Study of electrical and gas sensing properties of CeO_2 Thin films Prepared by Spin Coating Technique

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Abstract:
In the current research work, pure CeO_2 nanoparticles (NPs) were synthesized by using sol-gel method. The Cerium (III) nitrate hexahydrate [Ce $(NO_3)_3.6H_2O$] was used as source of Cerium. By using spin coating technique CeO_2 NPs thin films were prepared on glass substrate. The electrical and gas sensing properties of prepared thin films were studied. The electrical properties of prepared thin films were studied on the basis of resistivity, temperature coefficient ratio and activation energy. The prepared films were exposed to reducing gases like H_2S, LPG, methanol and ethanol. The maximum sensitivity has been found to the LPG which is 68.11% at 200 °C temperature and concentrations of LPG was 1000 ppm. Prepared films also show fast response time (~ 15 sec) and recovery time (~ 57 sec).

Keywords- *Sol-gel, Cerium nitrate, thin films, LPG, response time.*

1. INTRODUCTION:

In daily life, gas sensors are used in numerous applications such as food production, health care, and tracking pollution. Gas sensors made of metal oxide semiconductor (MOS) and nanocomposites are very well-liked because of their quick detection, easy operation, and low cost. They have long-lasting chemical and thermal characteristics. These sensors employ a semiconductor material, such as tin oxide, tungsten oxide and others, whose electrical conductivity changes in the presence of LPG gas [1]. The resistance or conductivity variations are detected to indicate the gas concentration. Semiconductor sensors are cost-effective and widely used in portable gas detectors. The sensors are mostly utilized to run a few constructions and estimate actual amounts. Electronic devices that detect many types of input signals include sensors. A challenge has arisen because of the demand for gas detection and monitoring [1, 2]. Exposure to poisonous and dangerous gases can lead to cardiac problems, respiratory disorders, and damage to cells in the lungs, hemoglobin loss, cognitive decline, a high blood pressure and numerous other problems [3, 4].

Cerium oxide (CeO_2) is a cubic-shaped rare earth oxide that plays a specific part in the degradation of organic contaminants. It is a common catalyst and shows promise for a range of applications [5]. It possesses a vital rare earth component that offers a variety of intriguing features. Wide surface areas, surface flaws, and oxygen vacancies characterize CeO_2. Oxygen vacancies have the ability to control both charge carrier transformation and separation, as well as change its photocatalytic behavior. It has received a lot of research attention because of its remarkable features, which can be used in a wide range of applications, such as gas sensors, solid oxide fuel cells, material polishing, UV blocking, and ceramic material additives. Gas sensors based on CeO_2 and doped CeO_2 have been studied with high operating temperatures [6, 7].

LPG (liquefied petroleum gas) gas sensors are devices designed to detect the presence of LPG gas in the environment. LPG is commonly used as a fuel in households for cooking, heating, and other applications. However, LPG is highly flammable, and a gas leak can pose serious safety hazards, including the risk of fire or explosion. LPG gas sensors are crucial in detecting such leaks and triggering appropriate actions to prevent accidents. LPG gas sensors are often used in combination with gas detection systems or alarms. When the sensor detects the presence of LPG gas, it can trigger an alarm, activate ventilation systems, or cut off the gas supply to prevent any potential accidents [8, 9].

The sol-gel method is a versatile and widely used technique for the synthesis of materials, particularly metal oxides. It involves the conversion of a sol (a stable colloidal suspension of solid particles in a liquid) into a gel (a three-dimensional network of interconnected solid particles immersed in a liquid). By carefully controlling the parameters of the sol-gel process, such as precursor concentration, pH, temperature, and drying conditions, it is possible to tailor the composition, structure, and properties of the resulting material. The sol-gel method offers advantages such as low processing temperatures, homogeneity, the ability to incorporate various dopants, and the possibility of forming thin films or complex shapes. The applications of sol-gel-derived materials are diverse and include optics, gas sensors, electronics, catalysis, coatings, sensors, energy storage, and biomedical devices [10]. For example, sol-gel silica is

commonly used in the production of optical fibers and anti-reflective coatings, while sol-gel titanium dioxide finds application in photo catalysis, and solar cells [9-11].
The current research work effort on the synthesis of pure CeO_2 and thin films were prepared using spin coating technique and studied films electrical and gas sensing properties for gas sensing application.

