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Thermally Evaporated ZrO_2

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The characteristics of zirconium oxide (ZrO_2) films, grown by standard thermal evaporation of zirconium while adding oxygen at constant partial pressure during evaporation, were investigated for the first time. The physical thickness (t_{phys} in Å) and electrical thickness of the as-grown and annealed samples were studied. The dielectric constant as measured by the capacitance-voltage (C-V) technique is estimated to be around 36. C-V measurements taken at 100 kHz show a low hysteresis of ~30 mV and the maximum capacitance seems to flatten out for the lower physical thickness, which might indicate presence of an interfacial oxide/silicate layer.
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Zirconium oxide (ZrO_2) as high-*k* gate dielectric has been under intense investigation recently for replacing conventional SiO_2 due to its high dielectric constant (~20-25), low leakage current, and good thermal stability on silicon. In addition to replacing gate oxide in complementary metal oxide semiconductor (CMOS) devices, other applications such as floating gate memory devices consider ZrO_2 as a potential candidate for replacement of the ONO stack dielectric, which is being used in the floating gate memory devices. Many such applications have led to numerous efforts to synthesize zirconium oxide by various methods compatible to standard CMOS technology. Techniques such as chemical vapor deposition (CVD,[1,2] atomic layer CVD (ALCVD),[3] sol-gel techniques,[4] chemical solution deposition,[5] anodization,[6] electron beam deposition,[7] ion-beam assisted deposition,[8] rf as well as dc sputtering,[9,10] and reactive direct current magnetron sputtering.[11] The properties of grown film and interface show a pronounced dependence upon the deposition process and the precise deposition parameters chosen. Each technique has their own set of advantages and disadvantages. However, most of these techniques show some or other kind of interface damage. Sputtering and e-beam assisted depositions create radiation induced surface damage during film growth. Thermal evaporation is a well-known technique that does not produce any kind of surface damage. Because this technique is a rather gentle process it creates very little or no damage to the interface. In this paper, we investigate the electrical properties of ZrO_2 deposited by standard thermal evaporation technique with adding oxygen at constant partial pressure during evaporation.

Experimental

Zirconium oxide (ZrO_2) films were grown on p-type ⟨100⟩ silicon wafers using standard thermal evaporation of zirconium while adding oxygen at constant partial pressure during evaporation. The base pressure was maintained at 10^{-6} Torr before oxygen was added. During evaporation the pressure in the chamber increased to 10^{-4} Torr when oxygen was added. Zirconium was evaporated using a specially designed tungsten boat. Before evaporation, the wafers were cleaned using standard RCA cleans (RCA-1 and RCA-2) followed by a 50:1 HF dip for 15 min immediately prior to the deposition. ZrO_2 of thickness as measured by ellipsometer of 59, 89, and 173 Å were deposited for the current work. Metal oxide semiconductor capacitance structure was achieved by using a mercury probe station. Samples were subjected to forming gas anneal (FGA) at 550°C and 650°C.

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Results and Discussion

Table I summarizes the physical thickness (t_{phys} in Å) of the as-grown ZrO_2 and after annealing, which shows a decrease in the thickness of the films after annealing. This decrease shows the thermal stability of these films. Figure 1 shows the capacitance-voltage (C-V) curves taken at 100 kHz for different film thickness annealed at 600°C. Using the known oxide thickness the dielectric constant as measured by the C-V technique is estimated to be around 36. This high value of dielectric constant can be attributed to possible tungsten contamination during evaporation. The accurate identification of tungsten is currently underway. One of the major concerns in High-*k* dielectrics is hysteresis because of its impact on threshold voltage instability. With post-deposition annealing at 600°C it can be seen that the hysteresis has reduced to ~ 30 mV. The maximum capacitance seems to flatten (Fig. 1) for the lower physical thickness, which might indicate presence of an interfacial layer between ZrO_2 and Si. The interfacial layer may be of either zirconium silicate ($ZrSi_xO_y$) because of oxygen deficiency or silicon oxide (SiO_x) due to the diffusion of excess oxygen through ZrO_2. The electrical *vs.* physical thickness are plotted in Fig. 2. A 9 Å interfacial film thickness was estimated using a quantum mechanical interface model.

