The Effect of Zirconium incorporation in La$_2$O$_3$ Nanocrystallites as Gate dielectric in MOSFET

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ABSTRACT

In this paper, the effect of Zirconium (Zr) incorporation on La$_2$O$_3$ nanocrystallites characteristics has been investigated that can be used as gate dielectric for the next MOSFETs (Metal-Oxide-Semiconductor Field Effect Transistors). Zr-doped La$_2$O$_3$ nanocrystallites were synthesized by a sol–gel method. The nanocrystallites size was determined by the Scherrer equation and X-powder method from the main peak of the sample phase observed in X-Ray Diffraction (XRD) patterns. The nanocrystallites properties were characterized with using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) techniques. Moreover, elemental qualitative analysis was performed Energy Dispersive X-Ray (EDX) spectrum. XRD spectra, AFM and SEM images indicate that the addition of Zr into La$_2$O$_3$ nanocrystallites can significantly increase the crystallization temperature.

KEYWORDS: MOSFET, High-k dielectric, Sol-gel, Zirconium-doped lanthanum oxide.

1. INTRODUCTION

The continuous advancement in the microelectronics industry relies on faster and higher density integrated circuits, which are made of millions of Metal-oxide-Semiconductor Field Effect Transistors (MOSFETs). As the channel length of these transistors reduces below 100 nm, the SiO$_2$ gate dielectric thickness is being scaled accordingly to an equivalent oxide thickness (EOT) below 2 nm [1]. Because of the gate leakage current and penetration of impurities from the gate into the gate dielectric, using SiO$_2$ as the gate dielectric material for standard Complementary Metal-Oxide-Semiconductor (CMOS) technology is a formidable task [2–4].

SiO$_2$ can easily crystallize during standard CMOS operation that a large leakage current may flow along the grain boundaries during the processing at high temperatures (~ 900 °C). Thus the ad-atoms which lie in the crystalline lattice can often be the pathways for dopants diffusion, large leakage current and breakdown [5-7].

This physical limitation imposed by SiO$_2$ has led the research into the study of many materials with high crystallization temperature and dielectric constants.

Many high-k dielectrics have been investigated to replace SiO$_2$ as possible gate dielectrics, such as Y$_2$O$_3$ [8], Al$_2$O$_3$ [9], Ta$_2$O$_5$ [10], Gd$_2$O$_3$ [11-12], HfO$_2$ [13], STO [14], ZrO$_2$ [15-16] and La$_2$O$_3$ [17-18].

In this work, we investigate the material and dielectric properties of Zr-doped La$_2$O$_3$ nanocrystallites. Since both lanthanum and zirconium atoms have high crystallization temperatures, high dielectric constant (~ 22-30), wide energy band gap (~ 6 eV), and good stability with Si. We expect that Zr-doped La$_2$O$_3$ nanocrystallites can be used as a good gate dielectric for the future of MOSFET generations [19-21].

2. Experimental Procedure and Details

Lanthanum nitrate hexahydrate [La(NO$_3$)$_3$.6H$_2$O] and zirconium propoxide [Zr(OCH(CH$_3$)$_2$)$_4$] were used as the metallic precursors for the nanocrystallites. Acetic acid [CH$_3$COOH] and ethylene glycol monomethyl ether [CH$_3$OCH$_2$CH$_2$OH] were used as solvents.

Zirconium lanthanum oxides nanocrystallites were prepared according to the following procedure: First, 10 g of lanthanum nitrate hexahydrate and 15 g of zirconium propoxide were dissolved in 10 ml of acetic acid and 15 ml of ethylene glycol monomethyl ether, respectively. Zirconia and lanthana solutions were stirred vigorously at 50 °C for 1 h. Then both solutions were mixed and the resultant sol was continuously stirred for 24 hours and kept at room temperature until it turned into a yellowish sol. Finally, the stabilized sol was rapidly heated to 60 °C for 10 h. Viscosity and color changed as the sol turned into a stick gel. The gel was heat-treated at 80 °C for 24 h and a fluffy, polymeric precursor was gained. The prepared nanocrystallites calcined at different temperatures in the air atmosphere. The crystal phases of the nanocrystallites were identified by XRD analysis. Microscopy analysis was performed using SEM. Surface morphology was observed by AFM.

