Preparation and Characterizations of High-\(k\) Gate Dielectric CaZrO\(_3\) Thin Films by Sol-gel Technology

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Abstract. Perovskite CaZrO\(_3\) gate dielectric thin films were prepared by the sol-gel wet chemical technology, followed by post annealing in O\(_2\) ambient at different temperatures from 550 to 700 °C. Based on our best knowledge, it is the first time in the literature to successfully prepare the CaZrO\(_3\) thin films using wet chemical deposition methods, including sol-gel and metallo-organic decomposition (MOD) technique. These thin films were systematically characterized using differential thermal analysis (DTA), thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), Auger spectra (AES) and electrical and dielectric measurements. Using these techniques, the different reactions in various processing steps have been clarified. The dielectric constant of crystalline CaZrO\(_3\) films is about 20 determined from the C-f measurement and the thickness. The sol-gel derived CaZrO\(_3\) films exhibit stable dielectric properties nearly independent on the applied electrical field and frequency at room temperature. The leakage current density of the CaZrO\(_3\) thin film annealed at 650 °C for 1 hour is approximately 9.5x10\(^{-8}\) A/cm\(^2\) at high applied electrical field 2.6 MV/cm. The high dielectric constant, low leakage current density and high breakdown strength suggest that the CaZrO\(_3\) thin film is a promising candidate for gate applications.

1. INTRODUCTION

As the dimensions of the microelectronic devices are scaled down, the tunneling current of SiO\(_2\) gate dielectric increases exponentially with decreasing the film thickness. For films below 20Å, the leakage current rises to 1~10 A cm\(^{-2}\) [1], which is becoming an increasingly critical problem. The material properties of alternative higher-\(k\) dielectrics have therefore attracted increasing attention. Metal-oxides with high dielectric constants have the potential to extend scaling of transistor gate capacitance beyond that of SiO\(_2\). Many materials have been investigated to replace silicon dioxide as possible gate dielectrics, such as Ta\(_2\)O\(_5\) [2], Al\(_2\)O\(_3\) [3], ZrO\(_2\) [4] and SrTiO\(_3\) [5], etc.

Materials with the perovskite phase are of fundamental significance for their electrical properties including ferroelectricity, piezoelectricity and superconductivity and they also offer interesting high temperature properties. CaZrO\(_3\)-based oxides belong to the class of high-temperature perovskite-type proton conductors. Their appreciable protonic conductivity makes them promising candidates to serve as a solid electrolyte in some novel electrochemical devices, such as solid oxide fuel cells and gas sensors [6]. But little work has been done on CaZrO\(_3\) perovskite oxides for its possible application as a gate material. The aim of the present study is to prepare and characterize the properties of CaZrO\(_3\) thin films using the sol-gel method.

2. EXPERIMENTAL

Zirconium butoxide solution and calcium acetate were used to synthesis the precursor. Zirconium butoxide was dissolved with glacial acetic acid by stirring and heating at 60 °C. Calcium acetate was mixed with glacial acetic acid diluted with water. Both solutions were mixed and stirred to form 0.2 M CaZrO\(_3\) precursor solution. The precursor solution was first spin-coated onto Pt/Ti/SiO\(_2\)/Si substrates at...
4000 rpm and then baked at 250 and 450 °C for 5 min respectively in air to remove most organics in the film. This process was repeated several times to obtain the desired film thickness. The dried films were post-annealed in the furnace at the temperature ranging from 550 to 700 °C for 1h in O$_2$ atmosphere. Top electrodes of Au with a diameter of 0.3 mm were evaporated for electrical measurement.

The decomposition behavior of the dried precursor was studied using program controlled thermogravimetry (TGA) and differential thermal analysis (DTA) up to a temperature of 1000 °C with a heating rate of 2 °C/min. For the DTA analysis, Al$_2$O$_3$ powder was used as a reference. XRD analysis was used to study the different phases in the calcined powder at temperatures between 150 and 1000 °C. The depth profile of the film was investigated by Auger Spectra (AES). Microstructure and morphology of the films were investigated by X-ray diffraction and scanning electron microscopy (SEM), respectively. Capacitance (C) and leakage current density (J) were measured by a HP 4284A LCR meter and a HP 4155B semiconductor parameter analyzer, respectively.

3. RESULTS AND DISCUSSION

The calcination behavior was studied at temperatures up to 1000 °C using DTA and TGA technique at a heating rate of 2 °C/min to distinguish the low-temperature reaction steps. Fig. 1 shows the typical DTA and TGA curves for the dried 0.2M CaZrO$_3$ precursor.

![FIGURE 1. DTA and TGA curves of CaZrO$_3$ precursor at a heating rate of 2 °C/min in air.](image)

It is seen from this figure that with the endothermic peaks at 56 °C and 180 °C in the DTA curve are due to the evaporation of adsorbed water and solvents. The exothermic peak at 378 °C is ascribed to the decomposition of the acetate complexes to carbonates. This decomposition causes a continuous decrease in sample weight in this temperature region. At 675 °C, an endothermic peak is found and attributed to the decomposition of the carbonates to oxides, accompanied by the loss of CO$_2$. It can be seen that the crystallization temperature for the CaZrO$_3$ perovskite phase is relatively high.

