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Conditional Optimization of Solution Combustion Synthesis for Pioneered La_2O_3 Nanostructures to Application as Future CMOS and NVMS Generations

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Abstract

The Present Research paper discuses the synthesis and characterization of lanthanum oxide (La_2O_3) nanoparticles by using a very low cost Solution Combustion Method. We are using Acetamide as fuel in present method. In future, most of manufacturer of integrated circuits recently announced and introduced hafnium and lanthanum based high-κ dielectrics materials in their next CMOS generations and also Lanthanum oxides show some important applications such as luminescent devices, sensors, up-conversion materials, and catalytic fields. Now a day's researches are focuses on "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) with EDAX spectra and Transmission Electron Microscopy (TEM) for morphological, percentage of metal and particle size determination. In XRD analysis, the average particle size was shown near 42 nm. Thermals analysis was done by TGA-DSC analyzer.

Keywords

Nanoparticles, Lanthanum Oxide, X-Ray Diffraction, SEM, FTIR, TEM

1. Introduction

Lanthanum exhibited the good diamagnetic properties and also having the largest band gap $E_g > 5$ eV in the rare earth group oxides. It having very highly dielectric constant, $\varepsilon = 27$ pF/m with the lowest lattice energy [1] [2]. La_2O_3 has

p-type semiconducting properties there for its resistivity decreases at high temperatures [3]. Thus the use of this material in the gated MOSFET devices will extensively reduce the leakage current density because of the larger band offset for electrons as compared to other high-κ materials [4] [5]. 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 oxide by Pechini method [6], Solution combustion method [7], and precipitation from aqueous solutions hydrothermal synthesis [8], sol-gel processing [9], microwave hydrothermal synthesis [10] [11], reverse micelle method [12] and solution combustion method using different fuel and chelating agent like Propylene glycol and Glutaric acid [13]. In this work satisfying the demand for higher integration density in microelectronics, the scaling of MOSFETs becomes more and more aggressive. In future, a leading manufacturer of integrated circuits recently announced to introduce hafnium and lanthanum based high-κ dielectrics in their next CMOS new generation [6].

In this article we have demonstrated to synthesis of La_2O_3 by at 600˚C temperature with using Solution combustion method for taking amount $\Psi = 1$ of Acetamide as fuel. It is very easy method for Preparation of La_2O_3 Nanoparticles. Synthesized La_2O_3 nanoparticles were characterized by various analytical techniques.

2. Materials and Method

2.1. Materials

Analytical grade Lanthanum nitrate and acetamide were used as received from the *s.d fine* chemicals (India). All reaction was performed using double distilled water.

2.2. Synthesis of La_2O_3 Nanoparticles by Using Solution Combustion Method

K. Bikshalu *et al.* have been reported synthesis of La_2O_3 Nanoparticles by using Pechini Method for Future CMOS Applications [14] and A. Pathan *et al.* have been reported Synthesis of La_2O_3 Nanoparticles using Glutaric acid and Propylene glycol for Future CMOS Applications [13]. Here, we used Acetamide as fuel. In this Method, We used mixing of the Lanthanum Nitrate with Acetamide as Fuel. Both reactant mix well and put it solution in muffle furnace at 600˚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 ratios *i.e.*, $\Psi = 1$.

$$4La(NO_3)_3 + 2CH_3CONH_2 \rightarrow 2La_2O_{3(s)} + 2NH_{3(g)} + 2H_2O + 4CO_{2(g)} + 11NO_{2(g)} + N_{2(g)}$$

Here, we are describing the amount of Precursor (fuel) Materials to be taken for in this synthesis (**Figure 1**).

Name of the sample	Composition			Weight of $La(NO_3)_3$ (gms)	Weight of Precursor
	Ψ	F_1	F_2		Acetamide C_2H_5NO (gms)
La_2O_3	1	50	50	6	1.630332

