

Effect of annealing temperature on the electrical properties of HfAlO thin films

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High-K gate dielectric HfAlO thin films with different temperature annealing treatment have been deposited on the Si substrate by atomic layer deposition. The electrical properties of Hf-films are analysed by measurement of high-frequency capacitance–voltage ($C-V$) and leakage current density–voltage ($J-V$) characteristics. The electrical measurement results indicate the decrease of equivalent oxide thickness (EOT) due to the great change of microstructure and densification after high temperature annealing and the increase of permittivity. However, the interface state density increases. Moreover, the leakage current increases with the increase of annealing temperature. The HfAlO film annealed at 650°C has the best electrical parameters, such as dielectric constant, EOT and leakage current density determined through capacitance–voltage and current density–voltage measurements were 23.5, 0.84, $6.8 \times 10^{-7} \text{ mA}\cdot\text{cm}^{-2}$, respectively.

1. Introduction: Numerous materials with a higher permittivity than SiO_2 have been studied as alternative gate oxide to overcome the limit of SiO_2 in downscaling of complementary metal–oxide–semiconductor (CMOS) field effect transistor dimensions, such as Al_2O_3 , HfO_2 , TiO_2 and ZrO_2 . Among the various potential high-k materials, HfO_2 is considered as one of the most promising materials, because of its desirable properties including relatively high dielectrics constant, large bandgap, excellent thermal and chemical stabilities [1–3]. However, pure HfO_2 film has its disadvantages, for instance, the density of active traps at and near the high-k dielectric/Si interface which is higher than the density of traps at SiO_2/Si interface, which can act as significant scattering centres for carriers and increase an interface-state density. HfO_2 is susceptible to crystallisation after high temperature processing and has a poor barrier to oxygen diffusion, and boron diffusion into the gate dielectric should be suppressed to maintain low equivalent oxide thickness (EOT) [4]. In order to solve these problems, Al_2O_3 was doped into the HfO_2 film because of its large energy gap, good thermal stability, and high crystallisation temperature [3, 5, 6].

On the research of Hf-based high-k gate dielectrics in CMOS, many works have been reported. Zhang *et al.* [7] reported the TiO_2 -doped HfO_2 gate dielectric thin films prepared by RF sputtering on the Si substrates. He *et al.* [8] reported the effects of nitrogen incorporation on properties of sputtering-derived HfTiO high-k gate dielectrics on GaAs substrates. He *et al.* [9] introduced DMAH-derived aluminium oxynitride interfacial passivation layer for p-type InGaAs and its application in HfTiO -InGaAs gate stacks grown by sputtering. He *et al.* [10] investigated the effect of ALD growth cycles on the $\text{Al}_2\text{O}_3/\text{InGaAs}$ interface. HfO_2 and HfAlO are applied in the new devices. Abunahla *et al.* [11] developed a novel memristive structure, which consists of a Pd/Hf/ HfO_2 /Pd stack. Orouji and Anvarifard [12] reported a new structure of SOI-MOSFETs with high-K dielectric HfO_2 as an insulator material.

An important advantage of ALD deposition is that it can alternately deposit a stacked film structure of two or more metal oxides, of which HfAlO, i.e. HfO_2 and Al_2O_3 are alternately grown, is a typical one. This alternately grown laminate structure can effectively improve the disadvantages of a single dielectric layer. Further, it has the advantages of two kinds of films, such as increasing the dielectric constant of the dielectric layer.

High-k gate dielectric HfAlO films have been deposited on the Si substrate by atomic layer deposition (ALD) in this experiment. The electrical properties of the as-deposited HfAlO thin films and

HfAlO films with different annealing temperatures have been investigated. High-frequency capacitance–voltage ($C-V$) and the leakage current density–voltage ($J-V$) characteristics were analysed systematically.

