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Synthesis of La_2O_3 Nanoparticles using Glutaric acid and Propylene glycol for Future CMOS Applications

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Abstract: In This Research paper deals with the preliminary studies on synthesis and characterization of lanthanum oxide (La_2O_3) nanoparticles follow Pechini method but using different reactants (Glutaric acid and Propylene glycol). In future, leading manufacturer of integrated circuits recently announced to introduce hafnium and lanthanum based high- κ dielectrics in their next CMOS generations and also Lanthanum oxides exhibit some important applications such as luminescent devices, sensors, up-conversion materials, and catalytic fields. The research focuses now - called "higher-κ" materials with a dielectric constant of above 30 in order to satisfy the demands for future CMOS applications. FTIR spectroscopy was done for observing the presence of La-O bond. The synthesized lanthanum oxide nanoparticles were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) for morphological and crystalline size determination. In XRD analysis, the average particle size was shown near 18-28 and 36-46 nm respectively Ψ=1 and Ψ=1.30. Thermals analysis was done by TGA-DSC Analyzer.

Keywords: Lanthanum Oxide (La_2O_3), Glutaric Acid, Propylene glycol, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Analyzer, FTIR Spectroscopy.

1 Introduction

Lanthanum exhibits the diamagnetic properties [1]. La_2O_3 has the largest band gap of the rare earth oxides at Eg > 5 eV, while also having the lowest lattice energy, with very-high dielectric constant, ε = 27 pF/m [1-2]. Thus the use of these materials in the gated MOSFET devices will importantly reduce the leakage current density because of the larger band offset for electrons as compared to other high- κ materials [3-4]. The higher κ - gate dielectric materials can thus be introduced as the alternative gate dielectrics for future of CIMS (I: insulator) devices. Rare earth oxides have lately received extensive attention in relation to the continuous scaling down of Nano-volatile memories (NVMs). In particular, La_2O_3 films are promising for integration into future NVMs because they are expected to crystallize above 400^0C [5]. Synthesis of fine and uniform crystallite size, chemical homogeneity, high-purity, complex oxide formulations have been studied for the past few deeades. At present, there are many techniques available to synthesize complex oxide by Pechini method. Solution combustion method, precipitation from aqueous solutions, hydrothermal synthesis, sol-gel processing, microwave hydrothermal synthesis and reverse micelle method [6-10]. In order to satisfy the demand for higher integration density in microelectronics, the scaling of MOSFETs becomes more and more aggressive. A leading manufacturer of integrated circuits recently announced to introduce hafnium and lanthanum based high- κ dielectrics in their next CMOS new generation [11]. In this article we have demonstrated to synthesis of La_2O_3 at 600 ^{0}C temperature with using Solution combustion method for taking different amount of chelating agent and fuel (Glutaric acid and propylene glycol).

2 Experimental Details

2.1 Synthesis of La_2O_3 Nanoparticles Using Pechini Method

K. Bikshalu et al. have been reported synthesis of La_2O_3 Nanoparticles by using Pechini Method for Future CMOS Applications [12]. Here we used the modified Pechini method (Solution combustion method). In this Method, We used mixing of the Lanthanum Nitrate with a Chelating agent, a mix 1:1 and 1:30 of Glutaric acid and also used Propylene Glycol as Fuel. All reactant mix well and put it solution in muffle furnace at 600-800 ^{0}C for 4-5 hrs. After that reaction we get solid particles. It cool at room temperature and give sample for various analysis. All reagents used were mixed in Double Distilled water. The experiment was carried out with two Fuel to Oxidizer ratios i.e., Ψ=1 and Ψ=1.30.

$$\mathbf{4\ La(NO_3)_3 + 2\ C_5H_8O_4 + 2\ C_3H_8O_2 \rightarrow 2\ La_2O_{3(s)} + 16}$$

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$$H_2O_{(g)} + 16\ CO_{2(g)} + 6\ N_{2(g)}$$

Here, we describe the amount of Precursor Materials to be taken for modified Pechini Method of Synthesis (solution combustion method).

