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Influence of Annealing Temperature on the Structural, Interfacial, and Dielectric Properties of ZrO_2 Thin Films

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Abstract: Zirconium dioxide (ZrO_2) thin films were deposited on silicon substrates using a sol–gel spin coating technique with a precursor concentration of 0.5 M. The deposited films were annealed at different temperatures (350 °C, 550 °C, and 750 °C) to investigate the influence of thermal treatment on their structural and surface morphological properties. X-ray diffraction studies reveal that the unannealed film is largely amorphous, while annealed films exhibit enhanced crystallinity with the coexistence of monoclinic and tetragonal ZrO_2 phases. An increase in annealing temperature leads to improved phase formation and grain growth. Field emission scanning electron microscopy images show uniform, crack-free surfaces with gradual densification and grain evolution upon annealing. The results indicate that annealing temperature plays a crucial role in tailoring the microstructural properties of ZrO_2 thin films, making them suitable for silicon-based microelectronic and sensor applications.

Keywords: ZrO_2 thin films, sol–gel, annealing temperature, XRD, FESEM.

1. INTRODUCTION

Zirconium dioxide (ZrO_2) is a technologically important metal oxide material owing to its high dielectric constant, wide band gap (~5–7 eV), excellent thermal stability, and superior chemical inertness. These properties make ZrO_2 a promising candidate for applications in microelectronic devices, gate dielectrics, sensors, optical coatings, and non-volatile memory elements [1–3]. In particular, ZrO_2 thin films deposited on silicon substrates are widely investigated as potential alternatives to conventional SiO_2 due to their ability to suppress leakage current while maintaining higher capacitance density in scaled devices [4,5]. ZrO_2 exhibits polymorphism and exists in monoclinic, tetragonal, and cubic phases depending on temperature, grain size, and processing conditions. While bulk ZrO_2 stabilizes in the monoclinic phase at room temperature, thin films often exhibit metastable tetragonal or mixed phases due to size confinement, substrate-induced strain, and oxygen vacancy effects [6,7]. The stabilization of specific crystalline phases is particularly important because the dielectric constant, loss behaviour, and electrical reliability of ZrO_2 thin films are strongly phase-dependent. Various deposition techniques such as sputtering, pulsed laser deposition, atomic layer deposition, chemical vapor deposition, and sol–gel processing have been employed for the fabrication of ZrO_2 thin films [8–10]. Among these methods, sol–gel spin coating is attractive due to its low cost, simplicity, precise control over stoichiometry, and suitability for large-area coatings. However, sol–gel derived ZrO_2 films are generally amorphous in the as-deposited state and require post-deposition annealing to achieve crystallization, phase transformation, and improved electrical performance [11,12, 13]. Annealing temperature plays a crucial role in tailoring the microstructure and dielectric behaviour of ZrO_2 thin films. Thermal treatment influences grain growth, defect density, oxygen vacancy concentration, and interfacial quality with the silicon substrate, all of which significantly affect dielectric constant and dielectric loss [14–16]. Moderate annealing temperatures often lead to enhanced dielectric properties due to improved crystallinity, whereas excessive annealing may induce grain boundary defects or interfacial reactions that degrade dielectric performance. Although several reports exist on ZrO_2 thin films, systematic studies correlating annealing-induced structural evolution with dielectric properties in low molarity sol–gel derived ZrO_2 films on silicon substrates remain limited. Therefore, a comprehensive understanding of the relationship between annealing temperature, phase formation, surface morphology, and dielectric behaviour is essential for device-oriented applications. In the present work, ZrO_2 thin films were deposited on silicon substrates using a sol–gel spin coating technique with a precursor concentration of 0.5 M. The films were annealed at different temperatures (350 °C, 550 °C, and 750 °C). The effect of annealing on structural properties, surface morphology, and dielectric characteristics was systematically investigated using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and dielectric measurements.