2. Experimental: The diagram of the experimental process and the metal–oxide–semiconductor (MOS) capacitor structure used in this Letter were shown in Fig. 1. The films were fabricated on 8-in, p-type Si substrates. First, p-type Si (100) wafers were cleaned with BOE solution ($\text{NH}_4\text{F}:\text{HF}=6:1$) and washed in deionised water to remove organic contamination and the native oxide, then a device interface was prepared. The substrates were immediately loaded into the ALD reactor. TEMA, $\text{Al}(\text{CH}_3)_3$ were used as the HfO_2 and Al_2O_3 metal precursor, respectively, and H_2O as the oxidant. Approximately 3.85 nm HfAlO films were deposited by ALD at 300°C. The predicted growths per cycle of HfO_2 and Al_2O_3 for this experiment are 0.75 and 0.1 Å, respectively. Different cycles of HfO_2 and Al_2O_3 were adopted to prepare the HfAlO film. After the ALD oxide layers deposition, MOS capacitors were formed with a TiN film of ~5 nm thickness as the top electrode formed by ALD. W of ~75 nm thickness was used to cap the reactive TiN metal electrode to prevent its subsequent oxidation on exposure to air. And the bottom electrodes (Al) were deposited with the good ohmic contact. Post metallisation annealing (PMA) with forming gas annealing was carried out in forming a gas (95% N_2 + 5% H_2) at 450°C for 20 min. After the fabrication process, the high-frequency $C-V$ characteristics and the gate leakage currents of the MOS capacitors were measured at a frequency of 1 MHz with Keithley 4200. The $C-V$ fitting was performed with QMCV simulation software developed by Berkeley University.

3. Results and discussion: To investigate the influence of doping Al on the electrical of HfO_2 film, we fabricate capacitors with pure HfO_2 film and 3.5% Al-doped HfO_2 film as the gate oxide, respectively. The films were annealed at 650°C, N_2 , 60 s. The dependence of high-frequency (1 MHz) $C-V$ characteristics on the annealing temperatures, swept from 0 to 1.2 V, is depicted in Fig. 2. Electrons are tunnelling from the substrate to the thin film. QMCV simulation software developed by Berkeley University is used to extract EOT and V_{FB} from the $C-V$ data. Table 1 shows the electrical parameters obtained through QMCV.

As shown in Fig. 2, it can be seen that the EOT of HfAlO film is smaller than HfO_2 film, which due to the rate of oxygen diffusion of Al_2O_3 is far slow, and the growth of the interfacial layer with

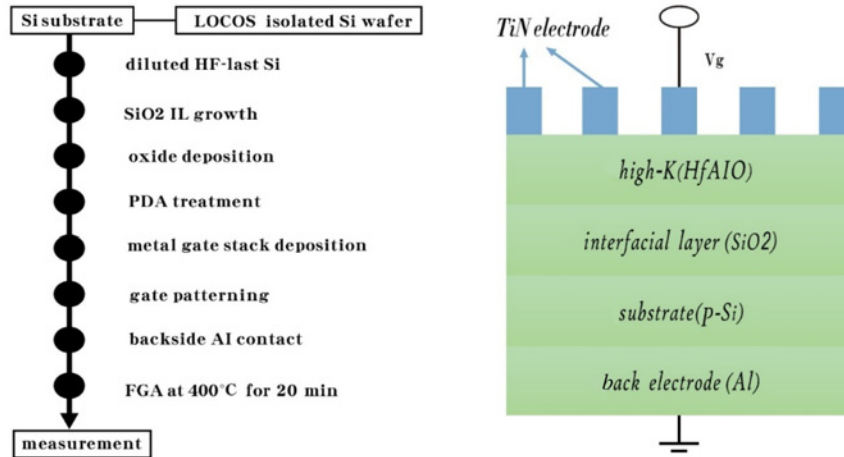


Fig. 1 Left is an experimental process diagram, right is a schematic diagram of the structure of TiN/HfAlO/SiO₂/p-Si MOS

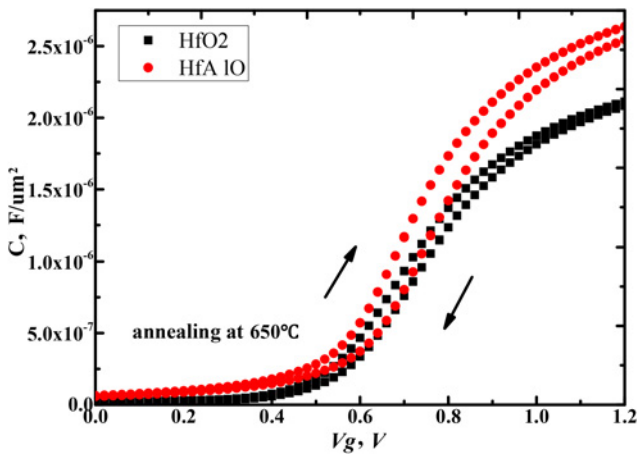


Fig. 2 High-frequency C - V curve of HfO₂ and HfAlO films with annealing at 650°C