The XRD spectra taken after calcining the precursor at 150 (1h) (drying), 450 (3h), 800 (3h), 1000 (5h), 1000 °C (10h) are presented in Fig. 2. All peaks with # mark observed for the dried precursor can be attributed to calcium acetate (Ca$_4$H$_6$CaO$_4$). If the precursor is calcined at 450 °C, the calcium acetate complex decomposes to CaCO$_3$, confirming the experimental results from the TG-DTA measurements. In the precursor calcined at 800 °C, two different phases are identified, a CaZrO$_3$ perovskite phase and a CaZr$_4$O$_9$ cubic phase. If the precipitated precursor is calcined at 1000 °C, then the solid-state reactions will progress even further towards formation of the desired CaZrO$_3$ phase, as shown in Fig. 2 of the XRD pattern obtained after calcining the precursor for 5h at 1000 °C. It can be easily seen that the XRD peaks of the CaZrO$_3$ perovskite phase have increased in intensity. The intensity of the CaZr$_4$O$_9$ phase has decreased dramatically, indicating a substantial decrease in the amount of this phase. If the precursor is calcined at 1000 °C for 10h, the conversion to CaZrO$_3$ phase progresses further and the CaZr$_4$O$_9$ phase nearly can not be detected.

![FIGURE 2. XRD patterns of the precursor calcined at different temperatures between 150 and 1000 °C. The labeled peaks are CaZrO$_3$.](image)
550 °C, which is much lower than the crystallization temperature, indicates that the film has its amorphous structure. It seems that the CaZrO₃ film begins to crystallize at 600°C. With further increasing the annealing temperatures, the intensity of perovskite CaZrO₃ phase is increased, indicating that the crystallization progresses in CaZrO₃ thin films further. There is no tendency of preferential orientation in the sol-gel–derived CaZrO₃ films fabricated on Pt/Ti/SiO₂/Si substrates.

The microstructure such as grain size is an important parameter determining the dielectric and electrical properties of thin films. Fig. 5 shows the SEM micrographs of the CaZrO₃ films annealed at different temperatures (550, 600, 650 and 700 °C) for 1 hour in O₂ atmosphere. From Fig. 5, it is seen that the grain size is increased with increasing the annealing temperature. Films annealed at 650 and 700 °C average consist of tiny crystal grains and they are dense and smooth, in consistent with the XRD results. Furthermore, the morphology is changed little with the increase of temperatures.

The AES depth profile of a flat thin film annealed at 550 °C is shown in Fig. 4. The buffer layer Ti may be assumed to infiltrate into the bottom electrode. It may have an effect on the leakage current.
Fig. 6 shows a typical cross-section image of thin film annealed at 600 °C. The thickness of the film is about 140 nm.

The characteristics of leakage current density versus applied field for capacitors of Au/Ti/CaZrO\textsubscript{3}/Pt are shown in Fig. 7. The leakage current density at room temperature fits a linear dependence of log J with E\textsuperscript{1/2}. It indicates that the Schottky emission is the dominant conduction process in the sol-gel derived CaZrO\textsubscript{3} thin films. The leakage current density of the CaZrO\textsubscript{3} thin film annealed at 650 °C for 1 hour is approximately 9.5×10\textsuperscript{-8} A/cm\textsuperscript{2} at high applied electrical field 2.6 MV/cm. For the film post-annealed at 700 °C, the poor leakage property is attributed to some defects resulted from the polycrystalline grain growth and thus open grain boundaries in thin films which are annealed at relatively high temperature [7].

The dielectric characteristics of CaZrO\textsubscript{3} thin films annealed at different temperatures of 550, 600, 650 and 700 °C in O\textsubscript{2} atmosphere as a function of frequency measured at room temperature are shown in Fig. 8. During the measurement the applied voltage was zero and the oscillation level was 50 mV. It can be easily seen from the Fig. 8 that the dielectric constant of these films is nearly independent of frequency. The dielectric loss is very low for the samples annealed in O\textsubscript{2}.

Perovskite CaZrO\textsubscript{3} dielectric thin films have prepared by the sol-gel wet chemical technology, followed by post-annealing in O\textsubscript{2} at different temperatures from 550 to 700 °C. It is found that CaZrO\textsubscript{3} film is in amorphous phase when annealed at temperature of 550 °C and crystallized into perovskite structure when annealed at temperature
above 600 °C on Pt/Ti/SiO₂/Si substrate, and the crystallinity is also supported by SEM surface morphology observation and dielectric measurements. The sol-gel derived CaZrO₃ films exhibit stable dielectric properties nearly independent from the applied electrical field and frequency at room temperature. The leakage current density of the CaZrO₃ thin film annealed at 650 °C for 1 hour is approximately 9.5×10⁻⁸ A/cm² at high applied electrical field 2.6 MV/cm. The high dielectric constant, low leakage current density and high breakdown strength suggest that the CaZrO₃ thin film is a promising candidate for gate applications.

REFERENCES