Effect of Al Inclusion in HfO_2 on the Physical and Electrical Properties of the Dielectrics

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***Abstract*—This letter presents the effect of Al inclusion in HfO_2 on the crystallization temperature, leakage current, band gap, dielectric constant, and border traps. It has been found that the crystallization temperature is significantly increased by adding Al into the HfO_2 film. With an addition of 31.7% Al, the crystallization temperature is about 400 °C–500 °C higher than that without Al. This additional Al also results an increase of the band gap of the dielectric from 5.8 eV for HfO_2 without Al to 6.5 eV for HfAlO with 45.5% Al and a reduced dielectric constant from 19.6 for HfO_2 without Al to 7.4 for Al_2O_3 without Hf. Considering the tradeoff among the crystallization temperature, band gap, and dielectric constant, we have concluded that the optimum Al concentration is about 30% for conventional self-aligned CMOS gate processing technology.**

***Index Terms*—Al-hafnium oxide, band gap, border trap, crystallization, dielectric constant, hafnium oxide, high-k dielectrics.**

I. Introduction

According to the International Technology Roadmap for Semiconductors (ITRS), the gate dielectric needs to be scaled down below 1.2 nm for 100-nm node CMOS technology and beyond [1] and the viability of SiO_2 will face severe challenges [2]. Therefore, high-k dielectrics are being pursued as possible replacements for SiO_2. Among these dielectrics, HfO_2 appears promising due to its relatively high dielectric constant ($\sim$ 25) as compared to Si_3N_4 and Al_2O_3 [3], its relatively high free energy of reaction with Si (47.6 kcal/mole at 727 °C) as compared to TiO_2 and Ta_2O_5 [4] and its relatively high band gap ($\sim$ 5.8 eV) among its high-k contenders [5]. However, the crystallization temperature of HfO_2 is quite low, which restricts the thermal budget after its deposition to avoid the higher leakage current and lateral nonuniformity associated with grain boundaries. Hf-silicate has been reported as a promising material with high crystallization temperature [6], [7]. However, the dielectric constants of silicates are usually less than 15 and therefore they may face the same scaling challenge as Al_2O_3.

This letter shows that the crystallization temperature of HfO_2 can be increased significantly by adding Al in the film while keeping the dielectric constant higher than 15. The effect of crystallization on the leakage current and the effect of Al-incorporation on the band gap and border traps of the HfO_2 film are also discussed.

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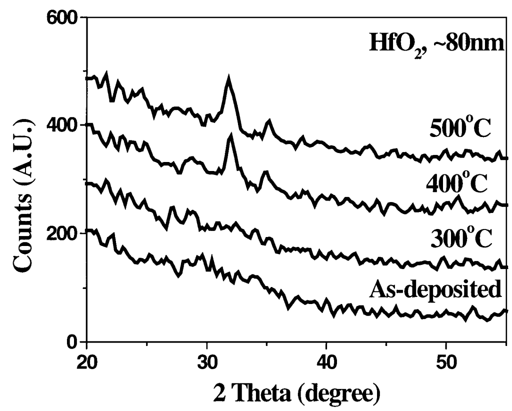

Fig. 1. XRD of HfO_2 after various PDA temperatures.

II. Experimental

HfO_2 and HfAlO films were deposited by jet vapor deposition (JVD) [8] at room temperature on Si substrates. The Hf vapor and Al vapor were generated by dc sputtering in separate nozzles. The metal vapors and O_2 were brought out of the source nozzles by supersonic Ar jets. The physical thicknesses of the HfO_2 and HfAlO films are about 3 nm for MOS capacitors and are about 80 nm for the X-ray diffraction (XRD), band gap, and ellipsometry measurement. The post deposition annealing (PDA) was performed in N_2 for 2 min in a rapid thermal anneal (RTA) chamber. The annealing temperature varied from 300 °C to 800 °C. Pt was used as the top electrode and Al was used as the backside contact for the MOS capacitors.

III. Results and Discussion

A. Effect of Crystallization on Leakage Current

Fig. 1 shows the XRD patterns of 80 nm of HfO_2 with various PDA temperatures. It can be seen that the (110) crystalline peak of HfO_2 starts to show up between 300 °C and 400 °C. As a result, the leakage current increase significantly when the annealing temperature increase from 400 °C to 500 °C, as shown in Fig. 2(a), due to the additional high-leakage path along the grain boundaries through the polycrystalline dielectrics. The subsequent decrease of the leakage current at temperatures higher than 500 °C is due to the growth of SiO_2 at higher temperatures, as shown in Fig. 3.