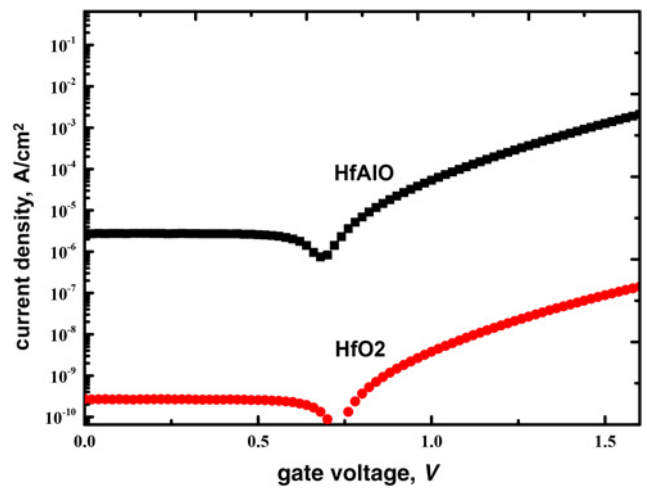


Fig. 3 I - V curves of HfO₂ and HfAlO films

Table 1 Electrical parameters obtained through QMCV from C - V curve

Electrical parameter	As-deposited	Annealed at 650°C	Annealed at 700°C	Annealed at 750°C
C_{acc} , pF/cm ²	218	258	230	223
K	17.3	23.5	22.8	22.1
EOT, nm	1.07	0.84	0.86	0.88
V_{FB} , V	0.38	0.46	0.44	0.48
ΔV_{FB} , mV	32.6	59.6	50.7	45.8
Q_m , $\times 10^{11}$ cm ⁻²	4.4	9.6	7.3	6.4

relative lower K can be slow down through doping Al. The interfacial layer can reduce the accumulation capacitance (C_{acc}) density, so the HfO₂ film has a smaller C_{acc} , which induce the relative dielectric constant K of HfAlO is larger than HfO₂. However, the oxide trap charge density (Q_m) of HfAlO is more than HfO₂, Q_m can be calculated from the equation $Q_m = C_{acc} \Delta V_{FB} / q$, the result as shown in Table 1, Q_m of HfAlO film is 9.6×10^{11} cm⁻². Since the HfAlO has a certain amount of Al-O or Hf-Al-O bond, these bonds have a better binding energy with oxygen located in the interface compared with Hf-O bond, inducing the formation of oxygen vacancy, the oxide trap charge density increase after oxygen vacancy trapping the charge.

Fig. 3 shows the I - V curves of HfAlO and HfO₂ films both are annealed at 650°C. We can see that the leakage current density of

HfAlO film is larger than HfO₂ film more than one order of magnitude. As we all know that the coordination number of Al atomic is larger than the SiO₂, which induce the increase of dangling bond, is easy to break up, increasing the density of interface state.

To investigate the electrical properties of HfAlO thin films, capacitors with TiN electrodes with an area of $100 \mu\text{m} \times 100 \mu\text{m}$ were measured. The annealing temperatures of the HfAlO films are 650, 700, 750 and 800°C. As shown in Fig. 4, comparing the annealing HfAlO films with the as-deposition film, it is found that the C - V curves are steeper in the depletion layer, which indicate the interface state densities are lower. Besides, the accumulation capacitances (C_{acc}) increase significantly. It is well known that the Cox is related to the interfacial layer, the application of post-deposition annealing (PDA) may be attributed to the suppression of the growth of interfacial layer and improvement of interface quality. The EOT values of capacitors are shown in Table 1. From Table 1, it can be seen that the EOT of samples after PDA are smaller than the as-deposition and the smallest EOT is 0.84 nm when the annealing temperature is 650°C. From the EOT, we can derive the dielectric constant K of HfAlO thin films through the equation [13]: $K_{high-k} = K_{SiO_2} \times T_{high-k} / (EOT - T_{SiO_2})$, the T_{high-k} and T_{SiO_2} are the thickness of HfAlO thin films and SiO₂ thin film, respectively. The dielectric constants (k) of samples are shown in Table 1. The sample after 650°C annealing has the highest dielectric constant, which reaches to about 23.5. The decrease of EOT and the increase of dielectric constant k after annealing could be due to the

