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Liquefied Petroleum Gas (LPG) Sensing Properties of Nanosized Sprayed $CdIn_2O_4$ Thin Films

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Abstract: The liquefied petroleum gas (LPG) sensing properties based on sprayed cadmium indium oxide ($CdIn_2O_4$) thin films were studied. The as-deposited films were annealed at 400 ^oC for 2 h in air atmosphere and studied structurally by SEM and TEM techniques. The annealed films are of $CdIn_2O_4$ with cubic spinel structure. Average particle size estimated from TEM analysis was observed to be 10-15 nm. Experiments with LPG at concentration levels of 400-1200 ppm and at operating temperatures ranging from 375-425 ^oC were performed. The maximum gas response of 26 % to 100 ppm of LPG at 400 ^oC achieved. At this temperature the response and recovery times were about 82 and 64 s, respectively. Improved gas response to relatively low LPG concentration was assigned to nanocrystalline nature of the deposits. *Copyright © 2009 IFSA.*

Keywords: Cadmium indium oxide, Thin films, Spray pyrolysis, X-ray diffraction, LPG sensor

1. Introduction

The complex oxide $CdIn_2O_4$ exhibits fcc spinel structure and is an n-type semiconductor because of existence of specific point defects. It has been extensively studied [1-2] for its very high transmittance in the visible spectrum and excellent electrical properties particularly in thin film form. At present, the search for new gas sensor materials and developing the properties of conventional gas-sensing materials has become an active research field. Several efforts have been made in this direction all over the world during last few decades [3]. Although commercially available gas sensors mainly included

Fe_2O_3, WO_3, and CuO-$BaTiO_3$ etc., however stability to LPG are still unsatisfactory and further efforts are needed [4-6].

$CdIn_2O_4$ thin films have been prepared by various physical as well as chemical deposition methods viz. ultrasonic spray pyrolysis [7-8], aerosol pyrolysis [9-10], co-precipitation [11], dc reactive magnetron sputtering [12-13], electron beam evaporation [14] and flux method [15]. However, cheapness is also one of the important criterions for sensor fabrication. Amongst these, chemical spray pyrolysis is a versatile technique for deposition of metal oxides, as demonstrated by Patil in his review [16]. It is possible to deposit nanocrystalline metal oxide deposits by chemical spray technique for LPG detection [17]. Recently, we reported the synthesis and characterization of $CdIn_2O_4$ thin films by chemical spray pyrolysis method [18]. Films exhibited cubic spinel structure and showed presence of direct optical transition having bandgap energy of 3.0 eV.

In continuation of this work, in this manuscript we present the results of the analysis on LPG sensitivity of these films. An effort is made to investigate the optimal measurements conditions of $CdIn_2O_4$ thin films with best gas sensing properties for lower concentrations of LPG.

2. Experimental

The $CdIn_2O_4$ thin films were spray deposited by mixing the appropriate volumes (1:2 ratio) of equimolar (0.025M) cadmium acetate (Cd $(CH_3COO)_2.2H_2O$) and indium acetate ($In(CH_3COO)_3$) in deionised water at different substrate temperatures [18] and 325^oC was found to be optimized substrate temperature. The as-deposited films were annealed at 400^oC for 2 h in air atmosphere. The thickness of the cadmium indium oxide thin films were measured by a weight difference method and counterchecked by Ambios, USA, XP-I surface profiler. The microstructural study was accomplished using JEOL (JSM-6360) scanning electron microscope (SEM). TEM analysis was carried out with a Philips CM-12 electron microscope (point resolution 2.8 Å). The LPG sensing properties of $CdIn_2O_4$ thin films were studied in an indigenous gas sensor unit, described in [17]. For electrical measurements, silver paste contacts (1mm) were made on the $CdIn_2O_4$ sample of area 1 cm^2. Gas concentration in the measurement chamber was monitored with calibrated gas flow meter.

3. Results and Discussions

3.1. Surface Morphology Studies

The SEM image of typical thin film annealed at 400 ^oC for 2 h is shown in Fig. 1. It can be seen that film surface is rough with large number of pores and overgrown particles, a common observation in the spray deposited thin films. Small crystallites are gathered together to form aggregate. It is proposed that such a kind of morphology might have resulted possibly due to homogeneous reaction of the ingredients before reaching the substrate at a given experimental conditions. We could observe a slight difference in the morphology of the $CdIn_2O_4$ thin films at other deposition temperatures.

