

Effect of Y, Gd, Dy, and Ce Doping on the Microstructural and Electrical Properties of Sol-Gel-Deposited ZrO₂ Film

Myung Soo Lee, Chee-Hong An, Kyung Park, Ju-Yun Choi, and Hyoungsub Kim^z

School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea

 ZrO_2 films doped with Y, Gd, Dy, and Ce at a concentration of ~13 cation atom % were deposited by a sol-gel technique, and the early-stage dopant effect on the stabilization of the high temperature phase and dielectric properties was systematically compared after a low-temperature annealing process (400°C). The high temperature phase formation of the ZrO_2 films was hindered by the Y, Gd, and Dy doping, thereby reducing the dielectric constant. In addition, the hysteresis was significantly increased via electron trapping, which was attributed to the increase in the number of oxygen vacancies possibly due to the difference in the valence number of the dopants with that of the substituted Zr atoms. However, the dielectric constant of the ZrO₂ film doped with tetravalent Ce atoms increased without retarding the stabilization of the high temperature phase and degrading the hysteresis characteristics. © 2011 The Electrochemical Society. [DOI: 10.1149/1.3562971] All rights reserved.

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For many decades, metal-oxide systems have been widely investigated as a major component in various application areas, such as a gate dielectric in complementary metal-oxide-semiconductor (MOS) devices^{1,2} and a capacitor dielectric in dynamic random access memory devices.² In particular, ZrO_2 and HfO_2 have attracted a lot of attention due to their high dielectric constant, wide band gap, and excellent electrical and chemical stability.³ According to their bulk phase diagrams, they hold a range of crystalline phases-monoclinic, tetragonal, and cubic phases-and the monoclinic is the equilibrium phase at typical device fabrication temperatures.⁴ Because the dielectric constant—one of the most important dielectric characteristics-strongly depends on the crystalline phase, many theoretical⁵⁻⁷ and experimental studies⁸⁻¹² have focused on the possible stabilization of these high-k dielectric films, especially HfO₂, from monoclinic to tetragonal and/or cubic phase by the doping of several elements, such as Si, Ge, Al, Sc, Y, and various rare earth elements. However, these studies have focused on the microstructural/dielectric properties of films undergoing either a nearlyequilibrium deposition environment or a post-deposition annealing process at high temperature, without revealing the initial, low-temperature kinetics. In addition, the trivalent doping atoms have been postulated to generate oxygen vacancies which may deteriorate the electrical properties of the dielectric film.^{13,14} However, experimental confirmation by a systematic and in-depth comparison using doping elements with different valence numbers is rare.

Although many studies on these high-k dielectric films have been performed by various vacuum-based deposition methods, such as sputtering, chemical vapor deposition, and atomic layer deposition, chemical solution deposition, e.g., sol-gel technique, is a useful method for fast and systematic studies of high-k films doped with various elements due to its precise and wide composition controllability.¹⁵ In addition, although solution-based deposition might not be a suitable choice for a current integrated circuit fabrication process compared to vacuum-based deposition, it can provide the following useful information: the effect of the dopant types on the stabilization strength and the microstructural/electrical properties of high-k films at a low temperature regime under an nearly-identical experimental condition.

In this study, moderately-thick ZrO_2 films (24–25 nm) doped with various elements—Y, Gd, Dy, and Ce—at an approximate cation concentration of 13 atom % to Zr were deposited by a sol-gel technique and the dopant effects on the microstructural evolution, especially stabilization process to tetragonal/cubic phase and the dielectric properties were studied after annealing at a relatively low temperature (400°C), with a particular focus on the effect of the valence number of dopants.

Experimental

In preparing the precursor solutions for the sol-gel deposition, acetic acid (CH₃CO₂H) and 2-methoxyethanol (CH₃OCH₂CH₂OH) were used as solvents, and the following metal-based nitrate hydrates were used as metallic components: zirconyl nitrate hydrate $[ZrO(NO_3)_2 \cdot xH_2O]$, yttrium nitrate hexahydrate $[Y(NO_3)_3 \cdot 6H_2O]$, gadolinium nitrate hexahydrate [Gd(NO₃)₃·6H₂O], dysprosium nitrate hydrate [Dy(NO₃)₃·xH₂O], and cerium nitrate hexahydrate [Ce(NO₃)₃·6H₂O]. All the chemical precursors were thoroughly mixed to form pure or doped ZrO₂ solutions having an identical concentration of 0.5 M by magnetic stirring at room temperature, and each solution was filtered using a 0.5 μ m hole-sized syringe filter for particle removal. In the case of the doped ZrO₂ films, the mixing ratios of the solutes were controlled to achieve a dopant concentration of 10 cation atom %. Before the sol-gel deposition, p-type Si (100) substrates of dimensions 2×2 cm were degreased using trichloroethylene to remove the possible organic contaminants without removing the native oxide layer. Each precursor solution containing different dopant species was then spin-coated on the cleaned Si substrates at a rotational speed of 3000 rpm for 30 s. The spin-coated films were dried at 100°C for 10 min to remove the solvents and finally sintered at 400°C for 60 min in air ambient.

