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Synthesis of CdO Thin Films for NO_2 Gas Sensor

Farhan Ahmad*[1], G. T. Bhalerao[2], P.R. Khawane[2], R. S. Nikam[3], R. K. Shirsat[4], H. J. Kharat[4], S. K. Devade[4]
*[1]Department of Physics, Shankarlal Khandelwal Arts, Science and Commerce College, Akola, Maharashtra, India
[2]Department of Physics, Mahatma Phule Arts and Science College, Patur Dist. Akola, Maharashtra, India
[3]Department of Physics, Vidnyan Mahavidyalaya Malkapur Dist. Buldhana, Maharashtra, India
[4]Department of Physics, Shankarlal Khandelwal Arts, Science and Commerce College, Akola, Maharashtra, India

ABSTRACT
Cadmium oxide thin films were successfully deposited on glass substrates using the chemical bath deposition method and annealed at 500^{0}C using Cadmium chloride and sodium hydroxide as starting precursors. These optimized films were tested for nitrogen dioxide (NO_2) as oxidizing gas using a static gas sensing unit at different operating temperatures at a constant gas concentration (NO_2) of 10ppm. The maximum response of the CdO thin film is at 100 °C as an operating temperature. The sensor's response and recovery time were calculated and reported. Our results show that the CdO thin film is suitable for NO_2 gas sensing applications at possible low operating temperature.

Keywords: chemical bath deposition, thin film, cadmium oxide, gas sensor

I. INTRODUCTION

With the growth of contemporary industry and technology in recent years, the emission of various toxic gases has become a major concern. Numerous studies have been done to develop novel solid-state gas sensors based on metal oxide semiconductors. As a result, low-cost detection and measurement of gaseous species in air are becoming more important for human health and safety, energy efficiency, and pollution control. [1,2].

Metal oxides, such as NiO, CdO ,ZnO, SnO_2 and others, have long been used as an active layer in gas sensors to detect toxic and hazardous environmental gases, such as NO_2, CO_2, and CO, because they are less expensive than other sensing technologies that are reliable, small in size, and lightweight. The recent growth of industries and improvements in quality of life have increased the importance of the problem of air pollution. As a result, the quality of urban air has recently become a public health issue. Nitrogen dioxide NO2 is one of the most dangerous air pollutants, causing toxic and harmful effects on the environment and human health. [3,4]. Car exhausts, as well as domestic and industrial combustion processes, are sources of nitrogen dioxide. NO2 has a threshold limit value of up to 25 ppm [5], so detection at this low concentration is required. However, widely used commercial gas sensors have significant limitations. These concerns arise from their high-power consumption, low sensitivity, and high operating temperature [6,7]. As a result, there is an urgent need for new gas sensors with improved performance. Several metallic oxides, such as ZnO [8], SnO_2 [9], CdO [10], NiO [11], and Fe_2O_3 [12], have attracted the attention of researchers and are being studied for this purpose. CdO is a well-known n-type semiconductor with a band gap energy of (2.2-2.7) eV. The electrical conductivity ranges between 102 and 104 S/cm. Cd interstitials (Cdi) and oxygen vacancies (Vo) act as doubly ionised (+ 2) charge donors in CdO, resulting in such high electrical conduction [13,14]. Its high electrical conductivity and optical transmittance in the visible region of the solar spectrum, combined with a moderate reflective index, make it suitable for a variety of applications such as photodiodes, gas sensors, and so on. [15,16]

Spray pyrolysis [17], electrochemical deposition [18], sol-gel [19], SILAR method [20], chemical bath deposition method [21] and other methods have been used to develop undoped CdO thin films. The chemical bath method has an advantage over other methods because it is simple, does not require sophisticated equipment, operates at low temperatures, and has a low deposition cost. In this article CdO films were deposited on a silica glass substrate using a chemical bath technique and their sensitivity to nitrogen dioxide (NO2) gas was tested for applications in environmental monitoring.

II. METHODS AND MATERIAL

All glass wares first washed in distilled water and HCl. 0.1 M concentration of cadmium chloride and 0.1M concentration of sodium hydroxide was prepared in 100 ml and 50 ml beaker respectively without any complexing agents. Drop by drop, NaOH solution was added to cadmium chloride solution until pH 10 was obtained at room temperature. The solution was then stirred with a magnetic stirrer after the well-cleaned glass substrate was rinsed in it for 3 hours using a thin film holder. After three hours, the substrate was removed from the solution and allowed to air dry at room temperature. On the substrate, a white-colored cadmium hydroxide film has formed. The film was annealed at 500 °C for 150 minutes to obtain pure CdO phase.