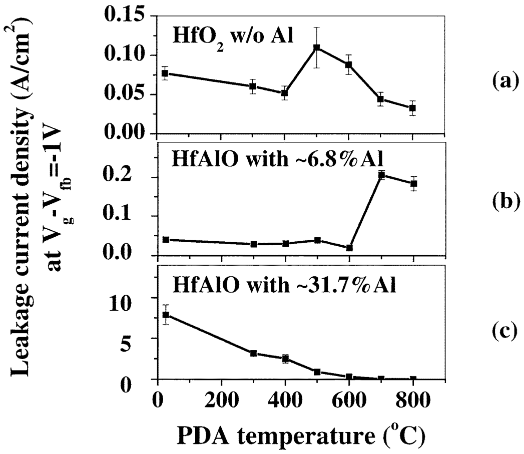

Fig. 2. Gate leakage currents of HfO_2, HfAlO with ~ 6.8% of Al and HfAlO with ~ 31.7% of Al, as functions of PDA temperature. The EOTs of these films are shown in Fig. 3.

B. *Effect of Al Inclusion in HfO_2 Film on the Crystallization Temperature of the Dielectric*

To raise the crystallization temperature, Al was added in the deposition process to form HfAlO films. Fig. 4 shows the crystallization temperature of HfO_2 or HfAlO as a function of Al atom percentage ($Al\% = N_{Al}/[N_{Al} + N_{Hf}]$). The Al percentage is measured by XPS. It can be seen that the crystallization temperature increases monotonically from 375 °C for HfO_2 to 1000 °C for HfAlO with 45.5% Al. This is probably because the Al acts as a network modifier and stabilizes the amorphous phase of the metal oxides.

The addition of Al also causes a corresponding increase of the temperature at which the peak gate current occurs, as shown in Fig. 2, where the leakage current for MOS capacitors with ~ 1.1 nm equivalent oxide thickness (EOT) of HfO_2, measured at $V_g - V_{fb} = -1$ V, is plotted as a function of PDA temperature from 300 °C to 800 °C. The temperature corresponding to the peak leakage current is ~ 500 °C for HfO_2, ~ 700 °C for HfAlO with ~ 6.8% of Al, and estimated to be well above 800 °C for HfAlO with ~ 31.7% of Al. Similarly, the onset of rising leakage current is probably due to crystallization of the film, causing increased leakage through grain boundaries; the subsequent current decrease is due to the growth of SiO_2 at higher temperatures, as shown in Fig. 3. The growth of the SiO_2 layer is probably due to the residual O_2 in the RTA chamber that diffuses through the HfO_2 or HfAlO film and react with the Si substrate to form the interfacial layer. It is worth noting that the EOT of the HfAlO film with ~ 31.7% of Al is thinner than that of either the HfO_2 or the HfAlO film with ~ 6.8% of Al, as shown in Fig. 3. As a result, the leakage currents for the HfAlO films with 31.7% Al are also generally higher than the other two. Another thing to be pointed out is that the leakage current decreases with increasing annealing temperature for temperatures below 500 °C, especially for HfAlO with 31.7% Al. We believe this is due to the decreased trap density with increasing annealing temperature, as reflected in the reduced hysteresis for samples annealed at higher temperatures, as shown in Fig. 5.

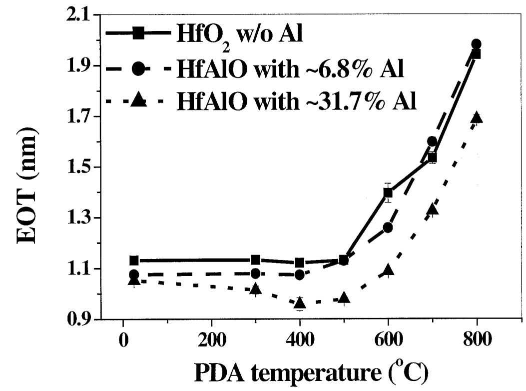

Fig. 3. EOTs of HfO_2, HfAlO with ~ 6.8% of Al and HfAlO with 31.7% of Al, as functions of PDA temperature.

