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Fabrication and Characterization of amorphous Lanthanum Zirconate Gate Capacitors

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Abstract*: *A novel high-k gate dielectric material, i.e., Lanthanum-doped Zirconium oxide (La-doped ZrO_2), has been thoroughly studied for applications in future metal oxide semiconductor field-effect transistor (MOSFET). The film's structural, chemical and electrical properties are investigated experimentally. The incorporation of La into ZrO_2 impacted the electrical properties in terms of leakage current while not sacrificing its dielectric constant. The dielectric constant of 25 is achieved which is calculated from the C-V analysis taken from Agilent 1500A Semiconductor Device Analyzer. XRD, FTIR, EDX analysis were conducted to confirm the stoichiometry and bond formation of $La_2Zr_2O_7$. The sol-gel spin coating method is adopted to form a uniform thin film over p-Silicon substrate and Aluminium is evaporated in the eBeam technique as gate electrode to form an MIS capacitor. The La-doped ZrO_2 film is hence a potential high-k gate dielectric for future application in MIS thin film transistors.

Keywords: $La_2Zr_2O_7$, MOS capacitor, High-k, Gate capacitor, dielectric constant, thin film.

I. INTRODUCTION

High-k materials presently under investigation are Al_2O_3, CeO_2, ZrO_2, TiO_2, HfO_2, Ta_2O_5, La_2O_3, Er_2O_3,Pr_2O_3, Gd_2O_3, Y_2O_3, etc. and some of their silicates such as $Al_xZr_{1-x}O_2$, $Zr_xSi_{1-x}O_y$, $Hf_xSi_{1-x}O_y$, etc. however, many of these materials show less thermodynamic stability on Si, also few other properties which need to be taken care of are; good adhesion, deposition at low temperature, large breakdown voltage, low defect density, ability to be patterned easily and low charge states on silicon. To find a best substitute for SiO2, in addition to the high-k value, the high-k materials should have several sophisticated characteristics. They should have good interface properties with the Si substrate, chemically stable with Si substrate and the gate electrode, should be thermally stable-at temperatures no less than 500°C. The structure can have high channel mobility, low interface trap density, large bandgap, low oxide trap density, low leakage current density, large band off-set energies and equivalent oxide thickness (EOT) – 10 to 15Å, High dielectric constant (10 < high-k < 50). All these guidelines are met by only few of these materials whereas many dielectrics are favorable in some of these areas. Including these, the bulk and interface properties of the new dielectric material must be comparable to the remarkable properties of SiO2. Since an important function of the gate dielectric is to isolate the gate terminal from the current-carrying channel region, it needs to be a good insulator. Lanthanum Zirconate nanocrystallites have high dielectric constant (k~22-30), wide energy band gap (~6eV), high crystallization temperatures, and good stability with Si. Also, it has been demonstrated as the thermal barrier coatings and showed excellent thermal stability because of its cubic pyrochlore structure [9–14]. Hence, we expect it can be used as a good gate dielectric for the future of MOSFET generations.

II. EXPERIMENTAL

$La_2Zr_2O_7$ solution was prepared using the sol-gel method. Initially, 5gms of Zirconium Oxychloride Octahedrate ($ZrOCl_2.8H_2O$) (Sigma Aldrich) powder was dissolved in 50ml of ethanol(C_2H_6O) and stirred at an optimum stirring speed using magnetic stirrer and the solution was leveled to form a clear and transparent solution. The mixture was then stirred continuously for 30min at 50^0C and 350rpm. 5.01gms of 99.9% pure lanthanum oxide (La_2O_3) (Sigma Aldrich) powder dissolved in 25ml of ethanol (C_2H_6O) in a 100ml beaker, this solution was then stirred for 5hrs at 90°C and 500rpm. Subsequently, lanthanum solution was added dropwise to the zirconium precursor solution and stirred for another 1hr at 100°C and 350rpm. To achieve a stoichiometric lanthanum zirconate in 1:1M ratio of La/Zr was maintained. After a homogeneous mixture was obtained, the resulting $La_2Zr_2O_7$ was cooled down before spin-coating on an RCA(Radio Corporation of America) Cleaned p-Si (100 orientation) substrate (with a resistivity of 5-10Ω-cm) wafers were cut down into small pieces of 1cm X 1cm square shape before depositing LZO solution. The spinning rate was 4000rpm and spinning time was 30sec. After spun, sample was placed in a furnace for post-deposition annealing at 130°C with a heating rate of 18°C-min^{-1} for 15min. The sample was then cooled down to room temperature. Spin deposition process was repeated ten times to achieve a uniform ultrathin LZO (Lanthanum zirconate) passivation layer. The novel procedure adopted in this work is to achieve a higher dielectric constant than that of the earlier reported works. Aluminium was deposited by e-beam evaporation method in a vacuum chamber at a background pressure up to 5x10^{-5} Pa.

