Indonesian Journal of Electrical Engineering and Computer Science
Vol. 28, No. 2, November 2022, pp. 686~692
ISSN: 2502-4752, DOI: 10.11591/ijeecs.v28.i2.pp686-692

Cadmium sulfide doped with silver as CO_2 gas sensor using pyrolysis technique

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Article Info

Article history:

Received Mar 17, 2022
Revised Jul 23, 2022
Accepted Aug 4, 2022

Keywords:

Atomic force microscope
CdS/Ag thin films
Chemical spray pyrolysis technique
CO_2 gas sensor
X-ray diffraction

ABSTRACT

The monitoring of CO_2 in our life safety, industrial, and chemical laboratory applications make it an inspiring task. The chemical spray pyrolysis technique was used to prepare CdS/Ag thin films. The nanocrystalline cadmium sulfide thin films were doped with Silver at different doping concentrations (0%, 2%, and 4%). The morphologies, structures, and gas sensing properties of CdS/Ag films are presented. The samples were characterized using X-ray diffraction (XRD) and atomic force microscope (AFM). The XRD results show that the films are a polycrystalline composition and hexagonal type with a favoured orientation along (111) direction. The average grain size (nm) of AFM is between 75 and 55 nm. As a result, Ag doping changes the sensitivity of the samples respectively with the percentage of doping with time. The synthesis samples show controlling sensitivity and the small response of sensitivity are the key point in this study.

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1. INTRODUCTION

Cadmium sulfide (CdS) belong to the II-VI group and considered popular material for a variety of devices. It has an average bandgap of 2.42 eV. For a heterojunction solar cell, used as the appropriate material as a window material. It has a high absorption coefficient, good transfer efficiency, reliable, and inexpensive [1]. CdS considered as interesting material because it used at different applications for instance diode sensor [2], transistor [3], photosensor [4], photodetectors [5], photodiodes [6]. CdS have been deposited by chemical bath deposition (CBD) method [7], sol-gel [8], pules laser deposition technique (PLD) [9], chemical vapour deposition (CVD) [10], RF-sputtering [11]. Spray pyrolysis offers certain benefits over the other techniques when compared to them. It has a flexible process mechanism, can create large-area and nanostructured films, and has a low-cost yet effective method. Therefore, it is used to fabricate the samples within this work.

The nanomaterial sensors have been introduced based on multiple principles of absorption for the ultraviolet-infrared (UV-IR) range [12], [13], the resistance of electric circuit [14]–[16], amperometry [17]. Current sensing techniques have been proven to improve in order to test the effectiveness, stability, reaction time, and sensitivity when nanomaterials are used. Organic, inorganic or hybrid components are used in sensing applications. Organic materials have several desired characteristics such as mass transfer, surface chemistry, and gas conductivity. However, inorganic nanomaterials are better in terms of their physical stability, resistivity, and optical characteristics [18], while hybrid nanomaterials combine between the organic and inorganic materials which improve the functional details [19].

In order to track and regulate indoor air quality, carbon dioxide (CO_2) detectors are essential [20]. Ecological, industrial, and sensors are all interested in CO_2 sensing using cheap, remotely controlled, extremely important sensors that operate at ambient temperature [21]. Because of the immense effect of CO_2 pollution on climate change, CO_2 tracking is important in the area of sensing applications [22]. CO_2 detectors are also essential in the agriculture sector [23], as well as breathing monitoring systems in medicine [24], [25], atmospheric institutes in nanotechnology [26], and petroleum refineries [27]. In addition, CO_2 sensors are in high demand for space and industrial uses, such as moderate fire alarm that detects chemical compounds suggestive of a fire [28]. Despite this, owing to the increase chemical stability of CO_2, there are about a few experiments in CO_2 detectors that can function at ambient temperature. In contrast to spectrometric CO_2 gas detectors, physical CO_2 gas sensors based on metal oxides have a low power consumption, convenience, and small size [29]. Gas sensors based on TiO_2 nanostructured has been introduced [30]. Gas sensing technology can be found in two leading commercial platforms: electronic (lambda sensors) and optical (nondispersive infrared (NDIR) sensors and optrodes) [31]

