Solid State Technology
Volume: 63 Issue: 2
Publication Year: 2020

Synthesis and Characterisation of ZnO–Ag Thin Films and Their use as Ammonia Sensors

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Abstract

This study involves the preparation of colloidal silver (Ag) nanoparticle solution using Turkevich method. Specifically, the solution is mixed with the zinc nitrate hexahydrate and hexamethylenetetramine solution with various volume ratios (e.g. 50, 70 and 90 AgNPs %V) to deposit zinc oxide (ZnO)–Ag thin films on glass substrates at 350 °C using chemical spray pyrolysis technique. Then, these thin films are used to measure the sensitivity of ammonia (NH_3) at room temperature (30 °C–32 °C). The thin films formed by this technique have been characterised by the following measurements: FE-SEM, XDR, AFM and EDXA; whereas, AFM, UV-Visible spectrophotometer and FT-IR spectrophotometer have been used to characterise the prepared Ag nanoparticles. The average size of ZnO–Ag nanoparticles formed on glass substrates is within the range of 68.93–86.64 nm, whereas the average size of Ag nanoparticles formed through Turkevich method is 48.9 nm. The XRD measurements show the wurtzite hexagonal and face centred cubic crystal structure of ZnO and Ag, respectively. The thin film that contains 50 %V of Ag has the highest gas sensitivity (69%). The high sensitivity of the ZnO–Ag sensor at room temperature is an indicator of the high efficiency of NH_3 gas sensing.

Keywords:Gas sensor, NH_3, AgNPs, Turkevich, ZnO

1. Introduction

Numerous gases, such as ammonia (NH_3), carbon monoxide (CO), sulphur dioxide (SO_2), nitrogen oxide (NOx) and hydrogen sulphide (H_2S), are considered toxic and polluting to the environment. These gases are a major concern for researchers [1-3]. NH_3 is a colourless, explosive, hazardous and flammable gas accompanied by pungent odour. NH_3 gas has a harmful effect on the throat, eyes and respiratory and pulse rates. It can also cause oedema of the lungs, permanent blindness and death upon prolonged exposure. This gas is produced in our environment from countless industrial sources, such as fertilizers, textiles, refrigeration, different chemicals, food processing industries, fire power plants and pesticides [4-8]. Therefore, NH_3 production has become important in the development of sensors for explosive and toxic gases that are considered sources of leaks and spills; it is also well-known for its use

in environmental monitoring and food quality control [9,10], industries, medical diagnosis, and agriculture [11].

Zinc oxide (ZnO) nanoparticles are used in different applications, such as UV sensors [12], transparent electrodes [13], optoelectronic devices [14], gas sensors [15,16], transducers [17] and solar cells [18]. In terms of gas sensing application, ZnO nanomaterials have been used for detecting and reducing oxidative gases with good performance, such as NH_3 [19], NO_2 [20], LPG [21], H_2 [22] and acetylene [23]. ZnO-based sensors are more preferred than other metal oxide-based conductive sensors to gas species because of their low cost, high sensitivity, ease of fabrication [24], long-term stability, short response–recovery time, fast response and excellent electrical performance [25-27].

Doping with noble metals, such as Ag [28–30], Ni, Pd, Pt [31–33] and Au [29], improves the electronic properties and increases the surface area of the ZnO nanoparticles, which are considered extremely important for enhanced gas sensor applications [34]. Ag nanoparticles can improve their gas-sensing performance greatly because it can accelerate the chemisorption process of metal oxides [35].

Various methods, such as spray pyrolysis [36,37], pulsed laser deposition [38] and sol–gel [39], can be used to synthesise ZnO films. Spray pyrolysis is a simple method that can be used to prepare thin films by spraying a solution on a preheated surface, wherein a chemical compound is formed through the reaction of the constituents. Spray pyrolysis is firstly used in 1966 to prepare a CdS-made thin film [40-42]. This method has many advantages [36], including its simplicity in doping the prepared films by adding any element in any proportion to the spray solution [43], does not require vacuum (evacuation) at any stage (vacuum conditions are not required) [44], does not require high-quality chemicals or substrates [45] and the thickness of the prepared films can be easily controlled by changing the parameters of spray process [46]. Accordingly, this research aims to prepare ZnO–Ag thin films using NH_3 gas sensors.

2. Materials and Methods

2.1Chemicals

Zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$, Ethanol C_2H_5OH, hexamethylenetetramine $C_6H_{12}N_4$ and silver (Ag) nitrate $AgNO_3$ were commercially purchased from Sigma–Aldrich. Trisodium citrate $Na_3C_6H_5O_7$ was purchased commercially from AppliChem GmbH in Germany. All these chemicals were used as received from the abovementioned manufacturers without using any additional purification.

2.2 Preparation of spray solutions

1. Solution A: $AgNO_3$ (0.1275 g) was dissolved in 250 ml of deionised water under continuous stirring and heated at 85 °C (±3) using a hotplate stirrer. Then, 25 ml of trisodium citrate (2%) was added slowly (Fig. 1).

