Dielectric Properties of Ta_2O_{5-X} Thin Films with Buffer Layers

In-Sung Kim, Jae-Sung Song, Mun-Soo Yun and Chung-Hoo Park

Abstract - The present study describe the electrical performance of amorphous Ta_2O_{5-X} fabricated on the buffer layers Ti and TiO_2. Ta_2O_{5-x} thin films were grown on the Ti and TiO_2 layers as a capacitor layer using reactive sputtering method. The X-ray pattern analysis indicated that the two as-deposited films were amorphous and the amorphous state was kept stable on the RTA(rapid thermal annealing) at even 700 ℃. Measurements of dielectric properties of the reactive sputtered Ta_2O_{5-x} thin films fabricated in two simple MIS(metal insulator semiconductor), structures, (Cu/Ta_2O_5/Ti/Si and Cu/Ta_2O_5/TiO_2/Si) show that the amorphous Ta_2O_5 grown on Ti showed high dielectric constant (23～39) and high leakage current density(10^{-3}～10^{-4} (A/cm^2)), whereas relatively low dielectric constant (～15) and low leakage current density(10^{-9}～10^{-10} (A/cm^2)) were observed in the amorphous Ta_2O_5 deposited on the TiO_2 layer. The electrical behaviors of the Ta_2O_5 thin films were attributed to the contribution of Ti-O_2 and the compositionally gradient Ta-Ti-O, being the low dielectric layer and high leakage current barrier. In additional, The Ta_2O_5/TiO_2 thin films exhibited dominant conduction mechanism contributed by the Poole-Frenkel emission at high electric field. In the case of Ta_2O_5/TiO_2 thin films were related to the diffusion of Ta, Ti and O, followed by the creation of vacancies, in the rapid thermal treated thin films.

Keywords - integrated passive device, buffer layer, capacitor, Ta_2O_5 thin films, dielectric properties, capacitance vs voltage, leakage current density vs electric field

1. Introduction

Ta_2O_5 is a promising material utilized in the film type capacitor because it has high dielectric constant (20~30) and easy of fabrication process. Because of good electrical properties of the Ta_2O_5, numerous investigations have been carried out on the material and its application to the advanced dynamic random access memory (DRAM) cell technologies [1-3]. Especially, the amorphous Ta_2O_5 film is known to have the low leakage current and high breakdown strength in comparison with the crystalline film [4]. Also, it has been reported that it can offer low leakage current and high dielectric constant on TiO_2 [5, 6].

Ta_2O_5 is also recognized as a candidate capacitor material used in the IPDs(integrated passive devices), including inductors, resistors and capacitors, which finally combines IC chips into the creation of new multi-functional electronics designed to be used as downsizing RF devices, DC blocks coupling filter elements, and microwave circuit resonant elements[7, 8]. The passive device of capacitor requires the particular characteristics such as moderate dielectric constant (ε_r=10), low leakage current density (<10^{-8}A/cm^2), low switching voltage, and the material fabrication processes available at low temperature[9]. Nevertheless, the capacitor used as a component of IPDs(integration passive devices) so far has been confined to the simple structure with only variations of size and shape, and thus there have little been the detailed investigations of IPDs capacitor material and structure. In the passive device, the dielectric constant of Ta_2O_5 should be reduced to 5～10, because the high dielectric material with larger than a relative permitivity of 10 is difficult to control accurately its capacitance in a very small size. However, it is not easy to keep the dielectric constant with the low leakage current density performance for the simple conventional capacitor structure (electrode/dielectric materials/ electrode). In addition, the direct contact of Ta_2O_5 film to Si substrate results in the formation of additional interlayer SiO_2 [10, 11] and the resultant degradation of electrical properties. The capacitance and leakage current of the simple MIS capacitor structure are expected to lower to the desired values by insertion of the other dense oxide layer with optimal dielectric constant between Ta_2O_5 and Si or electrode.

In the present study, we investigated the electrical properties of as-deposited and rapid thermal annealed Ta_2O_5 MIS capacitor grown onto metal layer Ti and oxide layer TiO_2. As an oxide buffer layer, TiO_2 was chosen because it possesses low crystallization temperature, relatively low dielectric constant, and dense crystal structure. Use of TiO_2 as a leakage current barrier was successful and gave an insight to the capacitor structure that meets the requirements of low capacitance and leakage current density. For comparison, Ti was used as a buffer layer to avoid oxide SiO_2 formable between

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Ta_2O_5 and Si wafer. The effect of RTA(rapid thermal annealing, capacitance vs voltage and leakage current density vs electric field characteristics of the films were studied. The electrical properties-microstructure relationship was investigated for as-deposited and rapid thermal annealed amorphous Ta_2O_5 films grown on metal Ti and oxide TiO_2 layer.