Danie *et al.* [32] synthesised a CdS/WOx nanocomposite that exhibits photocapacitive solar energy storage. They performed spectroscopy characterization and temporary photocurrent reaction comparative to an effect attributed to the extinction of electron-hole reconected in CdS due to hole transmission across the work sheds light on how the constituent materials could be used in the future self-charging solar device. Aishwarya et. al synthesized CdS nanoparticles under different concentrations of cadmium chloride and sodium sulphide used for applications in cancer therapy [33]. Under various doses of cadmium chloride and sodium sulfide, escherichia coli cells were utilized to produce CdS nanoparticles. Scanning electron microscopy (SEM) was used to examine the morphology of the nanoparticles, and X-ray spectroscopy (EDX) was utilized to examine the elemental composition of the nanoparticles. The functional groups of the nanoparticles were determined using Fourier-transform infrared spectroscopy. X-ray diffraction was used to determine the crystalline nature of nanoparticles. Foodborne pathogens were used to test the antibacterial properties of CdS nanoparticles. Zahra *et al.* [34] synthesized cadmium sulfide as quantum dots which have unique medical applications contains identifying cells, identifying viruses, and imaging intercellular proceedings.

This work is dedicated to fabricating CdS samples with Ag doping percentage (0%, 2%, and 4%. The method of the fabrication is Pyrolysis technique. The morphological, structural, and sensitivity towards CO_2 are presented. The homemade device was used to measure the sensitivity of the CO_2 for the three samples with the response time. The response time is very short compared to other works which open door for many applications. As a result, much effort has done into finding or developing new CO_2 sensitive mixtures that can operate at ambient temperature and provide particularly, ambient environment activities, fast response, and a rapid and reusable reaction.

2. PROPOSED METHOD

The CdS thin films were fabricated from a 0.1 M water solution of Cadmium Sulfide CdSO4.8H2O, by spray pyrolysis technique, onto a glass substrate. The silver (Ag) doping silver nitrate (AgNO3) powder dissolved in a precursor solution of CdSO4 with different weight percentages (W.%). The Ag-doped specimens fabricated with the different ratios of 0, 2, and 4 W.% silver concentrations. The CdS specimens fabricated with the same settings, of solution volume 100 ml and nozzle, to the resulting solution sprayed on preheated glass. The chemical equations can be describing the prepared samples as (1), (2).

$$CdSO_4.8H_2O \rightarrow Cd^{+2} + SO_4^{-2} + 8\ H_2O \quad (1)$$

$$Cd^{+2} + AgNO_3 \rightarrow AgSO_4 + CdS \quad (2)$$

After that, the CdS layer added to the CdS samples that resulted from (1) to have the doped samples as (3).

$$CdS + Ag \rightarrow CdSAg \quad (3)$$

The deposition parameters applied to the preparation of CdS thin films are present in Table 1.

Table 1. Deposition parameters applied in this research

Item	Details
CdSO4.8H2O solution concentration	0.1M
Gas pressure	1 bar
Substrate temperature (C_o)	350 C_o
Nozzle to substrate distance	25 cm
Solvent	Distilled water
Deposition of one time	10 Sec
Deposition total time (minutes)	15 min
Rat of spray	2.5 ml/ min
Spray time during each cycle	50 Sec

3. METHOD

The sensor element was linked in series with millimetre electrical impedance tests were done using two millimetres for current, external voltage measurements, and power source in the range of (0-20) Volt to examine the electrical characteristics of the examined specimens. Gas sensing tests carried out using a home-built gas sensing chamber (gas flow elements) as shown in Figure 1. Test chamber unit consists of a stainless steel almost cylindrical shape with diameter and height 20 cm and 16 cm respectively. The base has removable O – ring sealed. The chamber volume is 5024 cm^3 with 50 mbar pressure. The device located at ministry of science and technology. Where CO_2 gas preparation by the (4).