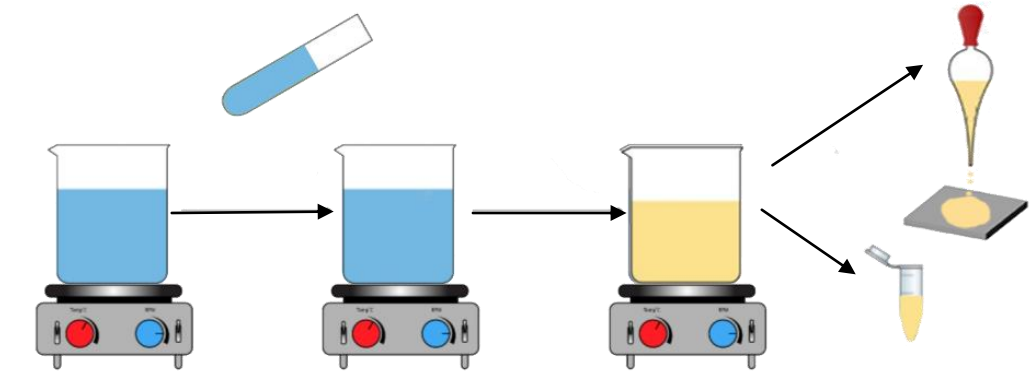

Fig. 1: Scheme of silver nanoparticles preparation

The golden-yellow colour was observed (i.e. an indication of Ag nanoparticles) after the addition of trisodium citrate solution (typically 6–7 min after addition). The hot plate stirrer was turned off, and the coloured solution was removed to cool it at room temperature for later use. Several drops of this solution were dispersed on clean glass substrate and dried in oven at 60 °C to gain the AFM and XRD data of the prepared Ag nanoparticles. Ag nanoparticles were formed according to Eq. 1 [47,48].

$$4Ag^{+}+C_6H_5O_7Na_3+2H_2O\rightarrow 4Ag^{0}+3Na^{+}+C_6H_7O_5H_3+H^{+}+O_2 \quad (1)$$

2.Solution B: 1 g of $Zn(NO_3)_2.6H_2O$ and 10 g of $C_6H_{12}N_4$ were dissolved in 200 ml of deionised water and heated under continuous stirring using a hotplate stirrer to 50 °C for 1 hour to be more homogenous and ready for the spraying process. This solution formed the ZnO nanoparticles during spraying process (Eqs. 2–5) [49].

$$C_6H_{12}N_4+6H_2O \xrightarrow{\Delta} 6HCHO+4NH_3 \quad (2)$$

$$NH_3+H_2O \rightarrow NH_4^{+}+OH^{-} \quad (3)$$

$$Zn^{+2}+2OH^{-} \rightarrow Zn(OH)_2 \quad (4)$$

$$Zn(OH)_2 \xrightarrow{heat} ZnO+H_2O \quad (5)$$

(on preheated substrates)

2.3Synthesis of thin films

Firstly, the glass substrates are cleaned successively using detergent to remove grease and oils over the surface. Secondly, they are ultrasonically cleaned by ethanol for 20 min, followed by washing with deionised water. The glass substrates are then dried using a hot oven to prepare it for use. The homemade spray pyrolysis system was used to deposit ZnO–Ag thin films on the preheated glass substrates by using an aqueous solution as a precursor. This aqueous solution is composed of (A) and (B) solutions with various solution volume ratios listed in Table 1. The scheme diagram of the homemade spray pyrolysis unit in our study is shown in Fig. 2. Compressed air is used as a carrier gas to carry the precursor to the spray nozzle to spray it into the preheated substrate. Crystalline growth was observed on ZnO–Ag thin films because of nucleation, and thermal decomposition

reaction occurred when the spray solution dropped and reached the hot substrates. After depositing the thin films successfully, the prepared thin films are annealed inside the furnace in air atmosphere for 3 hours at 500 °C. Various parameters associated with the thin-film deposition process are listed in Table 2.

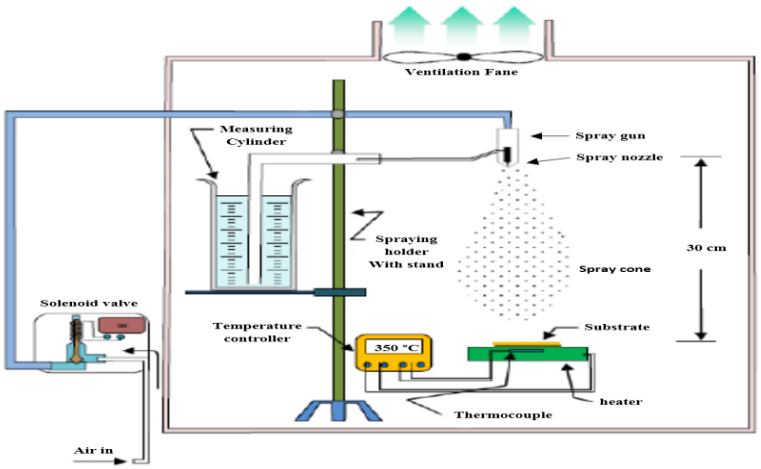

Fig.2:The scheme of the homemade spray pyrolysis system experimental setup used in our study

Table. 1: Various solution volumes ratios used in our study

Thin film symbol	Volumes ratios		Volume of (B)solution	Volume ofsolution (A)	Total volume
	Solution ratio (B)	Solution ratio (A)			
C1	10%	90%	10 ml	90 ml	100 ml
C2	30%	70%	30 ml	70 ml	100 ml
C3	50%	%50	50 ml	50 ml	100 ml

Table 2:The parameters associated with the thin film deposition process

Spray parameters	Optimum item/value
Substrate temperature	350±15 °C
Carrier gas	Compressed air
Nozzle	Stainless steel
Solvent	Deionized water
Substrate - nozzle distance	30 cm
Solution spray rate	13 ml/min
substrate	Glass
Spray time	9 Sec.
Time interval between sequent sprays	9 Sec.

