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Synthesis and Electrical Characterization of ZrO_2 Thin Films on Si(100)

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ABSTRACT

The ZrO_2 thin films deposited on Si(100) were successfully synthesized by sol-gel process and deposited by using spin-coating technique. The structural properties of ZrO_2 thin films were investigated by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), and electrical properties were studied by conventional techniques like Capacitance-Voltage (C-V) measurement and Current-Voltage (I-V) measurement. The XRD of ZrO_2 films shows the films crystallized and exists in two phases at 700˚C calcinations temperature. The C-V characteristics of all the dielectric films that involved distinct inversion, depletion, and accumulation were clearly revealed in MIS structure. I-V characteristics of ZrO_2 thin films on Si shows decreased saturation current on calcinations temperatures. The XPS measurement reveals that a zirconium silicate interfacial layer has formed in the ZrO_2/Si Systems.

Keywords: Sol-Gel Technique; ZrO_2 Thin Film; C-V; I-V

1. Introduction

With the metal-oxide-semiconductor (MOS) device scaling high dielectric constant (high-k) oxides are currently widely investigated as potential candidates for replacement of conventional SiO_2 gate oxide, zirconia based dielectrics is one of the most promising oxides because of their good thermal stability [1] and large band-offset in direct contact with the silicon substrate [2], high dielectric constant ($\varepsilon \approx 25$), and large band gap ($E_g \approx 5.8$ eV) [3-5]. In addition to the above advantages, ZrO_2 films are thermally stable with gate electrode materials during the deposition.

The oxide thin films are attracting an increasing interest because of their potential use as the material with high dielectric characteristics for manufacturing of the film capacitors and as a buffer layer with high chemical stability at creation of multi-layers systems [6]. Recently, oxide materials with high dielectric parameters have been suggested as an alternative to the currently used SiO_2 gate dielectric for complementary application of metal oxide for using in semiconductor technology. Several oxide materials with high dielectric constant have been investigated as an alternative gate dielectric. However, their application is limited due to the interfacial reaction between dielectric materials and tradition microelectronic substrates, such as Si substrates, during the post annealing processes are known various technologies, which can be used for fabrication of ZrO_2 films. But all suggested technologies include the stage of post-deposition annealing. Usually, optimum properties of ZrO_2 films have been achieved when they are deposited on a hot substrate and are annealed after deposition. Therefore, it is necessary to develop technology for deposition of ZrO_2 films at low temperature without considerable losses of their properties.

Various methods have been employed to prepare ZrO_2 films, such as reactive sputtering [7], metal-organic chemical vapor deposition [8], atomic layer chemical vapor deposition [9], and pulsed-laser ablation deposition [10]. Among these methods spin coating technique is the more perspective and supple method for preparation of ZrO_2 thin films, due to a high growth rate, simple means to drive of deposition processes. Hence, experimental definition of optimum parameters of spin coating technique for preparation of ZrO_2 films with good characteristics on Si substrate with and without annealing is very important for practical applications.

Sol-gel spin-coating techniques have proved a popular means of fabrication ceramic and dielectric films in the submicrometer thickness range [11,12]. The basis of the technique is to coat a substrate with a polymeric precursor solution containing the requisite metal components in the required proportion, which then, because of solvent evaporation and chemical reactions, transforms to a gel layer.

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The organic components of the gel are then eliminated by various heat treatments to form the desired crystalline film. The main advantage of the sol-gel process is the ability to form inorganic structures at relatively low temperature. Moreover, the process is a cost-effective way to produce thin homogeneous inorganic films on large scales.

The microstructure and electrical properties of ZrO_2 films on Si substrate prepared by spin coating technique were investigated. The microstructure of the films was characterized by X-Ray Diffraction (XRD) (Philips PW-1710). Scanning Electron Microscopy (SEM) (VPFE-SEM, SU-PRA 35VP) and Fourier Transform Infrared Spectroscopy (FTIR).