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200µm X 200µm front contact was made through hand-made shadow masking. Aluminium metal was evaporated on the complete back surface of Si substrate to act as a back contact. The use of a metal contact as the dielectric surface, and highly doped Si wafer as a substrate completes the parallel plate capacitor device. The metal contact deposition was established using e-beam evaporation for 200µm X 200µm area. The deposition rate was maintained at 1Å /s till the thickness reached to 150nm.

III. RESULTS AND DISCUSSION

X-ray diffraction analysis shown in figure 1 was conducted with a Philips X'pert System at 45KV and step size of 0.008Å using CuKα radiation (λ=1.5418 Å). Obtained results were analyzed using match!3 software. Crystallite size measured using Scherrer equaton,

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad -(3)$$

where, λ is X-ray wavelength = 0.15418nm, K is Scherrer constant=0.94, θ is diffraction angle and β is width of the XRD peak after corrections concerning the instrumental broadening. This gives the average crystallite size D.

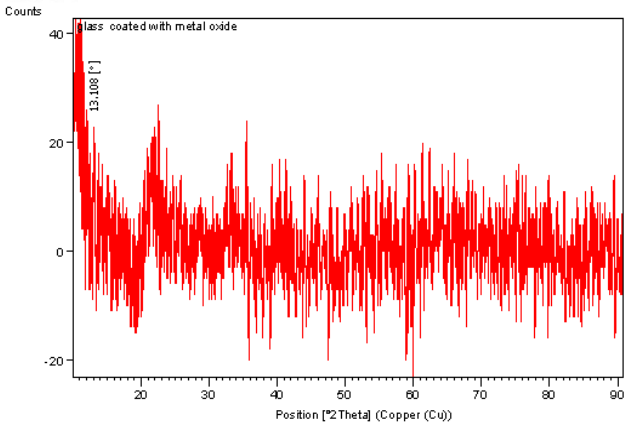

Figure 1: XRD diffraction pattern of lanthanum doped ZrO_2

The XRD diffraction pattern of Lanthanum doped ZrO_2 as in Figure 1. No clear peak in the graph represents the amorphous nature of the material. Crystallite size calculated using Bragg's law is 32nm. On heating, the material will acquire crystallite nature at 600^0C and the miller indices can be calculated.

Figure 2(a) shows the cross sectional SEM image of Lanthanum doped ZrO_2 film. Formation of a nano thin film is clearly visible. From the microstructure, it can be concluded that dopant has modified the film growth process and by consequence the microstructure and surface morphology. The Lanthanum doped ZrO_2 film shown in figure 2(b) represents a uniform coating and the surface appearing less porous. The cracks and delaminations that were found are consistent with the existing literature.

The Lanthanum doped thin film calcinated at 130^0C was analyzed by energy dispersive spectroscopy as shown in Figure 3 and Figure 4 respectively. EDS analysis of $La_2Zr_2O_7$ film shows that Lanthanum, Zirconium and Oxygen are the detected elements and thus presence of lanthanum and zirconium in the ratio of 1:1 was confirmed.

The following figure 4 indicated the bar chat for thin film of Lanthanum doped Zirconium high-k Dielectric gate capacitor confirming the presence of $La_2Zr_2O_7$. The atomic weight percentage proves that the sample synthesized has a good stoichiometry with a good compromise of materials

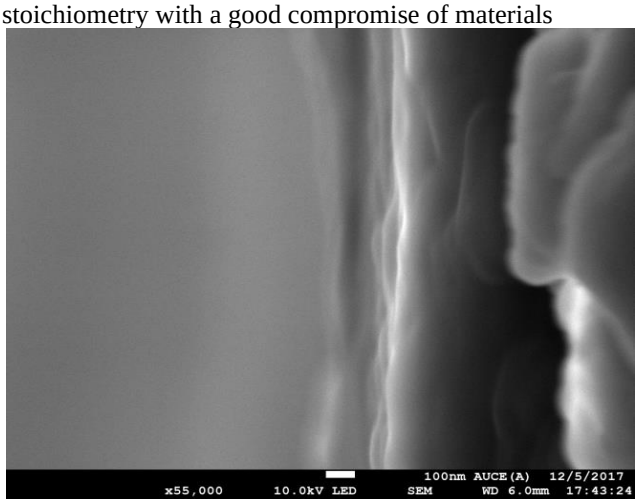

Figure 2: SEM images (a) Cross section, (b) surface of Lanthanum doped ZrO_2 films