2. EXPERIMENTAL WORK:

2.1 Synthesis of CeO_2 nanoparticles using sol gel method:

In the current research work, Cerium (III) nitrate hexahydrate [Ce $(NO_3)_3.6H_2O$] with 99.99 % purity, was used as source of cerium. The ammonia solution (NaOH), and citric acid [HOC $(CO_2H)(CH_2CO_2H)_2$] used during synthesis process to form gel. Figure 1 shows the graphically experimental work flow of synthesis of CeO_2 nanoparticles using sol gel method. The preparation of thin films of pure CeO_2 is also illustrate in Figure 1.

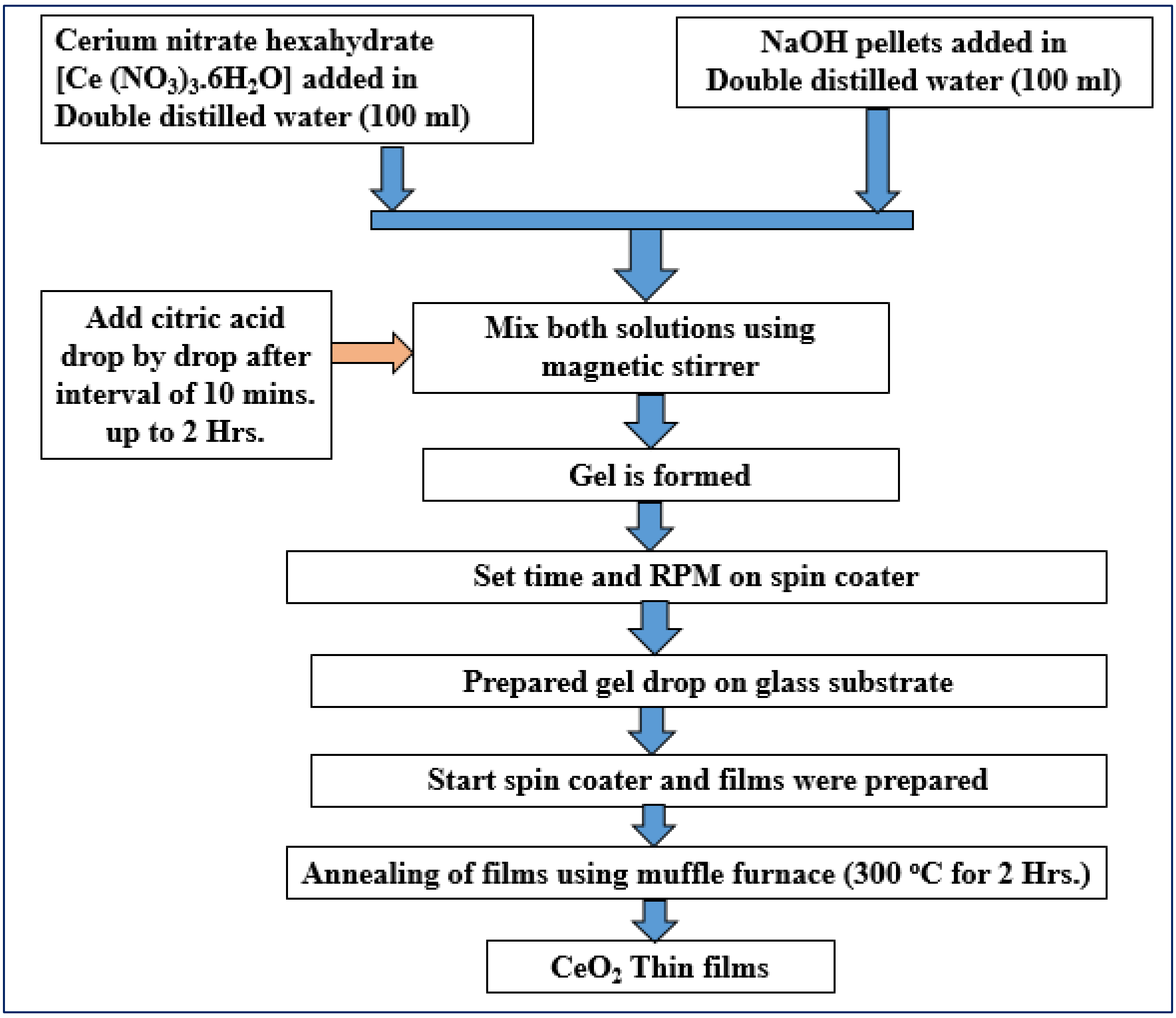

Figure 1: Steps of synthesis and preparation of CeO_2 thin films using spin coating technique

2.2 Measurement of Thickness of films:

The prepared films thickness were measured by weight difference method [12]. After calculations the thickness was observed as 68 nm.