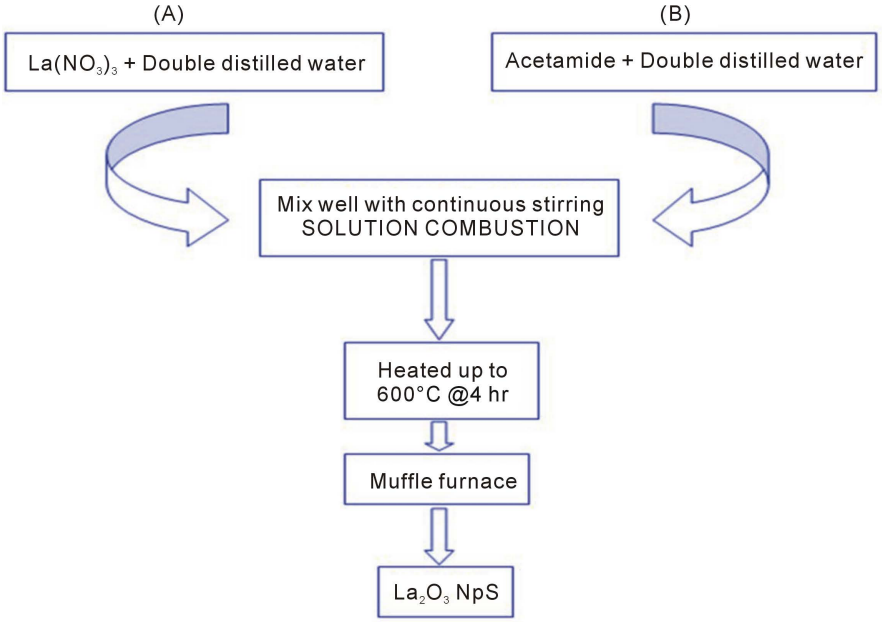

Figure 1. Schematic diagram of solution combustion method for La_2O_3 Nanoparticles.

3. Result and Discussions

3.1. X-Ray Diffractrometer Analysis

Figure 2 shows that the XRD pattern of the La_2O_3 Nanoparticles Prepared by using Solution Combustion method. This result indicates that the structure of the La_2O_3 Nanoparticles is in pure Cubic phase when synthesized at Ψ = 1. The extended peaks are representing the dimensions of the Nano range particles. Peaks are observed at 24.32˚, 31.90˚, 36.38˚, 47.71˚ and 56.79˚ respectively corresponding to the (*h k l*) values of the peaks (1 0 0), (1 1 0), (1 1 0), (2 0 0) and (2 1 0) respectively. The lattice parameters were in good agreement with JCPDS card number 04 - 0856 [15], having lattice parameters $a = b = c = 3.6180$ Å and $\alpha = \beta = \gamma = 90^\circ$. **Figure 2**: XRD Patterns of La_2O_3 Particles Synthesized by Solution Combustion method for Ψ = 1.

The crystallite size is calculated by Debye-Scherer's formula,

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

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 this method is 42 nm for ψ = 1.

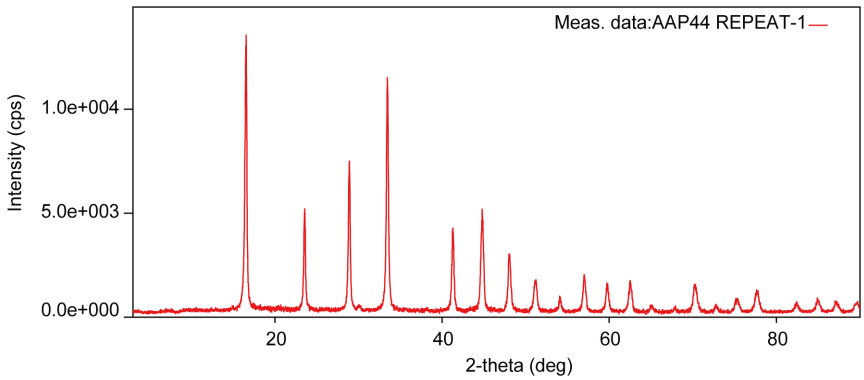

Figure 2. XRD patterns of La_2O_3 particles synthesized by this method for Ψ = 1.

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

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

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 $2\sin\theta$ is plotted against $\beta\cos\theta$, using a linear extrapolation to this plot, the intercept gives the crystallite size and slope gives the strain (ε). The average crystallite sizes were 42 nm and strain was 0.0028 for Nano particles synthesized by this method using ψ = 1. The lattice parameters of the hexagonal phase was measured by the below formula.

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

The measured values $a = b = 0.3919$ nm and $c = 0.63196$ 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 **Figure 3**.

The very weak absorption bands at 3607 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 1636 cm^{-1}, C-C Stretching, Medium strong band positions in the range of 1396 cm^{-1} to 1464 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 653 cm^{-1} were because of La-O stretching. Hence the existence of above mentioned bands identify the presence of La_2O_3.

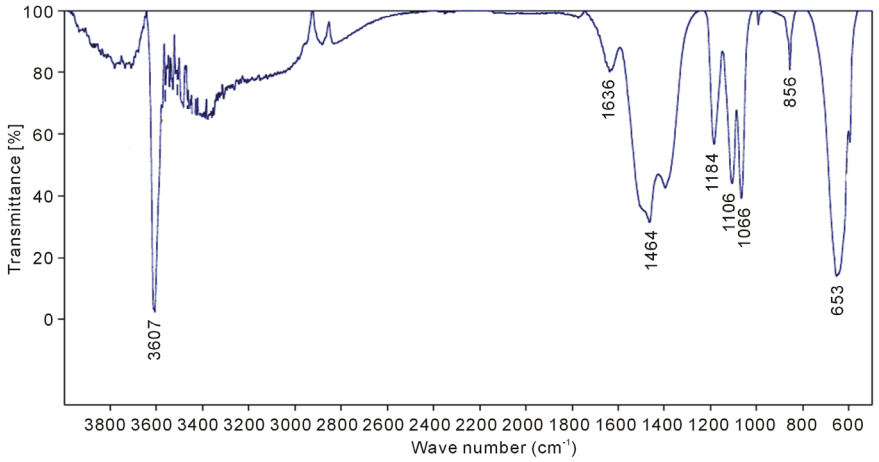

Figure 3. IR spectra of La_2O_3 Nanoparticles.