After the formation of the various doped-ZrO₂ films, the final doping concentrations (cation atomic ratio) were measured to be around 13 atom %, which is close to the initial concentration of the precursor solution (10 atom %), according to the separate energy dispersive X-ray spectroscopy measurements made during high-resolution transmission electron microscopy (HR-TEM) analyses. The phases and crystalline orientations of all the sintered ZrO₂ films were characterized by X-ray diffraction (XRD) with a Cu Ka X-ray source. Detailed microstructural analyses were performed using a HR-TEM operating at an acceleration voltage of 200 kV after making cross-sectional TEM samples. In order to investigate the doping effect with different elements on the electrical properties of the ZrO₂ films, MOS capacitors were fabricated by depositing TaN (50 nm) capped with Al (10 nm) as the gate electrode using DC magnetron sputter and patterning via a lift-off process. The capacitancevoltage (C-V) characteristics were measured by using an Agilent E4980A LCR meter to extract various MOS capacitor parameters and the leakage current characteristics were also measured by using an HP 4145B semiconductor parameter analyzer under a gate injection condition.

Results and Discussion

Figure 1a shows the XRD patterns obtained from the sol-gel-deposited, pure and doped ZrO_2 films after the densification process at 400°C. For the pure ZrO_2 film used as a reference, two diffraction peaks coming from the film were identified: one indexed as monoclinic phase and the other as tetragonal or cubic phase. The

^z E-mail: hsubkim@skku.edu



Figure 1. XRD spectra of the sol-gel-deposited pure ZrO_2 and doped- ZrO_2 films (Y, Gd, Dy, and Ce) after (a) a densification (400°C, 60 min in air) and (b) an additional high temperature anneal (1000°C, 1 min in N₂). The diffraction peaks from the monoclinic and tetragonal/cubic phase are labeled as M and T/C, respectively. The strong diffraction peak observed at ~33 degrees in all of the samples is the artifact coming from the substrate Si (200).

tetragonal and cubic phase could not be differentiated by XRD because the peak positions were too close with each other. Because the vacuum-deposited ZrO2 thin film was known to have a mixed state of monoclinic and tetragonal phases, i.e., a partially stabilized state, at this thickness range,¹⁶ it would be more reasonable to assign the low angle peak to the tetragonal (011) plane in our 25 nm-thick ZrO₂ film deposited by a sol-gel method. For the ZrO₂ sample doped with Ce atoms having the same tetravalent state with Zr, a similar mixed state was observed. The low angle diffraction peak from the Ce-doped ZrO₂ sample may have arisen from the tetragonal, cubic or mixed state. On the contrary, for the ZrO₂ films doped with elements having a trivalent state, i.e., Y, Gd, and Dy, only a monoclinic phase was observed, which implied the possible retardation of the high temperature phase formation by these doping ele-ments. Several published reports¹⁰⁻¹² have shown Y or rare earth element doping with trivalent states to be effective in stabilizing the HfO₂ film, which is similar to ZrO₂ in terms of the electrical and microstructural properties, to tetragonal or cubic phase, and increased the dielectric constant at an optimum doping concentration of around 10 atom %, which is close to our doping condition.

However, these results were obtained after reaching close to the equilibrium stabilized state due to the nearly-equilibrium deposition conditions or higher post-deposition annealing temperatures than in our experiment (400°C). Therefore, according to our low-temperature annealing experiment, we assumed that although all the dopants used in this experiment may eventually produce the tetragonal or cubic phase ZrO_2 film at a much higher temperature, their effectiveness at a low temperature regime is strongly dependent on the dopant identities. Furthermore, all the doped ZrO_2 samples were converted into a partially-stabilized state with tetragonal/cubic and monoclinic phases after high temperature annealing (1000°C, 1 min in N₂ ambient) as shown in Fig. 1b and exhibited a high dielectric constant (~28 for Y-doped ZrO_2 film),¹⁷ which corroborated our assumption.

In order to measure the thicknesses and study the detailed microstructural evolution of the sol-gel-deposited ZrO₂ films doped with various elements, cross-sectional HR-TEM pictures were taken and their images are shown in Fig. 2. For all the samples, the thicknesses of the high-k dielectric layers were within a similar range of 24-25 nm. Because the sol-gel deposition of all the ZrO₂ films was performed on the Si wafers having a native oxide without HF cleaning, the pure ZrO₂ sample had approximately 1.5 nm-thick interfacial oxide layer. Although an identical Si wafer was used, the interfacial layer thickness was increased to 2.1-2.4 nm for the doped ZrO₂ samples. The similar interfacial oxide thickening that was also observed in our previous experiment¹⁸—sol-gel deposition of 3.5-4 nm-thick ZrO2 films with different Ce contents on the HF-cleaned Si substrate-was attributed to the catalytic effect of the dopant in oxidizing the underlying Si substrate during the post-deposition annealing process. For the pure and Ce-doped ZrO₂ samples (see Figs. 2a and 2e), a crystalline image with relatively well-aligned grains was observed. However, Y, Gd, and Dy doping resulted in a random distribution of the crystalline directions of the nano-sized grains, with even some disordered structures appearing as shown in Figs. 2b-2d. A consideration of these HR-TEM analyses in conjunction with the previously discussed XRD results suggested that the Y, Gd, and Dy doping atoms having a valence number that differed



Figure 2. Cross-sectional HR-TEM images of the sol-gel-deposited (a) pure, (b) Y-doped, (c) Gd-doped, (d) Dy-doped, and (e) Ce-doped ZrO_2 films. I.L. stands for the interfacial layer.



