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Facile preparation of sol–gel-derived ultrathin and high-dielectric zirconia films for capacitor devices

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ABSTRACT

This study successfully prepared zirconia ultrathin films from the sol–gel solution with dispersion of zirconium halide in 1-octanol solvent. The film was subjected to annealing treatments after sol–gel spin-coating, and the films of interest were evaluated. The amorphous morphology of the zirconia film was identified using high-resolution transmission electron microscopy and X-ray diffractometry. The plot of the current density with respect to the electric field demonstrates that the as-deposited film at 500 °C annealing exhibited an inferior leakage current, whereas 600 °C annealing stabilized the film with a satisfactory leakage current of 10^{-8} to 10^{-9} A/cm^2. The out-gassing behavior of the sol–gel-derived thin film was evaluated using a thermal desorption system, that is, atmospheric pressure ionization mass spectrometry. The dielectric constant of the film was dependent on the retention effect of the preparation solvents. The low residual solvent for the preparation of the thin film with 1-octanol solvent and 600 °C annealing contributed to the superior high-k property.

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1. Introduction

Silicon-based technology has been used in microelectronics and electronics systems for more than 30 years. Several researchers focus on scaling down electronic devices to operate at higher speeds with multiple functions. Conventional SiO_2 gate dielectrics have reached their physical thickness limit (1.5 nm) and cannot be used as CMOS devices because of their high direct tunneling current and poor reliability. Advanced materials are crucial for smaller systems with scaled-down thicknesses. To address the issue of leakage current, various high dielectric materials such as zirconium oxide, hafnium oxide or tantalum oxide are the most promising candidates for use as an alternating thin material to replace SiO_2 film [1–8]. These electronic materials exhibit high temperature stability and excellent insulator properties against heat and electricity. In fact, dielectric films having higher permittivity allow the use of thicker films of equivalent electrical thickness as silicon dioxide; this situation will reduce the leakage current and improve the fabrication reliability of the dielectric films. Recently, numerous technologies have been developed for the preparation of various high-k films [9–12]. Atomic layer deposition (ALD), physical vapor deposition (PVD), and chemical vapor deposition (CVD) are the most useful technologies among the various methods to prepare metal oxide films. It is crucial to determine the manner in which to deposit and prepare the zirconia material for high dielectric thin films. In the ALD process, the precursor of $ZrCl_4$ and H_2O are used to prepare the zirconia films. For the PVD process, a zirconium metal target is used for sputtering under ambient oxygen to deposit the zirconia films. In the CVD method, a $ZrCl_4$ precursor is used to deposit zirconia films. However, these methods require ultrahigh vacuum conditions and expensive tools.

The sol–gel spin-coating method is an efficient approach to produce crack-free and smooth ceramic films with excellent surface conformity and uniformity over large areas [13–15]. In addition, such films can be fabricated at room temperature and normal pressure, thereby obviating the requirements for high-vacuum systems [16–18]. The sol–gel method can provide colloidal solvents or precursor compounds when metal halides are hydrolyzed under controlled conditions [18]. In the sol–gel process, hydrolysis, condensation, and polymerization steps occur to form metal oxide networks. These reactions play decisive roles in determination of the final material's properties. The most interesting feature of sol–gel processing is its ability to synthesize new types of materials known as "inorganic–organic hybrids." Films formation with the sol–gel spin-coating method is simpler method than using ALD, PVD or CVD because of its cost-effective precursor and tools. In addition, the film can be fabricated in the normal pressure system instead of high vacuum system. Typically, zirconia is an