2. Experimental Procedure

(100) p-type silicon wafers (25Ω · cm) were used as the base substrate. Ta_2O_5 films were reactive sputtered in an O_2 atmosphere. Two substrates were employed in this experiment: one is Ti 30nm coated Si wafer and the other is TiO_2 deposited on Si. Titanium was chosen to improve adhesion and to avoid the possibility of formation of additional oxide layer SiO_2 between Si and Ta_2O_5.

TiO_2 was employed as a barrier of oxygen diffusion from the SiO_2 layer. Cu bottom electrode beneath the Si wafer was deposited by thermal evaporation. Then Ti films were coated on the Si wafer for the layers of Ti and TiO_2 under Ar gas pressure and O_2 gas pressure, respectively. Ta_2O_5 films were deposited on the Ti and TiO_2 coated Si substrates by a conventional RF reactive sputtering.

The sputtering gas was 80 % Ar and 20 % O_2 mixture with a total pressure of 5 mtorr. Before deposition, the chamber was first back filled with Ar gas for pre-sputtering to clean the target for 10 min. Then Ar/O_2 gases were introduced into the chamber to reach a total pressure of 5 mtorr. Film thickness was estimated to be 50 nm using a Tencor Alpha-step 200 surface profile meter. Cu top electrodes with a thickness of 200 nm and a diameter of 1mm were patterned by a shadow mask process. The rapid thermal annealing treatments (a heating rate of 30 ℃/sec) of capacitor structures, $Ta_2O_5/Ti/Si$ and $Ta_2O_5/TiO_2/Si$ were carried out at 600, 650, 700, 750 ℃ on a vacuum of $< 5\times10^{-6}$ torr to reduce the defect of Ta_2O_5, prior to the formation of the electrodes.

Structures of Ta_2O_5 films were identified using X-ray diffraction. The composition depth profile was also analyzed by Auger electron spectroscopy (AES). The current-voltage (I-V) characteristics of the as-deposited and RTA Ta_2O_5 films were measured on the MIS structures ($Cu/Ta_2O_5/Ti/Si$ and $Cu/Ta_2O_5/Ti\text{-}O/Si$) with a KEITHLEY 237 high voltage measure unit. The capacitance-voltage (C-V) characteristic was read at frequency ranging from 100 Hz to 40 MHz with 0.5 V ac sweeping signal using a HP4194A impedance-gain phase analyzer.

3. Results and Discussion

The electrical properties of film type capacitor are dependent upon the structure and defects of the films which are varied with the post-deposition heat-treatment. To observe the effect of the rapid thermal annealing with the electrical characteristics, the dielectric constant of as-deposited and annealed Ta_2O_5/Ti and $Ta_2O_5/Ti\text{-}O$ MIS structures were measured as a function of annealing temperature as shown in the Fig. 1. For the Ta_2O_5/Ti, the dielectric constant ε_r increases from 23 to 39 with increasing of annealing temperature, whereas Ta_2O_5/TiO_2 films annealed at 650 ℃ showed the maximum dielectric constant ε_r 20 and TiO_2 capacitor structures annealed at the temperature exhibit lower ε_r 15.