2.4Sensor fabrication

To fabricate the sensor device, a metal mask was fixed on the surface of the thin films deposited on the glass substrates. Then, the substrates were placed in the high vacuum physical vapour deposition system to deposit two aluminium electrodes on the thin-film surface (Fig. 3). The homemade gas sensing system (Fig. 4) was used to determine the gas sensitivity measurements of the ZnO–Ag thin films. The fabricated sensors were tested at different concentrations of NH3 gas (50, 100 and 150 ppm) at room temperature. The gas sensitivity (S%) of fabricated sensors was calculated through Eq. (6) [50].

$S\% = (R_a - R_g / R_a) \times 100$, (6)

where R_a is the electrical resistance of thin film in fresh air, and R_g is the electrical resistance of thin films after test gas exposure.

The response and recovery times were calculated through sensitivity plot. These measurements were defined as the time required for the sensing element to achieve 90% and 10% of the change in resistance from its original resistance [51,52].

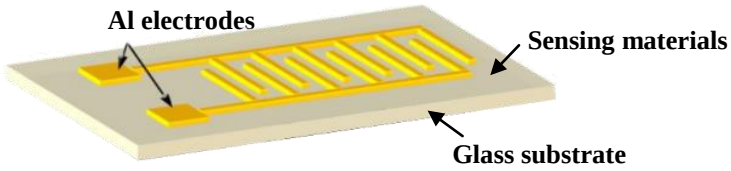

Fig. 3 A schematic of the patterned aluminum electrodes

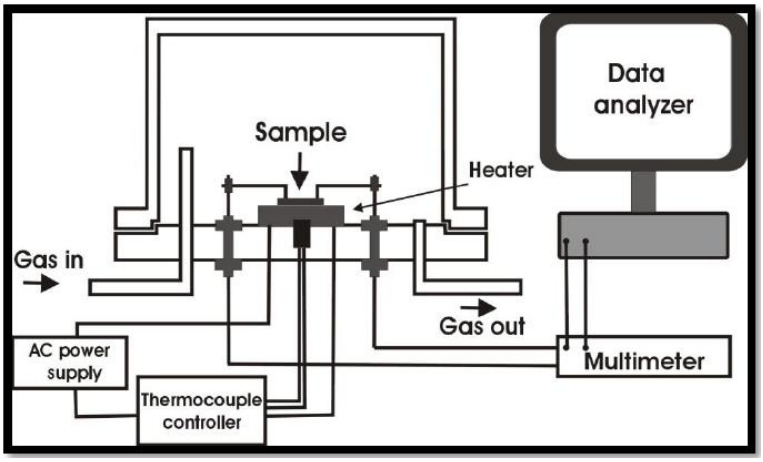

Fig. 4: A schematic of homemade gas sensing system

2.5Characterisations and measurements

The existing elements, crystal planes and crystallinity of Ag and ZnO–Ag nanoparticles thin films were investigated by using X-ray diffractometer (XRD) (SHEMADZU-600-Japan) with Cu–Kα radiation (λ = 1.5405 A°) with a range of 10°–80°. The morphology and composition of ZnO–Ag thin films were investigated by using atomic force microscopy (AFM) (CSPM-USA) and field emission scanning electron microscopy (FE-SEM) (FEI NovaSEM 450-USA) coupled with EDS. The morphology of prepared Ag nanoparticles was examined by scanning electron microscopy (SEM) (Hitachi-S 4160-Japan) and atomic force microscopy (AFM) (CSPM-USA). The absorbance measurements of Ag nanoparticle solution and prepared thin films were obtained by using spectrophotometer (UV-Vis) (Jenway-USA) with a range of 300–600 nm and 300–700 nm,

respectively. The vibration modes of the functional group of Ag nanoparticles solution were recorded through Fourier transformation infrared (FT-IR) spectra (Bruker–Germany) using KBr pellets with a range of 400–4000 cm^{-1}. The gas sensitivity of ZnO–Ag sensors was examined using a homemade test system.

3. Results and discussion

3.1 XRD

The observed diffraction peaks at 002, 110, 102 and 100 planes in the XRD patterns (Figs. 5–7) belong to the wurtzite hexagonal phase of ZnO when compared with JCPDS data file no. 00-036-1451 [53,54]. The observed diffraction peaks in the obtained XRD patterns (Figs. 5–8) at 111, 220, 311 and 200 planes belong to face-centred cubic phase of Ag when compared with JCPDS data file no. 00-004-0783 [55].