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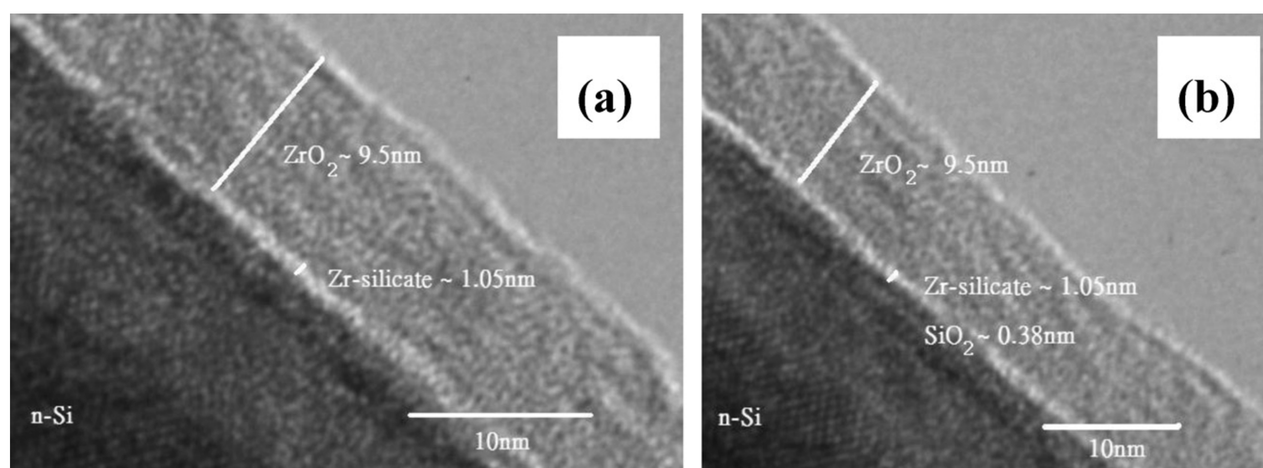

Fig. 1. Cross-sectional TEM images of sol–gel-derived ZrO_2/Si structures annealed at (a) 200 °C and (b) 600 °C under an oxygen atmosphere.

excellent heat-resistant and chemically durable material that is used, for example, as a material for furnaces [19]. Although zirconia-based materials generally provide good high-dielectric and thermal property, the electrical insulation issues such as leakage current and dielectric constant for sol–gel-derived ZrO_2 ultrathin film still require further improvement. In addition, the technique for achieving reliable property of ultrathin film under cost-effective manufacturing is also required to develop.

This study proposed the use of material from the dispersion of zirconium halide in organic solvent to fabricate the ultrathin film by sol–gel spin-coating. The thickness and structure of the film were identified by high-resolution transmission electron microscopy (HRTEM) and X-ray diffractometry (XRD). To determine the residual organic contamination in the fabricated zirconia ultrathin film, the out-gassing residual from the prepared thin film at a high temperature was evaluated by a thermal desorption system, that is, atmospheric pressure ionization mass spectrometry (TDS-APIMS). The electrical property of the thin film from simple and reliable sol–gel processing was evaluated for the capacitance–voltage and current density–electric field characteristics.

2. Experimental

2.1. Thin film material and fabrication

Zirconia thin films were prepared by using a spin-coating sol–gel method. $ZrCl_4$ (>99.5%, Aldrich, USA) was used as the precursor for the synthesis of zirconia. The thin films were prepared through polymerization in an organic solution. A mother sol solution was first prepared by dissolving $ZrCl_4$ in 1-octanol (Fluka, >99.5%) under vigorous stirring in an ice bath. The sol solution was obtained by fully hydrolyzing $ZrCl_4$ with a stoichiometric quantity of water in 1-octanol to yield a Zr:octanol molar ratio of 1:1000. The metal halide solution was subsequently subjected to ultrasonication at 0 °C for 20 min to accelerate the gelling rate.

The n-type wafers (10–15 Ω cm), which were served as substrates for the metal insulator semiconductor (MIS) structure, were RCA cleaned to remove the native silicon oxide film and particle. Zirconia films were deposited by spin-coating at 3000 rpm for 60 s at ambient temperature (25 °C) to obtain a thickness of ca. 9.5 nm on the n-Si (1 0 0) substrate. The films were initially annealed at 200 °C for 10 min. One of the samples was maintained at 200 °C for 1 min densification; the other samples were rapid thermal annealed (RTA) at different temperatures (500 or 600 °C) for 1 min under an oxygen atmosphere. Zirconia/n-Si structures were used in our experiments for the further characterization.

The Al top electrodes with a surface area of 3.14×10^{-4} cm^2 were deposited onto the top surface of the zirconia using a shadow mask and pure Al target evaporation. The thickness of the top electrode was 400 nm. A buffered oxide etch (BOE) solution was performed to remove the silicon back oxide and then the sample was thoroughly rinsed with deionized water. Finally, bottom electrodes were attached on the reverse side of the n-Si (1 0 0) substrates by vaporizing a pure Al target. The thickness of the bottom electrode was 100 nm. The dielectric properties were subsequently determined for the MIS capacitors with an Al/ZrO_2/n-Si/Al structure. The deposition technique allows the production of ultrathin gate dielectric films under excellent thickness control.

