Synthesis and characterization of Cr2O3:Al thin films by plasma of R.F. magnetron sputtering for gas sensing application

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Abstract

As a gas sensor for nitric oxide, thin films of Cr2O3:Al nanostructures have been created using the radio frequency (RF) magnetron sputtering process at various aluminum weight percentages (0, 2, 4, and 6). (NO2). X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), UV-Visible characteristics, and sensing properties were also examined as part of the characterization. The structural analysis revealed that the films had multiple crystal phases, including a hexagonal phase. According to the results of the sensing properties, the best sample was 4% Al, which had a sensitivity of 32% at 200 oC and response times of less than 15 s and 77 s for recovery.

Key words: *Gas sensor, NO2 gas, Plasma (RF) sputtering, Sensitivity%, Cr2O3:Al thin films.*

INTRODUCTION

Researchers have paid a lot of attention to semiconductors recently because of their unique optical, electrical, magnetic, and chemical features [1]. Due to its wide bandgap energy of 3 eV, chromium oxide, or Cr2O3, is one of the many significant semiconductor materials used in numerous applications. Furthermore, it is a p-type semiconductor. Gas sensors, an optical storage system, thermal protection, and corrosion resistance are only a few uses for Cr2O3 [3, 4]. Because of its size, surface area, and simplicity in combining with other metals and oxides, nanochromium oxide is regarded as one of the key materials. Researchers in this sector have therefore concentrated their attention on the synthesis and production of nanomaterials with large surface area to volume and strong chemical activity [5]. Many oxides of nanomaterials have been grown using sputtering with radiofrequency plasma, and these oxides have significant and beneficial uses with gas sensors. Some combustible or deadly gases, such as nitrogen oxide and NO2, have demonstrated the detecting capabilities of this metal oxide, Cr2O3. Due of the increase in surface area exposed to the gas, areas where nanotechnology has made significant strides have produced strong responses to various gases. This results in increased sensitivity and quicker response times for nanoscale thin films [6]. In this study, Cr2O3:Al thin films with various Al doping rates (0, 2, 4, 6) wt.% are intended to be used as NO2 gas sensors. Plasma R.F. magnetron sputtering was used as a method of preparation, and the characterization and sensitivity percentage for the produced films were examined.

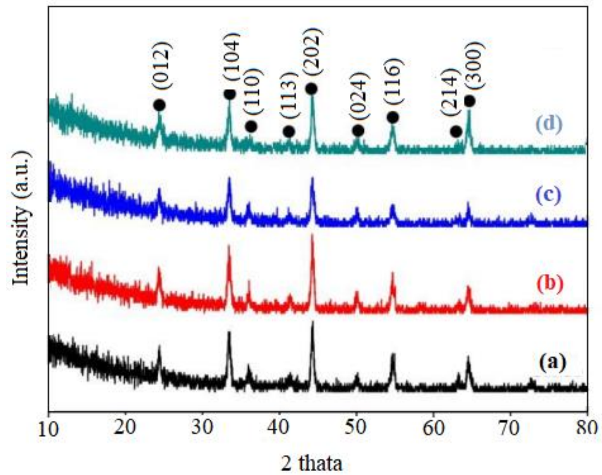
Materials and Method

In this study, Cr2O3 powder was combined with Al powder of high purity (99.99%) and different doping ratios (2, 4, and 6 wt%) before being pressed with hydraulic pressure under 10 tons to create a target with dimensions of 5 cm in diameter and 0.5 cm in thickness. RF magnetron sputtering with spent plasma was employed to deposit the thin layers. Vacuum pressure of 3 10-5 Torr and sputtering pressure of 6-7 10-3 Torr were the prepared conditions. Argon was the sputtering gas. The heat of the substrate was and 100 °C, and the power of the manufactured samples was (100)watt and 2 hours as the time of deposition [7]. Alcohol, ultrasonic, and distilled water were used to clean the substrate. At last, they were cleaned using soft, specialized cleaning paper. The substrate has the following dimensions: (20251.5 mm3). The acquired samples underwent a two-hour annealing process at 450 oC. The American-made CRC (Compact Research Coater600 Tor) apparatus were utilized to deposit the films. Cu was the target of the X-ray diffraction, with wavelengths of =1.5406 oA and a voltage of 40 Kv being employed. AFM stands for atomic force microscopy (SPM Nitegra NT. MDT). Scan electronic microscopy (SEM) devices were utilized to investigate the sencing properties, and they were of type JEOL, JSM67001.

Results and Discussion

Diagrams of Cr2O3:Al film X-ray diffraction (XRD) were displayed in Figure 1. Peaks in the spectrum were of a good crystalline nature, and hexagonal axes were the structure phase [8]. As can be seen in Fig. 1, the size of the crystals in planes 012, 104, and 110 increased as the Al concentration increased from (2 to 6) wt% before decreasing. Additionally, we can see that the peak intensities were higher at the ratio of 2% Al in plane (012) and 2=24.41, indicating that the addition of Al dopant increased the obtained films' crystalline size and slightly widened their dominant peaks. Peak Cr2O3 film intensity has been declining. It might go back to the impact of Al doping. This result is in agreement with those of Mohanapandian [9] and may be the result of a limited quantity of aluminum atoms having an effect on the arrangement of oxygen with Cr atoms, increasing the crystalline size. The area under the curve shrank as the intensity of the peaks increased in concentration from (2 to 6)Al wt%.

