Synthesis of La_2O_3 Nanoparticles by Pechini Method for Future CMOS Applications

[1]K. Bikshalu, [2]V.S.K. Reddy, [3]P.C.S. Reddy, [4]K.V. Rao

[1]Kakatiya University College of Engineering & Technology, Kakatiya University, Warangal, India
[2]Mallareddy College of Engineering and Technology, Secunderabad, India
[3]Jawaharlal Nehru Technological University Hyderabad, Hyderabad, India
[4]Centre for Nano Science and Technology, Institute of Science and Technology, Jawaharlal Nehru Technological University, Hyderabad, India

Abstract

Lanthanum oxides exhibit some important applications such as luminescent devices, sensors, up-conversion materials, and catalytic fields. The research focuses now on so- called "higher-κ" materials with a dielectric constant of 30 and above in order to satisfy the demands for future CMOS applications. This research paper deals with the preliminary studies on synthesis and characterization of lanthanum oxide or lanthana (La_2O_3) nano particles by Pechini method. The synthesized lanthanum oxide nano particles were characterized by X-ray diffraction (XRD) for crystal structure analysis, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) for morphological and particle size determination. The particle size histograms were studied with Particle size analyzer. Thermals analysis was done by TG-DTA Analyzer. FTIR spectroscopy was done for observing the presence of La-O bond.

Keywords

Lanthanum Oxide (La_2O_3) Nanoparticles, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Particle Size Analyzer, TG-DTA Analyzer and FTIR Specroscopy

I. Introduction

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 generation [1]. Lanthania exhibits the diamagnetic properties [2]. 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 [2, 3]. Thus the use of this material in the gated MOSFET devices will significantly reduce the leakage-current density because of the larger band offset for electrons as compared to other high-κ materials [5-6]. Synthesis of fine and uniform crystallite size, chemical homogeneity, high-purity, complex oxide formulations have been studied for the past few decades. At present, there are many techniques available to synthesize complex oxides by pechini method, sol-gel processing, precipitation from aqueous solutions, hydrothermal synthesis, microwave hydrothermal synthesis, reverse micelle method and combustion synthesis [7–11]. La_2O_3 was synthesized by chemical method namely Pechini Method.

II. Experimental Details

A. Synthesis of La_2O_3 using Pechini method

La_2O_3 which is considered as promising substitute for present SiO_2 has been synthesized by modified Pechini method at low temperature. The method involved the mixing of the Lanthanum Nitrate with a Chelating agent, a mix 1:1 of Citric acid. All reagents used were mixed in double distilled water. The experiment was carried out with two Fuel to Oxidizer ratios i.e., Ψ=1.25 and Ψ=1 as proposed by K. V. Rao et al. [12]. The balanced equation used for calculating the amount of precursor materials for complete combustion is given below as proposed by Jain et al. [13]

$14LaN_3O_9 + 7.5C_6H_8O_7 + 7.5C_2H_6O_2 \rightarrow 7La_2O_3(s) + 33.75H_2O(g) + 22.5CO_2(g) + 40.5N_2(g)$

Table 1: Table Representing the Amounts of Precursor Materials to be Taken for Pechini Method of Synthesis

Name of The Sample	Composition			Weight of LaN_3O_9 (gms)	Weight of Fuels
	Ψ	F1	F2		Citric Acid $C_6H_8O_7$ (gms)
La_2O_3	1	50	50	5	1.299882223
La_2O_3	1.25	50	50	5	1.624852778

III. Results & Discussions

A. X-Ray Diffractometer Analysis

Below fig. 1 shows that the XRD pattern of the La_2O_3 Nano particles obtained using Pechini Method. This result shows that the structure of the La_2O_3 nano particles is in pure Cubic phase when synthesized at Ψ=1 and partially mixed hexagonal phase at Ψ=1.25.The extended peaks are representing the dimensions of the Nano range particles. Peaks are observed at 23°, 28°, 32°, 40°, 48° and 54° 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 [14], having lattice parameters a=b=c=11.420A° and α = β = γ = 90°

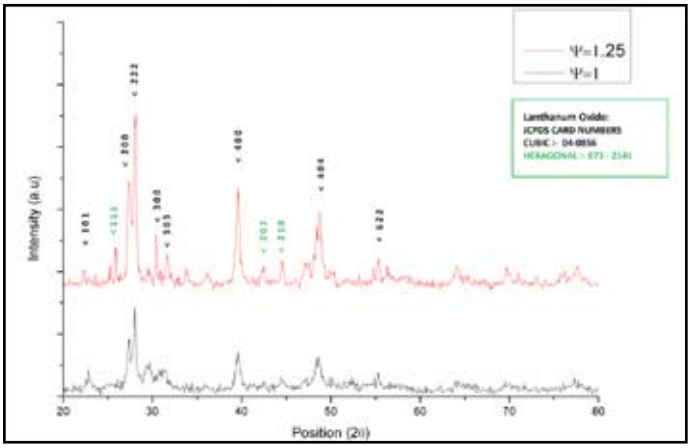

Fig. 1: XRD Patterns of La_2O_3 Particles Synthesized by Pechini Method for Ψ=1 and Ψ=1.25

The lattice parameters were in good agreement with JCPDS card number 73-2141 [15], 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 – Scherrer's formula,

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

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 nm for ψ= 1 and 30 nm for Ψ= 1.25.

