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

Chun Li[a], Zhiwei He[b*]

Department of Applied Physics, China Agricultural University, Beijing 100083, China

[a] lichunil@126.coml , [b*] hezw@cau.edu.cn,

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Abstract. High-K gate dielectric HfAlO thin films with different temperature annealing treatment have been deposited on Si substrate by Atomic layer deposition (ALD). The electrical properties of Hf-films are analyzed by measurement of high frequency capacitance-voltage (C-V) and leakage current density-voltage (I-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. But the interface state density increases. Moreover, the leakage current increases with the increase of annealing temperature. The HfAlO film annealed at 650℃ has the best electrical parameters, such as dielectric constant, EOT and leakage current density determined through CV measurement were 23.5, 0.84, 6.8×10^{-7}mA·cm^{-2}, respectively.

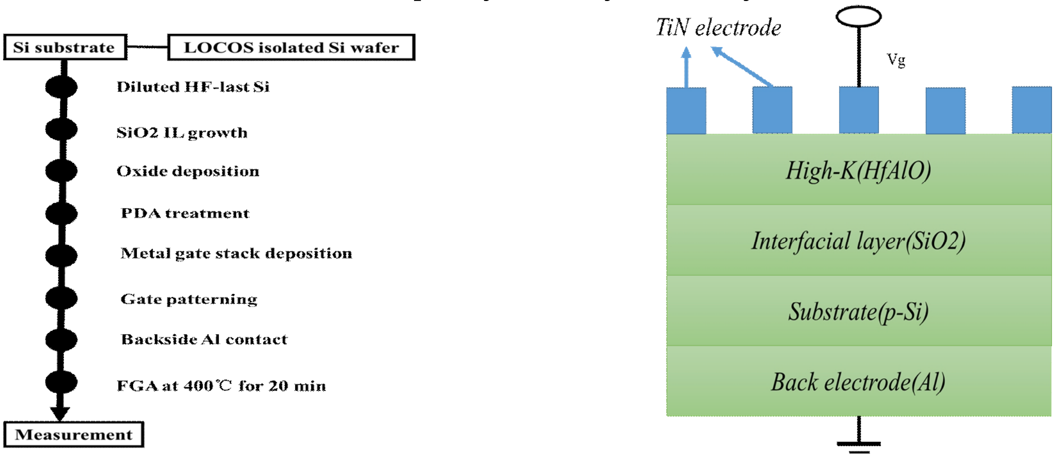
Introduction

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, 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 band gap, excellent thermal and chemical stability.[1,2] 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 centers for carriers and increase and interface-state density. HfO_2 is susceptible to crystallization after high temperature processing and has poor barrier to oxygen diffusion, and boron diffusion into the gate dielectric should be suppressed to maintain low equivalent oxide thickness (EOT).[3] 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 crystallization temperature. [4,5]

High-k gate dielectric HfAlO films have been deposited on 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 analyzed systematically.

Experimental

The diagram of the experimental process and the MOS capacitor structure used in this paper 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 (NH_4F: HF=6:1) and washed in deionized water to remove organic contamination and the native oxide, then a device interface was prepared. The substrates were immediately loaded into the ALD reactor. TEMAH, $Al(CH_3)_3$ were used as the HfO_2 and Al_2O_3 metal precursor respectively, and H_2O as the oxidant. ~3.85nm HfTiOx films were deposited by ALD at 300℃. The predicted growths per cycle of HfO_2 and Al_2O_3 for this experiment are 0.75Å 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, metal-oxide-semiconductor (MOS) capacitors were formed with TiN film of ~5nm thickness as 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 metallization annealing (PMA) with forming gas annealing were carried out in forming gas (95%N_2+5% H_2) at 450℃ 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.



(a) (b)

Fig 1 (a) Experimental process diagram ;(b)Schematic of structure of TiN/HfAlO/SiO2/p-Si MOS

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℃,N_2,60s. The dependence of high-frequency (1 MHz) C-V characteristics on the annealing temperatures, swept from 0 V to 1.2 V, is depicted in Fig 2. Electrons are tunneling 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. Tab 1 shows the electrical parameters obtained through QMCV.