The electrical properties of the deposited ZrO_2 thin films were studied using Current-Voltage (I-V) and Capacitance-Voltage (C-V) measurements. The C-V measurements were done at 1 MHz. The procedure of producing a MOS test structure is as follows. A layer of Al was deposited on top of the ZrO_2 film via thermal evaporation process. At the back of the MOS test structure, a layer of Al was deposited on the Si substrate (pressure ~1×10^{-6} Torr). This was ensured that a good back contact was achieved. The area of each MOS capacitor was 0.1×0.1 cm^2. The interface properties of ZrO_2 on Si studied by X-Ray Photoelectron Spectroscopy.

2. Experimental Details

10 g $Zr(OC(CH_3)_3)_4$, zirconium tetra-tert-butoxide was initially dissolved in 100 ml anhydrous ethanol and refluxed for 1 h at 50˚C ~ 70˚C. After that 1ml nitric acid was added to control its PH and subsequently the solution was further stirred for 2 h at the same temperature range. The precursor solution was kept in a pressure bomb at 130˚C up to 6 hours for gelification. This solution was then kept aside for two days so that it could undergo an aging process.

The thin films of ZrO_2 was deposited by Spin-coating technique in air at a speed of 3000 rpm for 30 sec on a cleaned Si wafer with an area of 1 cm × 1 cm. Multiple coatings were performed to increase the film thickness for structural characterizations. After the spin coating process, the samples were independently inserted horizontal tube furnace withtemperatures of 400˚C and 700˚C for 2 hours. In this paper, we investigated the structural and electrical properties of ZrO_2 films on Si substrate prepared by spin coating technique.

3. Results and Discussion

Figure 1 shows the XRD spectra of ZrO_2 thin films deposited on Si and calcined at temperatures of 400˚C and 700˚C. The peak (101) of tetragonal ZrO_2 was observed at 400˚C. At 700˚C calcinations temperature, in addition to tetragonal (101) peak, we could also observed monoclinic (022) peak of ZrO_2. The results indicate that ZrO_2 films crystallized at a temperature higher than 400˚C and two phases existed in the films deposited at 700˚C.