2.3 Characterizations of prepared CeO_2 thin films:

2.3.1 Electrical characterizations of CeO_2 thin films:

In the electrical characterization study, resistivity, Thermal coefficient of resistance (TCR) and activation energy at high and low temperatures were investigated.
Equations 1, 2 and 3 were used to calculate resistivity, TCR and activation energy, respectively [12].

$$\rho = \left(\frac{R \times b \times t}{l} \right) \Omega - m \qquad (1)$$

Where, ρ = Resistivity of prepared film, R = resistance at normal temperature, b = breadth of film, t = thinness of the film, L = length of the film.

$$TCR = \frac{1}{R_o}\left(\frac{\Delta R}{\Delta T}\right) \; /^{O}C \qquad (2)$$

Where,
ΔR = change in resistance between temperature T_1 and T_2,
ΔT = temperature difference between T_1 and T_2 and R_o = room temperature resistance of the film

$$\Delta E = Ae^{-Ea/kBT} \quad \text{eV} \qquad (3)$$

Where,
ΔE = Activation energy, T = Temperature in Kelvin and A = Arrhenius prefactor.

2.3.2 Gas sensing study of CeO_2 thin films:

The properties of gas sensing were studied using a static gas sensing apparatus. CeO_2 thin films were used for the sensing element. The resistance of the film was calculated at different operating temperatures and in the presence of a different gas concentrations. The sensitivity of the films was determined by using equation 4.

$$\text{Sensitivity (\%)} = Ra\text{-}Rg/Ra \times 100 \qquad (4)$$

Where, Ra -Film resistance in air and Rg- film resistance in a gaseous atmosphere.

3. RESULT AND DISCUSSION:

3.1 Electrical Characterization:

3.1.1 Resistivity:

The resistivity is one of the important property of thin films. The resistivity of the films is plays vital role in gas sensing mechanism. The resistivity of the film also depends up on the thickness of the film [13]. The figure 2 display the temperature versus resistance plot of pure CeO_2 thin film.

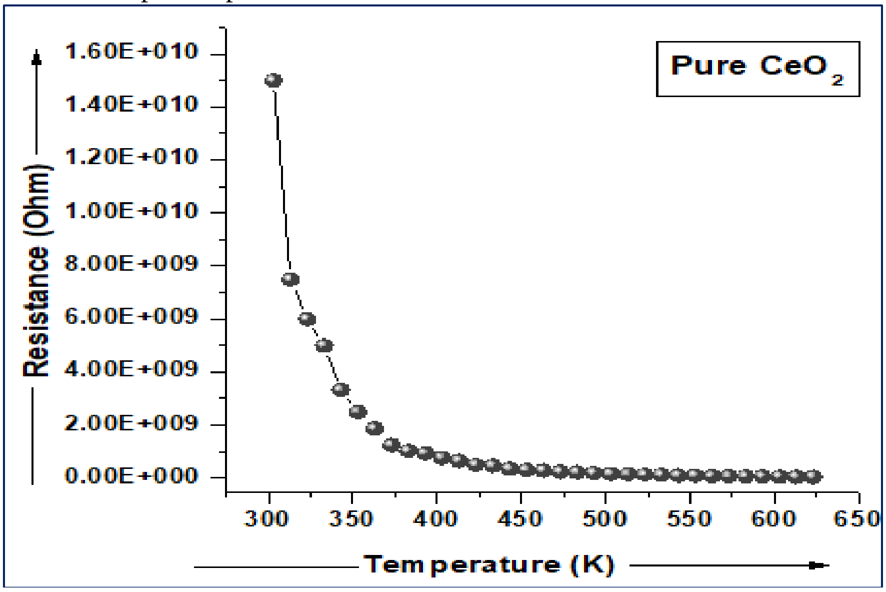

Figure 2: Resistance v/s temperature plot of CeO_2 thin film

The resistivity of CeO_2 thin film was calculated using Equation 1. The DC resistance of CeO_2 thin film as a function of temperature was determined using the half bridge method. As shown in Figure 2, the resistance of the film falls swiftly initially then drop down slowly, and the decrease in resistance with increasing surrounding temperature implies semiconductor behavior of the film [12, 14]. The resistivity of CeO_2 thin film was found to be 5097 **Ω**-m.