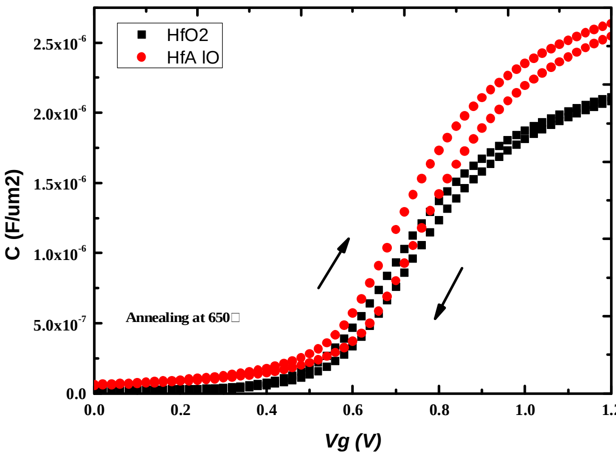


Figure 2 High frequency C-V curve of HfO2 and HfAlO films with annealing at 650℃

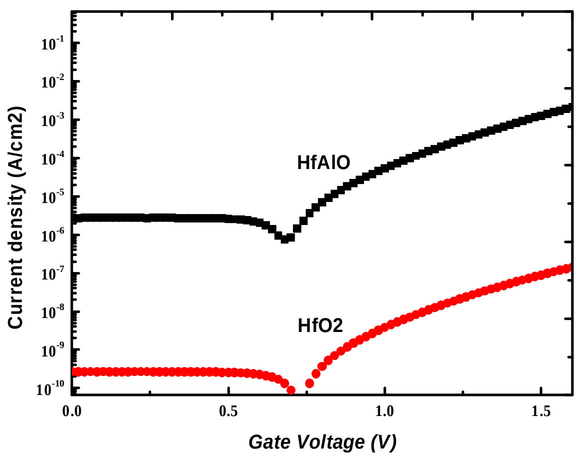


Figure 3 I-V curves of HfO2 film and HfAlO films

As shown in Fig 2, it can be seen that the equivalent oxide thickness (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 relative lower K can be slow down through doping Al. The interfacial layer can reduce the accumulation capacitance (C_{acc}) density, so the HfO_2 film has a smaller C_{acc} which induce the relative dielectric constant K of HfAlO is larger than HfO_2. However, the oxide trap charge density (Q_m)

of HfAlO is more than HfO_2, Q_m can be calculated from the equation $Q_m=C_{acc}\cdot\triangle V_{FB}/q$, the result as shown in Tab 1, Q_m of HfAlO film is $9.6\times10^{11}cm^{-2}$. Since the HfAlO has a certain amount of Al-O or Hf-Al-O bond, these bonds has 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 is the I-V curve of HfAlO film and HfO_2 film both are annealed at 650℃. We can see that the leakage current density of HfAlO film is larger than HfO_2 film more than one order of magnitude. As we all know that the coordination number of Al atomic is large than the SiO_2, 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 area of 100 μm*100 μm were measured. The annealing temperature of the HfAlO films are 650℃、700℃、750℃、800℃. As shown in Fig 4, comparing the annealing HfAlO films with as-deposition film, it is found that the C-V curves are steeper in depletion layer, which indicate the interface state densities are lower. Besides, the accumulation capacitances (C_{acc}) increase significantly. It is well know that the C_{ox} 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 equivalent oxide thickness (EOT) values of capacitors are shown in Tab 1. From Tab 1, it can be seen that the equivalent oxide thickness of samples after PDA are smaller than the as-deposition and the smallest EOT is 0.84 nm when annealing temperature is 650℃. From the EOT, we can derive the dielectric constant K of HfAlO thin films through the equation[6] : $K_{high-k}=K_{SiO2}\times T_{high-k}/(EOT-T_{SiO2})$,The T_{high-k} and T_{SiO2} are the thickness of HfAlO thin films and SiO_2 thin film respectively. The dielectric constants (k) of samples are showed in Tab 1. The sample after 650℃ annealing has the highest dielectric constant, which reaches to about 23.5. The decrease of EOT and increase of dielectric constant k after annealing could be due to the 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.[7,8]