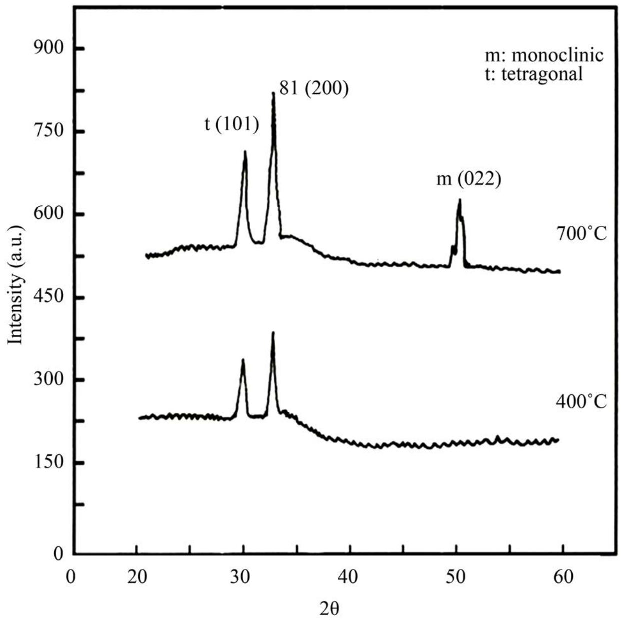


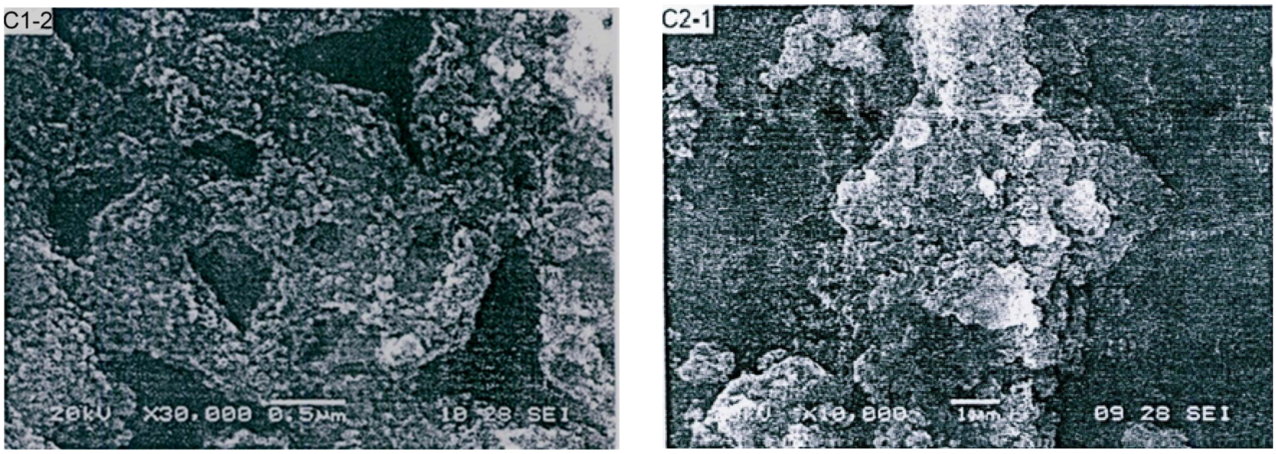
Figure 1. XRD Spectra of ZrO_2 thin film on Si(100) substrates grown at 400˚C and 700˚C.

The surface morphology of deposited ZrO_2 thin film was investigated using scanning electron microscopy, a field emission scanning electron microscope. The similar results were also observed by Zhu *et al*. [13]. **Figure 2** shows the SEM of ZrO_2 thin film calcined at 400˚C and 700˚C. The thin films of ZrO_2 shows a uniform, good coverage, and crack free surface. It has been observed that the average grain size increases with an increase in temperature from 400˚C to 700˚C, due to the thermal expansion of zirconia.

Figure 3 shows the FT-IR spectra of ZrO_2 thin films deposited by spin coating technique. The bands at 519 cm^{-1} and 792 cm^{-1} correspond to various vibrations of the Zr-O bond. Dhar [14] investigated ZrO_2 thin films deposited by MOCVD technique using beta ketoesterate complex and obtained similar type of microstructure.

It is to be noted that the FTIR spectra contain no features attribute to carbonate or hydroxide formation, even though the films were stored in the laboratory ambient.

Figure 4 shows the C-V characteristics of as deposited and calcined at 400˚C and 700˚C of ZrO_2 thin films on Si. As deposited and calcined at 400˚C, the C-V curve shows virtually flat which is an evidence of little modulation of the surface potential by the applied voltage. However when the film is subjected at 700˚C calcinations temperature the C-V plot shows a dramatic change in the 1MHz freq. C-V behavior and considerable reduction in the frequency dispersion suggest a much closer approach to surface accumulation *i.e.* usually observed in the metal insulator semiconductor structure. Hence, the electrical properties of



(a) (b)

Figure 2. SEM micrograph of ZrO_2 thin film annealed at (a) 400˚C and (b) 700˚C.

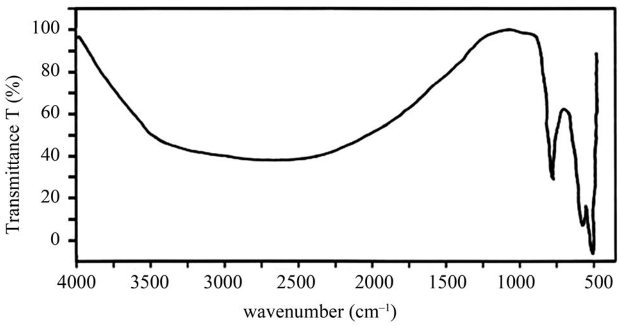


Figure 3. FTIR Spectra of ZrO_2 thin film as deposited.