2.2. Characterizations

The morphology of the zirconia ultrathin film was observed by a field-emission TEM tool (JEOL JEM-2100F). The structure of the obtained ultrathin film was characterized with an XRD instrument. The organic contamination of the sol–gel-derived thin film was analyzed by the TDS-APIMS tool from Hitachi company. The thermal desorption species were purged by nitrogen gas, and various species of interest were continually monitored using mass spectrometry. The high dielectric films were prepared in the MIS structure to characterize the leakage currents and capacitances. The capacitance–voltage was measured using an Agilent 4284A *C–V* analyzer; the current density with respect to electric field plot was measured using an Agilent 4156C analyzer.

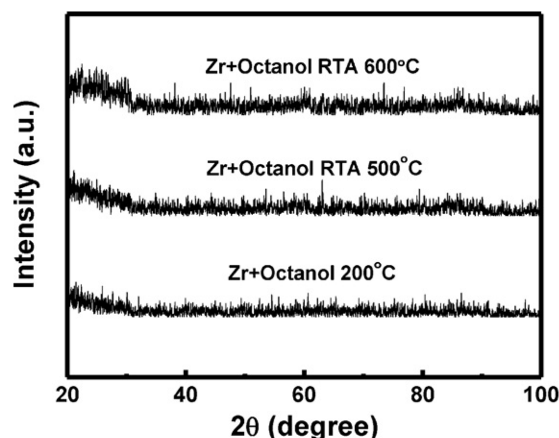

Fig. 2. XRD spectroscopy for ZrO_2 films of different annealing temperatures.

3. Results and discussion

3.1. Morphology of sol–gel-derived ultrathin films

The morphology of the sol–gel-derived zirconium dioxide films annealed at 200 and 600 °C is illustrated in Fig. 1. The TEM images indicate that the sol–gel deposited film consists of a ∼1.05-nm interfacial layer (Zr-silicate) and a ∼9.5-nm ultrathin ZrO_2 film. Smooth and conformal interfaces were observed in the sample. This observation of XRD pattern in Fig. 1a cannot form the SiO_2 layer. The interfacial layer formation of ultrathin SiO_2 in Fig. 1b was attributed to the excess oxygen in the RTA chamber under 600 °C annealing, not a chemical reaction of Zr-silicate and underlying silicon substrate [5]. The Zr-silicate layer in the interface was also observed, and the film had a higher dielectric constant than interfacial SiO_2 film. Both interface layers are important to reduce the interface traps and enhance the device reliability. Ensuring a smooth and crack-free interface for the MIS device is critical to achieve the high dielectric property. Our ultrathin film in Fig. 1 suggests the proposed sol–gel method is an efficient means for high dielectric device application.

The crystallinity of the ZrO_2 film-based samples was investigated using 1.5° glancing-angle XRD. The crystallinity of the high-k dielectric film was of concern because of the possible deterioration effects caused by the leakage paths and dopant/impurity diffusion along the grain boundaries, as well as for the control of device uniformity. Hence, an amorphous structure of high dielectric film was necessary. Liu et al. [3] used the sol–gel method to fabricate the 450-nm thickness of ZrO_2 film, and the crystalline structures were observed for annealing at 450–950 °C. This film is impractical for the electric device application on high-dielectric film. Fig. 2 suggests that our proposed 9.5-nm ultrathin film exhibits amorphous structure under 200–600 °C RTA. Broad features are present for the as-deposited film and they do not change significantly upon annealing up to 600 °C. This observation of XRD pattern is in the same with the TEM image in Fig. 1. All above results clearly identify the amorphous phase of the ZrO_2 films and suggest that they have high thermal stability to avoid phase transition and current leakage issue.

3.2. Contamination issue of sol–gel-derived ultrathin film

The most challenge issue for the sol–gel-derived film is the residual organic contamination. Because the precursor of the film is dispersed in the organic solvent, the residual solvent after annealing may degrade the electrical properties for high dielectric film. However, few studies have addressed this issue. We used TDS-APIMS characterization to measure residual organic compounds present in the films after annealing of 500 and 600 °C. We ramped the desorption temperature of the TDS-APIMS system from room temperature to 800 °C at 20 °C/min under an N_2 atmosphere. In Fig. 3, we simultaneously analyze the surface out-gasses at mass-to-charge ratio (m/z) of 16, 44, and 82. The sol–gel film contained Zr, Cl, C, H, and O elements, which were derived from the preparation solvents and the precursor. The out-gassing species with molecular weights of 16 and 44 may represent carbon elements in the

