La$_2$O$_3$ Nano powders by mixture of fuels approach through chemical combustion for dielectric studies

G Nithesh Sharma$^1$, K Venkateswara Rao$^1$, V Sesha Sai Kumar$^1$, Ch Shilpa Chakra$^1$, V Rajendar$^1$, P Ranjith reddy$^2$

$^1$Center for Nano Science and Technology, IST, JNTUH, India-500085.
$^2$Department of Physics, College of Engineering JNTUH, India-500085.

Presenting and Corresponding author: Mobile: +91 9290558256
Email: nithesh.sharma530@gmail.com

Abstract: La$_2$O$_3$ which is considered as a promising substitute for present SiO$_2$ Gate oxide material in CMOS devices has been synthesized by mixture of fuel method. The method involves the mixing of the Lanthanum Nitrate with, mixture 1:1 of Urea and Glycine. The fuel to oxidizer ratio ($\psi$) has been maintained as 1.25. The powders were studied by several physical characterization techniques such as X-ray diffraction (XRD), Thermo gravimetric analysis (TGA) and Differential Thermal analysis (DTA) and dielectric properties have been studied using LCR meter. Surface morphology has been studied by SEM. Particle size has been analysed using Particle analyzer.

1. Introduction: MOSFETs have become ubiquitous with their wide range of applications spanning over almost all fields starting from automobiles to communications. Miniaturization has played key role in this. Further scaling of transistors requires reducing Gate oxide layer thickness making SiO$_2$ Gate dielectric layer becoming so thin (1.4nm)[1]. This arises new issues such as Oxide breakdown, leakage current and light atom penetration through the film. Introducing physically thicker high-k dielectric materials while maintaining optimum value of capacitance needed for controlling the current flow in the channel, can resolve the afore mentioned problems[2].La$_2$ based dielectrics are considered as a promising substitute for present SiO$_2$ owing to their high dielectric constant(k~30) and better crystallization temperatures than other rare earth oxides[3-5]. La, has been prepared so far by several physical and chemical approaches such as sol-gel method [6], reverse micelle synthesis techniques [7], sputtering, SHS, Thermal decomposition [8] etc. In the present work, La, has been synthesized by mixture of fuel method through chemical combustion.

2. Experimental Procedure:

Lanthanum Oxide nano powders have been synthesized using Chemical Combustion by employing mixture of fuels approach. The initial precursor materials taken were Lanthanum nitrate (LaN$_3$O$_9$) by Merck Ltd., Urea (CH$_4$N$_2$O) by Finar and Glycine (C$_2$H$_5$NO$_2$) by Merck. All reagents used were of Analytical grade and mixed in double distilled water. Here LaN$_3$O$_9$ acts as Oxidizer and Urea, Glycine as Fuels. The Fuel to Oxidizer ratio has been maintained as 1 ($\psi = 1.25$). The fuels Urea and Glycine were taken in equimolar ratio. Stoichiometric amounts of reagents were taken as proposed by Jain et.al.[9]. $\psi$ value has been chosen such that the there exists a trade-off between combustion temperature and particle size since $\psi$ value has shown to have effect on the microstructure [10]. The balanced equation obtained for the above combustion is as follows.

$$6\text{LaN}_3\text{O}_9 + 7.5\text{CH}_4\text{N}_2\text{O} + 7.5\text{C}_2\text{H}_5\text{NO}_2 \rightarrow 3\text{La}_2\text{O}_3 + 33.75\text{H}_2\text{O} + 22.5\text{CO}_2 + 40.5\text{N}_2$$
The calculated amounts of reagents were weighed precisely using electronic weighing balance, Shimadzu, Japan. Lanthanum nitrate precursor was taken in a Borosilicate flask and double distilled water was added to it. Calculated amounts of Urea and Glycine were added to the beaker containing solution of La$_3$O$_9$ and stirred for 15 min using magnetic stirrer till clear solution is observed.

The clear solution comprising La$_3$O$_9$, CH$_4$N$_2$O and C$_2$H$_5$N$_2$O was kept on hot plate. Initially the solution started boiling, followed by frothing, fumes and instead of flames smoldering occurred indicating that combustion has been completed leaving behind white colored deposit. The sample was calcinated to 600°C for 1 hour in a muffle furnace for removing any carbonaceous impurity present in the as prepared sample. The samples Before calcination and After calcination were characterized using Particle Analyzer for average particle size. The crystal structure and crystallite size of the synthesized powder was determined by X-ray diffractometer (XRD), the X-ray diffraction analysis revealed that the synthesized La$_2$O$_3$ Nano powder has the perovskite structure having average crystallite size 30nm. Morphological studies were carried out by scanning electron microscopy (SEM), Energy Dispersive X-ray analysis (EDAX) was investigated by Scanning electron microscopy (SEM) coupled with an energy dispersive X-ray spectroscopy (EDAX). The phase purity of the Nano powder has been confirmed using differential thermal analysis (DTA), thermo gravimetric analysis (TGA) and the particle size was estimated from Nanoparticle size analyser.

3. RESULTS AND DISCUSSION

3.1 X-Ray diffraction (XRD):

X-Ray powder diffractograms (XRD) were recorded by means of a Bruker’s MODEL D8 Advance with Ni filtered Cu Kα radiation (λ=1.54056Å). The device operating controls were maintained at 40KV, 30 mA and scan rate of 1° per minute. The powder sample was packed into the depression in a sample holder mounted in a horizontal position. The intensity(I/I$_0$) versus d-spacing graphs representing diffraction pattern have shown resemblance with reported values.