Figure 1. XRD patterns for Cr2O3:Al films with different ratio., (a) Cr2O3 pure, (b) Cr2O3:2%Al, (c) Cr2O3:4%Al, (d) Cr2O3:6%Al.



In Fig. 2, three-dimensional pictures of Cr2O3:Al films with varying Al ratios were displayed along with the surface of the cart of gren size distribution. The AFM pictures revealed that each film had a granular texture. Additionally, the images demonstrated a larger surface area, which is suitable for a gas sensor because film roughness and gas sensitivity are inversely correlated [10, Deshpande's results]. At 4% Al doping, the average RMS and roughness values were (3.54 and 2.98 nm, respectively); see table 1. The finer some hillocks, which have an impact on the dispersed randomly, may be the cause of the increases in roughness value [11].

Figure 2. AFM images of Cr2O3:Al films and the chart of grain density distribution.

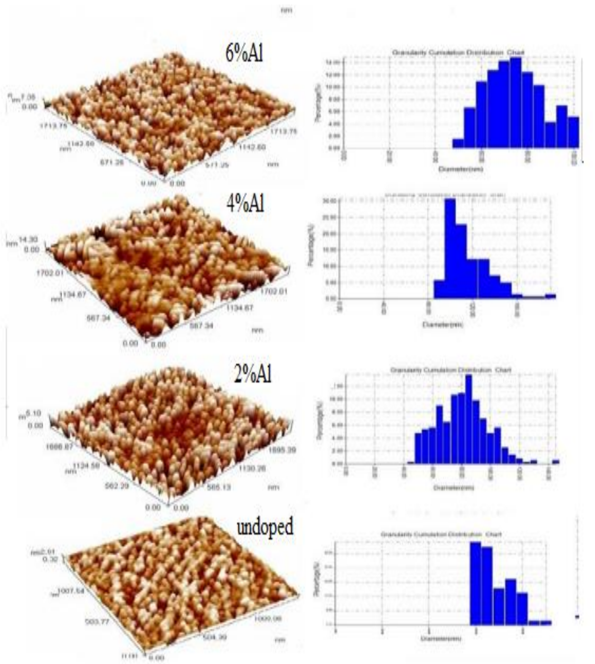


Table 1. Summarized the data of AFM images of Cr2O3: Al thin films

Samples	Average green size distribution (nm)	Average Roughness (nm)	RMS roughness (nm)
pure	65.80	0.45	0.53
2%Al	77.31	1.23	1.40
4%Al	82.51	2.98	3.54
6%Al	89.15	1.64	1.81

According to Fig. 3, the transmission spectra of Al-doped Cr2O3 films decreased as the doping ratio increased while transmittance increased as the photon wavelength increased.

According to the absorption coefficient spectra (Fig. 4), there was more absorption at 360 nm than at other wavelengths. According to Fig. 4, the absorption increased as the percentage of Al in the mixture rose from (2 to 6)% wt. On the other hand, as the wavelength increased, the value of the absorption coefficient decreased.

Figure 3. Transmission spectra of Cr2O3 :Al films as a function of wavelength.

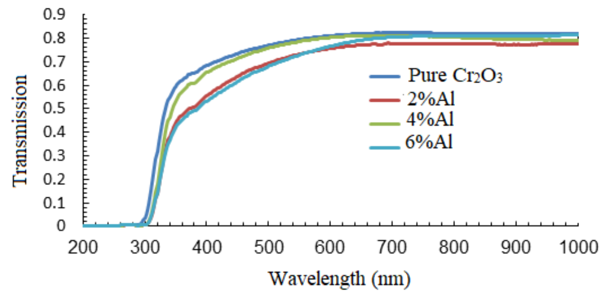


Figure 4. The absorption coefficient of Cr2O3:Al films with wavelength.

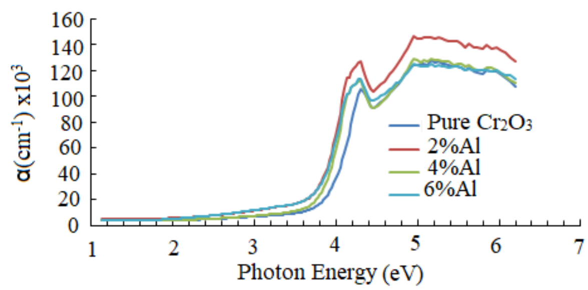
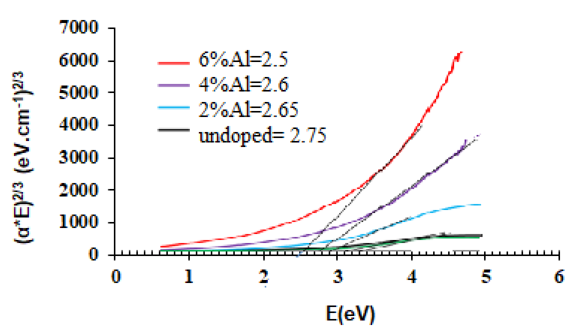


Figure 5. showed the (αhυ)2 versus hυ, where the extrapolation the linear portions on the curve to the hυ axis for measurement the energy gap.