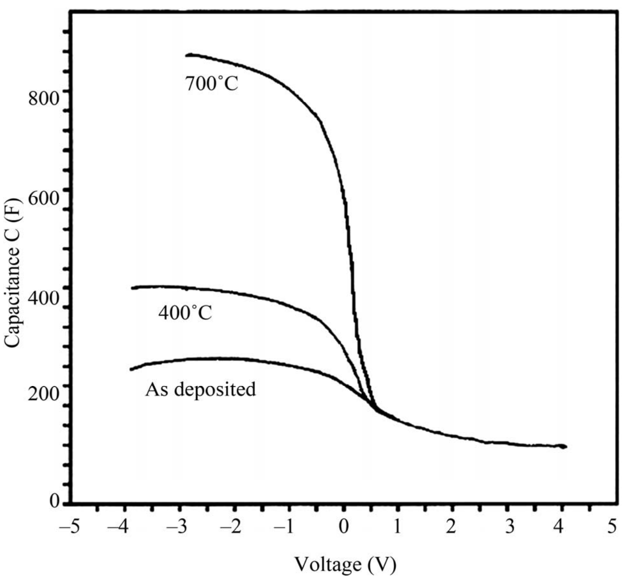


Figure 4. The C-V characteristics of ZrO_2 thin film on Si at as deposited, 400˚C and 700˚C.

ZrO_2/Si(100), MIS structure improved with annealing temperature at 700˚C. The measured capacitance density in accumulation was observed 1.95, 1.55 and 0.96 μf cm^{-2}, which correspond to equivalent oxide thickness t = 4.55, 6.85 and 7.3 nm respectively. The dielectric constant of ZrO_2 films is thickness dependent the dielectric constants are $\varepsilon \approx$ 19.8, 20.9 and 22.7 for 9.0, 12.0 and 21.0 nm ZrO_2 samples respectively. J. Zhu *et al*. [15] show similar behavior of ZrO_2 thin films deposited by pulsed laser deposition technique. The flat band voltage of ZrO_2 films from the C-V curves is in the range 0.86 - 0.88 V. The dielectric constant of the ZrO_2 film was calculated from the maximum capacitance (accumulation region) of the C-V curves, according to the relationship

$$C = \frac{\varepsilon \, \varepsilon_0 A}{d}$$

where ε is the relative dielectric constant, ε_0 is the dielectric constant, d is the oxide film thickness and A is the area of the capacitor system surface.

Figure 5 shows the I-V characteristics of ZrO_2 thin films on Si calcined at 400˚C and 700˚C. The saturation current decreased up on annealing. It was noticed that calcination temperatures affect the quality of the films. The improvement in leakage current by films calcined at 700˚C may be attributed to the removal of the interface traps and oxide changes at the ZrO_2 interface by Zr passivation. The ZrO_2 film exhibited a leakage current density of 10^{-5} A/cm^2 which was further improved to 10^{-6} A/cm^2 after annealing. S. J. Wang *et al*. [16] have grown ZrO_2 thin films on Si and obtained similar result. These low leakage currents due to several factors. ZrO_2 possesses a wide gap (5 - 7.8 eV), a high conduction band offset (1.4 ev) and valance band (3.3 eV) which means much high barrier heights for both electrons and holes carriers.

The ideality factor (n-value) was around 1.15 in the as deposited state shown in **Figure 6** which was not good. A poor ideality factor is due to low carrier density in the substrates. The thin insulating layer at the interface might be a candidate for poor ideality factor in the as deposited state. ZrO_2 thin films on Si at 400˚C and 700˚C did not change