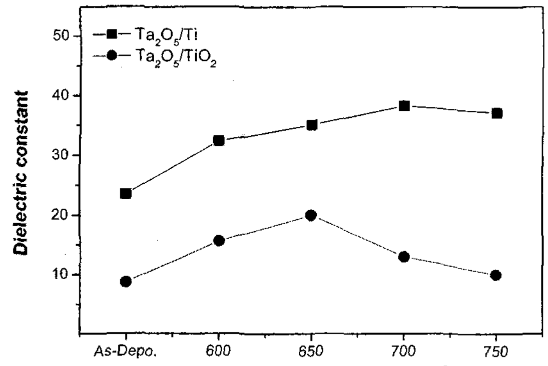
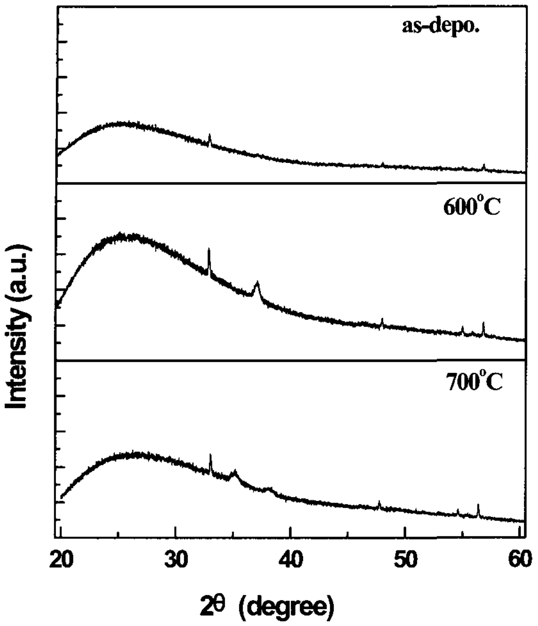


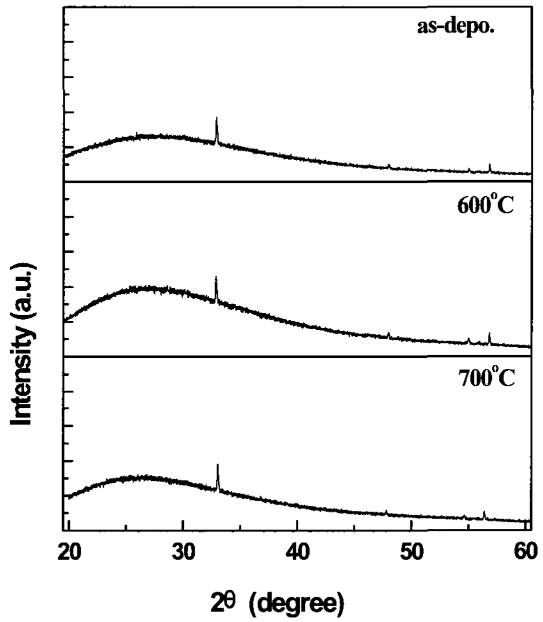
Fig. 1 Dielectric constants of Ta_2O_5 thin films on Ti and TiO_2 as a function of RTA temperature.

The change of the dielectric constant with annealing temperature are expected to be related to the crystal structures and defects of Ta_2O_5/Ti and Ta_2O_5/TiO_2. However the crystal structures of Ta_2O_5/Ti films obtained in this study were amorphous, irrespective of RTA temperatures up to 700 ℃, as shown in Fig. 2. Accordingly, the increase of dielectric constant for the Ta_2O_5/Ti film could be attributed to the reduction of defect existing in the oxide layer with higher RTA temperature. Similarly, XRD pattern of the Ta_2O_5/TiO_2 films represented the amorphous state at as-deposited condition and rapid thermal treatment up to 700℃.

To investigate the RTA effect on the structural modification of films obviously, the depth profiles of two kind of samples annealed at 700 ℃ annealed samples were carried out by Auger electron microscopy. In the case of Ta_2O_5/Ti thin films, as shown Fig. 3 (a), the oxygen profile have tailered into the Ti layer, which indicated that the annealing effect gave rise to the oxygen diffusion into the Ti layer and left oxygen vacancies in the Ta_2O_5 layer. The oxygen diffusion behavior was agreed with the annealing effect of Ta_2O_5/Si capacitor reported in the literatures [10-13]. In the Ta_2O_5/TiO_2 thin films capacitor (Fig. 3 (b)), on the other hand, Ti and Ta were found to diffuse each other into two layers upon 700 ℃ RTA, resulting in the formation of gradually composition-varied Ta-Ti oxide layer. The observation of