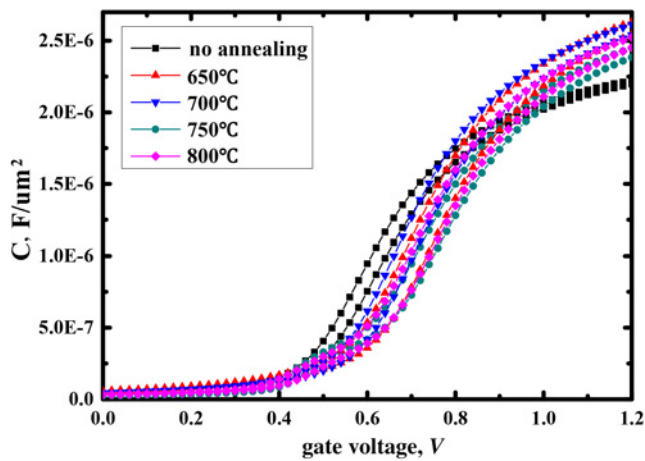


Fig. 4 High-frequency (1 MHz) C - V characteristics of HfAlO

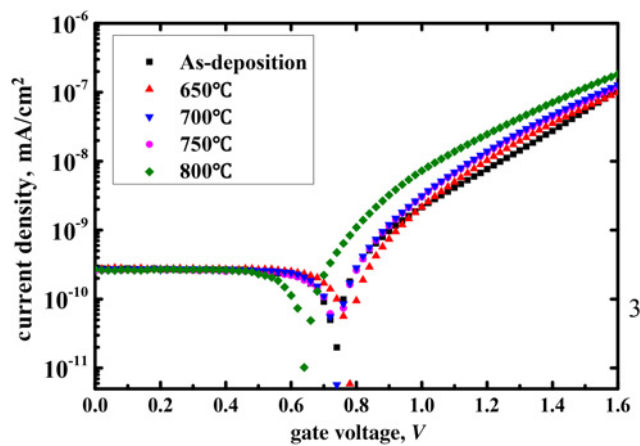


Fig. 5 I - V characteristics of HfAlO gate dielectric capacitors

great change of microstructure and densification of the films after high temperature annealing. Al atoms with small radius can diffuse into HfO_2 during PDA, which benefits the formation of tetragonal phase HfO_2 which exhibits high permittivity [14, 15].

The PDA treatment has an effect on V_{FB} that a positive shift can be seen compared with the sample without annealing. However, a negative V_{FB} shift is observed while after 700°C , which may be attributed to the oxygen vacancy generation caused by annealing. The values of V_{FB} with PDA are larger than without PDA, indicate that the films after annealing contain more defects and traps, which attributed to oxygen vacancies [16]. It also can be seen clearly that as-deposition HfAlO thin film has smaller flat band voltage hysteresis (ΔV_{FB}), which indicates that the sample with PDA has a larger border trapped oxide charge density. In brief, the interface quality is bader than that of as-deposition HfAlO thin film.

Fig. 5 demonstrates the I - V characteristics of HfAlO gate dielectric capacitors. The leakage current densities at the voltage of $V_{\text{FB}} + 1$ V of samples are 2.4×10^{-7} , 6.8×10^{-7} , 9×10^{-7} , 11.8×10^{-7} , $12.2 \times 10^{-7} \text{ mA}\cdot\text{cm}^{-2}$. The as-deposition HfAlO thin film has the lowest leakage current density. The high annealing temperature could make films to produce crystals, which is a pathway to deliver the leakage current. Due to the interfacial layer between HfAlO films after annealing and substrate has more interface states, which have a bad influence on the leakage current. Therefore, with the increase of annealing temperature, the leakage current densities increase obviously. The results show that the HfAlO thin film with 650°C has the best electrical properties.

4. Conclusion: In this work, $\sim 3.85 \text{ nm}$ HfO_2 and HfAlO films annealed at 650°C were deposited by ALD, the HfAlO film showed better electrical properties compared with HfO_2 film. Then, we investigated the property of as-deposition HfAlO film and annealed HfAlO films with different annealing temperatures were deposited by ALD at 300°C . From the results, it can be seen that the increase of dielectric constant k and the decrease of EOT and leakage current density with the increase of annealing temperature. The film annealed at 650°C has a dielectric constant of 23.5, an EOT of 0.84 nm , and leakage current of $6.8 \times 10^{-7} \text{ mA}\cdot\text{cm}^{-2}$ at a gate bias of $V_g = V_{\text{FB}} + 1 \text{ V}$. The HfAlO film annealed at 650°C has the best electrical properties.

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6 References

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