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3. RESULTS AND DISCUSSIONS

Figure 1 shows the EDX analysis obtained from nanocrystallites confirms that the nanocrystallites consisted of La, Zr, O.

Figure 1: EDX spectrum of the Zr<sub>0.3</sub>La<sub>0.7</sub>O<sub>y</sub> nanocrystallites.

Figure 2 shows the XRD spectra of Zr<sub>0.3</sub>La<sub>0.7</sub>O<sub>y</sub> sample at different temperatures. As the annealing temperature of Zr<sub>0.3</sub>La<sub>0.7</sub>O<sub>y</sub> nanocrystallites increases, more peaks appeared, their intensity also increases, peaks shifted toward right at higher temperatures (900 °C), nanocrystallites were not formed in an amorphous and as temperature increases, nanocrystallites sizes increases that can be derived from the full width-at-half-maximum (FWHM) of the XRD peaks, using the Debye-Scherrer formula, and X-powder method (figure 3) which gives the nanocrystallites size in terms of the half-width β as follow:

\[ D = \frac{0.94\lambda}{\beta \cos \theta} \]

Here 0 is half the grazing angle.

Figure 2: XRD patterns of the Zr<sub>0.3</sub>La<sub>0.7</sub>O<sub>y</sub> at different temperatures.

Figure 3 shows sizes of Zr<sub>0.3</sub>La<sub>0.7</sub>O<sub>y</sub> nanocrystallites at different temperatures that have been determined by X-powder method. X-powder calculations show that nanocrystallites size increase at higher temperatures.
Figures 3: The size nanocrystallites determined with using X-powder method: (a) 22 nm (Scherrer) and 25 nm (correct Scherrer) at as-deposited; (b) 26 nm (Scherrer) and 30 nm (correct Scherrer) at 500 °C; (c) 64 nm (Scherrer) and 36 nm (correct Scherrer) at 700 °C; (d) 41 nm (Scherrer) and 52 nm (correct Scherrer) at 900 °C.

Figure 4 (a, b and c) shows AFM topographical images of calcined Zr$_{0.3}$La$_{0.7}$O$_y$ nanocrystallites at 700 °C. The scan size was 25.2 pm$^2$. $S_s$ of the Zr$_{0.3}$La$_{0.7}$O$_y$ nanocrystallites is about 24,902 nm. Uniform surface was observed. The AFM results of the calcined Zr$_{0.3}$La$_{0.7}$O$_y$ nanocrystallites at 700 °C demonstrate that crystallites contours are clearly visible. Zr$_{0.3}$La$_{0.7}$O$_y$ nanocrystallites had partly a flat and smooth surface morphology. Nanocrystallites showed similar surface roughness which can affects the electrical properties of the Zr$_{0.3}$La$_{0.7}$O$_y$ nanocrystallites. Figures 4 d shows the image of height distribution of calcined Zr$_{0.3}$La$_{0.7}$O$_y$ nanocrystallites at 700 °C.
Figure 4: (a, b and c) AFM topography images of Zr$_0.3$La$_0.7$O$_y$ nanocrystallites at 700 °C; (d) the image of height distributions of Zr$_0.3$La$_0.7$O$_y$ nanocrystallites.

Figure 5 shows the SEM images of the Zr$_0.3$La$_0.7$O$_y$ nanocrystallites. On the sample surface of figure 5a (as-deposited), no recognizable crystal grains were found. Signs of severe brittle fracture are also visible on the worn surface. In figure 5b (calcined at 700 °C) one can see that the shape of grain is regular and the grain boundary is clear. Delamination happened on the surface and the tetragonal and monoclinic nanocrystallites of ZrO$_2$ have growth during the calcination treatment.

Figure 5: SEM images of Zr$_0.3$La$_0.7$O$_y$ nanocrystallites: (a) as – deposited; (b) at 700 °C.
Conclusion

In the present work, the properties of the \( \text{Zr}_{0.2}\text{La}_{0.8}\text{O}_{3} \) nanocrystallites prepared by sol-gel method were studied. The experimental results reveal that the incorporation of \( \text{Zr} \) into \( \text{La}_{2}\text{O}_{3} \) nanocrystallites can increase the crystallization temperature up to at least 700 °C. Results show zirconium lanthanum oxide nanocrystallites as gate dielectric is suitable for MOSFETs to achieve low leakage current.

REFERENCES


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