![XRD diffraction patterns of La$_2$O$_3$ powders Obtained Before and After calcination.](image_url)

Figure 1. XRD diffraction patterns of La$_2$O$_3$ powders Obtained Before and After calcination.

The crystallite size was calculated using the scherrer’s formula [11],

\[ D = \frac{Kλ}{βcosθ} \]

where

- \( D \) is the crystallite size
- \( K \) is the shape factor (0.89 for a cubic structure)
- \( λ \) is the wavelength of the X-ray (1.54056 Å for Cu Kα)
- \( β \) is the full width at half maximum (FWHM) of the diffraction line
- \( θ \) is the Bragg's angle
\[ d = \frac{0.9\lambda}{\beta \cos \theta} \]  

(1)

Where \( d \) is the crystallize size, \( \lambda \) is the wavelength of incident X-ray, \( \beta \) is full width at half maximum of diffracted peak and \( \theta \) is diffracted angle.

| S.No. | Intensity | d-spacing [Å] | 2Theta [°] | h k l |
|-------|-----------|---------------|------------|------|
| 1     | 34        | 3.41000       | 26.111     | 1 0 0 |
| 2     | 31        | 3.06300       | 29.131     | 0 0 2 |
| 3     | 100       | 2.98000       | 29.961     | 1 0 1 |
| 4     | 58        | 2.27800       | 39.528     | 1 0 2 |
| 5     | 63        | 1.96800       | 46.085     | 1 1 0 |
| 6     | 52        | 1.75300       | 52.133     | 1 0 3 |
| 7     | 4         | 1.70500       | 53.717     | 2 0 0 |
| 8     | 24        | 1.65600       | 55.441     | 1 1 2 |
| 9     | 17        | 1.64200       | 55.955     | 2 0 1 |
| 10    | 3         | 1.53200       | 60.372     | 0 0 4 |
| 11    | 5         | 1.49000       | 62.260     | 2 0 2 |
| 12    | 2         | 1.39800       | 66.871     | 1 0 4 |
| 13    | 7         | 1.30900       | 72.096     | 2 0 3 |
| 14    | 2         | 1.28900       | 73.396     | 2 1 0 |
| 15    | 12        | 1.26100       | 75.304     | 2 1 1 |
| 16    | 6         | 1.20900       | 79.157     | 1 1 4 |

Table 1: The peak parameters of the obtained diffractogram matched with JCPDS data card number 05-0602

3.2 Scanning Electron Microscopy (SEM):

![Figure 2. SEM images of La$_2$O$_3$ nanopowder a) before calcinations  2 b) after calcinations](image)

Figure 2. SEM images of La$_2$O$_3$ nanopowder a) before calcinations  2 b) after calcinations

The surface morphology of La$_2$O$_3$ nanopowder was investigated by SEM and images are shown in Figure 2(a) and Figure 2(b) with different magnifications. The SEM shows that, the clusters of nanoparticles like porous structures. It has been observed that powder of the combustion reaction has a morphology forming a porous and fuzzy network of Nano crystalline La$_2$O$_3$, which may be due to the rapid release of gaseous byproducts during the combustion reaction. The La$_2$O$_3$ agglomerated particles which consists of tiny nanoparticles having average size 40nm, which is in agreement with XRD results.
Figure 3. EDAX spectrum of La$_2$O$_3$ Nano powder

3.3 Particle Analyser studies

Table: Energy Dispersive X-ray analysis (EDAX) results

| Element | Weight% | Atomic% |
|---------|---------|---------|
| O       | 36.05   | 83.03   |
| La      | 63.95   | 16.97   |
| Total   | 100%    | 100%    |

Energy Dispersive X-ray analysis (EDAX) was investigated by Scanning electron microscopy (SEM) coupled with an energy dispersive X-ray spectroscopy (EDAX) unit. Figure 3. Shows the chemical compositional analysis of La$_2$O$_3$ nanopowder is nearly stoichiometry.

Figure 4(a) and Figure 4(b)

Figure 4. (a) Particle size analysis of La$_2$O$_3$ solid solution (b) Zeta potential of La$_2$O$_3$ solid solution

The particle size of nano powders is done by particle size analyzer (Nano particle size analyzer SZ100). Figure 4 shows the distribution of particle size of La$_2$O$_3$ nano powders. The size is estimated as 37.5nm from the graph and Zeta potential as (-15.7) mV.

3.4 LCR Meter Analysis

Figure 5. frequency Vs K curve for La2O3 nanopowder

LCR analysis shows that the dielectric constant of La$_2$O$_3$ nano powder sharply decreases at low frequencies and stabilizes at higher frequencies. The average per gram Dielectric constant is measured to be $K = 31$. 
4. Conclusions
La$_2$O$_3$ nanopowder have been successfully synthesized via mixture of fuel approach in solution chemical combustion. It is observed that from the XRD analysis, the obtained crystallite size varies from 30 nm to 50 nm. Structural properties were examined by SEM. The average particle size is deduced as 47.2nm from Particle size analyser and Zeta Potential as -15mV indicating that the obtained sample is chemically less reactive and stable. The LCR meter results show high-k dielectric nature of material such that it can be employed as gate dielectric material.

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