3.3. Thermo Gravimetric and Differential Thermal Analysis

The TGA analysis of La_2O_3 Nano particles synthesized using this Method was representing in **Figure 4** respectively. The temperature range is 50˚C to 1000˚C. The initial weight loss observed at 350˚C to 500˚C corresponds to that of loss of carbonaceous compounds. The peak observed after 450˚C to 550˚C 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 640˚C to 810˚C can be observed due to desorption and decomposition of carbonaceous materials.

The weight loss of the La_2O_3 Nano Particles are Shown in Above **Figure 4** Shows the Weight Loss for the Sample Synthesized this Method is 14.006% for at $\psi = 1$.

3.4. Scanning Electron Microscopy and EDAX

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 this Method at $\psi = 1$ was shown in **Figure 5** respectively.

EDAX spectrum of La_2O_3 shows the peaks for lanthanum and oxygen elements indicating the formation of La_2O_3 nanoparticles. Peak indexing of the elements are oxygen 0.52 keV and lanthanum 4.71 keV. The compositions in mass percentage of the elements are oxygen 35.15% and lanthanum 64.42%. The observed composition matches with the theoretically calculated composition (**Figure 6**).

3.5. 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 this Method.

From TEM analysis, it has been found that the samples particles not good in crystal due to severe agglomeration. But the particles are well below Nanometer range to conclude that the obtained particles are Nano particles (**Figure 7**).

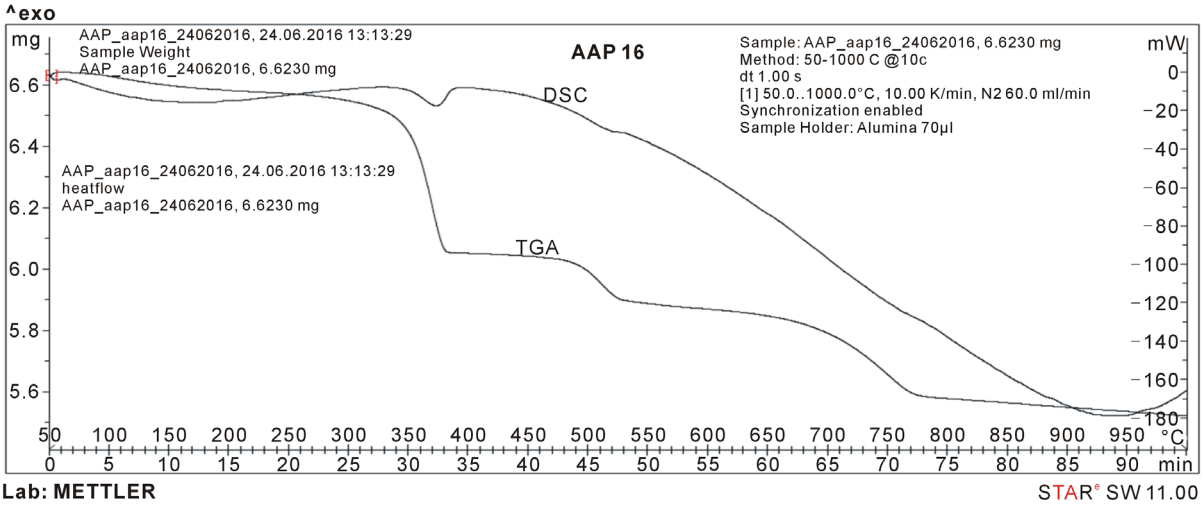

Figure 4. TGA/DSC curves of La_2O_3 Nanoparticles.

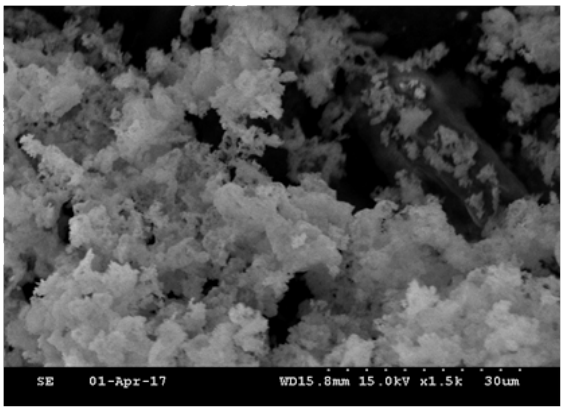

Figure 5. SEM images of La_2O_3 Nanoparticles synthesized by maintaining carried out this method using $\psi = 1$. It shows that, the particles are agglomerated and porous properties. It show that the size of the porous or porosity shows to be increased as the fuel to oxidizer ratio increased.