III. RESULTS AND DISCUSSION

A. Measurement of response

The sensor's gas response (S) is defined as the ratio of change in conductance to sensor conductance after target exposure (at same operating conditions).

Sr = Ig-Ia/Ia (for reducing gases) -------------- (1)

So = Ia-Ig/Ig (for oxidising gas) ------------- (2)

where Ia = the conductance of the sensor in air

Ig = the conductance on exposure of a target gas.

B. Gas sensing mechanism of CdO thin film towards NO2 gas.

As we know, the key points of gas sensing phenomena are the morphology of the synthesised materials, oxygen vacancies, grain size, and the nature of the gas. The CdO layers were used for gas sensing measurements after they were physiochemically characterised. Most metal oxides-based gas sensors require high temperatures for oxygen chemisorption, which is the foundation for oxygen mediated transition metal oxide gas sensors. To determine the operating temperature for the CdO sensor, it was tested from 50 °C to 300 °C with an interval of

50 °C at constant gas concentration of 10 ppm of NO_2. As shown in Fig. 2, the responses of CdO samples initially increase with increasing operating temperature, reaching maximum sensitivity at 100 °C, and then decrease for higher temperatures.

Because the particles of NO_2 gas do not have enough energy to become active at low operating temperatures, the sensor's sensitivity is limited. The response decreases as the operating temperature exceeds 100 °C, which could be attributed to a decrease in NO_2 particles adsorption on the surface of the CdO thin films due to the decomposition of NO_2 gas into oxygen and NO gases at higher temperatures.

NO_2, N_2O, CO_2, and NO gases are oxidising, whereas, CO, CH_4, NH_3, SO_2 and H_2S gases are reducing [22]. When metal oxide surfaces are exposed to these oxidising gases they trap the more electrons from material surface resulting in an increase in resistance. [23] It is well known that oxygen molecules adsorbed O_2^-, O^-, and O^{2-} ions depending on temperature in the air atmosphere.on the surface of CdO which is shown in Fig.1. The stable oxygen ions are O_2^- below 100^0 degrees Celsius, O^- between 100 and 300 degrees Celsius, and O^{2-} above 300 degrees Celsius [24]. We can understand the by chemical reactions when CdO is exposed to NO_2 gas.[25, 26]

$NO_{2\,(gas)} + e^- \longrightarrow NO_2^-{}_{(ads)}$ ---------- (3)

$NO_2^-{}_{(ads)} + O^-{}_{(ads)} + 2e^- \longrightarrow NO_{(gas)} + 2O_2^-{}_{(ads)}$ ------ (4)

When the CdO films are exposed to NO_2 gas, the NO_2 gas reacts with the adsorbed O^- ions which is on the surface of the CdO films. This ions help the adsorbed NO_2 ions to take electrons from the conduction band of bulk CdO ,resulting concentration of electrons on the surface of the CdO film decreases and the resistance of the CdO film increases. However, as the temperature rises, the O^{2-} dominant at the surface, and the response of the CdO sensor further decreases. At the high temperatures, all species desorb gradually and the response decreases. The optimum working temperature for pure CdO thin film sensor towards a concentration of 10 ppm NO_2 was determined to be 100^0C as shown in Fig.2. At this working temperature the CdO sensor had a response time of 125 seconds and recovery time of 175 seconds which is shown in Fig.3.