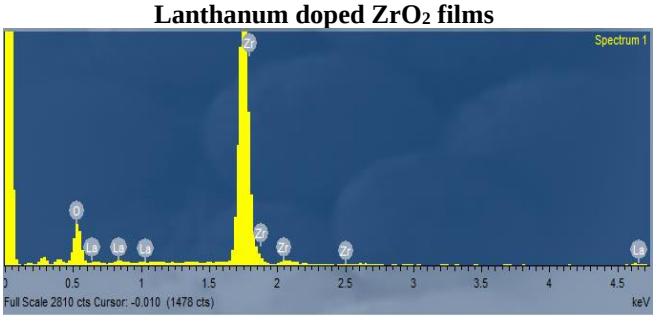

Figure 3: EDX Spectrum analysis of lanthanum doped zirconium oxide

Element	Weight%	Atomic%
OK	0.57	88.26
Zr L	0.21	5.65
La L	0.34	6.09
Totals	1.12	-

TABLE1: ELEMENTAL COMPOSITION OF $La_2Zr_2O_7$

Figures 3 and 4 describes the EDX spectrum obtained from FESEM [JEOL JSM-7100F] through OXFORD's EDX attachment connected to it. This is showing the presence of Zirconium, Oxygen and Lanthanum in various Quantities. Strength of each peak representing the quantity of the material. EDX data is collected at a working distance of 10mm, probe current of 8mA and the accelerating voltage maintained is 10KV.

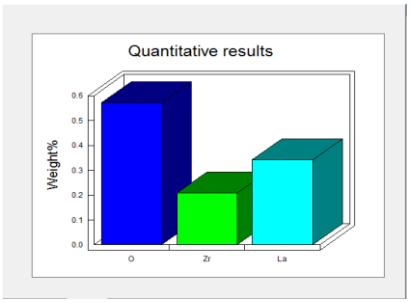

Figure 4: Bar chart of lanthanum and zirconium

Figure 5 shows the FTIR spectra of spin coated $La_2Zr_2O_7$ thin films. The band at 2560.43cm^{-1} indicates vibration of Zr-O bond. Ali Bahari [5] investigated ZrO_2 thin films deposited by sol-gel spin coating technique and obtained a similar type of microstructure. The band at 3700cm^{-1} corresponds to the vibration of the Si-O bond.

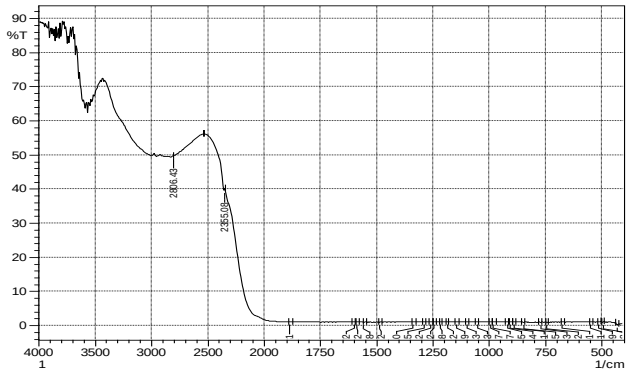

Figure.5: FTIR Spectra Of Spin Coated La2Zr2O7

Figure 6 indicates the AFM images of sol-gel spin coated Lanthanum Zirconate high-k dielectric thin film. The 3D image the layer shows a smooth surface with uniform distribution of material. Scan is performed at a random location in an area of 1µm x 1µm. These results are further correlated with electrical properties achieved in other characterizations. The film resulted in a surface area ratio of 4.31% representing large linearity of the deposited film. A random location is chosen from the scanned region to plot the line profile of the film. It shows an average variation of 6.5nm in the surface profile shown in Figure 8. Uniform thin film has resulted from the sol-gel spin coat technique at room temperature. The grain boundary results of AFM shown in Figure 8 supports the film linearity as it showed very fewer grains.