3.1.2 Activation energy:

The activation energy is can be defined as the amount of required energy for charges or carrier form valance band to conduction band. Figure 3 shows the Arrhenius plot of CeO_2 thin film. The plot is reversible in both heating and cooling cycles, according to the Arrhenius equation [12, 15]. At lower temperature region, the activation energy of CeO_2 thin film was found to be 0.263854 eV, and at higher temperature region it was 0.281663 eV.

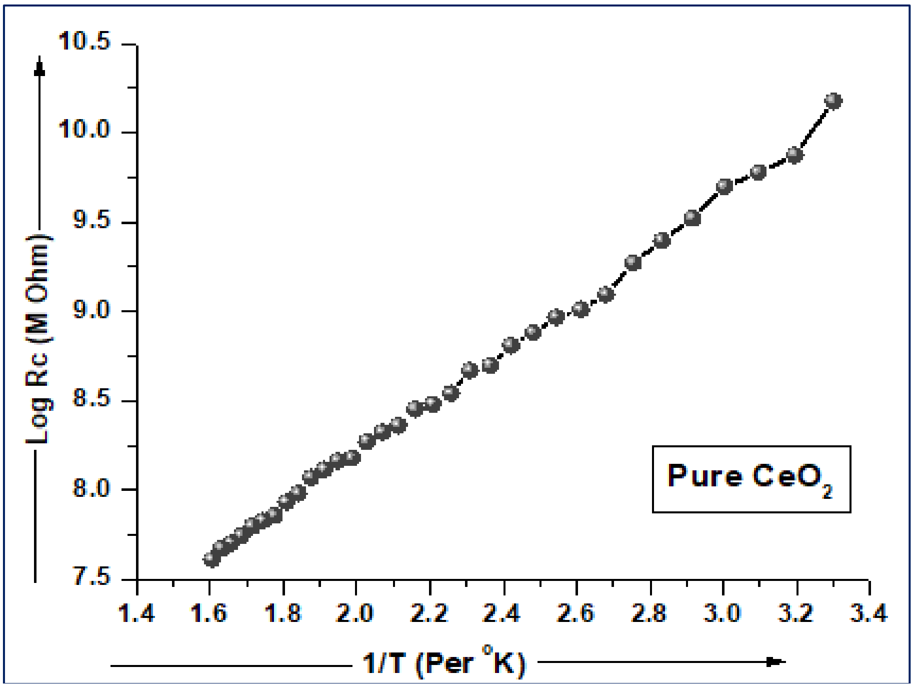

Figure 3: Arrhenius plot of CeO_2 thin film

3.1.3 Temperature coefficient of resistance (TCR):

TCR is a critical important parameter of thin films. The temperature coefficient of resistance for CeO_2 thin film is found to be -0.00036/˚C. TCR of CeO_2 thin film was found to be negative. The TCR of thin films is negative, signifying that CeO_2 thin film is a semiconducting material nature [15].

Table-1: Electrical outcomes of CeO_2 thin film

Thickness (nm)	Resistivity (Ω-m)	TCR (/ºC)	Activation energy (eV)	
			LTR	HTR
68	509660	-0.00036	0.263854	0.281663

3.2 Gas sensing study of CeO_2 thin film:

The selected gases like H_2S, ethanol, methanol and LPG were exposed on CeO_2 thin film using a static gas system. Among the gases these selected gases; LPG shows the maximum sensitivity to CeO_2 thin film as shown in Figure 4.