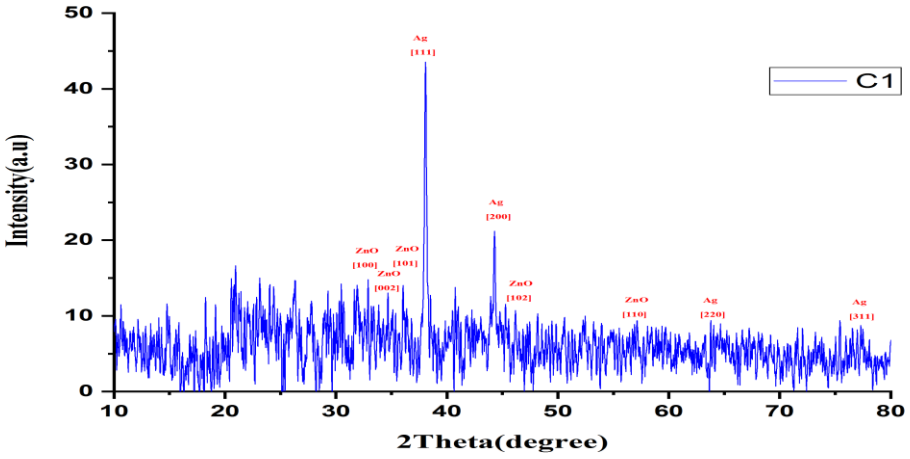

Fig. 5: XRD of (C1) thin film

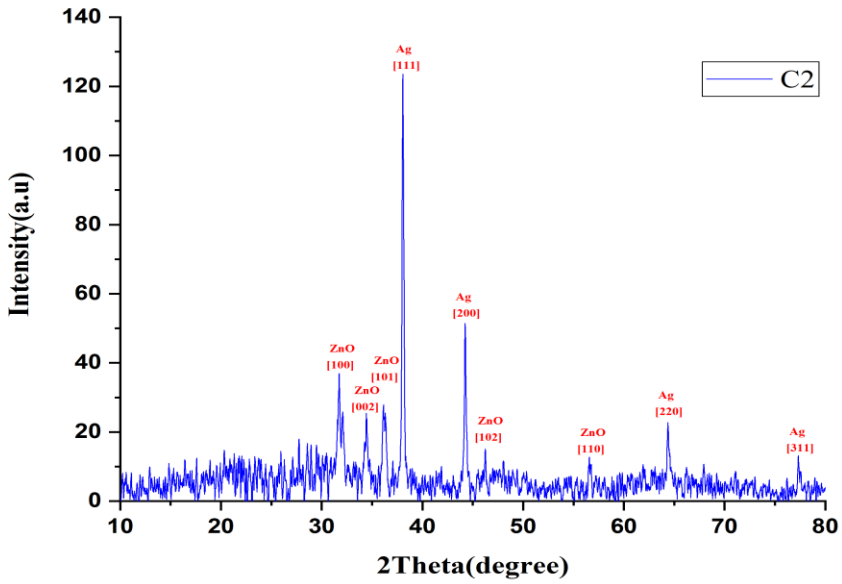

Fig. 6: XRD of (C2) thin film

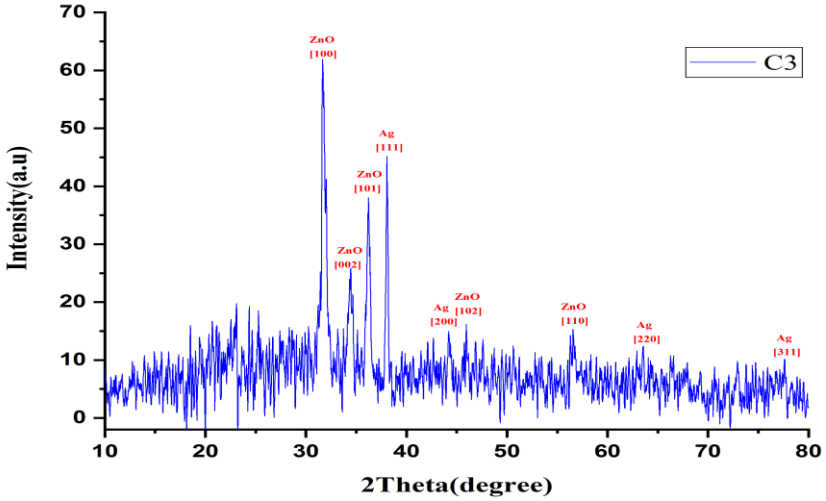

Fig. 7: XRD of (C3) thin film

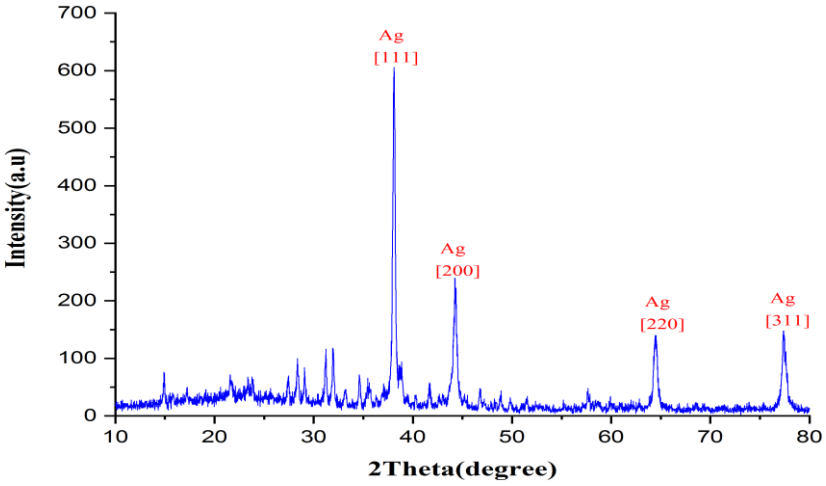

Fig. 8: XRD of AgNPs solution

3.2 FESEM and EDXA analysis

The surface morphology of the films is important given the key role it plays in gas sensing applications [56]. The high-resolution FESEM image of C2 thin film (Fig. 9) shows that ZnO has a nanoneedle structure, which agrees with Yas Al-Hadeethi et al.'s [28] research results. In addition to the sodium produced from the trisodium citrate (reducing agent) used to reduce Ag ions and the other impurities that appeared, Fig. 10 shows that the EDXA spectra of C2 thin film, which contains ZnO and Ag, may have come from materials that are used for manufacturing glass substrates.