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

$$\beta \cos\theta = \frac{K\lambda}{t} + 2\varepsilon \sin\theta \quad (2)$$

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, 30 nm and strain was 11.7 x 10^{-2}, 8 x 10^{-2} for Nano particles synthesized by Pechini method using ψ= 1, ψ= 1.25 respectively.

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

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

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

B. Particle Size Analyzer Analysis

The as-prepared La_2O_3 nanoparticles were ultra-sonicated and suspended in the ethanol solution. The sizes of the agglomerated colloids in the suspensions were estimated using particle size analyser. From the analysis of Historams and average Particle size of the samples, we can infer that the results are in coherence with XRD results, that is, the average particle size is nearerly comparable to the average crystallite size.

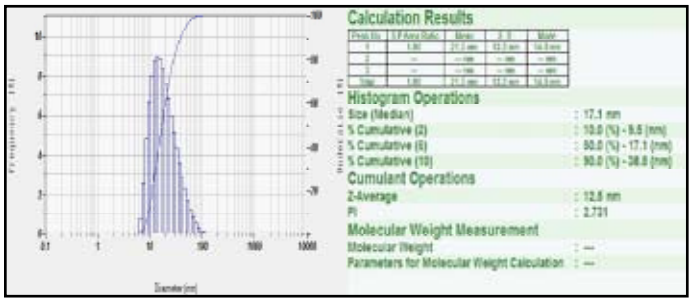

Fig. 2: Particle Size Distribution and Average Particle Size La_2O_3 Nano Particles Synthesized Using Calculated Using ψ= 1 in Pechini Method

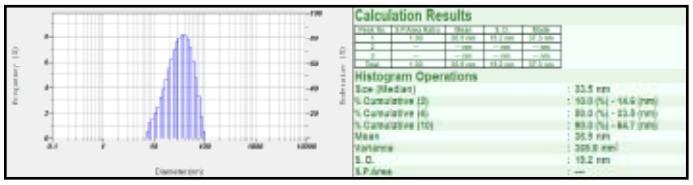

Fig. 3: Particle Size Distribution and Average Particle Size La_2O_3 Nano Particles Synthesized Using Calculated Using ψ = 1.25 in Pechini Method

C. Scanning Electron Microscopy

The grain size, shape and surface properties like morphology were observed using SEM with different magnifications. The SEM images of La_2O_3 nanoparticles which were prepared using using Pechini Method at ψ= 1 and ψ= 1.25 respectively were shown in fig. 4 respectively.

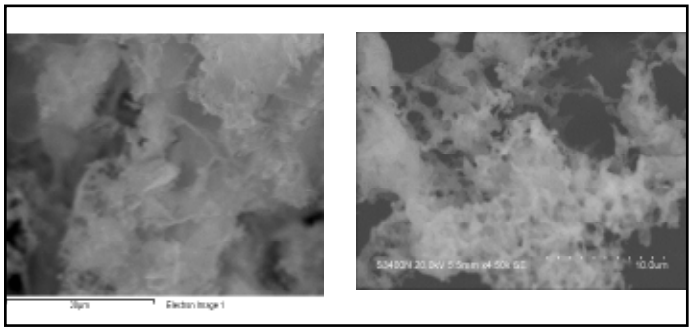

Fig. 4: SEM Images of La_2O_3 Nanoparticles Synthesized by Maintaining Using Pechini Method Using ψ= 1 and ψ= 1.25 Respectively

It shows that, the particles are agglomerated and porous. The size of the pores or porosity sees to be increased as the fuel to oxidizer ratio increased.

D. Energy Dispersive X-ray Spectrometry

The elemental composition percentages of Nano powders were obtained from EDX pattern. The EDX spectrums of La_2O_3 Nano particles synthesized La_2O_3 nanoparticles which were prepared using Mixture of Fuels Method and using Pechini Method at ψ= 1 and ψ= 1.25 respectively were shown in fig. 5. Respectively.