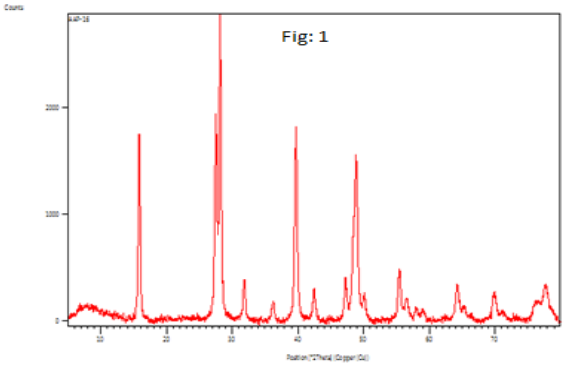
Table 1

Name of the sample	Composition			Weight of $La(NO_3)_3$ (gms)	Weight of Precursor Glutaric Acid $C_5H_8O_4$ (gms)
	Ψ	F1	F2		
La_2O_3	1	50	50	6	1.830762
La_2O_3	1.30	50	50	6	2.387408

3 Result and Discussions

3.1 X-Ray Diffractometer Analysis

Below fig. 1 shows that the XRD pattern of the La_2O_3 Nano particles Prepared by using Pechini method. This result indicates that the structure of the La_2O_3 nano particles is in pure Cubic phase when synthesized at Ψ=1 and slightly mixed hexagonal phase at Ψ=1.30. The extended peaks are representing the dimensions of the Nano range particles. Peaks are observed at 15°, 27°, 28°, 39° and 48° respectively corresponding to the (h k l) values of the peaks (1 0 1), (2 2 2), (3 0 0), (4 0 0), (4 0 0) and (6 2 2) respectively. The lattice parameters were in good agreement with JCPDS card number 04 - 0856 [13], having lattice parameters a=b=c=11.420 A° and α = β = γ = 90°. Fig. 1 and 2: XRD Patterns of La_2O_3 Particles Synthesized by Pechini Method for Ψ=1 and Ψ=1.30.



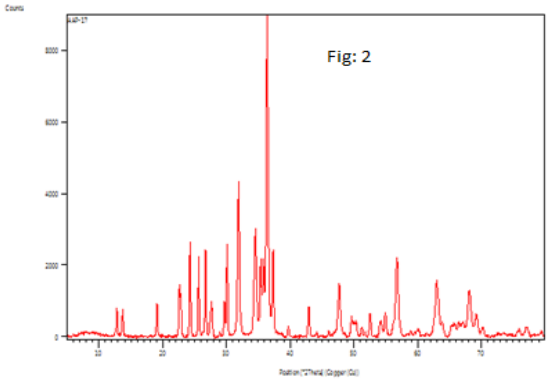


Fig: 1: XRD Patterns of La_2O_3 Particles Synthesized by Pechini Method for Ψ=1 and Ψ=1.30.

The lattice parameters were in good agreement with JCPDS card number 73-2141 [14], having lattice parameters a = b = 3.940 A° and c = 6.130 A° and α = β = 90° and γ =120°. The crystallite size is calculated by Debye-Scherer's formula,

$$D = \frac{K\lambda}{\beta\ Cos\theta} \quad \ldots\ldots(1)$$

Where, D is the average crystallite size of the particle, λ is the wavelength of the radiation, β is the full width at half maximum (FWHM) of the peak, θ is the Bragg's angle. The average crystallite sizes of samples synthesized by Pechini method are 18-28 nm for ψ = 1 and 36-46 nm for Ψ= 1.30.

Here, Calculate the strain and crystallite size of the sample are from the Williamson – Hall equation. The equation is as follows:

$$\beta\ Cos\theta = \frac{K\lambda}{t} + 2\varepsilon\ Sin\theta \quad \ldots\ldots(2)$$

Where β is the full width at half maximum (FWHM) of the XRD corresponding peaks, K is Debye-Scherer's constant, t is the crystallite size, λ is the wave length of the X-ray radiation, ε is the lattice strain and θ is the Bragg angle. In this process 2 sin θ is plotted against β cos θ, using a linear extrapolation to this plot, the intercept gives the crystallite

size and slope gives the strain (ε).

The average crystallite sizes were 18 nm, 36 nm and strain was 11.7 x 10^{-2}, 8 x 10^{-2} for Nano particles synthesized by Pechini method using ψ= 1, ψ= 1.30 respectively.