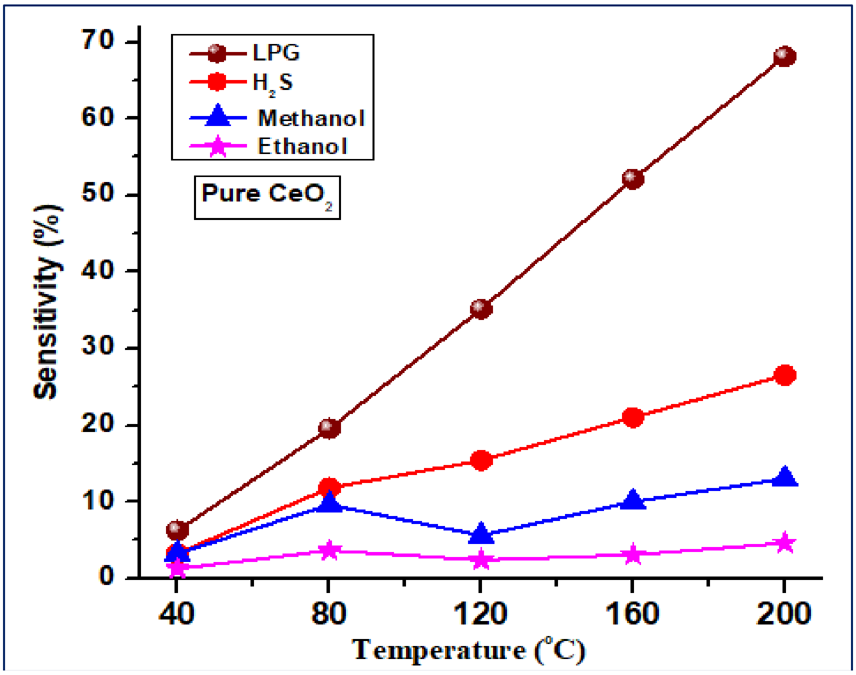

Figure 4: Sensitivity verses operating temperature of CeO_2 thin film

From figure 4, it has been observed that, as operating temperature is increases the sensitivity of the CeO_2 thin film also increases. It could be at higher operating temperature more oxygen vacancies are created and the rate of absorption of LPG gas molecules with films surface enhance the response of film and change the resistance of the film drastically [15, 16]. The CeO_2 thin film were exposed to LPG concentrations of 100, 300, 500, and 1000 ppm. The PPM versus sensitivity plot is shown in Figure 5.

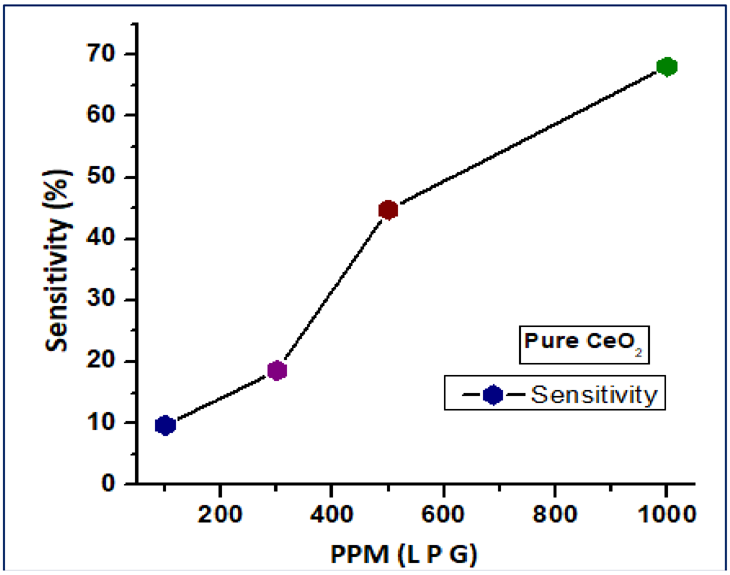

Figure 5: Sensitivity verses LPG concentration in PPM.

Figure 5 depicts the sensitivity of CeO_2 thin film to various LPG concentrations in ppm. At 1000 PPM, the maximum sensitivity was obtained. From figure 5, it has been observed that, as LPG ppm was increases the sensitivity of the CeO_2 thin film also increases. In comparison to other selected gases, Figure 6 indicates that LPG has the highest selectivity. The selectivity of a sensor for a certain gas is directly correlated with the temperature at which it operates. Selectivity = Sx/Sy represents the selectivity of a target gas to a distinct gas, where Sx and Sy are the sensor's response to a target gas X and an intruder gas Y, respectively.