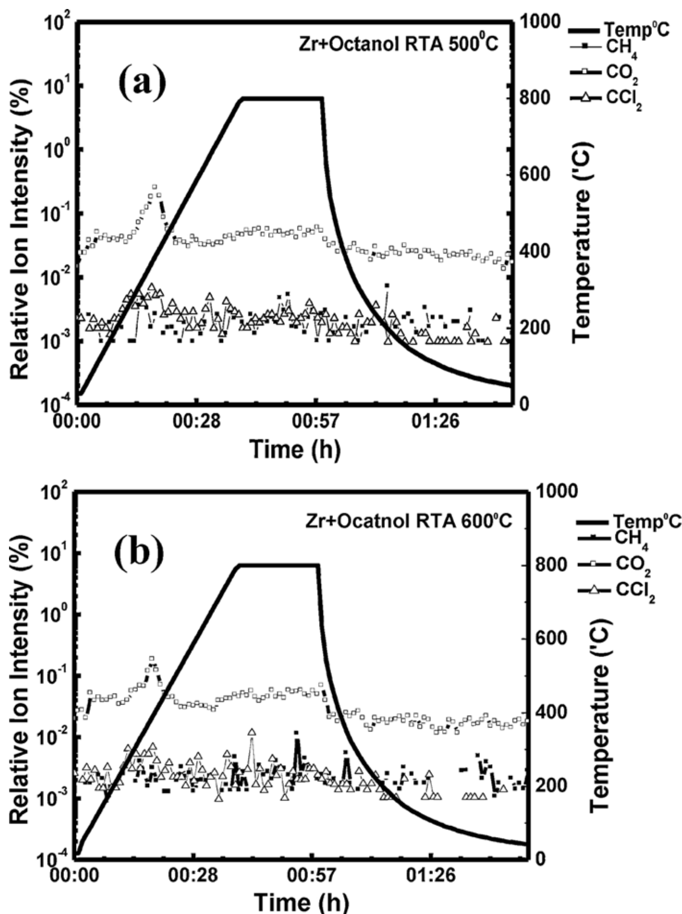

Fig. 3. TDS-APIMS analyses of the sol–gel-derived ZrO_2 films prepared from (a) 1-octanol solvent and RTA 500 °C, (c) 1-octanol solvent and RTA 600 °C.

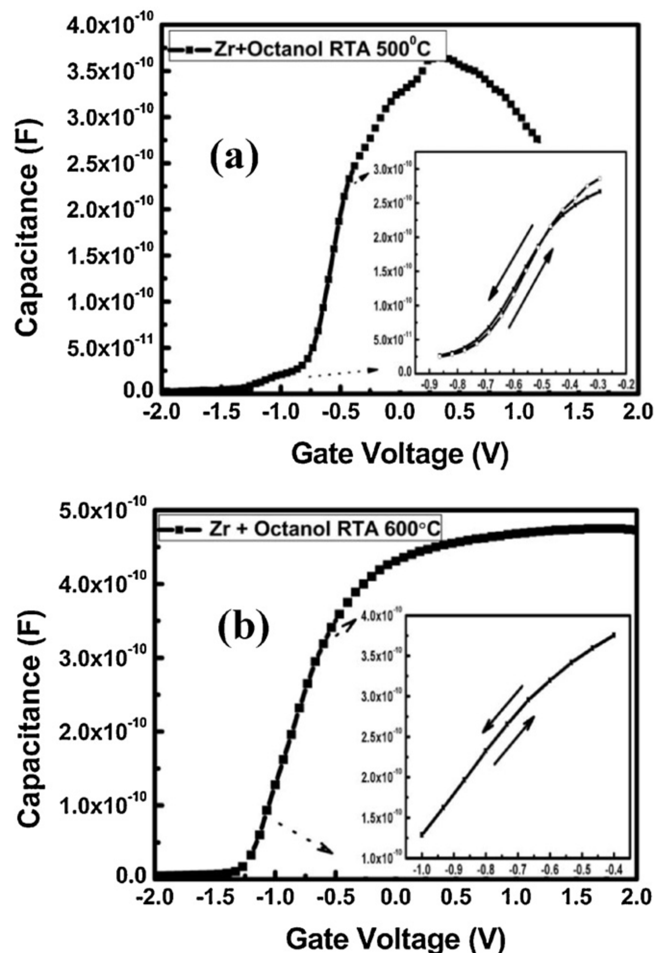

Fig. 4. High-frequency (at 1 MHz) $C–V$ characteristics of the sol–gel-derived ZrO_2 dielectric film upon RTA at (a) 500 °C and (b) 600 °C under an O_2 atmosphere.