Fig. 2 shows TEM micrograph of annealed sample. The micrographs indicate the complete coverage of the substrate by the film and uniform distribution of nanosized particles. The average size of particles estimated from the TEM micrograph is 12 ± 2 nm. The inset in Fig. 2 shows the selected area diffraction (SAD) pattern of the sample. The ring pattern observed in the SAD pattern clearly reveals the crystalline nature of the film. This observation is consistent with crystallite sizes obtained from XRD patterns [18]. The SEM and TEM shows the porous and nanocyrstalline morphology respectively, which is useful for achieving higher sensitivity of the resistive gas sensor.

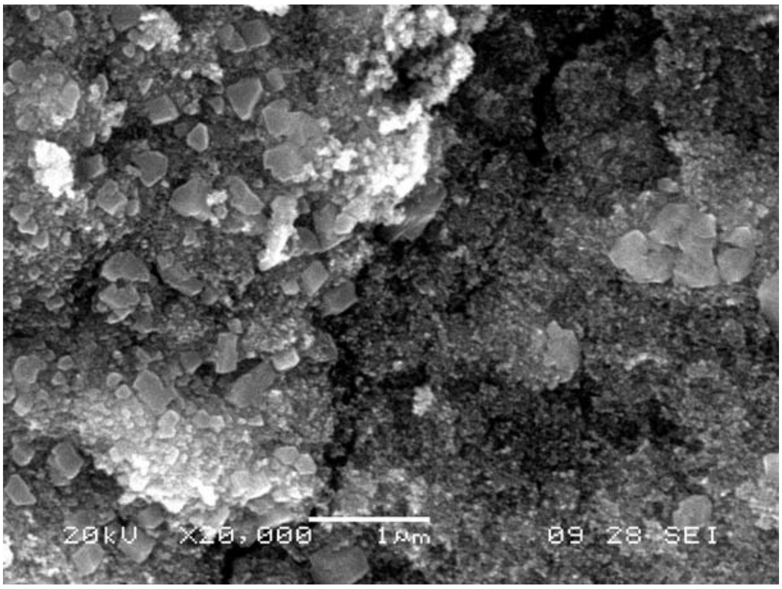

Fig. 1. SEM image of annealed $CdIn_2O_4$ thin film.

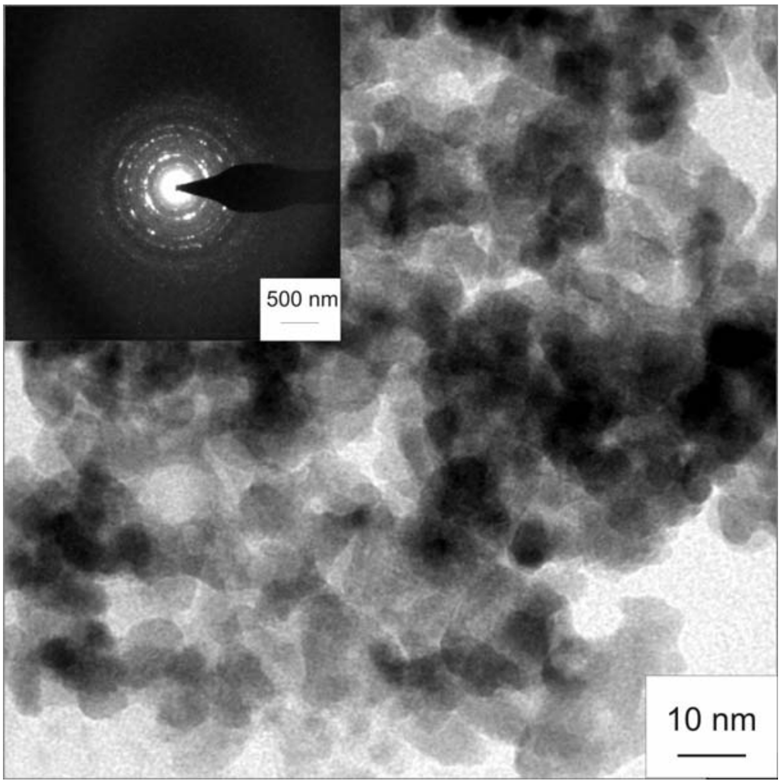

Fig. 2. TEM micrograph of annealed $CdIn_2O_4$ thin film.