$$H_2SO_4+CaCO_3\ CO_{2\ +}CaSO_{4+}H_2O \quad (4)$$

The film surface adsorbed CO_2 gas which causes increasing the total resistance of the sample. It is promising to reduce the required effective temperature by reducing the heating power and improve the sensor productivity reaction. The nanoscale layer changes the surface exhaustion and can lead to a different reaction with the nanostructure. The increase of crystalline size increased boundary resistance, indicating that the roughness average contributes to gas sensitivity. This lead to a change in the response of the sensitivity of the doped sample. The literature shows that resistance of the detector at RT amplified or reduced because of the electrolytic separation of the tested gasses in the exterior sample [35]. Because Cd atoms occupy the majority of the tetrahedral sites and there are vacant sites, the specimen structure is rather open. As a result, CdS has plenty of places to tolerate inherent defects and immutable doping. The gas sensitivity of thin film elements for CO_2 gas was evaluated at room temperature.

For lowering and oxidizing gases, the resistance reaction of each sensor structure was converted into a sensitivity value using the frequently used formula 5 [36].

$$S = \Delta R/R$$

$$S = Rair – Rgas/Rair \quad (5)$$

where S is the sensitivity, Rair is the resistance in air and Rgas resistance with gas. Figure 1 shows the setup of the suggested system in the lab.

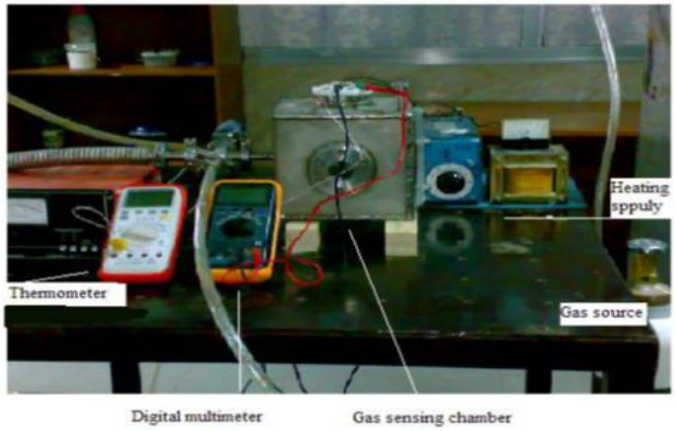

Figure 1. The setup of homemade gas sensing measurement

4. RESULTS AND DISCUSSION

In this section, it is explained the results of research and at the same time is given the comprehensive discussion. The results devided itno three sections regarding to cover the details and data of the suggested samples. These sections are morphological, structural, and sensing properties.

4.1. Morphological properties

The morphology of the deposited films examined using an atomic force microscope (AFM) (Angstrom AA3000). Characteristic 3D and 2D AFM pictures of the CdS: Ag specimen synthesized at different doping concentrationfs (pure (0%), 2%, and 4%) are shown in Figure 2. Figure 2(a) has homogenouse structure surface because it is pur without any adding materials. While Figures 2(b) and 2(c) has different surface morphology because of the metallic Ag.