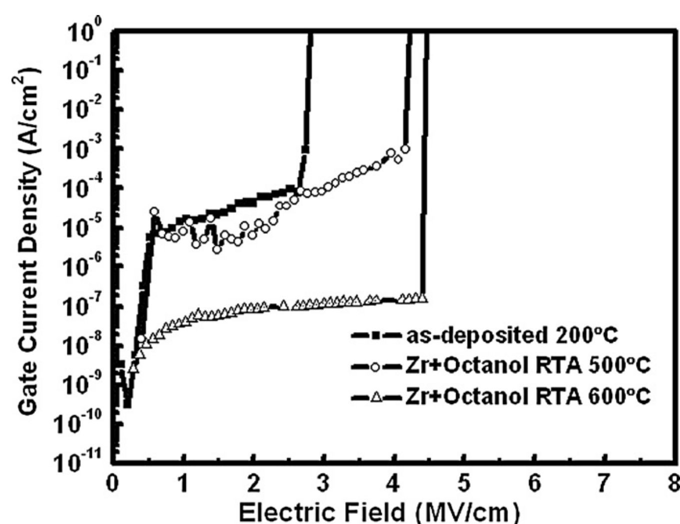

Fig. 5. Gate current density vs electric field (*J*–*E*) characteristics of the ultrathin film after various RTA treatments.

forms of CH_4 and CO_2, respectively. In contrast, the chlorine components (in precursor) of the film combined with carbon atoms (in solvent) to form CCl_2 ($m/z = 82$). In comparison with our previous study [1], we find that the desorption gases or species from the sol–gel film prepared by 1-octanol solvent were considerably lower than the preparation solvent of 2-propanol/hexanol. This observation suggests the 1-octanol solvent was more easily removed from the high-k film by using the annealing method than the 2-propanol/hexanol solvent because of the intermolecular hydrogen bonding in the high-k film. The proportion of the hydroxyl group in the 1-octanol molecule was lower than that in the 2-propanol or hexanol molecule, which indicated that the 1-octanol molecule had a low hydrogen bonding interaction with the ZrO_2 molecule. Therefore, the film prepared from the 1-ocatanol solvent had a lower desorption peak than that from the 2-propanol/hexanol solvent. The solvent type plays a critical role in the dielectric property of the sol–gel-derived thin film. This residual species in the high dielectric film may affect the dielectric constant and leakage current mentioned later.

3.3. Electrical property of sol–gel-derived ultrathin film

We measured the quantitative capacitance and leakage current to evaluate the dielectric performance of the high-k ZrO_2 ultrathin film in the MIS configuration. Fig. 4 illustrates the high-frequency (1 MHz) capacitance versus gate voltage characteristics (*C*–*V* curves) for the MIS capacitors prepared from 1-octanol solvent under the various annealing conditions. The hysteresis from the *C*–*V* characteristics was used to evaluate the reliability of the film. By sweeping the voltage from accumulation to inversion and sweeping back (from +2.0 to −2.0 to +2.0 V), all of the films exhibited a shift of less than 30 mV for the hysteresis phenomenon. The *C*–*V* curve for the sample annealed at 500 °C was inferior; several steps occurred in the curve, which indicates that the films were unstable after annealing at 500 °C. Hence, the sample annealed at 500 °C did not exhibit an excellent electrical property because of the excessive residual organics in the film. When the annealing temperature was increased to 600 °C, the ZrO_2 films exhibited excellent and reversible electrical properties.

Table 1
Dielectric constant (k) and equivalent oxide thickness (EOT) of ZrO_2 thin films prepared using two different solvents and annealed at 600 °C.