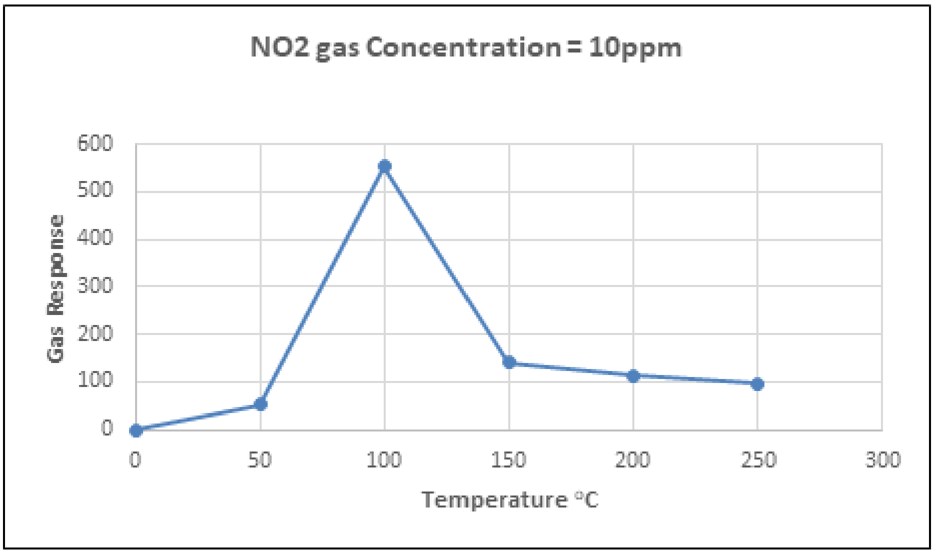

Fig.1 Gas Sensing mechanism of CdO thin film

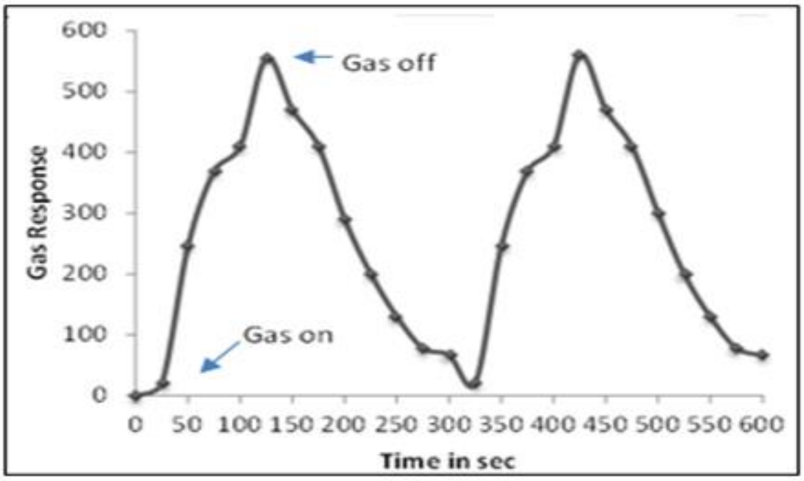

Fig.2 Variation of operating temperature with gas sensor response

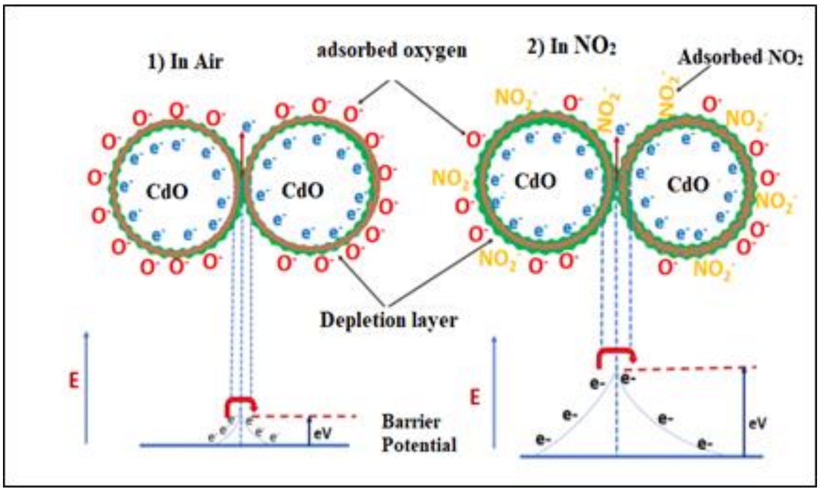

Fig.3 Response time and recovery time of CdO thin film operating at 1000C

IV. CONCLUSION

Pure CdO thin film was successfully deposited by chemical bath deposition method. Temperature dependent NO_2 gas sensing behaviour was studied towards a concentration of 10ppm.The optimal operating temperature was found to be 100^0C with response and recovery times of 125 sec and 175 sec respectively.

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