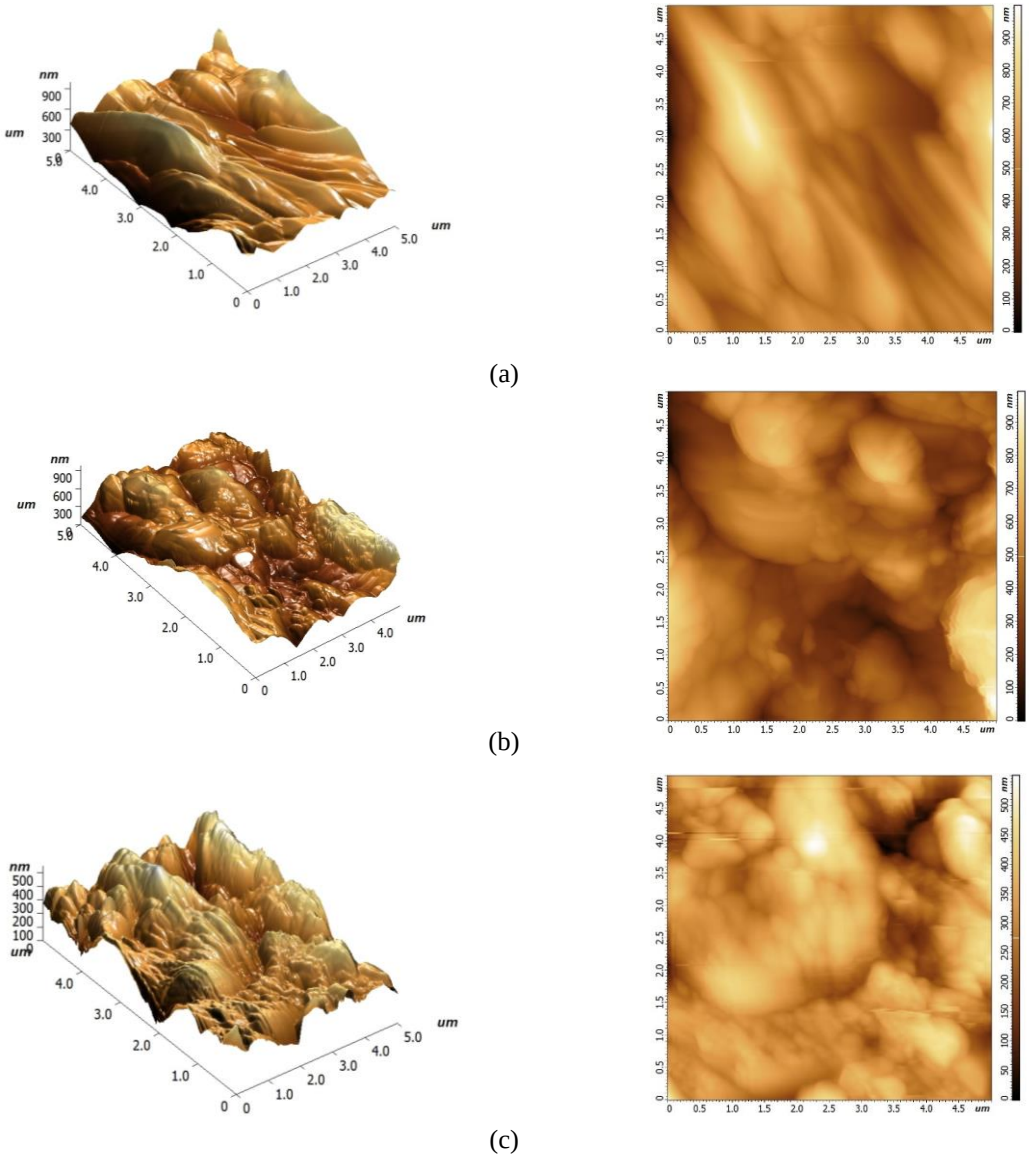

Figure 2. 3D and 2D of AFM images of (a) pure (0%), (b) 2%, and (c) 4% Ag-doped CdS films

Table 2 shows the average crystal size, average roughness, and root mean square (RMS) roughness as determined by AFM. The crystallite size and RMS roughness of the film have risen as the doping concentration has grown. Columnar grain development in the structure might be causing the crystallite size to rise. The crystalline size findings acquired by AFM research differ from those obtained from X-ray diffraction (XRD) observations using the Scherrer equation [37]. This due to that AFM results were described exterior crystalline surface but the XRD results were described interior crystalline structure, as shown in Table 2.