Figure 5. Energy gap for Cr2O3: Al films at different ratios of Al



When compared to the undoped Cr2O3 (2.75eV), the absorption peaks showed a longer wavelength shift as the ratio of Al dopant in the mixture [12,13]. As a result, by increasing the doping from 2.75 to 2.50 eV, the energy gap was reduced. These findings concur with those of the researchers [14, 15].

Sensitivity% of the Cr2O3: Al films calculate by used Eq. 1 [7].

S%= Gg - Ga / Ga ----------------(1)

Where Ga: the sensor's conductance in air; Gg: the sensor's conductance when the target gas is present. This study looked into the Cr2O3:Al films' sensitivity to oxidized gas (NO2). Figures 6, 7, respectively, illustrate the response and recovery times of Cr2O3:Al films for NO2 gas. It is evident that the response time increased when adding 2% aluminum, decreased when adding 4% aluminum, and then returned to its height at 6% aluminum and high response temperatures, respectively, of (200, 250) o C. The effect of Al concentration on the structure of Cr2O3 film and this effect on the response of prepared films is the cause of the oscillation in the value of response time [16]. The Cr2O3:Al films' sensitivity percentage to the NO2 gas presence was shown in Fig. 8. We observe that the sample 4%Al had the highest sensitivity at 200 o C, reaching 32%. This is because the sample 4%Al performed better than the other prepared samples in terms of structural and optical properties, and this is consistent with research findings that follow in the same direction. [17].

Figure 6. The response time of Cr2O3: Al films at different concentration of Al

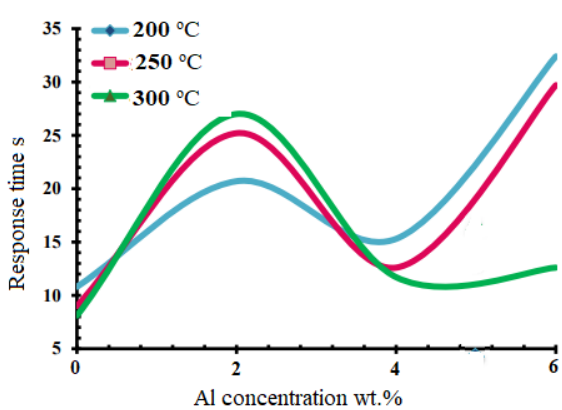


Figure 7. The recovery time of Cr2O3: Al films at different concentration of Al

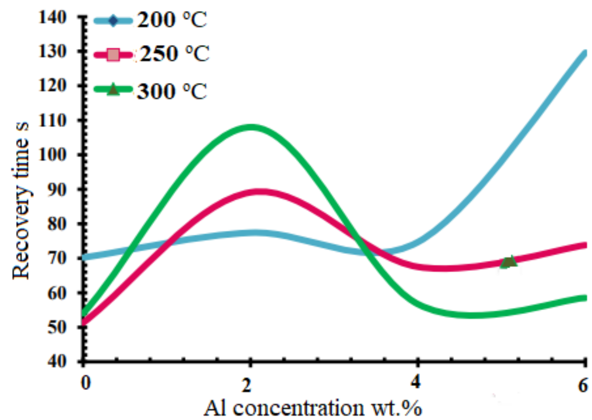
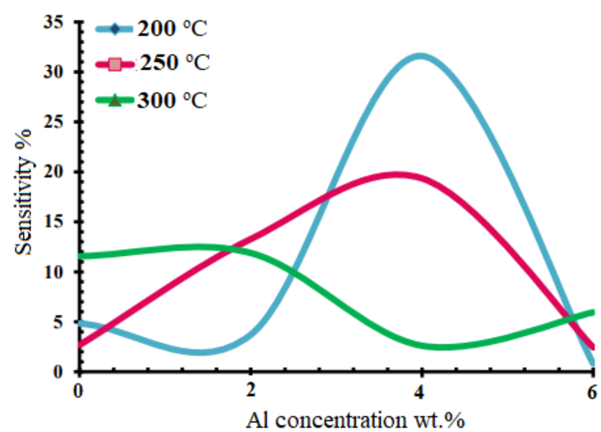


Figure 8. The sensitivity of Cr2O3: Al films at different ration of Al-doping at (200,250, and 300) °C



Conclusions

An oxidation NO2 gas sensor made by plasma RF magnetron sputtering was investigated for its structural, optical, and gas sensor properties. The XRD results revealed a hexagonal phase in the structure with a rotation peak of Cr2O3: Al in plane (104) at 4% weight. The AFM images showed a granular structure, and as the Al concentration ratio was increased, the roughness also increased, peaking at 4%Al (2.98) nm. With an increase in the ratio of Al concentration, the energy gap shrank from 2.75 to 2.5 eV. The best sensitivity to NO2 gas was found in the

4% Al doped Cr_2O_3 film, which was 32% at 200 oC.

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