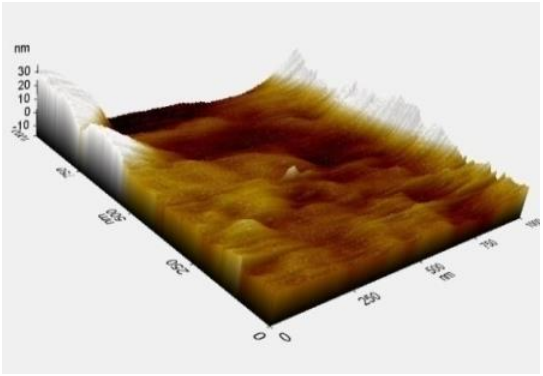

Figure.6: 3D Surface Image obtained from PARK XE-7 AFM

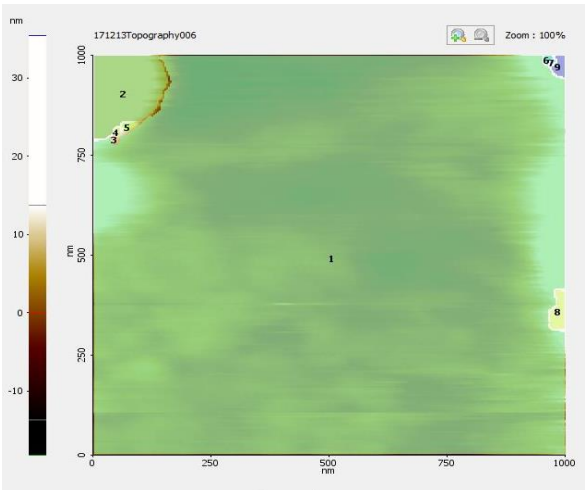

Figure 7. Grain boundaries on film surface

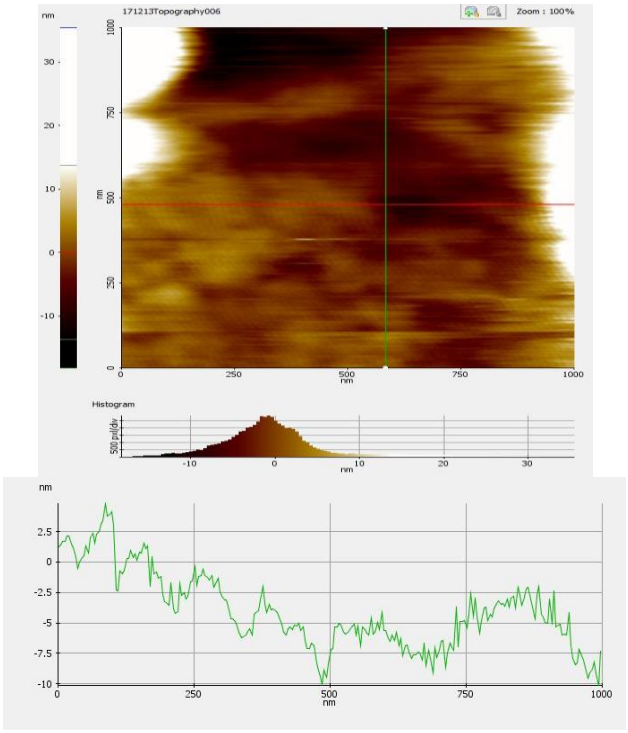

Figure.8: Line Profile of the deposited film

C-V measurements of Al/$La_2Zr_2O_7$/p-Si were carried out by using Agilent 1500A Semiconductor Device Analyzer and plotted in Figure 9. Three distinct regions of the C-V graph are accumulation, depletion and inversion which are clearly visible at the interface. The maximum capacitance was achieved in the accumulation for negative voltage. Because, the majority charge carriers (holes) of p-substrate will form a conduction layer at the interface. The maximum capacitance in this region was found to be 859pF,163pF and 2.74pF respectively for 1KHz, 100KHz and 1MHz applied frequencies respectively. This wide dispersion observed in the accumulation region is because of the substrate series resistance. Effect substrate series resistance will be more prominent as the frequency increases. The dielectric constant calculated with the values of C-V curve is 25 using equation 4. The curves were corrected for the calculation of dielectric constant (Wu *et al* 2006).