Figure 3. (Color online) (a) C–V curves of the sol-gel-deposited ZrO_2 films as a function of the doping species measured at a frequency of 100 kHz. (b) The extracted dielectric constant and the amount of hysteresis in the ZrO_2 films with different doping species.

with that of Zr, hindered the stabilization of the ZrO_2 film to the tetragonal or cubic phase and deteriorated the crystallinity of the film during the annealing process at the relatively low temperature.

Electrical analyses, such as C-V and leakage current densityvoltage (J-V) measurements, were performed after fabricating MOS capacitor structures using Al/TaN gate electrodes. Figure 3a shows the C-V curves measured at a frequency of 100 kHz as a function of the dopant species, and the extracted dielectric constant and the amount of the hysteresis are plotted in Fig. 3b. The dielectric constants of the high-k films were calculated from the accumulation capacitance values measured at a gate bias of -2 V. In order to decouple the effects of the interfacial oxide and high-k layers, the physical thicknesses of all the layers measured from the HR-TEM images were used to extract the dielectric constants of the high-k films. Also, the interfacial oxide was assumed to be a pure SiO₂ layer with a dielectric constant of 3.9. For the sol-gel-deposited pure ZrO_2 film, the extracted dielectric constant was close to 20. When Y, Gd, and Dy atoms were added to the ZrO₂ film, the dielectric constant of the high-k layer was slightly lowered to 16-18 possibly due to the retardation of the tetragonal/cubic phase formation and/or decreased crystallinity, which were evidenced in the previous XRD and HR-TEM results. However, the Ce doping significantly increased the dielectric constant of the ZrO_2 film up to ~26, which could be explained not only by the Ce-O bond formation, but also by the densification and tetragonal/cubic phase formation effect.

Another interesting trend observed in the C–V measurement results was the effect of doping on the hysteresis characteristics of the doped ZrO_2 films. For the pure and Ce-doped ZrO_2 films, the measured hysteresis was lower than 30 mV, exhibiting excellent



Figure 4. (Color online) Leakage current characteristics of the pure and doped- ZrO_2 films measured under a gate injection condition.

low trapping characteristics during the voltage sweep. However, the apparent increase of the hysteresis over 300 mV was incurred with the other doping elements and a typical electron trapping behavior was observed: a positive shift of the C–V curve during a reversal voltage sweep after a positive-to-negative initial sweep. Because the doping elements used in this study were incorporated into the ZrO_2 film through a substitutional mechanism rather than an interstitial one,^{13,19} the observed increase of the bulk trapping characteristics in the Y, Gd, and Dy-doped samples was believed to be strongly related to the formation of the oxygen vacancies due to the difference of their number of valence electrons from that of ZrO_2 . Because the formed oxygen vacancies are positively charged, they are eager to trap the injected electrons and become neutralized, which coincides well with the observed positive shift of the C–V curve during the voltage sweeping.

Figure 4 shows the leakage current characteristics of the sol-geldeposited doped-ZrO₂ films as a function of the dopant species measured under a gate injection condition. Y, Gd, and Dy doping were expected to increase the leakage current of the ZrO₂ film due to their generation of oxygen vacancy defects. However, the leakage current was significantly decreased compared to the pure ZrO₂ film. Because the physical thicknesses of all the doped ZrO₂ films are quite similar, this suppression of the overall leakage current was attributed mainly to the doping-induced thickening of the interfacial oxide, as observed in the aforementioned HR-TEM results (see Fig. 2). In addition, the Ce-doped ZrO₂ film exhibited the lowest leakage current in the high field region at similar high-k and interfacial oxide thicknesses, compared to the other doped samples, possibly due to an additional densification effect induced by the Ce doping.

Conclusion

The dopant effect on the phase stabilization and dielectric properties of ZrO_2 films after a low temperature anneal was investigated by doping trivalent (Y, Gd, and Dy) or tetravalent (Ce) atoms at ~13 cation atom % into the sol-gel-deposited ZrO_2 films. After a densification process conducted at a temperature as low as 400°C for 60 min in air ambient, the trivalent dopants retarded the stabilization of the tetragonal or cubic phase and decreased the dielectric constant as a result. In addition, the C–V hysteresis was significantly increased by the trivalent atom doping, which was attributed to the formation of numerous oxygen vacancies due to the difference of the valence number with that of the substituted Zr atoms. On the contrary, doping with Ce atoms, having the same valence number as that of Zr, yielded an enhanced densification effect without hindering the tetragonal or cubic phase formation and hysteresis

characteristics, and increased the dielectric constant compared to the pure ZrO₂ film.

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