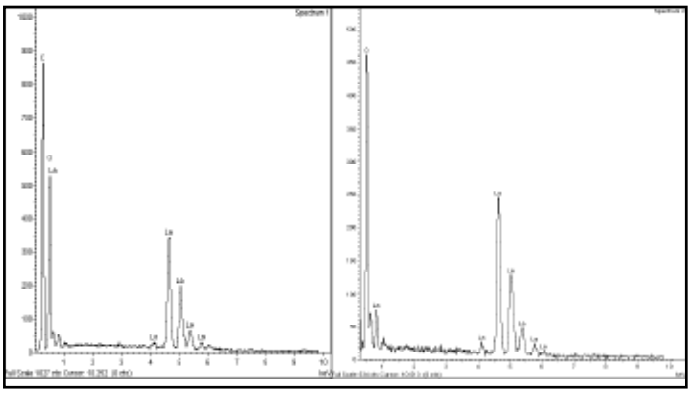

Fig. 5: EDX Pattern of La_2O_3 Nanoparticles by Pechini Method

Table 2: Elemental Compositions of La_2O_3 Nanoparticles by Pechini Method

Elements	Weight Percentage of Sample ψ= 1	Weight Percentage of Sample ψ= 1.25
Oxygen	28.82 %	35.08%
Lanthanum	29.94 %	64.92%
Carbon	41.24%	0%
Total	100.00 %	100.00 %

From the above table it can be inferred that the La_2O_3 nano particles synthesized at constant using Mixture of Fuels Method shows optimum percentages of La and O compared to that of using Pechini Method.

E. Fourier Transform Infrared Spectroscopy

FTIR analysis has been done in the wave number range from 450 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 PERKIN FTIR spectrometer as shown in fig. 6.

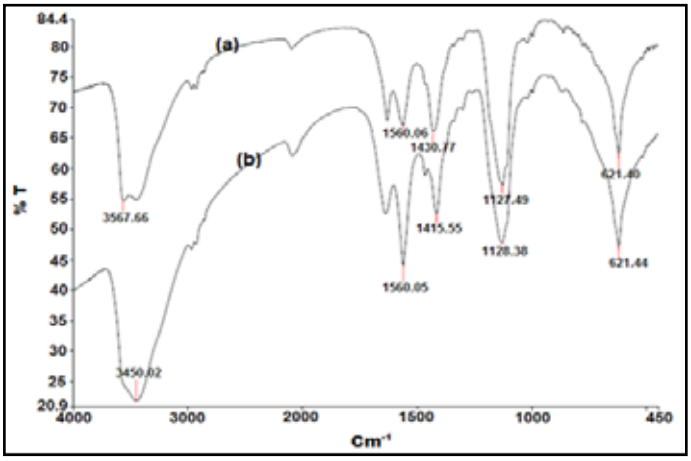

Fig. 6: FTIR Spectrum of La_2O_3 Nanoparticles Synthesized Using Pechini Method

The very weak absorption bands at 3567.66 cm^{-1} is assigned to O-H stretching vibration of water molecules, due to presence of moisture in the sample. Very weak bending vibrations of water molecules appeared at 1560.06 cm^{-1}, C-C Stretching, Medium strong band positions in the range of 1430 cm^{-1} to 1560 cm^{-1} are possibly due to stretching vibrations of ions. The narrow absorption peak observed around at 1120 cm^{-1} can be ascribed to the C=O bonding. The medium to strong absorption bands at 620 cm^{-1} were because of La-O stretching. Hence the existence of above mentioned bands identify the presence of La_2O_3.

F. Thermo Gravimetric and Differential Thermal Analysis

The TG analysis of La_2O_3 nano particles synthesized using Pechini Method were representing in fig. 7 (a) & (b) respectively. The temperature range is 50°C to 800°C. The initial weight loss observed at 450°C corresponds to that of loss of carbonaceous compounds. The peak observed after 450°C corresponds to decomposition of covalently bond organic material, mainly carbon which was converted into CO_2 at the time of synthesis. From DTA curves of La_2O_3 nano particles the exothermic peak present in between 500°C to 600°C can be observed due to desorption and decomposition of carbonaceous materials.