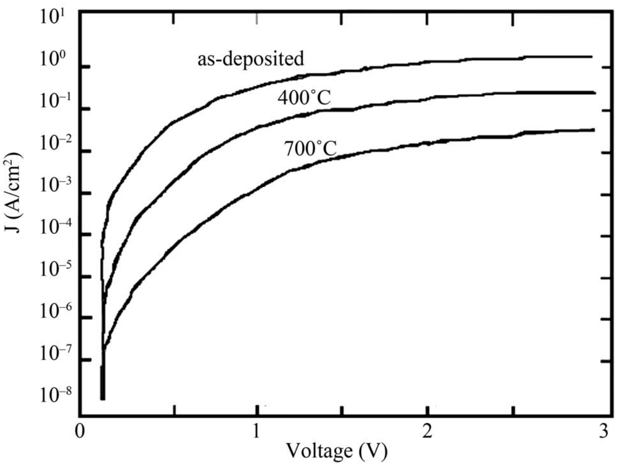


Figure 5. The I-V characteristics of ZrO_2 thin film as deposited and annealed at 400˚C and 700˚C.

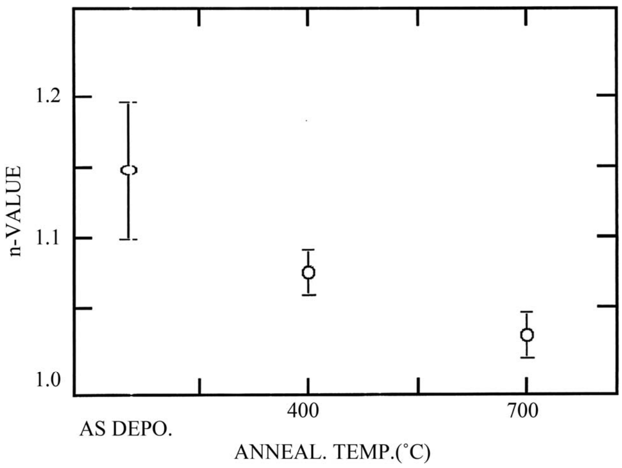
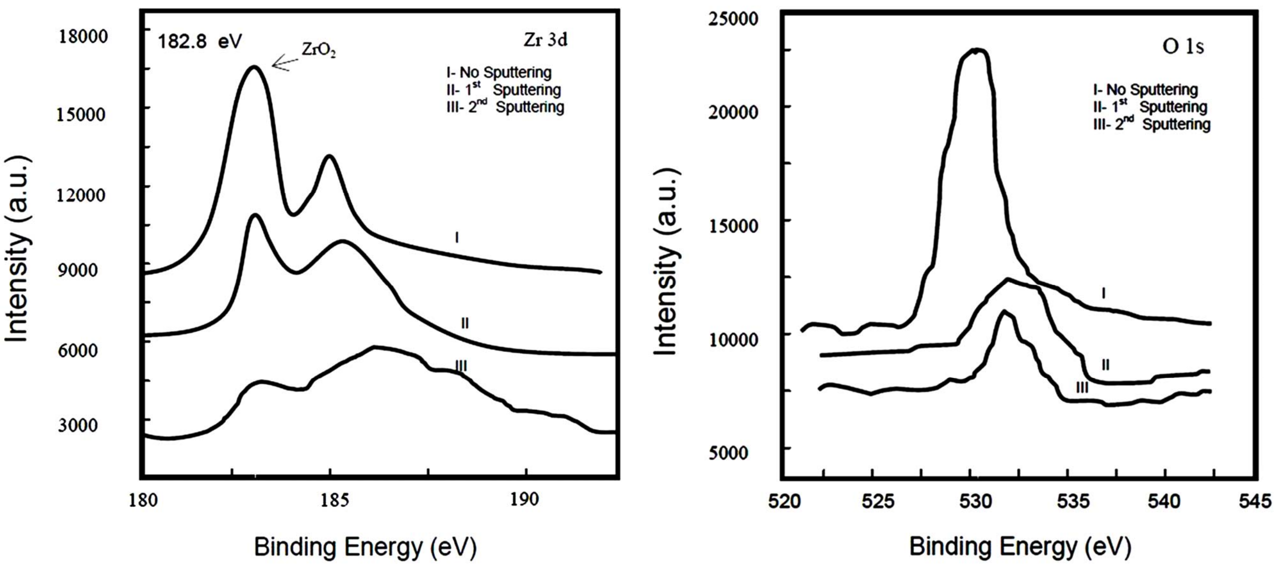


Figure 6. Change of the n-value (ideality factor) at different calcinations temperature.