2. EXPERIMENTAL DETAILS

ZrO_2 precursor solution was prepared with 0.25 M $ZrO_2.8H_2O$ in 25ml ethanol under continuous stirring. A stabilizing agent was added dropwise to control hydrolysis and condensation reactions, ensuring the formation of a homogeneous and stable sol. The solution was stirred for several hours at room temperature until a clear and uniform sol was obtained, indicating complete precursor dissolution and reaction.

Single-side polished p-type silicon (100) substrates were used for film deposition. Prior to coating, the substrates were sequentially cleaned ultrasonically in acetone, ethanol, and deionized water for 10 minutes each to remove organic contaminants and surface impurities. The cleaned substrates were dried using nitrogen gas and stored in a dust-free environment before deposition.

The ZrO_2 thin films were deposited on silicon substrates using a spin coating technique. A few drops of the prepared sol were dispensed onto the substrate surface, followed by spinning at a fixed speed for a predetermined duration to ensure uniform film thickness. After each coating cycle, the films were pre-heated on a hot plate at moderate temperature to remove residual solvents and initiate organic decomposition. This coating–drying cycle was repeated to obtain films of desired thickness. The as-deposited films were subjected to post-deposition annealing in ambient air at temperatures of 350 °C, 550 °C, and 750 °C for a fixed duration. Annealing was carried out to promote densification, remove residual organic species, and induce crystallization and phase transformation in the ZrO_2 films. The effect of annealing temperature on structural and electrical properties was systematically studied.

The crystalline structure and phase evolution of the films were examined using X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.5406 Å) over a 2θ range of 20°–70°. Surface morphology and grain evolution were analysed using field emission scanning electron microscopy (FESEM). To study the dielectric characteristics, metal–oxide–semiconductor (MOS) capacitors were fabricated by depositing circular metal electrodes on the ZrO_2 film surface through a shadow mask. High-frequency capacitance–voltage (C–V) measurements were performed using an LCR meter at room temperature. From the C–V characteristics, key electrical parameters such as oxide charge density (Q_{ox}) and interface trap density (D_{i}□) were extracted to evaluate the dielectric quality and interfacial behaviour of the ZrO_2/Si system.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

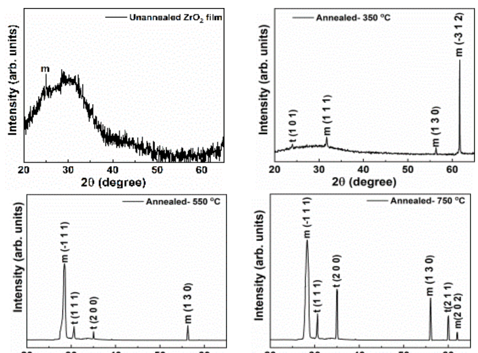

Fig. 1. X-ray diffraction (XRD) patterns of sol–gel derived ZrO_2 thin films deposited on silicon substrates: (a) as-deposited, and annealed at (b) 350 °C, (c) 550 °C, and (d) 750 °C.

Figure 1 shows the XRD pattern of the as-deposited ZrO_2 thin film deposited on Si, annealed at various temperatures. In Fig. 1 (a), the unannealed ZrO_2 films show a monoclinic peak at 25°. Figure 1 (b) shows diffraction peaks at 24°, 31.6°, 56.3°, and 61.6° corresponding to t (1 0 1), m (1 1 1), m (1 3 0), and m (-3 1 2) planes, respectively, for ZrO_2 thin film annealed at 350 °C. Figure 1 (c) shows the diffraction peaks obtained around 28.4°, 30.4°, 35°, and 56.3°, corresponding to the m (-1 1 1), t (1 1 1), t (2 0 0), and m (1 3 0) planes, respectively, for ZrO_2 thin film annealed at 550 °C. Figure 1 (d) shows diffraction peaks at 28.4°, 30.4°, 35°, 56.07°, 60°, and 62° correspond to m (-1 1 1), t (1 1 1), t (2 0 0), m (1 3 0), t (2 1 1), and m (2 0 2), respectively, for ZrO_2 thin film annealed at 750 °C [17, 18].