The flatband voltage shift as a function of physical thickness is shown in Fig. 3. It seems the flatband voltage shift for the 650°C annealed films is quite reliable where as the other data is very scattered. The significant deviation in as grown sample is believed to be due to interface-trapped charges (Q_{ot}). For 550°C annealed film the flatband voltage shift looks unreliable. Even though it is currently being explored further, it is believed that for thermally evaporated ZrO_2 films the activation annealing temperature is higher than 550°C. In addition, the flatband voltage shift indicates an effective negative charge as high as 2.7×10^{13} cm^{-2} in the oxide. However, the net charge decreases due to annealing. The nature of the interfacial layer in thermal evaporated ZrO_2 can determine the polarity as well as the quantity of oxide-trapped charges.

Figure 4 shows the leakage current *vs.* electrical thickness of ZrO_2 at a flatband voltage of −1 V. Note that even though the

Table I.

Samples	t_{phys} as-grown (Å)	t_{phys} 550C FGA (Å)	t_{phys} 650C FGA (Å)
1	59	49	49
2	89	72	70
3	173	150	146

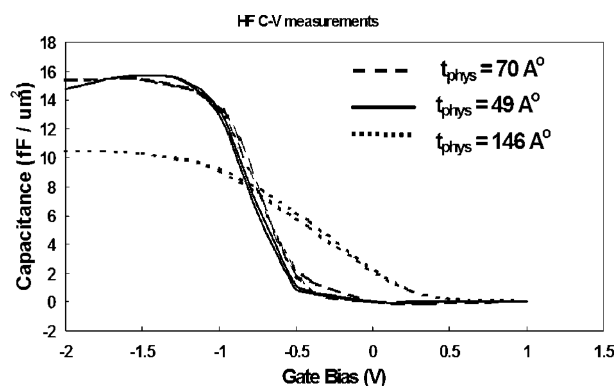

Figure 1. C-V measurements for 650°C-annealed ZrO_2 taken at 100 kHz.

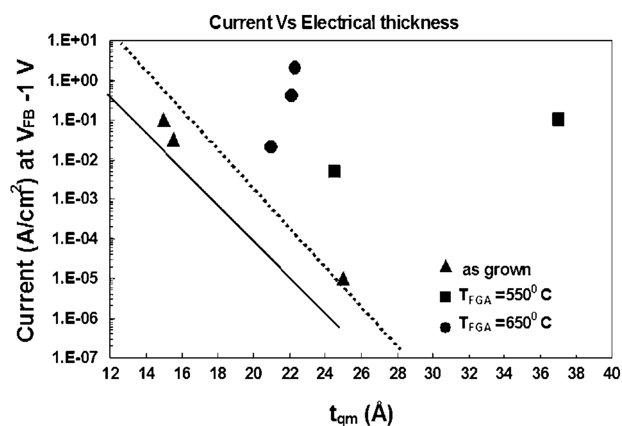

Figure 4. The leakage current *vs.* electrical thickness of ZrO_2 films as deposited, 550°C annealed, and 650°C annealed.

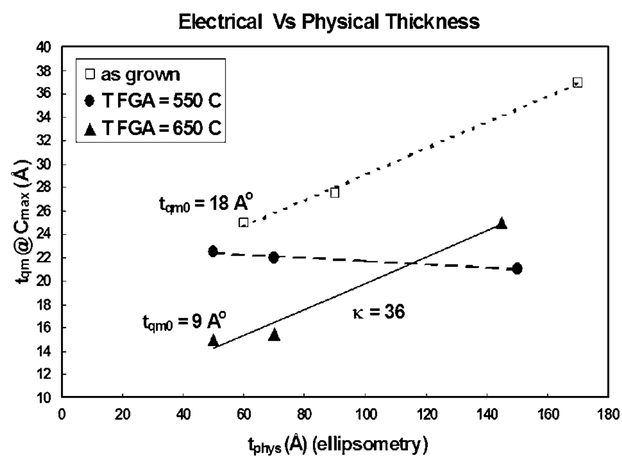

Figure 2. Electrical *vs.* physical thickness of ZrO_2 films.