(a) (b)

Figure 7. XPS Spectra of ZrO_2 film deposited on Si with sputtering (a) O 1s (b) Zr 3d.

the barrier height very much, but improved the ideality factor slightly.

The XPS sputtering depth profile was carried out to investigate the features of the substrate interface and interfacial layer that were crucial to good performances of MOS structures. The ZrO_2 film deposited on Si at 400˚C was sputtered. The results are shown in **Figure 7(a)** Top scanning revealed ZrO_2 bonding of both O 1s binding energy 530.2 eV and Zr 3d binding energy 182.8 eV. Obvious shifts to higher binding energy of O 1s and binding energy of Zr 3d energy were observed after the second sputtering. The Zr 3d peak was shifted to higher binding energy for ZrO_2. This also confirmed the formation of a zirconium silicate interfacial layer.

It is suggested that the greater donation of electron density to the Si-O bond in silicate should result in the higher binding energy of Zr 3d in Zr-O-Si than that in ZrO_2. The Zr 3d peak after the second sputtering was relatively complicated, as shown in **Figure 7(b)**. We attribute it to the fact that the interfacial layer is a mixture of non-stoichiometric ZrOx and Zr Silicate. This may be caused by Argon ion sputtering damage which leads to a change of binding energy and is inevitable, no peak of binding energy 178.4 eV of Zr 3d corresponding to Si-Zr bonding was observed [17], suggesting a lack of silicide formation at the substrate interface and Si-Zr bonding with in the interfacial layer.

4. Conclusion

The structural and electrical properties of ZrO_2 thin films on Si(100) substrate by simple and low cost, spin coating technique was investigated. The XRD of ZrO_2 films shows the films crystallized at higher temperature and exists in two phases at 700˚C calcinations temperature. The C-V characteristics of all the dielectric films that involved distinct inversion, depletion, and accumulation were clearly revealed in MIS structure. I-V characteristics of ZrO_2 thin films on Si shows decreased saturation current on calcinations temperatures. The XPS measurement reveals that a zirconium silicate interfacial layer has formed in the ZrO_2/Si Systems.

REFERENCES

[1] K. J. Hubbard and D. G. Schlom, "Thermodynamic Stability of Binary Oxides in Contact with Silicon," *Journal of Material Research*, Vol. 11, No. 11, 1996, pp. 2757-2776. doi:10.1557/JMR.1996.0350

[2] R. Puthenkovilakam and J. P. Chang, "Valence Band Structure and Band Alignment at the ZrO_2/Si Interface," *Applied Physics Letters*, Vol. 84, No. 8, 2004, pp. 1353-1355. doi:10.1063/1.1650547

[3] J. Robertson, "Band Offsets of Wide-Band-Gap Oxides and Implications for Future Electronic Devices," *Journal of Vacuum Science Technology*, Vol. B 18, 2000, p. 1785.

[4] K. S. Krisch, J. D. Bude and L. Manchanda, "Gate Capacitance Attenuation in MOS Devices with Thin Gate Dielectrics," *IEEE Electron Device Letter*, Vol. 17, No. 11, 1996, pp. 521-524. doi:10.1109/55.541768

[5] S. Chatterjeea, S. K. Samantaa, H. D. Banerjeeb and C. K. Maiti, "Electrical Properties of Stacked Gate Dielectric (SiO_2/ZrO_2) Deposited on Strained SiGe Layers," *Thin Solid Films*, Vol. 422, No. 1-2, 2002, pp. 33-38. doi:10.1016/S0040-6090(02)00995-1

[6] Y. S. Lin, R. Puthenkovilakam, J. P. Chang, C. Bouldin, I. Levin, N. V. Nguyen, J. Ehrstein, Y. Sun, P. Pianetta, T. Conard, W. Vandervorst, V. Venturo and S. Selbrede, "Interfacial Properties of ZrO_2 on Silicon," *Journal of Applied Physics*, Vol. 93, No. 10, 2003, pp. 5945-5952.