3.2 Surface Morphological Analysis

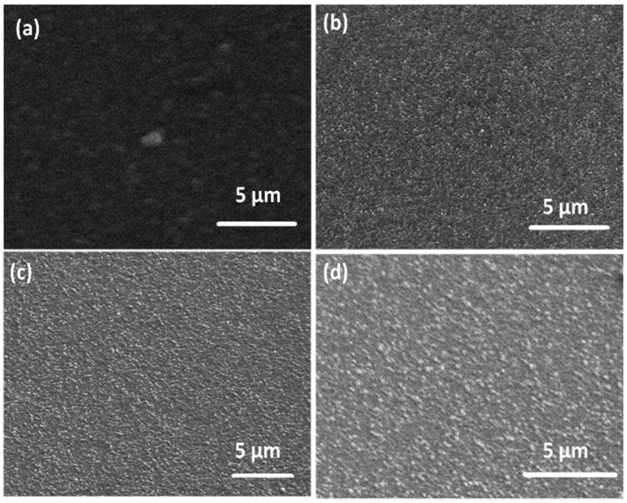

Fig.2. FESEM surface micrographs of ZrO_2 thin films on silicon substrates: (a) as-deposited, and annealed at (b) 350 °C, (c) 550 °C, and (d) 750 °C.

Figure 2(a–d) shows the FESEM images of ZrO_2 thin films at different annealing temperatures. The unannealed film exhibits a relatively smooth but featureless surface with low contrast, consistent with its amorphous nature. Upon annealing at 350 °C, the surface becomes more uniform with the formation of fine granular features. Further annealing at 550 °C leads to noticeable grain development and surface densification. At 750 °C, the film surface appears compact and uniformly distributed with well-developed grains, without visible cracks or pinholes. The observed morphological evolution is attributed to enhanced atomic diffusion and grain coalescence at higher annealing temperatures, which improves film density and structural integrity.

3.3 Dielectric Study

The dielectric characteristics of the ZrO_2 thin films annealed at different temperatures were investigated by high-frequency C–V measurements and subsequent extraction of oxide charge (Q_{ox}) and interface trap density (D_{it}). As shown in Fig. 3(a), all samples exhibit typical MOS capacitor behaviour, reaching normalized capacitance values close to unity under accumulation bias, confirming that the ZrO_2 films act as effective dielectrics on Si. A clear systematic shift in the flat-band region is observed with annealing. The as-deposited film presents a pronounced negative shift, indicating the presence of significant negative charge within the film or at the dielectric/Si interface, which can be attributed to oxygen vacancies (V_O) and residual organic components originating from the sol–gel precursor. Upon annealing at 350 °C, the C–V curve moves toward more positive voltages, suggesting effective elimination or passivation of these negative charge centers. The 550 °C annealed film exhibits