(a) Ta_2O_5/Ti

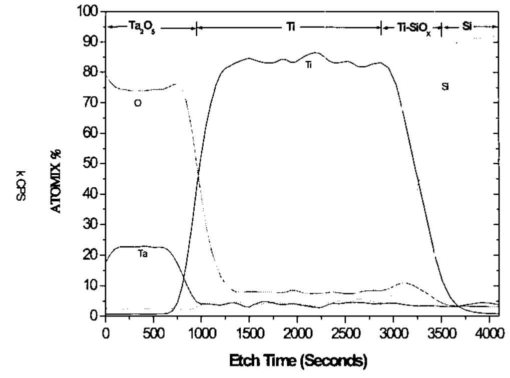


(b) Ta_2O_5/TiO_2

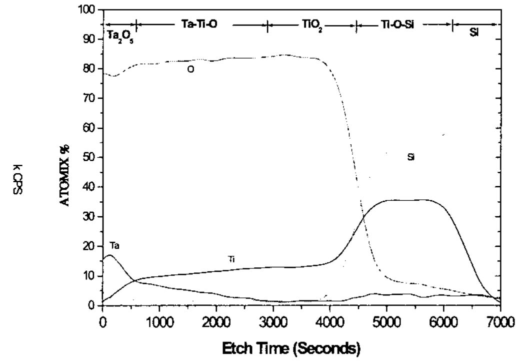
Fig. 2 X-ray diffraction patterns of as- deposited, 600 ℃ and 700 ℃ RTA treated Ta_2O_5 /Ti and Ta_2O_5/TiO_2

inter layer with compositional gradient was different from the report [14]. In which TiO_2 layer acted as only the protection layer avoiding the formation of SiO_2 layer between Ta_2O_5 and Si substrate. By contrast, RTA process of Ta_2O_5/TiO_2 investigated in the present study allowed the diffusion of the Ta and Ti to induce Ta-Ti oxide formation with compositional gradient.

The existence of the layer with compositional gradient implies that ε_r decreases with RTA at temperatures beyond 650 ℃.

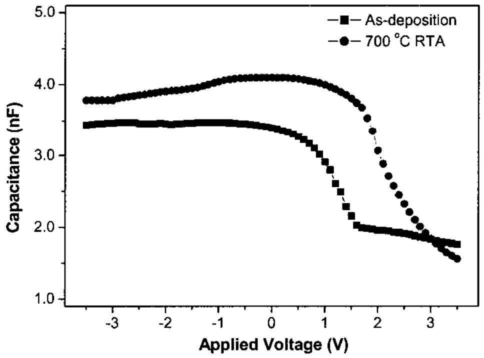


(a) Ta_2O_5/Ti

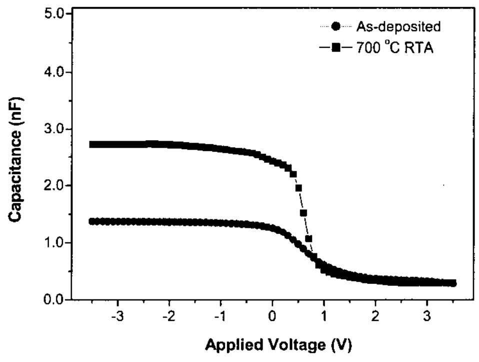


(b) Ta_2O_5/TiO_2

Fig. 3 AES depth profile of 700 ℃ RTA treated Ta_2O_5 /Ti and Ta_2O_5/TiO_2.



(a) Ta_2O_5/Ti

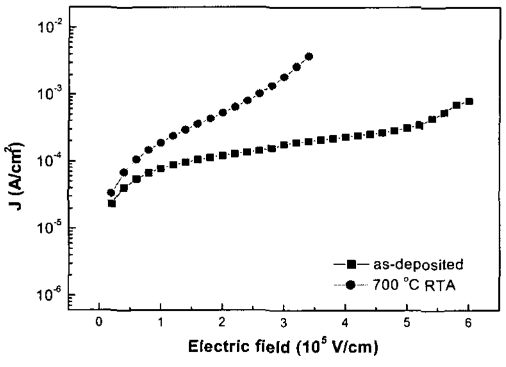


(b) Ta_2O_5/TiO_2

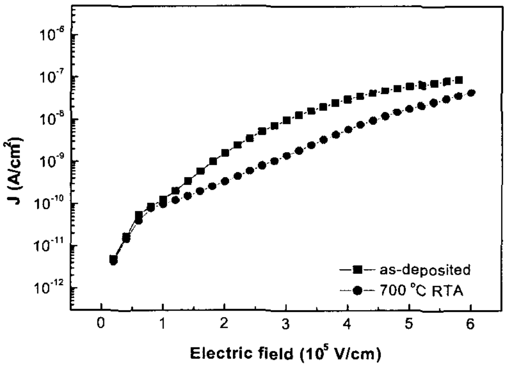
Fig. 4 Capacitance vs applied voltage of as deposited and 700 ℃ RTA treated Ta_2O_5 /Ti and Ta_2O_5/TiO_2.