3.2. LPG Sensing Properties

As-deposited $CdIn_2O_4$ films (deposition temperature = 325^{o}C) didn't show enough response to the LPG. Therefore, with regard to the gas-sensing properties, attention was devoted only to the thermally annealed $CdIn_2O_4$ samples. In general, the response of the sensors is affected by the operating temperature.

Gas-sensing experiments were performed at different operating temperatures to find the optimum operating condition. Before exposing to LPG, the $CdIn_2O_4$ films were allowed to be stable for electrical resistance for 30 min. For the present study, initially the gas response to 1000 ppm of LPG was studied as a function of operating temperature. From, Fig. 3, it is found that the sensor response (normalized conductance) reaches maximum at 400°C (gas response = 26.05 %) and then decreases at 425°C (gas response =19 %). It is observed that high operating temperature is necessary for a pure $CdIn_2O_4$ film to interact with LPG [19]. At lower temperature; 375°C, the speed of chemical reaction restricts the response and at high temperature; 425°C, it is restricted by the speed of diffusion of gas molecules. At some intermediate temperature, the speeds of the two processes become equal and gas response is maximum [20]. The maximum gas response of 26.05 % is observed for 400°C, therefore, for further studies 400°C is selected as an optimum operating temperature.

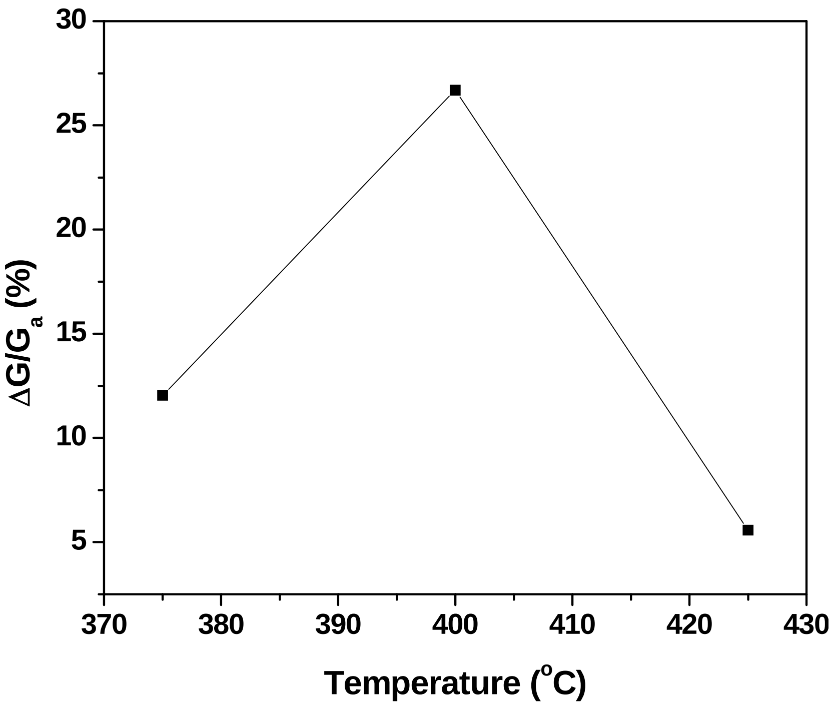

Fig. 3. The variation of gas response to 1000 ppm LPG for $CdIn_2O_4$ film at different temperatures.

Fig. 4 shows the response of a $CdIn_2O_4$ film as a function of LPG concentration at 400°C operating temperature. The figure reveals that the response increased from 7 to 27.3 % as the LPG concentration increased from 400 to 1200 ppm. However, at higher concentrations the increase in gas response value was gradual and saturated at LPG concentrations more than 1200 ppm. The response of a sensor depends on removal of adsorbed oxygen molecules by reaction with a target gas and generation of electrons. For a small concentration of gas, exposed on a fixed surface area of a sample, there is a lower coverage of gas molecules on the surface and hence lower surface reaction occurs. An increase in gas concentration increases the surface reaction due to a larger surface coverage. A further increase in surface reaction will be gradual when the saturation point on the coverage of molecules is reached. Relatively higher sensitivity for resistive gas sensor based on sprayed $CdIn_2O_4$ thin films in the present investigation might be due to formation of nano-sized grains and exhibition of porous surface morphology. The sensor performance obtained in this work is relatively higher than reported by Xiangfeng et al. [21] and Patil et al [22]; for $CdIn_2O_4$ thin film that too for 1000 ppm LPG. Xiangfeng et al. [23] have obtained an average response of 5 % to LPG (1000 ppm) for Y and Nd doped $CdIn_2O_4$ films obtained by coprecipitation method.