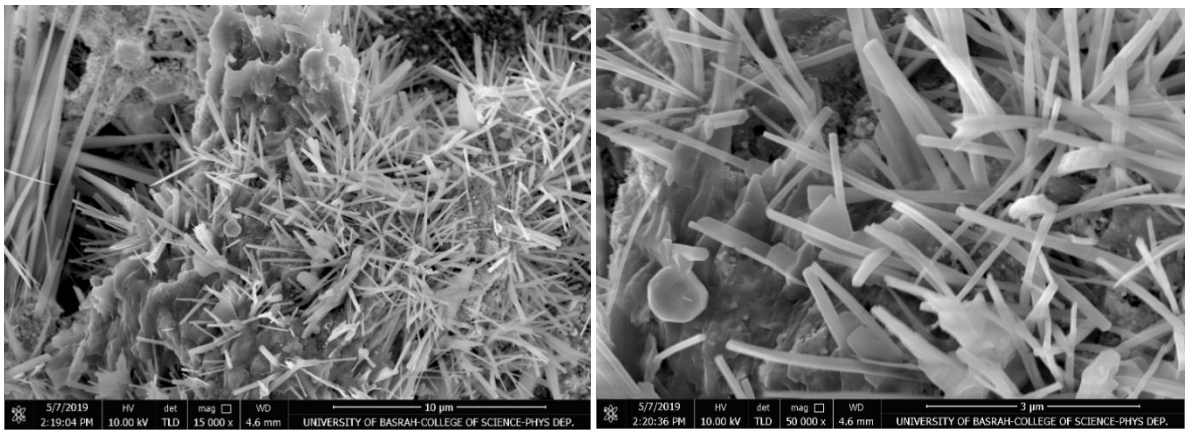

Fig. 9: FE-SEM (C2) thin film

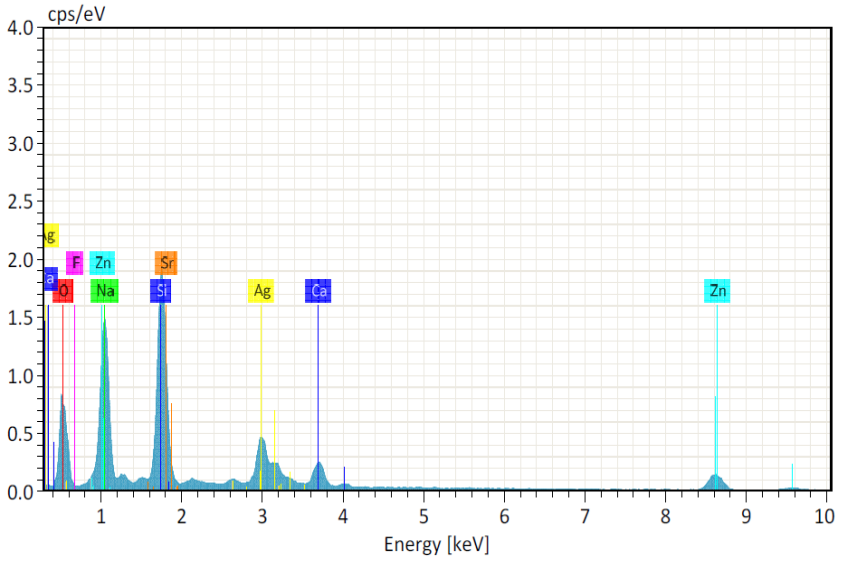

Fig. 10: EDXA spectra of (C2) thin film

3.3 AFM

The form of the prepared thin films was investigated using AFM. Surface roughness and particle size play important roles in the interaction of gases within the surface [57]. AFM images of C1, C2 and C3 thin films deposited on glass substrates are shown in Fig. 11. These images have a highly regular and homogeneous granular distribution. The C1, C2 and C3 films obtained the following results: root mean square (RMS) of 7.65, 5.22 and 8.88 nm, respectively; average grain size of 81.17, 68.93 and 86.64 nm, respectively; and average roughness of 6.68, 4.52 and 7.66 nm, respectively. The AFM image of dried AgNPs on the glass substrate has an average grain size of 48.9 nm (Fig. 12).