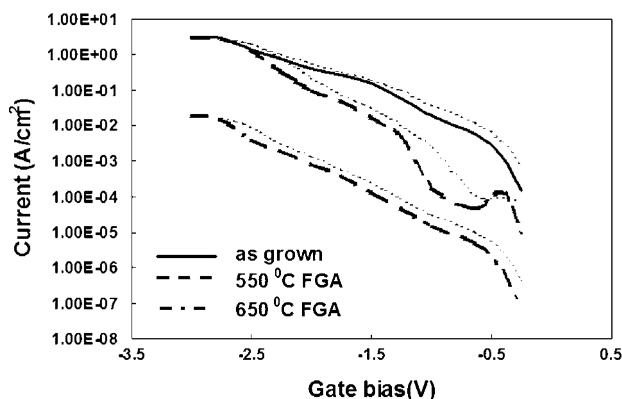

Figure 5. Leakage current as a function of bias voltage.

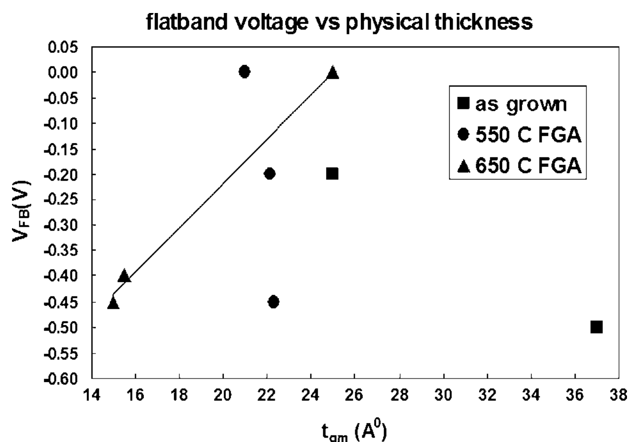

Figure 3. Flatband voltages *vs.* physical thickness for all the ZrO_2 films.

physical thickness decreases for annealing at higher temperatures, the leakage current decreases. For 650°C annealed ZrO_2 samples the leakage current shows a linear dependence and consistent with Schottky emission mechanism, where the interface layer between ZrO_2 and the Si substrate dominates the conduction process. The decrease in leakage current suggests that ZrO_2 bulk traps contributing to the leakage paths are reduced after the activation annealing. As mentioned before the formation mechanism and the nature of interfacial layer could control the leakage current. Note that the current as a function of bias voltage (Fig. 5) also shows identical behavior.

MOS capacitors with ZrO_2, deposited by ALCVD, a widely used technique, show an increase in leakage current when post deposition annealing temperature is increased.[12] The leakage current increase is attributed to increase in defect density. In thermal evaporation technique, on the other hand, a decrease in leakage current indicate annealing of defects and improvement in electrical characteristics occur when ZrO_2 films are annealed at 650°C. Possible condensation of the ZrO_2 films may be the reason for the decrease in leakage current due to improvement in film density. ZrO_2 films annealed at 550°C show poor electrical characteristics. It is believed that for thermally evaporated films an appropriate annealing temperature is necessary to obtain high quality ZrO_2 films. Even though detailed study is still underway it seems that excellent quality ZrO_2 films can be grown by standard thermal evaporation method.

Conclusions

In summary, zirconium oxide (ZrO_2) films, grown by standard thermal evaporation of zirconium while adding oxygen at constant partial pressure during evaporation, show encouraging results for 650°C annealed films. The estimated dielectric constant is found to be around 36. CV measurements taken at 100 kHz show the maximum capacitance seems to flatten out for the lower physical thickness, which might indicate presence of an interfacial layer.

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