Fig. 5 shows the variation in normalized conductance $\Delta G/G_a$ with the time of a $CdIn_2O_4$ film when exposed to 1000 ppm LPG in dry air at three different operating temperatures (375, 400 and 425°C). G is the conductance due to the introduction of gas and Ga is the conductance before gas injection (in air). It is evident in all cases that the sensor conductance increases upon the introduction of LPG and returns to its initial value when the film is exposed to pure dry air. This proves that the adsorption process is reversible. Moreover, the rise in conductance suggests that $CdIn_2O_4$ films have an n-type conduction in this temperature range.

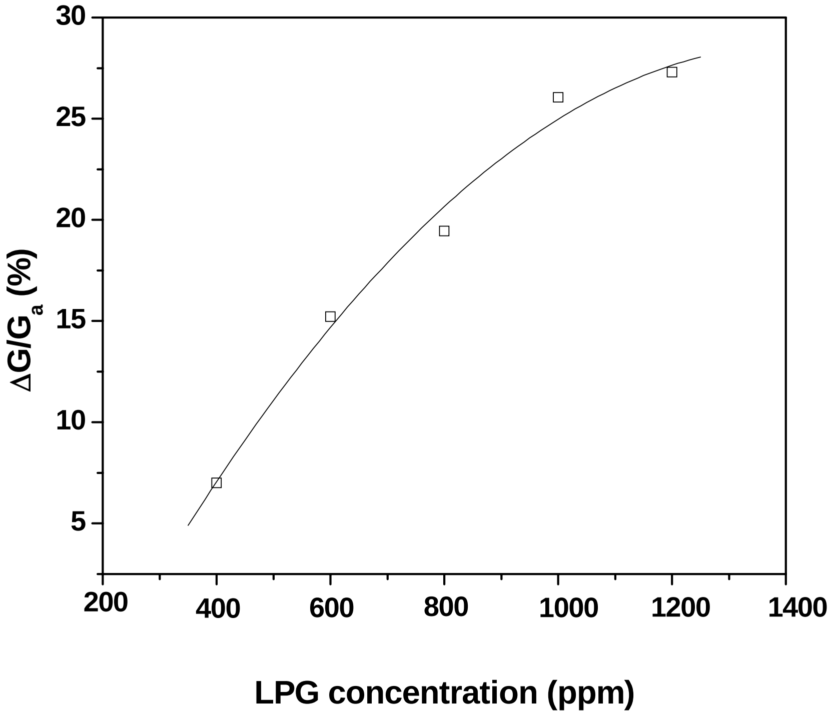

Fig. 4. Sensor response to 1000 ppm LPG of a $CdIn_2O_4$ film as a function of LPG concentration (operating temperature 400 °C).

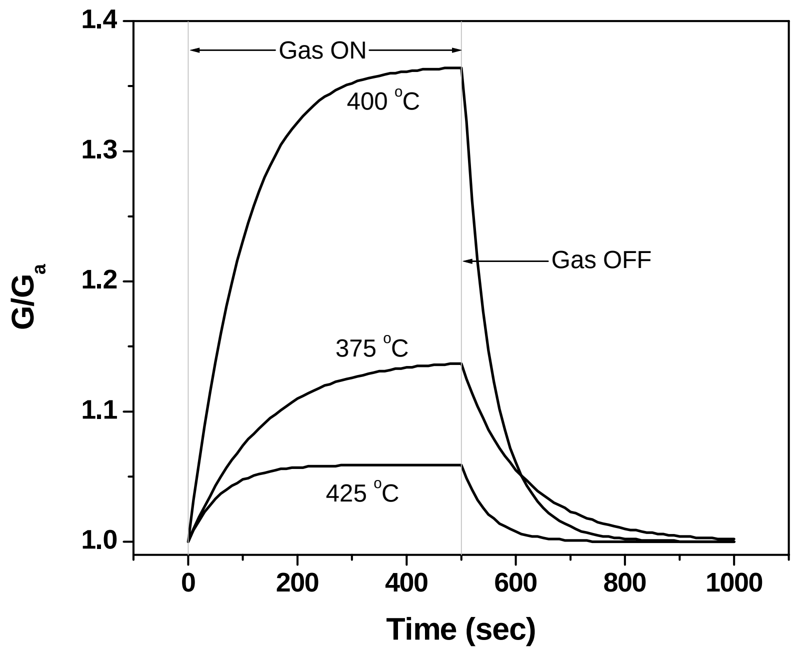

Fig. 5. Normalized conductance of a $CdIn_2O_4$ thin film to 1000 ppm LPG at 375 °C, 400 °C and 425 °C.