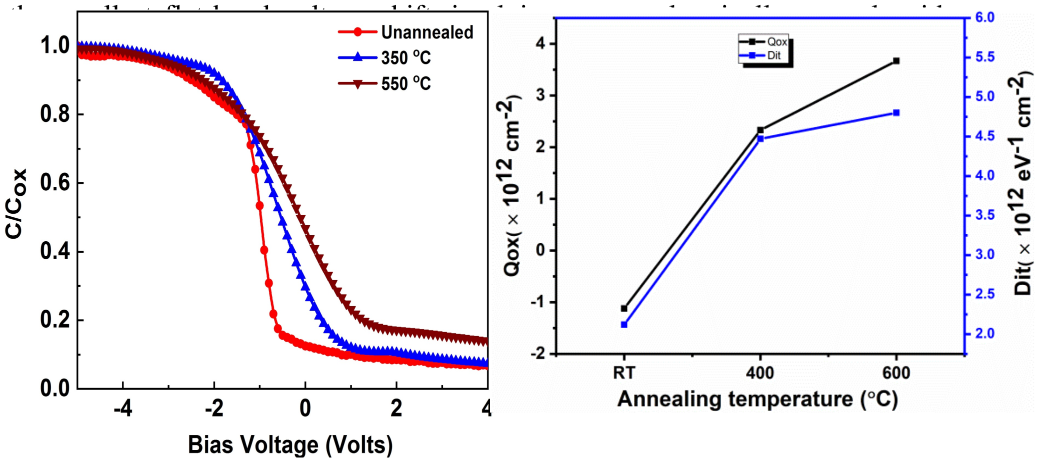

Fig.3 (a) High-frequency capacitance–voltage (C–V) characteristics of ZrO_2/Si MOS capacitors for films annealed at different temperatures. **(b)** Extracted oxide charge density (Q_{ox}) and interface trap density (D_i□) of ZrO_2 thin films as a function of annealing temperature.

The transition from accumulation to depletion becomes progressively broader at higher annealing temperatures, which points to an increase in interface-related states capable of interacting with the AC signal. These traps exchange charge with the semiconductor as the Fermi level sweeps, causing distortions and stretching in the C–V slope. This behaviour is corroborated by the parameter extraction plotted in Fig.3 (b), where Q_{ox} changes from negative values in the unannealed film to positive values at elevated annealing temperatures. The reduction of negative Q_{ox} is consistent with thermally assisted densification and the removal of weakly bonded hydroxyl groups, carbon residues, and incomplete ligands that are commonly present in sol–gel derived oxide films. However, the improvement in Q_{ox} at higher temperatures occurs concurrently with a rise in interface trap density (D_{it}). The D_{it} value increases from the unannealed to the 550 °C treated film, indicating that while bulk defects diminish, interface states become more dominant with temperature. This effect is likely associated with microstructural evolution: ZrO_2 is known to undergo a transition from amorphous to partially crystalline phases above ~450 °C. The onset of monoclinic or tetragonal crystallites and their associated grain boundaries can induce interfacial stress and form dangling bonds at the ZrO_2/Si boundary, thereby generating electrically active interface centres. Such a trade-off between improved bulk stoichiometry and deteriorated interfacial quality is commonly reported in high-κ metal oxides processed at elevated temperatures. Furthermore, high-frequency C–V measurements for the film annealed at 750 °C could not be reliably analysed due to increased leakage current and non-ideal MOS characteristics, which hindered stable capacitance response. Therefore, dielectric parameter extraction was limited to films annealed at 350 °C and 550 °C.

4. CONCLUSION

ZrO_2 thin films were successfully deposited on silicon substrates using a sol–gel spin coating technique with a precursor concentration of 0.5 M, and the influence of post-deposition annealing temperature on their structural, morphological, and dielectric properties was systematically investigated. X-ray diffraction analysis revealed that the as-deposited film is predominantly amorphous, while annealed films exhibit enhanced crystallinity with the coexistence of monoclinic and tetragonal ZrO_2 phases. Increasing annealing temperature leads to improved phase formation and grain growth, which is corroborated by the evolution of surface morphology observed in FESEM images. Dielectric characterization using high-frequency C–V measurements confirm typical MOS capacitor behaviour for all samples, demonstrating that the ZrO_2 films function as effective dielectric layers on silicon. The as-deposited film exhibits a significant negative flat-band voltage shift due to the presence of negative oxide charges associated with oxygen vacancies and residual precursorrelated defects. Annealing at moderate temperatures effectively reduces these charge centres, leading to a near electrically neutral oxide–semiconductor interface, as evidenced by the minimized flat-band voltage shift and reduced oxide charge density. However, higher annealing temperatures result in a gradual increase in interface trap density, attributed to microstructural evolution and the formation of crystalline phases and grain boundaries at the ZrO_2/Si interface. This highlights a trade-off between improved bulk dielectric quality and interfacial electrical stability in sol–gel derived ZrO_2 films. Overall, the film annealed at an intermediate temperature exhibits the most favourable balance between structural crystallinity and dielectric performance, indicating its potential suitability for silicon-based high-κ dielectric and microelectronic applications.

5. ACKNOWLEDGEMENTS

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