Table 2. Structural characteristics of CdS: Ag specimen

Doping Concentration	RMS (nm)	Average grain size (nm) of AFM	Max crystalline size (nm) of XRD	Roughness average (nm)
pure	81.822	75	27.7	62.716
2%	131.893	65	37.5	100,479
4%	150.547	55	53.3	117.626

4.2. Structural properties

Structural details of the CdS/Ag samples presented by XRD technique of Shimadza-6000 using Cu Kα radiation. Figure 3 shows the XRD data of pure and CdS doped with Ag thin film. These samples show polycrystalline and peaks that are ascribed to the hexagonal structure. The peaks of the film corresponding to Miller planes (111) and (102) reflections position at 2θ=26.6 and 2θ=36.7 with (x= 0, 2% and 4%) respectively, for the pure and doping samples. The CdS structure films reported by many studies confirming the cubic and hexagonal crystalline shape [38].

There are no peaks associated to metallic Ag or Ag compounds. As a result, Ag atoms can be exchanged for sulphite atoms or integrated into the CdS lattice's interstitial sites. This indicates that the precursors have been fully converted to the CdS phase, and that Ag doping has had no effect on the CdS lattice's hexagonal structure. Despite the variations in the atomic radius of the server and the dopant, there are no changes in the peak position.

4.3. Sensing properties

The sensitivity response time is changed with the doping ratio 4%, which means we can control the sensitivity time. The previous reports show long sensitivity response time for CdS [35]. However, the sensitivity percentage is changed with changing the doping ratio. The lowest sensitivity (%) with the doping ratio 4% due to the effect of the Ag. The high interaction to CO_2 can be explain to the sample modification. In the two-dimensional system, the electron-electron interaction in the presence of periodically heightened disorders can establish the adsorption, ionization, and diffusion interaction resulting in different sensitivity.

There are two significant indicators for the time response and recovery curve to show sensor performance. The response time or the raising time describe the sensor resistance that reach 90% from the steady point, while the recovery or falling time describes the sensor resistance to recover about 90% from the total changing after test gas stopped pumping. The faster response and recovery sample time of the sensor is due to adsorption at the sample surface. The small response time means that sample has fast oxidization with gas. The sensitivity CdS:Ag thin films (0%, 2% and 4%) shown in Figure 4.

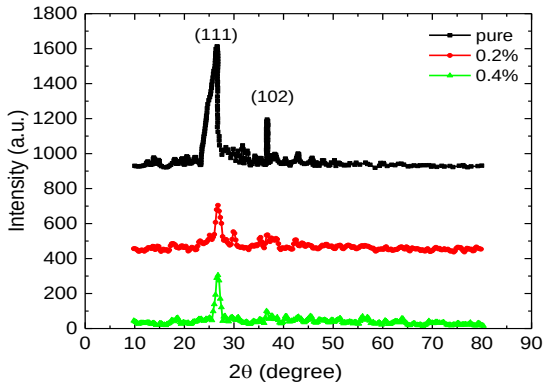

Figure 3. XRD data of pure, 2%, and 4% Ag-doped CdS films

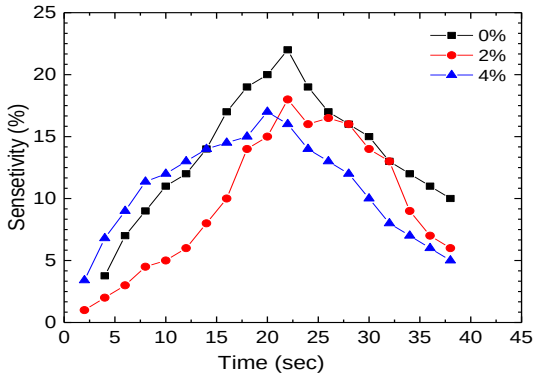

Figure 4. The relation between the sensitivity and time in second

5. CONCLUSION

Pure and Ag-doped CdS specimens were deposited using the chemical spray pyrolysis technique. The size of the molecular of the doped samples is larger than that of the pure sample. In this research, we found CdS has a polycrystalline composition with Hexagonal type, and has favourite directions for the growth of granule (111) and (102). We observed the sensitivity was decreased with an increased doping ratio because Silver is oxidized before the formation of a crystalline compound. We observed the sensitivity was very low

because the CO_2 gas was inert gas. The roughness was increased with doping increased too. The response time is very short comparing with other studies which make these samples are desirable to detect CO_2.

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