The lattice parameters of the hexagonal phase was measured by the below formula

$$\frac{1}{d^2} = \frac{4(h^2+hk+k^2)}{3a^2} + \frac{1}{c^2} \quad \ldots\ldots (3)$$

The measured values a=b=0.3819 nm and c=0.61196 nm were shows the similar values, which is from the XRD pattern.

3.2 Fourier Transform Infrared Spectroscopy

FTIR analysis has been done in the wave number range from 500 cm^{-1} to 4000 cm^{-1}. The samples have been admixed with KBr, thoroughly mixed and pelletized by pressing under sufficient pressure, before FTIR analysis. La_2O_3 nano particles were analysed with the BRUCKER (αT Model) FTIR spectrometer as shown in fig. 2.

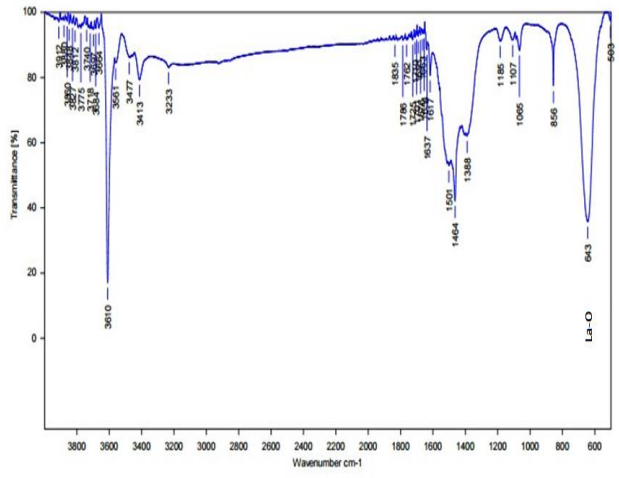


Fig 2: FTIR of La_2O_3

The very weak absorption bands at 3610 cm^{-1} is assigned to O-H stretching vibration of water molecules, its shows the presence of moisture in the sample. Very weak bending vibrations of water molecules appeared at 1501 cm^{-1}, C-C Stretching, Medium strong band positions in the range of 1388 cm^{-1} to 1501 cm^{-1} are possibly due to stretching vibrations of ions. The narrow absorption peak observed around at 1066 cm^{-1} can be ascribed to the C=O bonding. The medium to strong absorption bands at 643 cm^{-1} were because of La-O stretching. Hence the existence of above mentioned bands identify the presence of La_2O_3.

3.3 Thermo Gravimetric and Differential Thermal Analysis

The TGA analysis of La_2O_3 nano particles synthesized using Pechini Method were representing in fig. 3 respectively. The temperature range is 50^0C to 800^0C. The initial weight loss observed at 350^0C corresponds to that of loss of carbonaceous compounds. The peak observed after 350^0C corresponds to decomposition of covalently bond organic material, mainly carbon which was converted into CO_2 at the time of synthesis. From DSC Curves of La_2O_3 Nano particles the exothermic peak present in between 400^0C to 600^0C can be observed due to desorption and decomposition of carbonaceous materials.

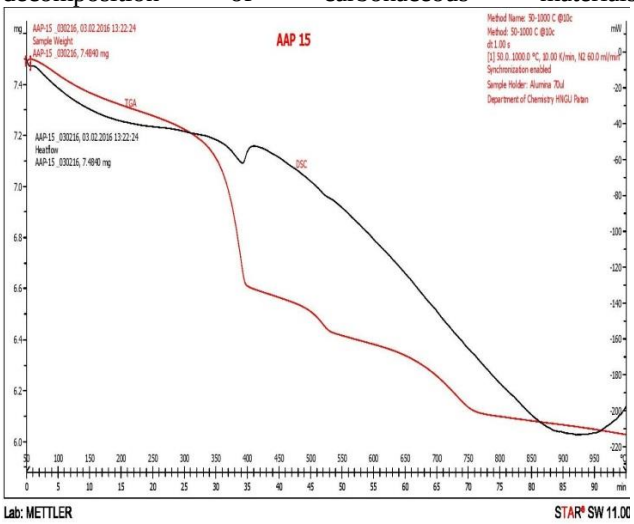


Fig. 3: TGA/DSC Curves of La_2O_3 Nanoparticles Synthesized Using Pechini Method The weight loss of the La^2O_3 Nano Particles are Shown in Above fig. 3 Shows the Weight Loss for the Sample Synthesized Using Pechini Method is 16.6%, 18.4% for at ψ= 1 and ψ= 1.30 respectively.