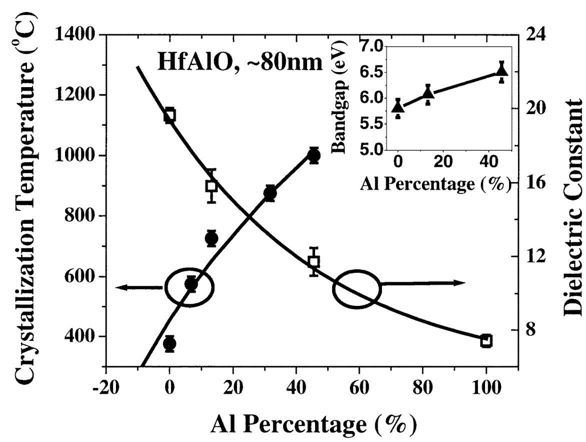

Fig. 4. Crystallization temperature, dielectric constant of HfAlO as functions of Al percentage. The inset shows the band gap of HfAlO as a function of Al percentage.

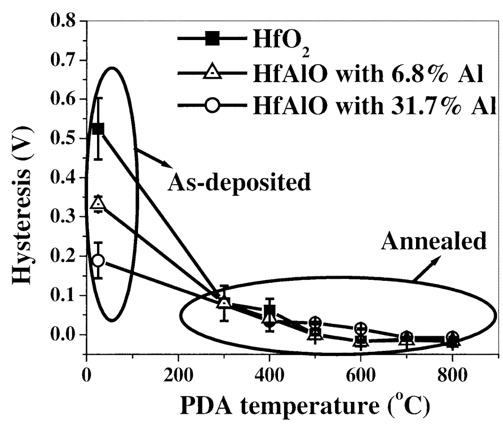

Fig. 5. C–V hysteresis for capacitors made of HfO_2, HfAlO with 6.8% Al, and HfAlO with 31.7% Al.

C. *Effect of Al Inclusion in HfO_2 Film on Band Gap of the Dielectric*

The band gap is measured by n and k analyzer [9] on the thick films of ~ 80 nm. As shown in the inset of Fig. 4, Al incorporated in the HfO_2 film induced an increase of band gap from 5.8 eV for HfO_2 without Al to 6.5 eV for HfAlO with 45.5% Al, which is consistent with the large band gap of Al_2O_3 (8.1 eV)

[10]. Since the tunneling current can be reduced exponentially as the band offset of the dielectric increases, this increased band gap is another advantage of the Al-incorporated film.

D. Effect of Al Inclusion in HfO_2 Film on Dielectric Constant

The dielectric constant is determined on films of 80 nm in thickness, by measuring the physical thickness with ellipsometry and the electrical thickness from the capacitance in strong accumulation measured at 100 kHz. As shown in Fig. 4, the dielectric constant of the film decrease from 19.6 for HfO_2 without Al to 7.4 for Al_2O_3. If the dielectric constant is required to be higher than $\sim$ 15, then it will limit the Al percentage to be less than $\sim 30\%$.It should be noted that the dielectric constants reported in Fig. 4 are the effective dielectric constants that include the effects of the high-k films and the interfacial layers, which are lower than that of a single high-k layer, although the dielectric constant value for HfO_2 we report here is very close to that reported by Gusev at IBM [11].

E. Effect of Al Inclusion on Hysteresis of the Capacitance–Voltage (C–V) Characteristics

The capacitance–voltage (C–V) hysteresis of capacitors made of HfO_2 and HfAlO with various Al concentrations are shown in Fig. 5. It can be seen that, for as-deposited sample, the hysteresis for the HfAlO sample is much smaller than that for the HfO_2 sample, indicating that the former has much fewer border traps. The reason for this is not yet clear. After annealing in N_2 at 300 °C and above, the hysterisis decreases dramatically and becomes less than 50 mV when the temperature is higher than 500 °C for both HfO_2 and HfAlO, probably due to the removal of some dangling bands near the interface. Although it is not yet confirmed, we suspect that the large hysterisis for as-deposited films may be due to the radiation damage during the e-beam evaporation of the Pt gate.

IV. SUMMARY

The effect of Al inclusion in HfO_2 film on the crystallization temperature, leakage current, band gap, dielectric constant, and C–V hysterisis have been studied. It has been found that the crystallization of HfO_2 could result in significant increase of the leakage current. Al inclusion in HfO_2 increases the crystallization temperature from 375 °C for HfO_2 without Al to 1000 °C for HfAlO with 45.5% Al. This additional Al also results in an increase of the band gap from 5.8 eV for HfO_2 without Al to 6.5 eV for HfAlO with 45.5% Al and a decrease of dielectric constant from 19.6 for HfO_2 to 7.4 for Al_2O_3. Considering the tradeoff among the crystallization temperature, band gap, and dielectric constant, we have concluded that the optimum Al concentration is about 30% for conventional self-aligned CMOS gate processing technology.

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