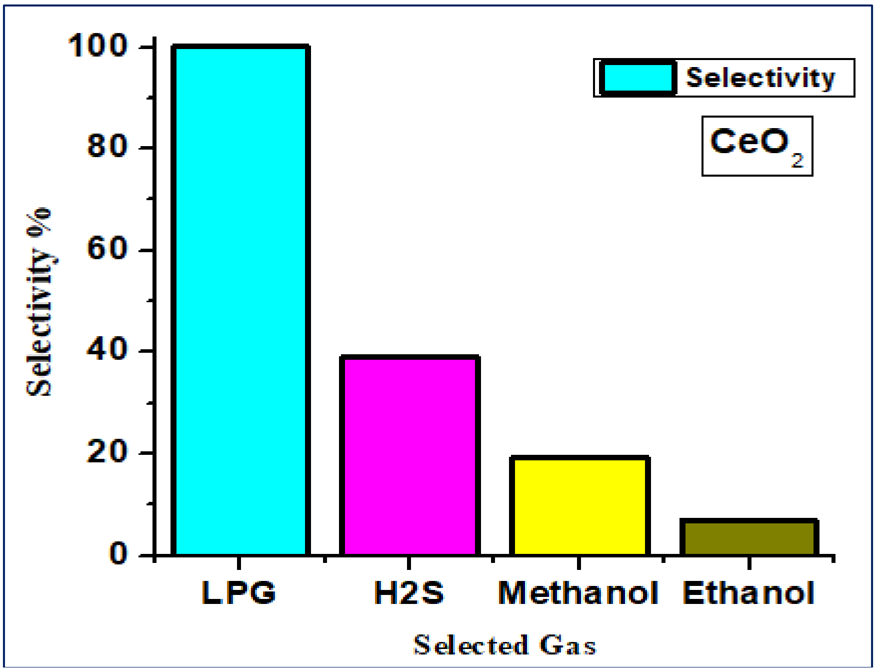

Figure 6: Selectivity of CeO_2 thin film

Figure 7 depicts the CeO_2 thin film sensor's response-recovery characteristics at its ideal operating temperature.

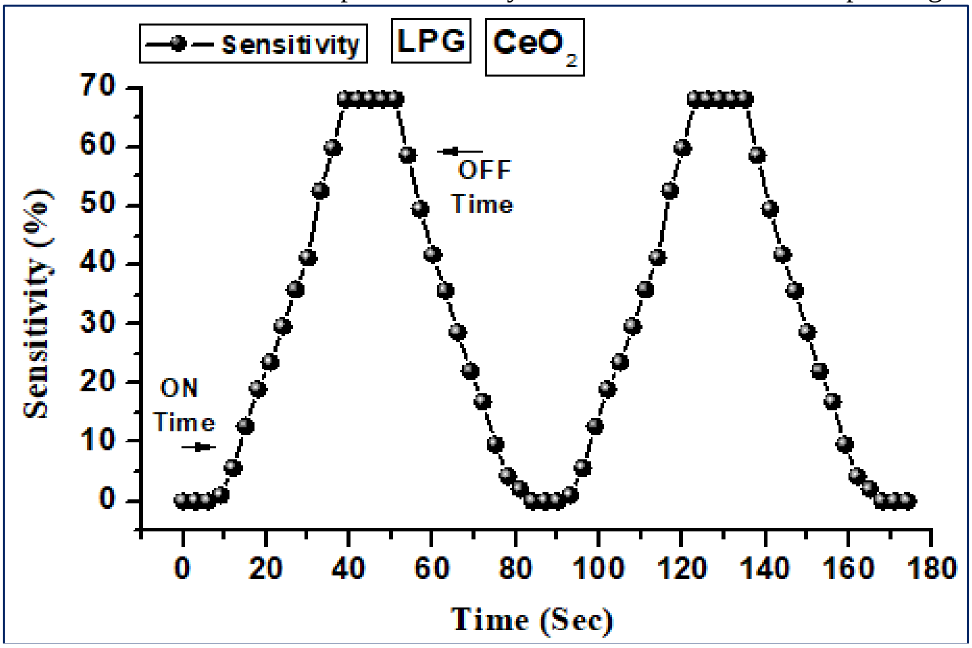

Figure 7: Response and recovery time of CeO_2 thin film for LPG

The amount of time required to reach 90% of the maximum response while gas is present and 10% when gas absence occurs, respectively, is referred to as the response time and recovery time of a gas sensor [17]. The response and recovery durations of the CeO_2 thin film for LPG were found to be 45 and 78 seconds, respectively, as shown in Figure 7.

CONCLUSIONS:

The thin film of CeO_2 can be prepared using a spin coating technique on a glass substrate. At working temperature 200°C and gas concentration of 1000 ppm, the CeO_2 thin film showed maximum sensitivity to LPG. The response and recovery time also found to be very rapid in seconds. CeO_2 thin film could be used for the development of novel LPG gas sensors.

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