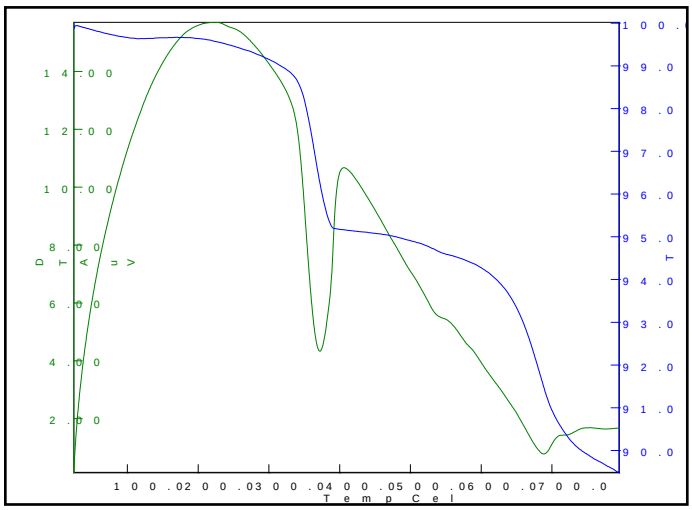

Fig. 7(a) and (b): TG/DTA Curves of La_2O_3 Nanoparticles Synthesized Using Pechini Method

The weight loss of the La_2O_3 Nano Particles are Shown in Above figs. 7 (a) and (b) Shows the Weight Loss for the Sample Synthesized Using Pechini Method is 19.5%, 17.1% for at ψ= 1 and ψ= 1.25 respectively.

E. Transmission Electron Microscopy (TEM) Analysis

The TEM analysis show the agglomerated sample in Nano range. The below figure shows the TEM micrograph of the sample synthesized using Pechini Method.

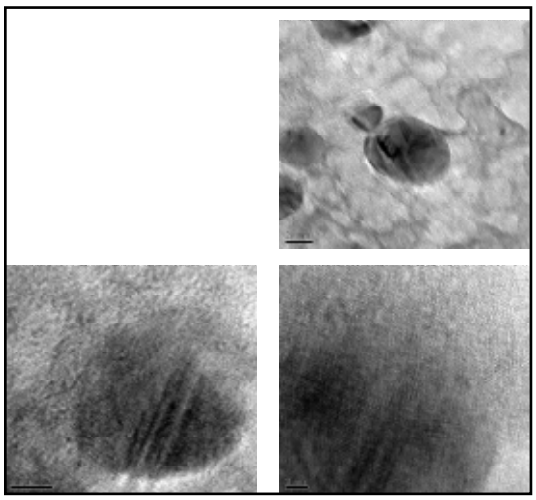

Fig. 8: TEM Micrographs at Different Magnifications of Pechini Method Sample

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.

IV. Conclusion

La_2O_3 Nano powders have been successfully synthesized via Pechini method using different F/O ratios i.e., Ψ=1 and Ψ=1.25. The average crystallite sizes of samples synthesized by Pechini method are 18 nm for Ψ = 1 and 30 nm for Ψ= 1.25 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.

References

[1] [Online] Available: http://www.intel.com/technology/silicon/45nmtechnology.htm.

[2] Zhang N. et al.,"Materials Chemistry and Physics", 2009. 114. pp. 160–167.

[3] Bedoya C. et al.,"Chemical Vapor Deposition. 2006. 12. pp. 46–53.

[4] Hattori T. et al.,"Microelectronic Engineering", 2004. 72. pp. 283–287.

[5] Wu Y.H. et al. IEEE Electron Device Letters. 2000. 21(7), pp. 341–343p.

[6] Yamada H. et al. Journal of the Electrochemical Society. 2003. 150(8). pp. G429–G435.

[7] Yi X. et al.,"Materials Science and Engineering", B. 1995. 34. L1– L3p.

[8] Kim W.C. et al. Journal of Magnetism and Magnetic Materials. 2001. 226. 1418–1420p.

[9] Wang H.W. et al. Journal of Magnetism and Magnetic Materials. 2004. 270. 230–236p.

[10] Krishnaveni T. et al. Journal of Materials Science. 2006.4. pp. 1471–1474.

[11] M. Pechini, U.S. Patent no. 3.330.697 (1967).

[12] K.Venkateswara Rao, C.S. Sunandana, J. Mat. Sci., 43, pp. 146–154, 2008.

[13] S.R.Jain, K.C. Adiga, V.R. Pai Vernicar, Comb. Flame 40: 71-79(1981)

[14] Powder diffraction file; Card no 04-0856 Joint committee on Powder Diffraction Standards (JCPDS), Pennsylvania, 1988.

[15] Powder diffraction file; Card no 73-2141 Joint committee on Powder Diffraction Standards (JCPDS), Pennsylvania, 1988.

[16] D. Berger, N. Van Landschoot, C. Ionica, F. Papa, V. Fruth,"Synthesis of pure and doped lanthanum cobalaite by the combustion method", J. Optoelectron. Adv. Mater., 5 [3] (2003) 719.

[17] Lachezar Radev et al "Sol-gel synthesis and structure of La_2O_3–CoO–SiO_2 powders", Processing and Application of Ceramics 2 [2] (2008) pp. 103–108.