3.4 Scanning Electron Microscopy

The grain size, shape and surface properties like morphology were observed using SEM with different magnifications and also its shows diameter of particles. The SEM images of La_2O_3 nanoparticles which were prepared using Pechini Method at ψ= 1 and ψ= 1.30 respectively were shown in fig. 4 respectively.

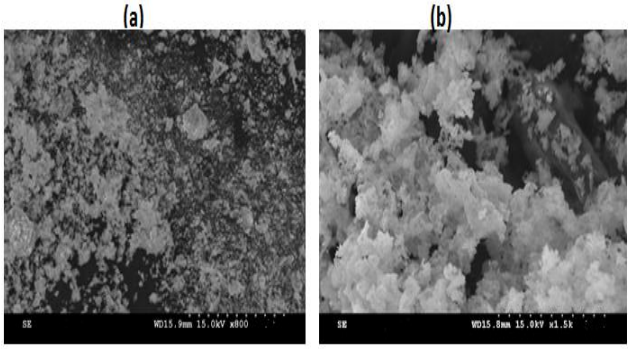


Fig. 4: Fig. 4: SEM Images of La_2O_3 Nanoparticles

Synthesized by Maintaining Using Pechini Method Using ψ= 1 and ψ= 1.30 respectively. It shows that, the particles are agglomerated and porous the size of the pores or porosity shows to be increased as the fuel to oxidizer ratio increased.

3.5 Transmission Electron Microscopy (TEM) Analysis

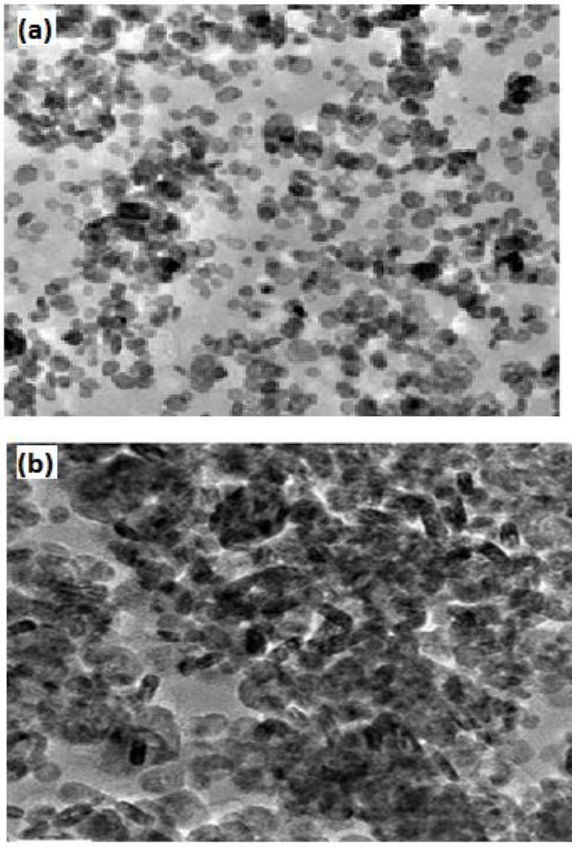


Fig 5: (a) and 5(b) TEM Images of La_2O_3 Nanoparticles Synthesized by Maintaining Using Pechini Method Using ψ= 1(a) and ψ= 1.30(b).

The TEM analysis show the agglomerated sample in Nano range. The below figure shows the TEM micrograph of the sample synthesized using Pechini Method. From TEM analysis, it has been found that the samples particles shapeless, due to severe agglomeration. But the particles are well below Nanometer range to conclude that the obtained particles are Nano particles.

4 Conclusion

La_2O_3 Nano powders have been successfully synthesized via Pechini method using different F/O ratios i.e., Ψ=1 and Ψ=1.30. The average crystallite sizes of samples synthesized by Pechini method are 18-28 nm for Ψ = 1 and 36-46 nm for Ψ= 1.30 and those are in good agreement with PSA results. Structural properties were examined by SEM reveals porous and fuzzy network of Nano crystalline La_2O_3. From the above characterizations we inferred that the sample obtained from higher F/O ratio was phase pure and more crystalline in nature..

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