LETTER TO THE EDITOR

Amorphous (CeO$_2$)$_{0.67}$(Al$_2$O$_3$)$_{0.33}$ high-$k$ gate dielectric thin films on silicon

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Abstract

The electrical and physical characteristics of (CeO$_2$)$_{0.67}$(Al$_2$O$_3$)$_{0.33}$ (CAO), for use in metal-oxide-semiconductor gate dielectric applications were investigated. The CAO thin films have been deposited at 650 $^\circ$C in different oxygen pressures by pulsed laser deposition. The CAO thin film was found to exhibit excellent characteristics such as atomic-scale smooth surface, thin interfacial layer, high accumulation capacitance and low leakage current density. This demonstrates that CAO thin film is a promising gate dielectric replacing SiO$_2$ in future for its good physical and electrical properties.

In order to maintain lower power consumption performance of complementary metal-oxide-semiconductor (CMOS) transistors, high dielectric constant ($k$) gate dielectrics must be employed to replace conventional SiO$_2$/SiON as the scale of the channel length goes down to sub-0.1 $\mu$m feature size. An alternative gate dielectric needs stringent requirements for practical replacement of SiO$_2$/SiON [1]. These requirements include high permittivity, thermal stability, high level film and interface quality, processing and materials compatibility with fabrication of CMOS devices and long-term reliability. Many materials have been investigated as candidates for this replacement. Among all the high-$k$ dielectrics, amorphous metal oxides, such as unary metal-oxide of Al$_2$O$_3$ [2, 3], CeO$_2$ [4–6], HfO$_2$ [7, 8] and ZrO$_2$ [9, 10] and binary systems of (Y$_2$O$_3$)$_x$(ZrO$_2$)$_{1-x}$ (yttria-stabilized ZrO$_2$) [11, 12], LaAlO$_3$ [13] and (HfO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ [14, 15], have been shown to be the most promising high-$k$ gate dielectrics due to their high dielectric constant, excellent thermal stability and good compatibility with modern microelectronics processing technique. Aluminium oxide (Al$_2$O$_3$) is considered as a candidate for gate dielectric replacement of SiO$_2$ for its high dielectric constant ($k = 10$), large bandgap (9 eV), thermodynamic stability on Si and good interface with Si substrate [16]. And also, cerium oxide shows to be a potential alternative to replace the standard SiO$_2$ based silicon on insulator technology [4, 6, 17]. Recently, Al$_2$O$_3$ was proposed to form alloy with HfO$_2$ to raise the crystallization temperature so that improvement in the interfacial characteristics could be achieved [14]. However, although significant progress has been made, none of the above-mentioned materials has been found to fulfil and fit the requirements for practical applications. As a result, searching for new high-$k$ gate dielectric materials is still under way.

(CeO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ (CAO) system is an effective catalyst for oxidation of various hydrocarbons [18]. In this letter, we report an investigation on the CAO thin films deposited by using pulsed laser deposition (PLD) from a target of (CeO$_2$)$_{0.67}$(Al$_2$O$_3$)$_{0.33}$, as an alternative candidate for high-$k$ gate dielectric material. Our results have shown that the amorphous CAO thin film possesses excellent physical and electrical properties, such as a smooth surface morphology, high oxide capacitance, low hysteresis characteristics and low leakage current density.

The amorphous CAO thin films were deposited on n-type silicon substrate by PLD technique. The target with a composition of (CeO$_2$)$_{0.67}$(Al$_2$O$_3$)$_{0.33}$ was made via the conventional ceramic processing. CeO$_2$ (99.9%) and Al$_2$O$_3$ (99.99%) powders were thoroughly mixed and then sintered at 1200 $^\circ$C for 12 h. CeAlO$_3$ was not formed in the (CeO$_2$)$_{0.67}$(Al$_2$O$_3$)$_{0.33}$ target, as evidenced by x-ray diffraction...
amorphous. AFM examination demonstrated that no particles were deposited by a PLD system, using a KrF excimer laser. The deposition was conducted with a focused energy density of 2 J cm\(^{-2}\) at a laser pulse frequency of 2 Hz and substrate temperature of 650 °C. Oxygen pressure was varied from 5.5 \times 10^{-2} \text{Pa} to 4.5 \text{Pa}. After deposition, all the samples were in situ annealed for 30 min at the deposition oxygen pressure. The thickness of the CAO thin films was in the range from 6 Å to 150 Å.

The phase composition of CAO thin films was characterized by an XRD measurement. Surface morphology was observed by atomic force microscopy (AFM). The morphological characteristics were examined by x-ray photoelectron spectroscopy (XPS). For electrical characterization, MOS capacitor was fabricated using Pt-gate electrodes with an area of 2 \times 10^{-2} \text{cm}^2, deposited using magnetic sputtering equipment. Capacitance–voltage (C–V) and leakage current density (J) versus voltage of CAO were measured using an HP 4192 LCR meter and Radiant Technology RT6000S ferroelectric tester, respectively. The capacitance equivalent thickness (CET) was calculated including the quantum mechanical effect.

XRD measurement showed that no diffraction peak related to CeAlO\(_3\), CeO\(_2\), Ce\(_2\)O\(_3\) or Al\(_2\)O\(_3\) was observed in CAO/Si samples, indicating that the CAO films were amorphous. AFM examination demonstrated that no particles and islands were found. The average root-mean-square surface roughness of CAO thin films was about 5.8 Å in an area of 2 \mu m \times 2 \mu m, which indicated that the surface of CAO thin film is atomic-scale smooth.