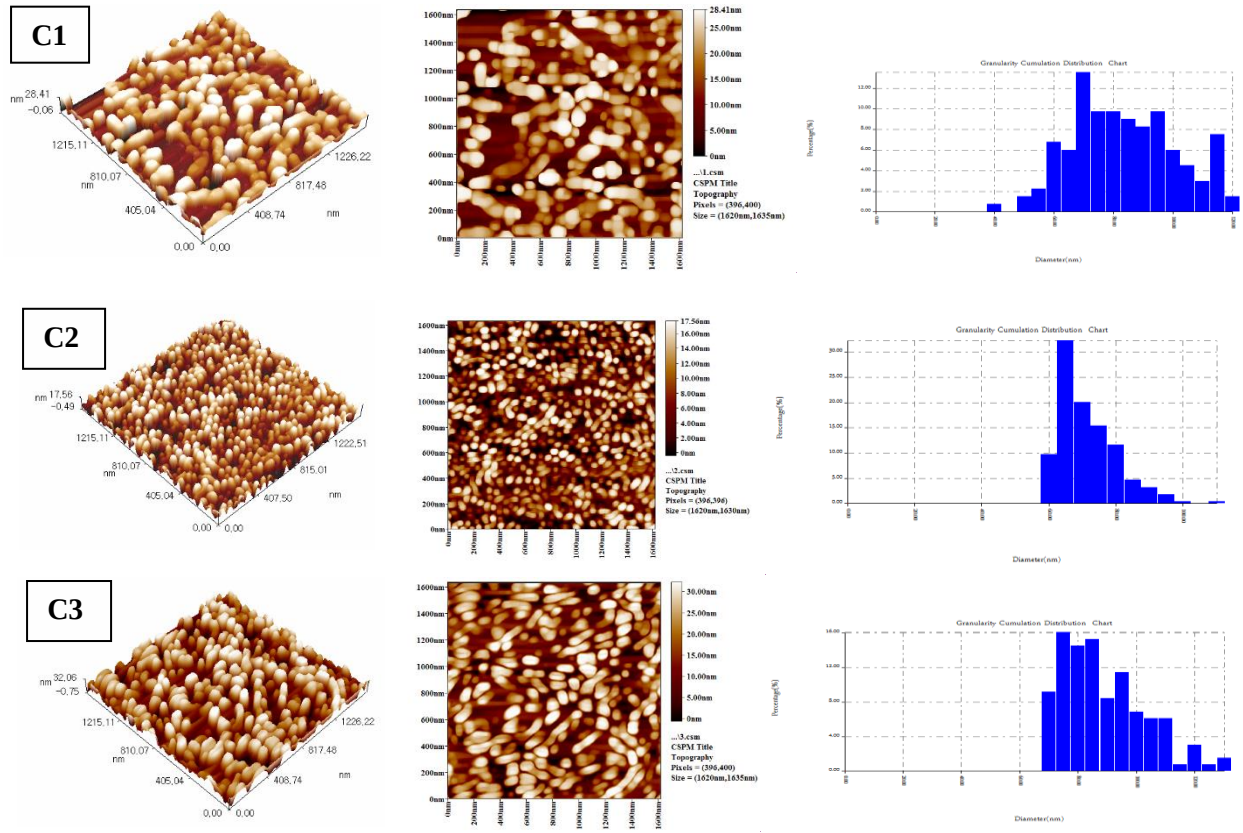

Fig. 11: AFM images of C1, C2 and C3 thin films

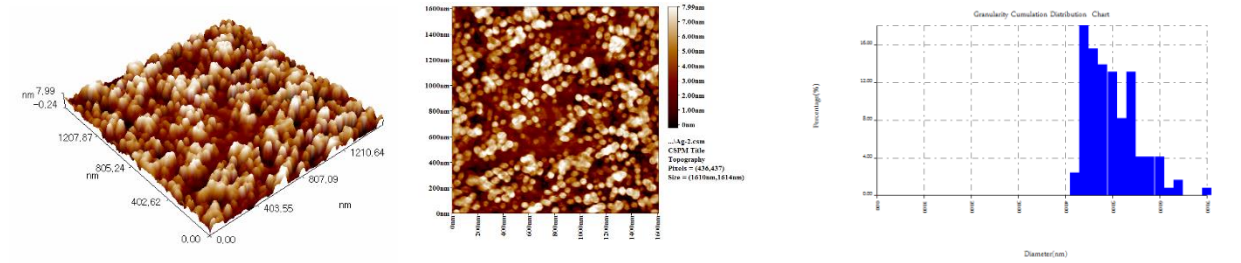

Fig. 12: AFM images of AgNPs

3.4 UV-Vis measurements

Figs. 13 and 14 show the recorded UV-Visible spectra of the deposited thin films and colloidal Ag nanoparticles, respectively. These recorded spectra have good agreement with Ismail and Shameli's research results [58, 59]. The decreasing intensity of the peaks in UV-Visible spectra (Fig. 13) from C1 to C3 thin films is due to the difference in the percentage of Ag nanoparticles in these films.