Therefore, the two layer in the Ta_2O_5/TiO_2 structure are connected in a serial pattern under equivalent circuit concept and all specimens showed lower ε_r than those of Ta_2O_5/Ti thin films capacitor. Nevertheless, the apparent double oxide layers (Ta_2O_5/TiO_2) structure has a proper dielectric constant ε_r 10~20 available for the film capacitor used in the integrated passive devices[15, 16].

The high frequency (100 kHz) capacitance (C) vs applied voltage (V) characteristics were measured for the as-deposited and 700 ℃ annealed amorphous Ta_2O_5/Ti and Ta_2O_5/TiO_2 MIS capacitors. For both as-deposited and 700 ℃ annealed Ta_2O_5/Ti films (Fig. 4 (a)), the relatively large residual capacitances were seen at even applied bias voltages up to 2.0 V. As shown in the Fig. 4 (b), the Ta_2O_5/TiO_2 films showed the distinct flat band bias voltages 0.7 V at 700 ℃ RTA and 1.3 V at as-deposited condition. The relatively small capacitance of the annealed Ta_2O_5/TiO_2 was probably due to a low dielectric constant of compositionally gradient Ta-TiO_2 layer formed in the MIS structure during high temperature (700 ℃) annealing[17]. The different flat band voltage observations of the two capacitors indicated that Ta_2O_5/TiO_2 structure was a preferred one in that capacitor must lose easily the capacitance when given switching bias voltage. Keeping the small cut-off voltage for the Ta_2O_5/TiO_2 capacitor was probably caused by forming Ta-Ti-O inter layer as well as reducing broken bond between Ta and O which diffuse through the new oxide interface from TiO_2 to Ta_2O_5 layers. The I-V characteristics of two films were measured to observe the leakage current density behaviors. The voltage was applied at a step of 0.1V and the current was measured in an interval of 2 sec at every measurement. The leakage current densities of Ta_2O_5/Ti and Ta_2O_5/TiO_2 thin films were in the order of $10^{-3}\sim10^{-4}$ and $10^{-9}\sim10^{-10}$ (A/cm^2) respectively at an applied electric field of 2×10^5 V/cm, as shown in the Fig. 5(a) and (b). In as-deposited and 700 ℃ annealed Ta_2O_5/Ti, the current density increased linearly with increasing electric fields up to 3.5×10^5 V/cm for RTA and 5.2×10^5 V/cm for as-deposited condition. Then, the Ta_2O_5/Ti film exhibited dramatic increase of leakage current density when the higher electric field was applied. In the case of Ta_2O_5/TiO_2 films as shown in the Fig. 5 (b), in the range of low electric field up to 1×10^5 V/cm, current density increased exponentially with applied electric field. In the higher electric fields than 1.5×10^5 V/cm, the current density was observed to increase linearly with electric field for as-deposited and 700 ℃ RTA conditions. The current density behaviors as a function of electric field was different from those of Ta_2O_5/Ti films.



(a) Ta_2O_5/Ti



(b) Ta_2O_5/TiO_2

Fig. 5 Current density vs electric field of as-deposited and 700 ℃ RTA treated Ta_2O_5 /Ti and Ta_2O_5/TiO_2.

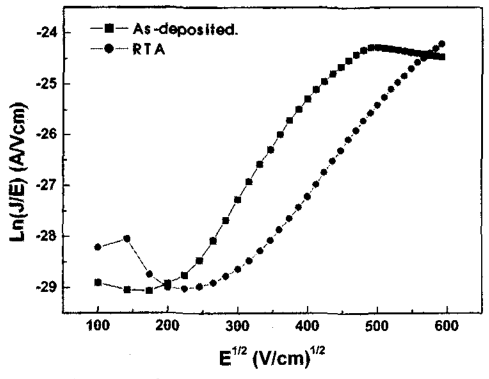


Fig. 6 J-E characteristics plotted of Ta_2O_5/TiO_2 thin in films as ln(J/E) vs $E^{1/2}$.