$$K = Ct_{ox}/(\varepsilon A) \quad (4)$$

where C is Accumulation capacitance, t_{ox} oxide thickness, ε is permittivity of free space and A is the area of the gate electrode. Equivalent Oxide thickness was measured using

$$EOT = (k_{sio2}.t_{ox})/k_x \quad (5)$$

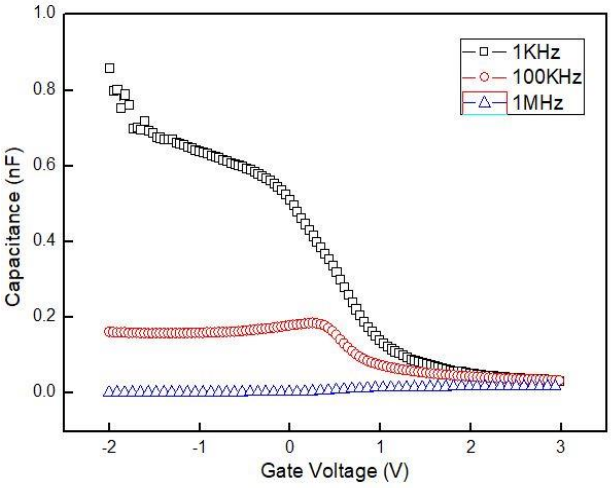

Figure 9: C-V Characteristics of spin coated $La_2Zr_2O_7$ film

where value of k_{sio2} is 3.9, t_{ox} is oxide layer thickness(44 nm) and k_x dielectric constant of $LaZrO_4$ layer fabricated (25); value of EOT calculated is 5.4 nm. A slight positive shift of 0.4V in the flatband voltage(Vfb) is observed. This is because of the negative charges present in the LZO thin film.

Effective oxide charges (Q_{eff}) located in $La_2Zr_2O_7$ thin film. Q_{eff} is given by

$$Q_{eff} = \frac{\Delta V_{FB} C_{OX}}{q A_G} \quad (6)$$

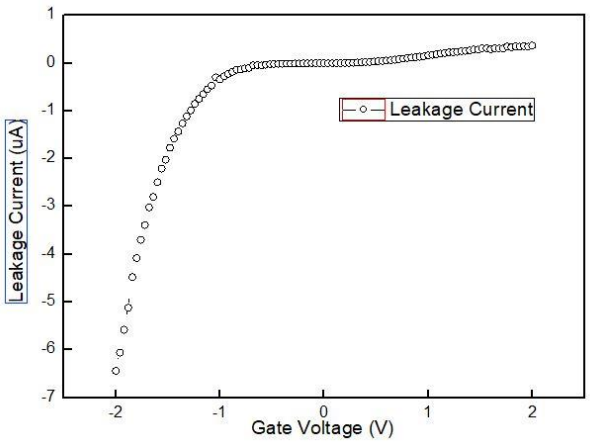

Figure 10: Leakage current Vs Gate voltage

which is calculated as $1.098x10^{15}Cm^{-12}$. A positive shift in flatband voltage V_{fb} can be identified from CV analysis. Maximum leakage current measured is 10nA; which is shown in figure 10. This value is lower than the reported leakage current..

IV. CONCLUSION

The main focus of this work was to study structural, topographical and electrical characteristics of high-k dielectric layer of Lanthanum zirconate ($La_2Zr_2O_7$). Initially, $La_2Zr_2O_7$ solution is prepared through sol gel method and it is deposited using spin coating method at 4000 rpm spun for 30Sec. The as prepared film's amorphous nature was confirmed by XRD analysis, the EDX report obtained is supporting stoichiometry of 1:1 nature of the prepared gel. The deposited film thickness is measured to be 31.5nm using ellipsometer. Calculated EOT is 5.4nm. Presence of uniform thin dielectric layer was confirmed by cross sectional SEM image. Aluminium is thermally evaporated using eBeam evaporation as a gate electrode. Thus an Al/$La_2Zr_2O_7$/p-Si/Al capacitor is formed; and analysed for AC and DC characteristics with Agilent 1500A Semiconductor Device Analyzer electrometer for C-V analysis and I-V analysis. The measured dielectric constant (k) is 25 and the gate leakage current measured to be 10nA. All the calculated values are tabulated in table number 2.

V. FUTURE SCOPE

The deposited films can be undertaken for annealing at various temperatures like 400^0C, 500^0C, and 600^0C to study the crystal orientation of the material (phase formation) which in turn changes the dielectric constant, leakage current and Equivalent Oxide thickness.

Physical Oxide layer thickness - tox	31.5nm
Dielectric Constant - k	25
Equivalent Oxide thickness (EOT)	5.4nm
Q_{eff}	$1.098x10^{15}Cm^{-12}$
Gate Leakage Current	10nA
V_{fb}	0.4V

TABLE 2: MEASURED / CALCULATED PARAMETERS OF THE GATE CAPACITOR

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