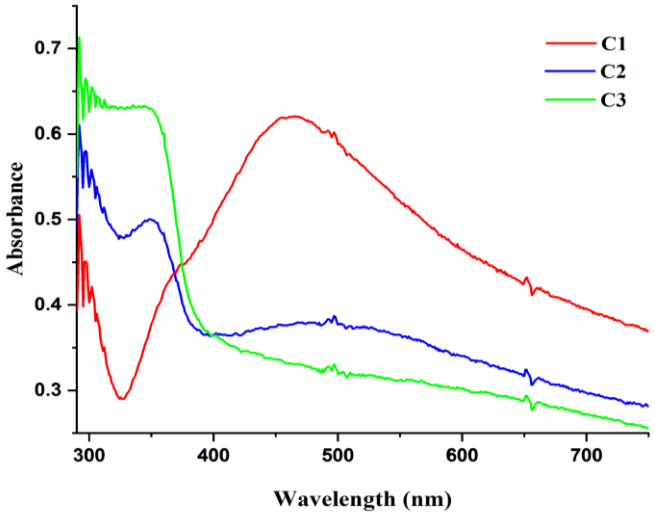

Fig. 13: UV-Vis spectra of C1, C2 and C3 thin films

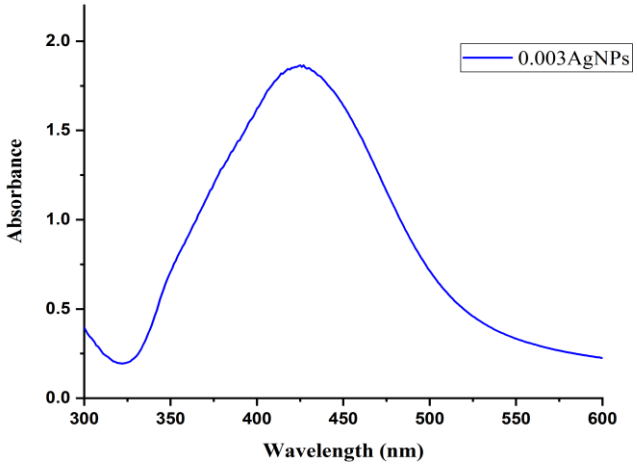

Fig. 14: UV-Vis spectra of AgNPs solution

3.5 FT-IR spectra of AgNPs solution

FT-IR spectroscopy can be applied to the gain information about functional groups of stabilisation and capping of the nanoparticles through peak positions in the spectrum. A drop of colloidal Ag nanoparticles was placed between two NaCl plates and in FT-IR spectrophotometer to scan within a range of 4000–400 cm^{-1}. The FT-IR spectra of the prepared Ag nanoparticles are shown in Fig. 15. The peaks around 1400 cm^{-1} and 1600 cm^{-1} correspond to the anti-symmetric and symmetric stretching of COO^- vibrations of COO^- groups in citrate capped AgNPs, respectively. The broad bands in the 3600–2800 cm^{-1} region correspond to the O−H stretching vibrations of the −OH groups in citrate capped AgNPs [60]. The observed peaks at 1380 cm^{-1}–1390 cm^{-1} belong to the vibrations of the nitro compound (NO_2), which are produced by $AgNO_3$ salt [61]. Ag–Ag vibrates at a wave value below 400cm^{-1} [62]. Thus, it will not be presented in Fig. 15.

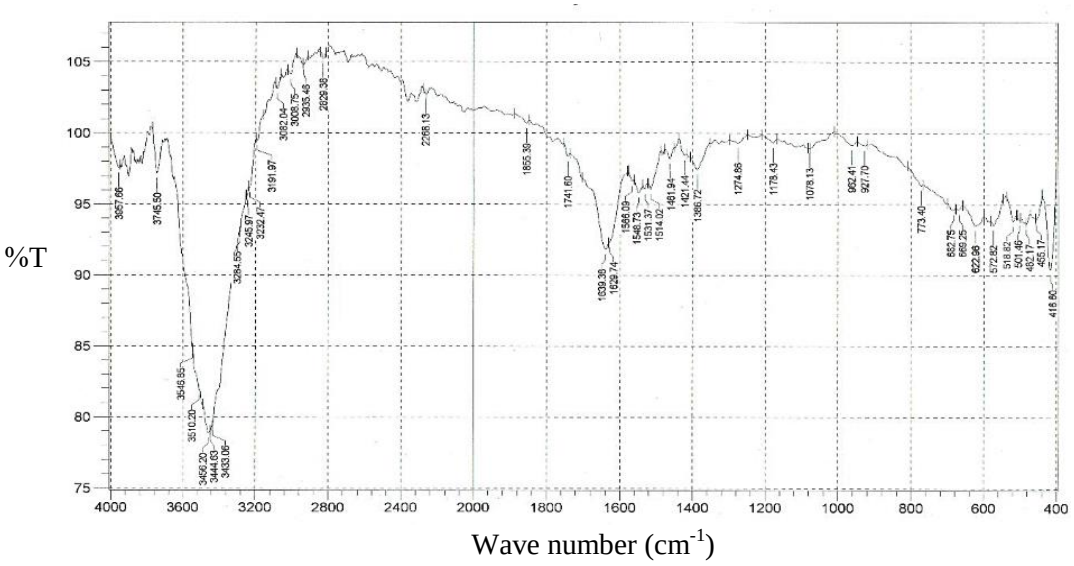

Fig. 15: FT-IR spectra of AgNPs

3.6Gas test

The value resistance of the prepared thin films was converted into sensitivity S (%) using Eq. 6 (Fig. 16). A sharp increase in sensitivity was observed as the NH_3 concentration rose from 50 ppm–150 ppm. This rapid response may be due to the large surface to volume ratio of the nanoneedle and the small grains of the nanostructured film. The sensitivity, response (τ_{res}) and recovery times (τ_{rec}) of C1, C2 and C3 sensor devises are listed in Table 3. The decrease in sensitivity from C3 to C1 was due to the increment in the amount of sodium (provided by the trisodium citrate) in the thin films, which increased the resistance of thin films [63] from C3 to C1.

