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The Effect of Zirconium incorporation in La₂O₃ Nanocrystallites as Gate dielectric in MOSFET

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ABSTRACT

In this paper, the effect of Zirconium (Zr) incorporation on La_2O_3 nanocrystallites characteristics has been investigated that can be used as gate dielectric for the next MOSFETs (Metal-Oxide-Semiconductor Field Effect Transistors). Zrdoped La_2O_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_2O_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 SiO₂ as possible gate dielectrics, such as Y_2O_3 [8], Al₂O₃ [9], Ta₂O₅ [10], Gd₂O₃ [11-12], HfO₂ [13], STO [14], ZrO₂ [15-16] and La₂O₃ [17-18].

In this work, we investigate the material and dielectric properties of Zr-doped La₂O₃ nanocrystallites. Since both lanthanum and zirconium atoms have high crystallization temperatures, high dielectric constant ($k \sim 22$ -30), wide energy band gap (~ 6 eV), and good stability with Si. We expect that Zr-doped La₂O₃ 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(NO₃)₃.6H₂ O] and zirconium propoxide [Zr(OCH(CH₃)₂)₄] were used as the metallic precursors for the nanocrystallites. Acetic acid [CH₃CO₂H] and ethylene glycol monomethyl ether [CH₃OCH₂CH₂OH] 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 lanthania 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 show The EDX analysis obtained from nanocrystallites confirms that the nanocrystallites consisted of La, Zr, O.



Figure 1: EDX spectrum of the Zr_{0.3}La_{0.7}O_v nanocrystallites.

Figure 2 shows the XRD spectra of $Zr_{0.3}La_{0.7}O_y$ sample at different temperatures. As the annealing temperature of $Zr_{0.3}La_{0.7}O_y$ 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 θ is half the grazing angle.





Figure 3 show sizes of $Zr_{0.3}La_{0.7}O_y$ 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 asdeposited; (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 pm². S_a 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 $Zr_{0.3}La_{0.7}O_y$ nanocrstallites. 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_ynanocrystallites: (a) as – deposited; (b) at 700 °C.

Conclusion

In the present work, the properties of the $Zr_{0.3}La_{0.7}O_y$ nanocrystallites prepared by sol-gel method were studied. The experimental results reveal that the incorporation of Zr into La_2O_3 nanocrystallites can increase the crystallization temperature up to at least 700 °C. Resuls show zirconium lanthanum oxide nanocrystallites as gate dielectric is suitable for MOSFETs to achieve low leakage current.

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