The response and recovery times as function of the operating temperature are evaluated by applying the first order kinetic equations to adsorption and desorption phenomena as reported by Tepore et al. [24, 25]. According to them the conductance variation is given by

$$\Delta G = \Delta G_{\max}(1 - \exp^{(-t/\tau_d)} \quad (1)$$

in the response process, and

$$\Delta G = \Delta G_{\max} \exp^{(-t/\tau_a)} \quad (2)$$

in the recovery process, where ΔG_{max} is the maximum value of conductance variation under stationary conditions, and τ_d and τ_a represent the response and the recovery times, respectively. In the equation (2) t = 0 means the switching off of test gas, that is t = ∞ in Eq. (1). According to Eq. (1) the response time τ_d can be obtained from the slope of the linear plot of log $(1-\Delta G/\Delta G_{\max})$ versus time. Similarly, for the recovery transient, the Eq. (2) allows us to obtain the recovery time τ_a from the experimental data by fitting log ($\Delta G/\Delta G_{max}$) versus time. This analysis is illustrated in Fig. 6 for the normalized conductance variation $\Delta G/\Delta G_{\max}$ induced by 1000 ppm of LPG at 400°C. The response and recovery times versus operating temperature of the sensors to 1000 ppm LPG are shown in Fig. 7. Both the response and recovery times decrease in a non-linear manner by increasing operating temperature. In particular at the optimum operating temperature of 400°C, the response and recovery times are about 82 and 64 sec respectively. Usually, it is observed that the recovery time for resistive gas sensor is relatively higher than the response time. In the present case, it is observed that the response times are slightly higher than the recovery times. This reflects that the adsorption process is reversible and the rate of desorption process is higher.

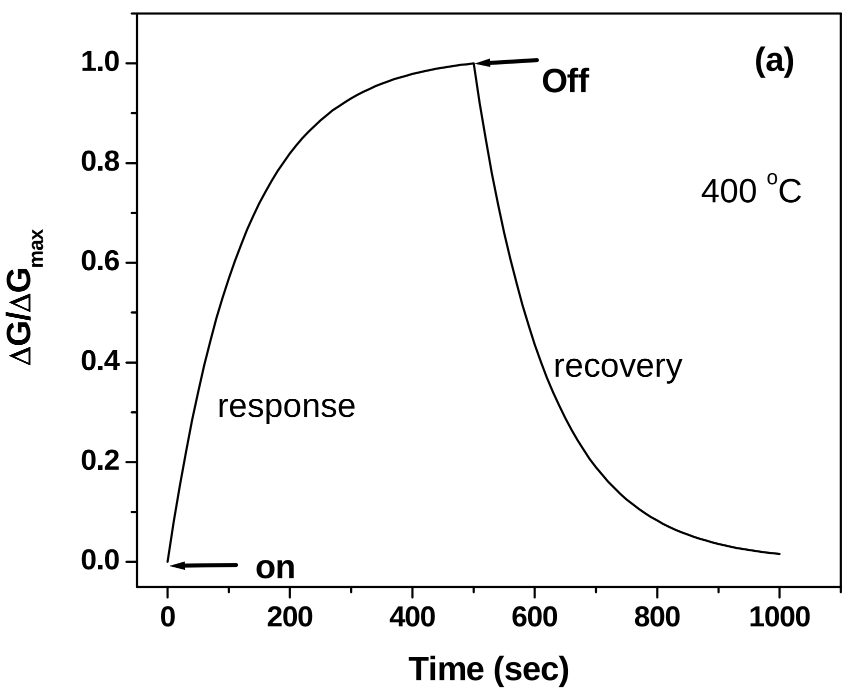

Fig. 6(a). Typical normalized response and recovery curve to 1000 ppm LPG.