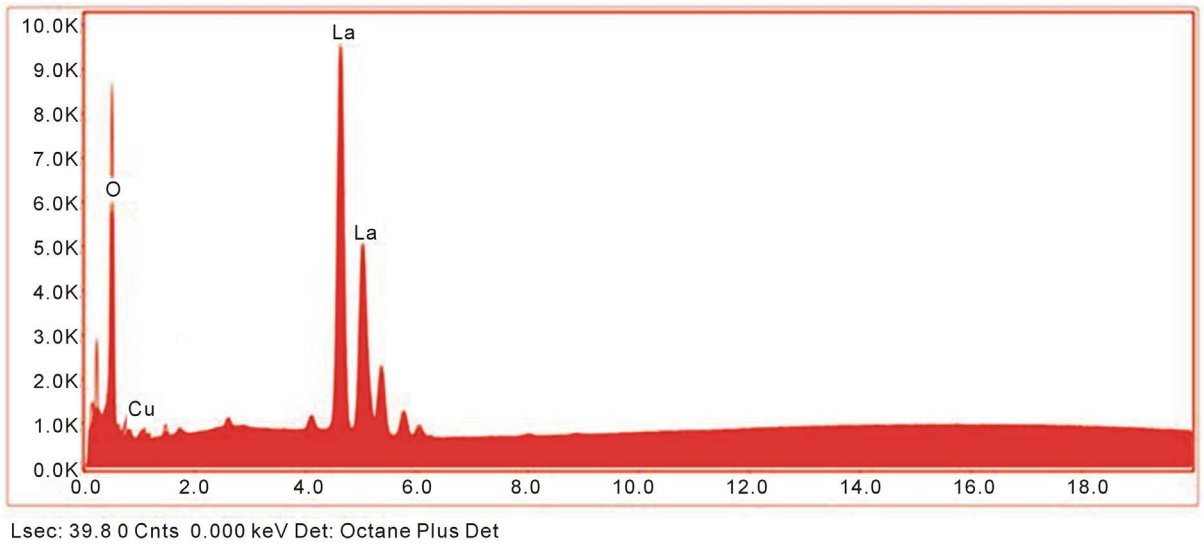

Figure 6. EDAX spectrum of La_2O_3 Nanoparticles.

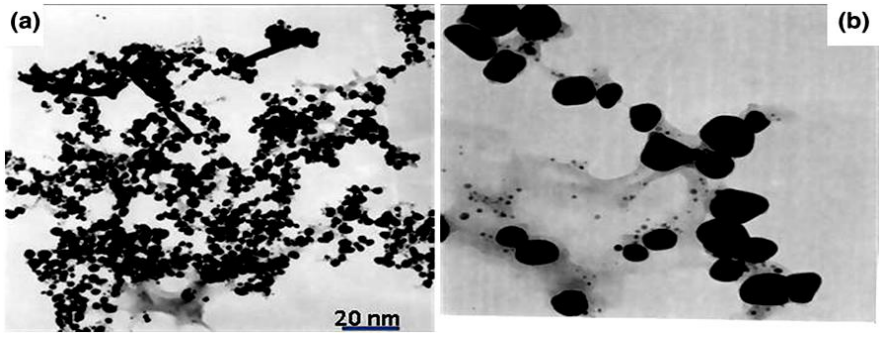

Figure 7. (a) and (b) TEM images of La_2O_3 Nanoparticles synthesized by maintaining carried out this method using $\psi = 1$.

4. Conclusion

La_2O_3 Nano powders have been successfully synthesized by very low cost Solution Combustion method using Acetamide as fuel and taking F/O ratios *i.e.*, $\Psi = 1$. The average crystallite sizes of samples synthesized by using this method are 42 nm for $\Psi = 1$. From FTIR analysis, it shows good formation of La_2O_3 NPS for La-O band at 653 cm^{-1} and TGA/DSC reveal the effective weight loss of materials at 350˚C and exothermic peak of La_2O_3 at 800˚C. Structural properties were examined by SEM reveals porous and porosity was good in network of Nano crystalline La_2O_3. The EDAX shows the purity and percentage of the La_2O_3 nanoparticles. From the above TEM characterizations we inferred that the sample obtained from higher F/O ratio was phase pure and more crystalline in nature.

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