In order to investigate the interfacial properties of CAO thin film on silicon, very thin CAO layers with thicknesses of 6 Å, 10 Å and 20 Å were deposited at 650 °C under an ambient oxygen pressure of 3.2 \times 10^{-1} \text{Pa}. Figure 1 shows the Si 2p core-level spectra of the three CAO/Si samples. It has been reported that the Si 2p binding energies of Si–O for SiO\(_2\) in the native silicon oxide and Si–Si for pure silicon are about 103.1 eV and 99.2 eV, respectively, with a difference of about 3.9 eV [16]. For the 6 Å CAO layer, the peak binding energy measured was 103.1 eV, indicating that the interfacial layer was SiO\(_2\) in this sample. As the CAO thickness increased, the binding energy of Si–O shifted to lower values. For example, the Si–O binding energy of the 20 Å thick CAO thin film was only about 102.5 eV, which was equal to the bonding energy for Si\(^{3+}\) [20]. This observation indicated that the band valency state of Si in the interfacial layer decreased with the increasing thickness of the CAO film. At the same time, the intensity of the Si 2p binding energy peak decreased as the thickness of the CAO thin films increased. It is necessary to note that no Si 2p peak could be detected by the XPS measurement as the CAO thin film was thicker than 40 Å. The XPS results showed that there was a thin SiO\(_x\) (0 < x < 2) interfacial layer between the CAO thin film and the Si substrate and the CAO thin film could prevent the ambient oxygen from diffusing through it to react with the Si substrate. For a 45° XPS detector, the thickness of the interfacial SiO\(_x\) layer \(t_{\text{SiO}_x}\) can be estimated by the following equation,

\[
f_{\text{SiO}_x} = \frac{\lambda_{\text{SiO}_x}}{\sqrt{2}} \ln \left( 1 + \frac{\lambda_{\text{Si}}}{r_{\lambda_{\text{SiO}_x}}} \right) \tag{1}
\]

where \(\lambda_{\text{SiO}_x}\), \(\lambda_{\text{Si}}\), and \(r\) are the electronic inelastic mean free paths for SiO\(_x\), Si and the ratio of SiO\(_x\) peak area to substrate peak area [21]. The values of \(\lambda_{\text{SiO}_x}\) and \(\lambda_{\text{Si}}\) are about 36 Å and 30 Å, respectively [22]. Using this equation, the thicknesses of the interfacial layer SiO\(_x\) for the 6 Å, 10 Å and 20 Å thick CAO samples were 10.8 Å, 9 Å and 6 Å, respectively.

Figure 2 shows the capacitance–voltage (C–V) curves at 100 kHz of the 80 Å thick CAO/Si sample deposited at ambient oxygen pressures of 5.5 \times 10^{-2} \text{Pa}, 2.7 \times 10^{-1} \text{Pa} and 5.5 \text{Pa}, respectively. The effective dielectric constant and CET of the corresponding CAO thin films were 16.8, 20.5 and 22.6, and 18.6 Å, 15.2 Å and 13.8 Å, respectively. The flat band voltage (\(V_{fb}\)) calculated from the C–V curves was 1.19 V, 0.59 V and 0.77 V, respectively. It is noted that the effective dielectric
constant of the films increased, while the $V_B$ decreased with increasing oxygen pressure. This could be attributed to the fact that high oxygen pressure led to dense films with less oxygen vacancies. It is therefore suggested that high oxygen pressure be used for the deposition of films with high dielectric constant. However, high oxygen pressure inevitably increases the fixed positive charges in the films, which in turn increases the $V_B$. The reason why $V_B$ of the CAO samples deposited at low oxygen pressure was larger than that of those deposited at high oxygen pressure might be due to the fact the Ce$^{3+}$ was reduced to Ce$^{4+}$ at low ambient oxygen pressure [23].

The EOT of the CAO films with different thicknesses of 36 Å, 50 Å, 85 Å, 90 Å and 140 Å is shown in figure 3. All the CAO thin films were deposited at 650 °C at the oxygen pressure of 3.3 Pa. It can be concluded that the EOT of the CAO decreases with CAO physical thickness correspondingly. At the same time, one can find that the effective dielectric constant of the CAO thin films is less than 10 as the CAO physical thickness is thinner than 30 Å. It implies that there was a SiO$_2$ interfacial layer between the CAO and the Si substrate. The thickness of the interfacial layer in the thin CAO film was thicker than that in the thick one. This observation is in good agreement with the XPS result.

Figure 4 shows the leakage current density ($J$) at +1 V bias voltage of the CAO/Si samples with different EOT. The leakage current density of the CAO film with 20 Å EOT is only $2.74 \times 10^{-5}$ A cm$^{-2}$, which is much lower than that of a 20 Å SiO$_2$ on silicon (about 100 mA cm$^{-2}$) [24].

In summary, amorphous CAO thin films, with good electrical and physical properties, were deposited on silicon by PLD method. The CAO film had good interfacial characteristics with Si substrate. The good dielectric and electrical properties of the amorphous CAO thin films make them a promising candidate of future high-$k$ gate dielectrics to replace SiO$_2$.

References