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High-\(k\) cobalt–titanium oxide dielectrics formed by oxidation of sputtered Co/Ti or Ti/Co films

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High-\(k\) cobalt–titanium oxide (CoTiO\(_3\)) film was formed by directly oxidizing sputtered Co/Ti or Ti/Co films. Al/CoTiO\(_3\)/Si\(_3\)N\(_4\)/Si capacitor structures were fabricated and measured. Excellent electrical properties with an effective dielectric constant (\(k\) value) as high as 40 have been achieved for a CoTiO\(_3\) gate dielectric with a buffer layer. The metal–oxide thus appears to be a very promising high-\(k\) gate dielectric for future ultralarge scale integrated devices. © 2001 American Institute of Physics. [DOI: 10.1063/1.1352044]

As conventional SiO\(_2\) gate dielectric scales down to less than 20 Å, a high leakage current is inevitable due to the occurrence of direct tunneling. To solve this problem, high-\(k\) (>3.9 of oxide) dielectric materials that allow a physically thicker film for the required equivalent oxide thickness (\(E_{\text{OT}}\)) are proposed to replace the conventional SiO\(_2\).\(^1\) Thus, gate dielectric materials having high dielectric constant, low interface state density and good thermal stability appear to be promising for future gate dielectric application. Recently, Si\(_3\)N\(_4\) (\(k\) = 7), Al\(_2\)O\(_3\) (\(k\) = 9), Ta\(_2\)O\(_5\) (\(k\) = 25), and TiO\(_2\) (\(k\) = 40) gate dielectric films have been widely studied.\(^2\)–\(^5\) However, these high-\(k\) films still exhibit undesirable high leakage current. The formation of an interfacial silicon oxide layer during the metal–oxide deposition process is a serious issue in high-\(k\) gate dielectric development. An interfacial SiO\(_2\) layer with a thickness over 20 Å was obtained when Ta\(_2\)O\(_5\) was deposited directly on silicon. This interfacial oxide layer seriously limits the scalability of high-\(k\) dielectrics and causes poor interface quality.\(^6\) Besides, thermal stability of the high-\(k\) dielectric material is another major concern. Severe degradation of the dielectric quality has been shown to occur after Ta\(_2\)O\(_5\) is subjected to processing temperature above 800 °C.\(^7\) In this letter, we report a cobalt–titanium oxide (CoTiO\(_3\)) film as an alternative gate dielectric. This CoTiO\(_3\) film is formed by direct oxidation of Co/Ti or Ti/Co films. From our results, the dielectric constant can reach as high as 40, while depicting excellent electrical properties.

Samples were fabricated on \(p\)-type (100)-oriented Si wafers with resistivity of 14–21 Ω cm. All wafers were first cleaned by a standard Radio Corporation of America clean. To avoid reaction between metal and silicon during the sputtering process and later high-temperature oxidation step, a 10 Å Si\(_3\)N\(_4\) film was first grown by NH\(_3\) nitridation of the Si substrate in low-pressure chemical vapor deposition system at 800 °C for 1 h. Afterwards, samples were immediately deposited in sequence first with a 50 Å Ti and then a 50 Å Co (Co/Ti), or first a 50 Å Co and then 50 Å Ti (Ti/Co) film from independent targets by using a physical vapor deposition method. Direct thermal oxidation was carried out at 700 or 800 °C in diluted O\(_2\) (N\(_2\)/O\(_2\) = 2/1) gas for 5 min and annealed in N\(_2\) ambient for 5 min to form CoTiO\(_3\) films. A 5000 Å Al film was deposited on the wafer by a thermal coater to serve as the gate electrode. The gate of the metal–oxide–semiconductor (MOS) capacitor was defined by lithography, and then the Al was etched by a wet etching solution. Finally, a 5000 Å Al film was also deposited on the back side of the wafers after stripping the oxide on the back side. X-ray diffraction (XRD) was used to identify the composition and the phase of these new metal–oxide films. The gate dielectrics of MOS capacitors with an area of 2.5 \(\times\) 10\(^{-5}\) cm\(^2\) were measured. The \(E_{\text{OT}}\) (17.9–21.2 Å) of CoTiO\(_3\) with a Si\(_3\)N\(_4\) buffered layer structure was obtained by high frequency capacitance–voltage (C–V) of 0.1 MHz at an operating range of −2–2 V in a strong accumulation

![Graph showing XRD spectra of CoTiO\(_3\) films with various stack structures and temperatures.](image-url)
region without considering quantum mechanical effects. The physical thickness (~200 Å) was doubly checked by transmission electron microscopy to obtain the $k$ value. The $k$ value ~36.8–43.6 is calculated by timing 3.9 to the physical thickness and dividing it by the $E_{OT}$. The electrical properties and reliability characteristics of the metal oxide were measured by using an Hewlett-Packard 4156 semiconductor parameter analyzer.

Film crystallization and degradation during a back-end thermal process is a major concern for high-dielectric-constant metal–oxide materials. Figure 1 shows the resultant XRD spectra. From the results, Co/Ti and Ti/Co samples oxidized at either 700 or 800 °C are found to react with oxygen and form CoTiO$_3$ films as shown in Fig. 1. The sample oxidized at 800 °C has a stronger spectrum than that of the sample oxidized at 700 °C, suggesting insufficient time for crystallization, as shown in Fig. 1. Figure 2(a) shows current density–voltage ($J$–$V$) curves for different gate dielectric films. With a thinner $E_{OT}$ of 1.8 nm, the CoTiO$_3$/Si$_3$N$_4$/Si sample shows a lower leakage at low field and a higher breakdown voltage than those of Ta$_2$O$_5$ ($E_{OT}$=2.0 nm, in Ref. 4), TiO$_2$ ($E_{OT}$=2.2 nm, in Ref. 5), or oxynitride ($E_{OT}$=2.5 nm). Figure 2(b) shows $J$–$V$ curves of CoTiO$_3$ capacitors. Co/Ti and Ti/Co capacitors oxidized at 700 and 800 °C were compared. It is found that the Co/Ti capacitor oxidized at 800 °C demonstrates the highest breakdown voltage among all samples. In addition, the metal oxide oxidized at 800 °C exhibits a lower leakage current than that oxidized at 700 °C, implying that samples oxidized at 800 °C may exhibit CoTiO$_3$ crystallization.

The formation of an interfacial silicon oxide layer during sputtering and thermal processing makes it very difficult to
realize a high-\( k \) value. An effective method to solve this problem is to use a high quality silicon nitride buffer layer.\(^8\) Figure 3 shows the high frequency (\( C-V \)) curves for Co/Ti and Ti/Co capacitors oxidized at 700 and 800 °C. It is found that the Co/Ti stack capacitor exhibits a higher capacitance (\( k \) value) than the Ti/Co stack capacitors. Figure 4 shows the result after constant voltage stress at \(-4.5\) V for Co/Ti stack capacitors. No significant stress induced leakage current (SILC) was observed for these four samples even after \( 10^4 \) s stressing.

In summary, we have demonstrated a high-\( k \) CoTiO\(_3\) which is formed by direct oxidation of the sputtered Co/Ti and Ti/Co film. The CoTiO\(_3\)/Si\(_3\)N\(_4\)/Si stack by sputtering Co/Ti film oxidation shows higher \( k \) value and better electrical properties, such as low gate leakage current at low voltage operation, and high reliability after stressing. This high-\( k \) material with CoTiO\(_3\) thus appears to be very promising for future ultralarge scale integrated devices.

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\(^1\)International Technology for Semiconductor Roadmap (Semiconductor Industry Association, San Jose, 1999).