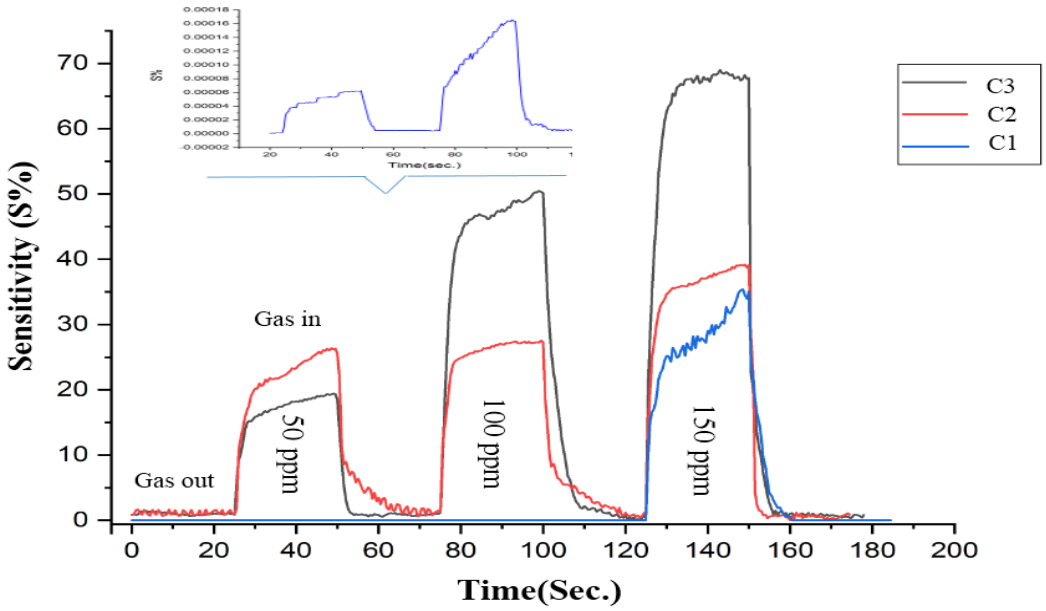

Fig.16: sensitivity of C1, C2 and C3 thin films towards (50, 100 and 150) ppm of NH_3

Table. 3: The sensitivity(S%), response and recovery times of C1, C2 and C3 sensor devises

Sensor devise	Gas concentration (ppm)	Sensitivity (S%)	Response time (Sec.)	Recovery time (Sec.)
C1	50	Little	17.7	4.4
	100	Little	18.9	3.9
	150	35	20	5.7
C2	50	26	15.7	8.5
	100	27	4.2	10.3
	100	39	6.1	1.6
C3	50	19	10.9	2.2
	100	50	5.7	6.7
	150	69	5	3.6

4. ProposedNH_3-sensing mechanism

The NH_3 gas sensor mechanism can be summarised in three steps:

Step 1: Oxygen molecules in the air are adsorbed after being exposed on the Ag surface.

Step 2: The adsorbed oxygen molecules in Step 1 are spilled over to ZnO, wherein the molecules are converted into another oxygenated anionic form, such as O_2^-, O^- and O^{-2}, after capturing the electrons (Eqs. 7–10) from the conduction band of ZnO, thereby increasing the value of the electrical resistance of the sensor.

$$O_{2(gas)} \rightarrow O_{2(ads)} \quad (7)$$

$$O_{2(ads)} + e^-_{(from\ ZnO)} \rightarrow O_2^-{}_{(ads)} \quad (8)$$

$$O_2^-{}_{(ads)} + e^-_{(from\ ZnO)} \rightarrow O^-_{(ads)} \quad (9)$$

$$O^-_{(ads)} + e^-_{(from\ ZnO)} \rightarrow O^{-2}{}_{(ads)} \quad (10)$$

Step 3: After the exposure of the thin films to NH_3, absorbed oxygen (O_2^-, O^- and O^{-2}) can react with NH_3 molecules and break it into H_2O, N_2 and three electrons (Eq. 11). These electrons will be transmitted into the conduction band of ZnO, thereby causing high signal given the decrease in the resistance of the sensor [64,65]. All these steps are illustrated in Fig. 17.

$$2NH_3 + 3O^-_{(ads)} \rightarrow N_2 + 3H_2O + 3e^-_{(to\ ZnO)} \quad (11)$$

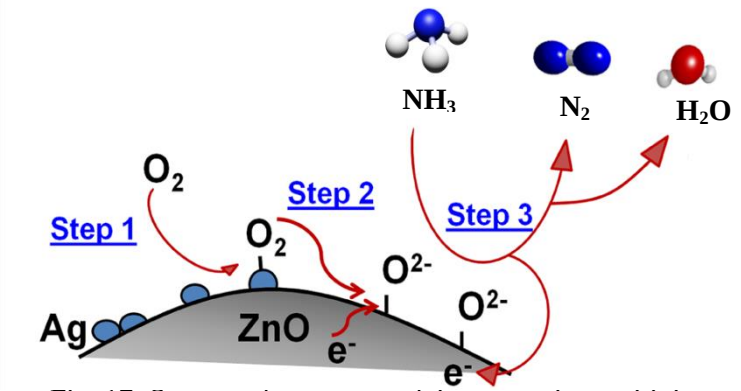

Fig. 17: Suggested steps to explain ammonia sensitivity

5. Conclusion

The prepared ZnO–Ag thin films showed high sensitivity (69%) to NH_3 at room temperature (30 °C–33 °C). The sensitivity to NH_3 gas at room temperature (30 °C–33 °C) is inversely proportional to the increased concentration of the prepared Ag nanoparticles because of the rising concentration of sodium produced from the reducing substance (e.g. sodium citrate) used for the preparation of Ag nanoparticles.

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