first thing is that binding energy for Hf_{4f} and Al_{2p} does not

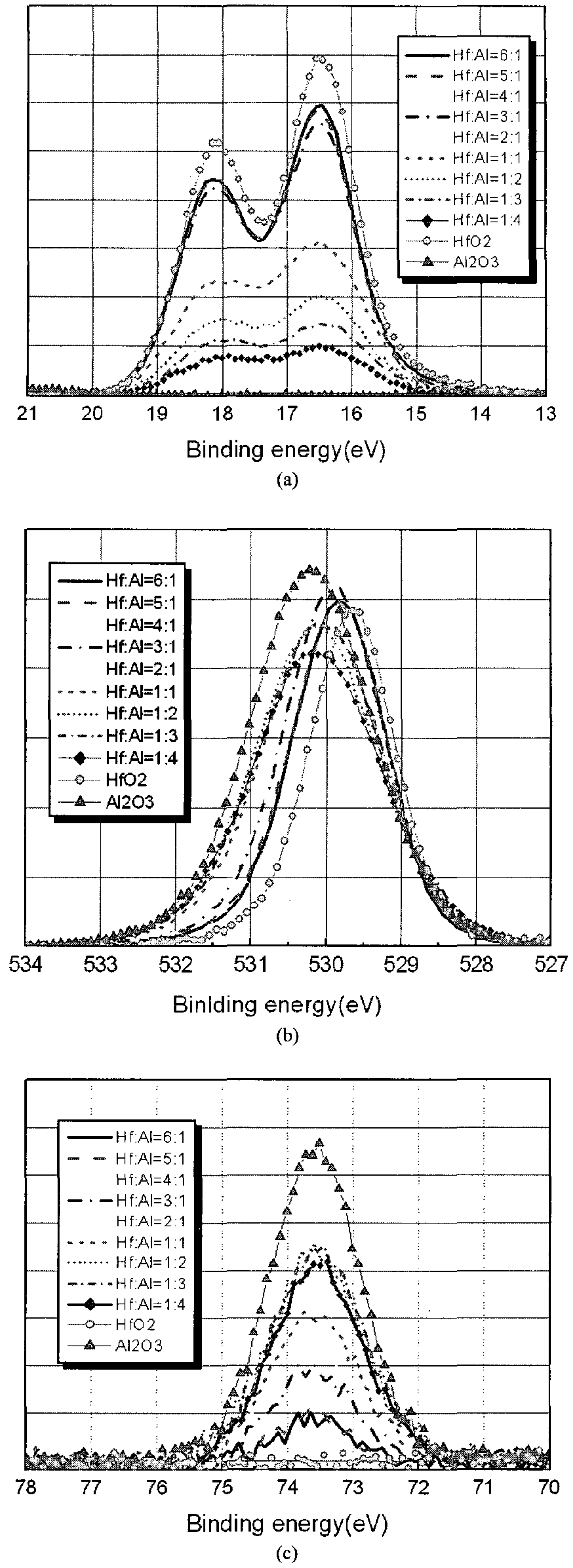


Fig. 5. Binding energy of core electrons for Hf_{4f} (a), Al_{2p} (b) and O_{1s}(c) with Hf/Al ratio

change at all in spite of composition change. On the other hand, O_{1s} peak monotonously shifts from 529.65eV to 530.23eV with the increase of Al contents.

The behavior of Hf_{4f} and Al_{2p} might be originated from that there is no interaction and chemical bonding between Hf and Al like Hf-O-Al. However, the shift of O_{1s} to the higher energy can imply that overall $Hf_xAl_yO_z$ films are just mixing of HfO_2 and Al_2O_3 without any interaction with each other. That is to say, higher binding energy of O_{1s} for higher Al contents is considered to be due to the higher Al_2O_3 portion in $Hf_xAl_yO_z$ films. From the XPS results, we can think that overall $Hf_xAl_yO_z$ film is a mixture composed of HfO_2 and Al_2O_3 acting independently without any chemical nature. This postulation can be indirectly supported from the fact that growth rates change with good linearity as a function of Hf/Al feeding ratio.

From the above XPS analysis, it is thought that the good agreement of calculated atomic ratio with real measured one is attributed to the independent behavior of HfO_2 and Al_2O_3 during deposition.

IV. CONCLUSIONS

It has been firstly proposed that elemental concentration in multi component oxide films by ALD can be estimated by some experimental data like film density and growth rates. For the calculation of composition, we newly defined two thickness factors (R_{HfO2}, R_{Al2O3}) and concentration factor(C). From these two factors, initial source feeding ratio could be transformed into thickness ratio by thickness factors and then finally changed to atomic ratio through concentration factor. Moreover we could successfully demonstrate that predicted concentration was in good agreement with the real concentration by ICP-MS analysis using ALD processed $Hf_xAl_yO_z$ thin film system. It was inferred that good agreement between predicted value and analyzed one was attributed to the fact that HfO_2 and Al_2O_3 independently contribute to the film formation without any chemical interaction.

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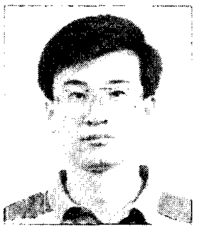

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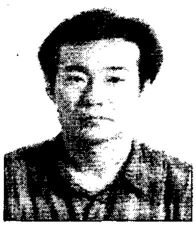

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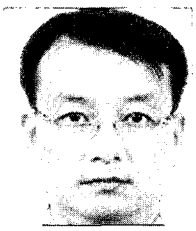

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