Solvent type	Anneal (°C)	k	EOT (nm)	Reference
1-octanol	500	12.8	2.89	This work
1-octanol	600	16.4	2.26	This work
2-propanol/hexanol	600	13.9	3.04	[1]
2-propanol/hexanol	900	12.8	3.91	[1]

Table 1 shows a comparison of the devices with various solvents and annealed at different temperatures. The value of equivalent oxide thickness (EOT) is 3.04 nm and the dielectric constant is 13.9 for the preparation from 2-propanol/hexanol solvent and annealed at 600 °C under an O_2 atmosphere [1], while 2.26 nm EOT and 16.4 (dielectric constant) from 1-octanol at 600 °C under an O_2 atmosphere. If annealed temperature is at 500 °C, both the dielectric constant and EOT are degraded due to carbon-contamination issue. This observation suggests the dispersion solvent for sol–gel-derived devices is favor for low portion of hydroxyl group solvent. Hence, the research proposes that 1-octanol solvent is suitable for the ZrO_2 sol–gel preparation to fabricate the high-k ultrathin film.

The electric field (E) in the *J*–*E* curve of Fig. 5 was obtained using the equation $E = V/t_{ox}$, where V is the applied voltage and t_{ox} is the EOT determined through *C*–*V* measurement. The samples annealed at 200 and 500 °C contained a couple of organics in the ZrO_2 film. Hence, their breakdown electric fields were relatively low at 2.6 and 4.2 MV/cm. The unsatisfactory breakdown field was related to the effect of residual organic contamination as mentioned early. The breakdown electric field increased to 4.5 MV/cm when the annealing temperature was increased to 600 °C. Similarly, the 600 °C RTA demonstrated the leakage current of 10^{-8} to 10^{-9} A/cm^2. A high and suitable annealing temperature led to the removal of the unstable carbon-containing compounds from ZrO_2 film and stabilized the thin film. Table 2 compares various methods [1,2,4–7] for the fabrication of thin ceramic film. On the issue of dielectric constant and leakage current, our device has better performance than methods of photo-assisted sol–gel spin-coating, oxygen plasma-enhanced sol–gel spin-coating and chemical vapor deposition [2,4,6,7]. In comparison with expensive physical vapor deposition [5], the electrical property on leakage current from our simple and cheaper sol–gel-derived method

Table 2
Comparison of electrical properties of various high-k dielectric materials.

Preparation method/solution	Film/substrate material	Annealing temperature (°C)	Dielectric constant	Lowest leakage current density (A/cm^2)	Reference
SGSC/octanol	9.5-nm ZrO_2/Si	RTA/600	16.4	1×10^{-9}	This work
SGSC/*1	9.3-nm ZrO_2/Si	RTA/600	13.9	1×10^{-9}	[1]
LA-SGSC/ethanol	50-nm ZrO_2/Si	CA/400	–	8×10^{-8}	[2]
PE-SGSC/ethanol	9.5-nm ZrO_2/PI	CA/250	14.8	9×10^{-9}	[4]
PVD/in vacuum	5.0-nm ZrO_2/Si	CA/550	18.4	$2\times10^{-1\circ}$	[5]
PE-SGSC/ethanol	10-nm HfO_2/PI	CA/250	11.7	4×10^{-9}	[6]
CVD/in vacuum	7.0-nm Ta_2O_5/Si	RTA/800	7.91	4×10^{-8}	[7]

*1: mixing solvent of 2-propanol and hexanol. PI: polyimide substrate, SGSC: sol–gel spin-coating, LA-SGSC: photo-assisted sol–gel spin-coating, PE-SGSC: oxygen plasma-enhanced sol–gel spin-coating, RTA: rapid thermal annealing (~1 min), CA: conventional oven or furnace annealing, PVD: physical vapor deposition, CVD: chemical vapor deposition.

is also comparable. In addition, the electrical quality of zirconia ultrathin film is excellent than the hafnium oxide and tantalum oxide films [6,7]. This observation suggests that the match solvent in the sol–gel solution is an important issue to prepare an ultrathin and reliable film for future electronic materials on gate dielectric devices.

4. Conclusions

This study successfully fabricated a 9.5 nm ZrO_2 ultrathin film using a simple sol–gel spin-coating technique. Prior to rapid thermal annealing, the precursor of $ZrCl_4$ powder was dissolved in 1-octanol solvent. This film demonstrated excellent electrical performance because of the suitable precursor solvent and annealing condition. The ZrO_2 ultrathin film after 200–600 °C annealing remained in an amorphous phase. The out gassing study of these ultrathin films indicated the 600 °C annealing was the most suitable condition to minimize the residual organics in the ZrO_2 ultrathin films. The MIS capacitor with the proposed procedures had lower fabrication cost, superior dielectric constant, higher breakdown field, and lower leakage current than those using other techniques.

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