[7] R. Mahapatra, J. H. Lee, S. Maikap, G. S. Kar, A. Dhar, N.-M. H. Wang, D. Y. Kim, B. K. Mathur and S. K. Rayc, "Electrical and Interfacial Characteristics of Ultra-Thin ZrO_2 Gate Dielectrics on Strain Compensated SiGeC/Si Heterostructure," *Applied Physics Letters*, Vol. 82, No. 14, 2003, pp. 2320-2327. doi:10.1063/1.1566480

[8] S. Harasek, A. Lugstein, H. D. Wanzenboeck and E. Bertagnolli, "Slow Trap Response of Zirconium Dioxide Thin Films on Silicon," *Applied Physics Letters*, Vol. 83, No. 7, 2003, p. 1400. doi:10.1063/1.1602577

[9] A. Stesmans and V. V. Afanas'ev, "Si Dangling-Bond-Type Defects at the Interface of Si(100) with Ultrathin Layers of SiO_x, Al_2O_3, and ZrO_2," *Applied Physics Letters*, Vol. 80, No. 11, 2002, pp. 1957-1959. doi:10.1063/1.1448169

[10] J. M. Howard, V. Craciun, C. Essary and R. K. Singh, "Interfacial Layer Formation during High-Temperature Annealing of ZrO_2 Thin Films on Si," *Applied Physics Letters*, Vol. 81, No. 18, 2002, pp. 3431-3433. doi:10.1063/1.1517407

[11] N. Sriprang, D. Kaewchina and J. D. Kennedy, "Processing and Sol Chemistry of a Triol-Based Sol-Gel Route for Preparing Lead Zirconate Titanate Thin Films," *Journal of American Ceramic Society*, Vol. 83, No. 8, 2000, pp. 1914-1920.

[12] X. R. Huang and Z. T. Huang, "Preparation of Asymmetric Alumina Membrane by Sol-Gel Techniques," *Journal of Inorganic Material*, Vol. 13, No. 4, 1998, p. 534.

[13] L. Q. Zhu, Q. Fang, G. He and M. Liu, "Interfacial and Optical Properties of ZrO_2/Si by Reactive Magnetron Sputtering," *Material Letter*, Vol. 60, No. 7, 2006, pp. 888-891. doi:10.1016/j.matlet.2005.10.039

[14] S. Dhar and M. S. Dharmaprakash, "MOCVD of ZrO_2 Films from Bis(t-Butyl-3-oxo-butanoato) Zirconium (IV): Some Therotical (Thermodynamics) and Experimental Aspects," *Material Science*, Vol. 31, 2008, pp. 67-72.

[15] J. Zhu and Z. G. Liu, "Structure and Dielectric Properties of Ultra-Thin ZrO_2 Films for High-k Gate Dielectric Application Prepared by Pulsed Laser Deposition," *Applied Physics*, Vol. 78, No. 5, 2004, pp. 741-744. doi:10.1007/s00339-002-2025-0

[16] S. J. Wang and C. K. Ong, "Rapid Thermal Annealing Effect on Crystalline Yttria-Stabilized Zirconia Gate Dielectrics," *Semiconductor Science and Technology*, Vol. 18, No. 2, 2003, pp. 154-157. doi:10.1088/0268-1242/18/2/316

[17] T. S. Jeeon, J. M. White and D. I. Kwong, "Thermal Stability of Ultrathin ZrO_2 Film on Si(100)," *Applied Physics Letter*, Vol. 78, No. 3, 2001, p. 368. doi:10.1063/1.1339994