The leakage current in the Ta_2O_5 films can be explained by the several conduction mechanisms[18] including Ohmic emission, Schottky emission, Poole-Frenkel emission, Fowler-Nordheim tunneling and a space charge limited current. Among them, the current density due to the Ohmic emission[19] was expressed by,

$$J \propto E\exp(-Q_B/kT) \tag{1}$$

The current density owing to Schottky emission[20, 21] can be given as,

$$J \propto T^2\exp\left[\frac{q(-Q_B+\sqrt{qE/4\pi\varepsilon_r})}{kT}\right]. \tag{2}$$

In addition, the current density due to Poole-Frenkel emission [21, 22] can be written as,

$$J \propto E \exp\left[\frac{q(-Q_B + \sqrt{qE/\pi\varepsilon_r})}{KT}\right] \qquad (3)$$

where, J denotes the current density, T the absolute temperature, k the Boltzmann constant, q the electronic charge, E the electric field, Q_B the barrier height to conduction quantity and ε_r the dielectric constant of the insulator material. The dominant leakage current mechanisms of the two MIS capacitors were determined by plotting the logarithmic current density as a function of electric field. As shown in the Fig. 6, for the Ta_2O_5/TiO_2 thin films, the increase of logarithmic current density as a function of square root of electric field was found to continuously obtain at given high electric field range (up to $300(V/cm)^{1/2}$) as compared with that in the low electric filed. By contrast, when imposing the high electric field for the Ta_2O_5/TiO_2 thin films capacitor, the logarithmic current density divided by the electric field has a linear relation as a function of electric field. Therefore, the conduction mechanism in the high field range for Ta_2O_5/TiO_2 thin films was determined to be the Poole-Frenkel (PF) emission[22-24].

The leakage current was in association with the defects existing in the film caused by the oxygen and Ti diffusion phenomenon. As shown in Fig. 5, upon annealing of the Ta_2O_5/TiO_2 and Ta_2O_5/Ti thin films, the Ti absorbed the oxygen from Ta_2O_5 layer, resulting in the degradation of leakage current behavior. In the Ta_2O_5 thin films, the RTA induced the formation of compositional gradient oxide layer to provide interface defect giving high leakage current, and the reduction of the broken bonds to improve the barrier of leakage current. These two effects would cancel out each other and then gave rise to similar leakage current value at RTA as comparison with as-deposited condition.

In general, four possible defects including interface defect, grain boundary defect, shallow trap levels, and oxygen vacancies can be considered in multilayer capacitor[25]. Among such defects, the interface defect gives rise to the formation of conduction level within the forbidden gap due to the interruption of the periodic lattice. Consequently, the dominant conduction mechanism is caused by the presence of TiO_2 whose role as an oxygen donor and new interface formation were likely responsible for the low leakage current level for the Ta_2O_5/Ti-O film.

4. Conclusions

This study demonstrated the passive devices capacitors of $Cu/Ta_2O_5/Ti/Si$ and $Cu/Ta_2O_5/TiO_2/Si$ capacitor structures. X-ray pattern analysis showed that the two kind of as-deposited films in this study were amorphous after the annealing treatment at even 700 ℃. Measurement of electrical characteristics of the $Cu/Ta_2O_5/Ti/Si$ and $Cu/Ta_2O_5/TiO_2/Si$ capacitor structures indicated that the amorphous Ta_2O_5/Ti showed high dielectric constant ε_r 23~39 and high leakage current density $10^{-3} \sim 10^{-4}$ (A/cm^2). In the amorphous Ta_2O_5 deposited on the TiO_2, a relatively low dielectric constant ε_r 15 and low leakage current $10^{-9} \sim 10^{-10}(A/cm^2)$ were observed. The different electrical behaviors for the two Ta_2O_5 films were caused by the contribution of Ti-O as the other capacitor layer and an oxygen donor. The Ta_2O_5/TiO_2 thin films exhibited the dominant conduction mechanism regimes contributed by the Poole-Frenkel emission at high electric film.

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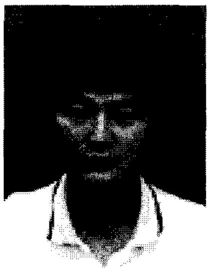

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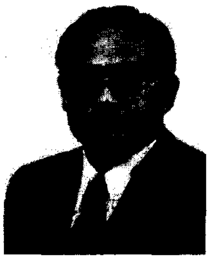

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