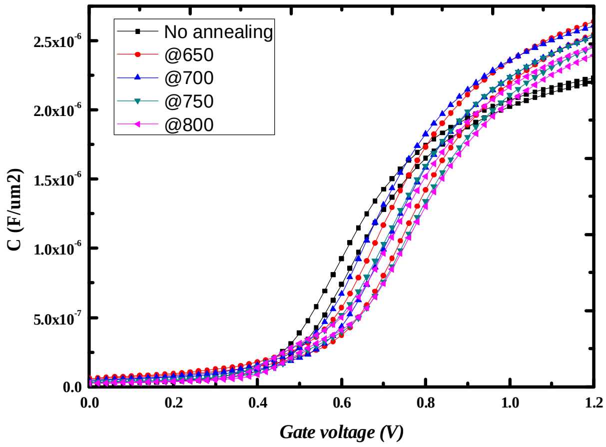
Tab 1 The electrial parameters obtained through QMCV from C-V curve

Electrical parameter	As-deposited	Annealed at 650℃	Annealed at 700℃	Annealed at 750℃
C_{acc}(pF/cm2)	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
$\triangle V_{FB}$(mV)	32.6	59.6	50.7	45.8
Q_m($\times10^{11}cm^{-2}$)	4.4	9.6	7.3	6.4

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℃,which may be attribute to the oxygen vacancy generation caused by annealing. The value 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.[9] It also can be seen clearly that as-deposition HfAlO thin films has smaller flat band voltage hysteresis (ΔV_{FB}) which indicate that the sample with PDA has larger border trapped oxide carge 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 density at the voltage of V_{FB}+1 V of samples are $2.4\times10^{-7}mA\cdot cm^{-2}$、$6.8\times10^{-7}mA\cdot cm^{-2}$、$9\times10^{-7}mA\cdot cm^{-2}$、

$11.8\times10^{-7}mA\cdot cm^{-2}$、$12.2\times10^{-7}mA\cdot cm^{-2}$, respectively. 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 bad influence on the leakage current. Therefore, with the increase of annealing temperature, the leakage current densities increase obviously. The results show that HfAlO thin film with 650℃ has the best electrical properties.



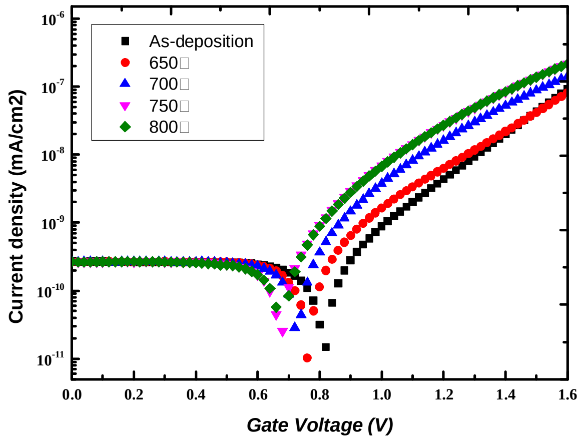


Fig 4 High frequency (1MHz) C-V characteristics of HfAlO   Fig 5 I-V characteristics of HfAlO gate dielectric capacitors

Conclusions

In this work, ~3.85nm HfO_2 and HfAlO film annealed at 650℃ were deposited by Atomic layer deposition (ALD), the HfAlO film showed a 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 temperature were deposited by ALD at 300℃. 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℃ has a dielectric constant of 23.5, a EOT of 0.84 nm, and leakage current of $6.8\times10^{-7}mA\cdot cm^{-2}$ at a gate bias of $V_g=V_{FB}+1$ V. The HfAlO film annealed at 650℃ has the best electrical properties.

Acknowledgment

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