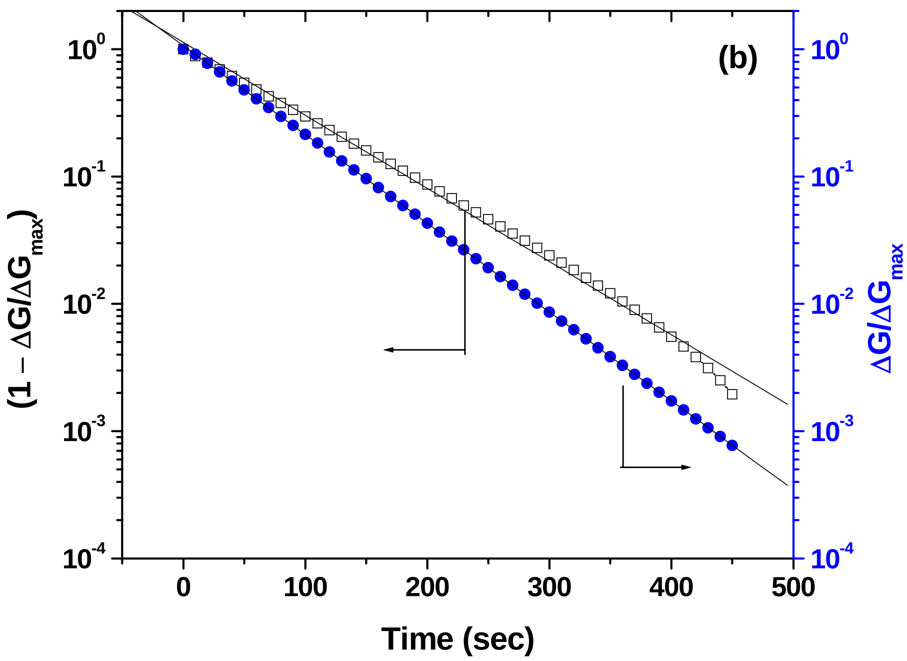

Fig. 6(b). Response and recovery conductivity transient analysis.

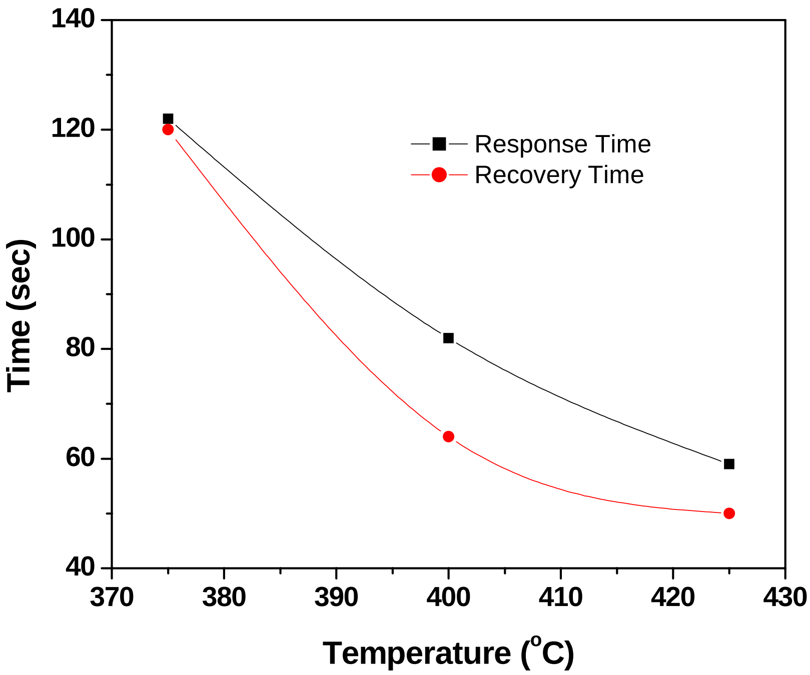

Fig. 7. The response and recovery times vs. temperature of a $CdIn_2O_4$ thin film exposed to 1000 ppm LPG.

4. Conclusions

The $CdIn_2O_4$ thin films synthesized by a chemical spray pyrolysis method have been used for LPG sensing properties. Annealed $CdIn_2O_4$ films are polycrystalline with cubic spinel structure. TEM studies revealed that the particle sizes are in the range of 10-15 nm. As-deposited films present a poor response to $CdIn_2O_4$. Contrarily, the thermally annealed films were found to be sensitive to $CdIn_2O_4$ with the maximum response observed at 400°C. Response time was observed to be higher than the recovery time. These results can be improved significantly by doping and/or noble metal sensitization.

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- Sensor instrumentation;
- Virtual instruments;
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