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COPPER DOPED ZINC OXIDE THIN FILMS FABRICATED BY SOL-GEL DIP COATING: PIONEERING DIABETES DETECTION IN EXHALED BREATH

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Abstract. This research paper presents an in-depth investigation into Copper-doped Zinc oxide (Cu-ZnO) thin films, fabricated using the sol-gel dip coating method, with a focus on enhancing acetone sensing for non-invasive diabetes detection through breath analysis. The study systematically explores the structural, morphological, optical, and gas sensing characteristics of these thin films using advanced characterization techniques. The analysis of the X-ray diffraction (XRD) confirms a highly crystalline wurtzite structure in both undoped and Cu-doped ZnO thin films. The successful incorporation of copper into the ZnO lattice is evident from the shift in the XRD peaks, indicating successful doping. Scanning electron microscopy (SEM) investigations reveal changes in surface morphology with increasing copper doping concentration, including enlarged grain size and smoother film surfaces, which may impact the sensing properties. Utilising UV-visible spectrophotometry, the researchers demonstrate that Cu-doped ZnO thin films exhibit higher optical transparency compared to undoped films. Moreover, as the copper concentration increases, the optical band gap decreases, suggesting a modification in the band structure of the thin films. To evaluate gas sensing capabilities, an acetone sensing test is conducted. The results show that Cu-doped ZnO thin films outperform undoped films with an enhanced acetone sensing response. The most effective doping concentration of 3 at % of Cu results in the greatest sensitivity, with a 46% level of selectivity, a response time of 31 sec., and a recovery time of 66 sec. to acetone vapor. These results propose its potential as a non-invasive diabetes detection candidate through human breath analysis.

Key words: Copper-doped zinc oxide, Sol-gel dip coating, Acetone sensing, Gas sensing characteristics, non-invasive diabetes detection

1.INTRODUCTION

Millions of people worldwide suffer from the chronic metabolic illness known as diabetes mellitus. Diabetes must be identified and monitored as soon as possible in order to be effectively managed preventing problems from developing. Recently, there has been an increase in interest in non-invasive diabetes detection techniques, such as breath analysis, which presents a potential strategy for the creation of portable and practical diagnostic tools [1]. Due to its higher levels in diabetic patients, acetone, one of the volatile organic compounds (VOCs) found in exhaled breath, has been identified as a possible biomarker for diabetes [2]. Individual differences in breath acetone content are possible and are impacted by a number of variables, including food, metabolism, and general health. However, investigations have shown that both healthy people and diabetic patients have average breath acetone concentrations [3].

Diabetes mellitus is a chronic metabolic illness characterised by increased blood glucose levels. Type 1 and type 2 diabetes are two different types of the disease [4]. Despite having the same name, their underlying causes, onset ages, and treatment methods vary. It is crucial to remember that type 1 and type 2 diabetes have different underlying processes, which has a substantial impact on how they are managed and treated. Unlike type 1 diabetes, which needs lifelong insulin therapy, type 2 diabetes is frequently treated with a mix of oral medicines, lifestyle modifications, and, occasionally, insulin or other injectable therapies [5]. For all kinds of diabetes, regular blood glucose monitoring and healthcare management are crucial to preventing complications and maintaining good health.

The average breath acetone content in people without diabetes (non-diabetics) is normally modest, ranging from 0.9 to 1.8 parts per million (ppm) [6]. It is believed that the body's typical metabolic processes are to blame for this low concentration. Conversely, persons with diabetes who have uncontrolled or poorly regulated blood glucose levels may have greater quantities of acetone in their breath. The body's changed metabolic state, especially the increased synthesis of ketone bodies owing to insulin insufficiency or insulin resistance, is the cause of the elevated breath acetone content in diabetes patients [7]. Patients with diabetes who have diabetic ketoacidosis (DKA), a potentially fatal condition marked by exceptionally high amounts of ketones, may have breath acetone values that vary from 1.5 to 4 ppm or even higher.

This work provides a thorough analysis of the improved acetone sensing capabilities of copper-doped zinc oxide (Cu-ZnO) thin films. These thin films were created using the versatile and economical sol-gel dip coating technique. In order to maximise the efficacy of the Cu-ZnO thin films for non-invasive diabetes detection by breath analysis, the study concentrated on analysing their structural, morphological, optical, and acetone gas sensing properties.

Due to its distinctive qualities, such as high sensitivity, cheap cost, and environmental durability, zinc oxide (ZnO) has become a viable material for gas sensing applications. In particular, ZnO has demonstrated excellent promise in the detection of acetone, a volatile organic compound (VOC) present in human breath and important in the non-invasive diagnosis of diabetes [8]. Zinc oxide (ZnO) is a versatile material with applications across various fields. As a direct-bandgap oxide semiconductor, it is renowned for its remarkable optical and electrical properties. Zinc oxide finds applications in various devices and technologies, such as UV light-emitting devices [9], UV photodetectors [10], solar cells [11], thin film transistors [12], gas sensors [13], and photocatalysts [14, 15]. ZnO thin films are frequently doped with additional elements to improve their optical and/or electrical characteristics [16–19].

Intrinsic ZnO thin films typically exhibit n-type conductivity due to inherent point defects like oxygen vacancies and zinc interstitials. Consequently, achieving stable P-type ZnO materials through doping has become a significant research focus. Theoretical studies suggest that in oxygen-rich environments, Cu serves as a promising candidate for doping to attain n-type ZnO [20]. The effect of Cu doping on the electrical and optical characteristics of ZnO has therefore been the subject of several investigations [21–24].

Due to its cost-effectiveness, uniform film formation, tailored film properties, versatility in substrate compatibility, compatibility with additive doping, scalability and reproducibility, etc., the sol-gel dip coating method was used in this study to prepare pure and Cu doped zinc oxide (ZnO) thin films.

Using X-ray diffraction (XRD) analysis, the structural investigation of the thin films was carried out, indicating the production of a highly crystalline wurtzite structure in both the undoped and Cu-doped ZnO films. The observed change in XRD peaks served as confirmation that copper had been successfully incorporated into the ZnO lattice. With increasing copper doping concentration, the surface morphology of the films changed, showing a larger grain size and smoother film surfaces in scanning electron microscopy (SEM) pictures.

Additionally, compared to films that weren't doped, UV-visible spectrophotometry studies showed that Cu-doped ZnO films had better optical transparency. The observed reduction in the optical bandgap with increased copper content pointed to a change in the films' band structure, which would improve their acetone gas gas sensing capabilities.

The thin films were subjected to an acetone gas sensing test in order to assess their acetone gas sensing capabilities. The improved response to acetone vapour displayed by the Cu-doped ZnO films over undoped films suggests the possibility of selective acetone detection, a crucial biomarker for diabetes. The experiment also determined that a 3 at. % Cu doping concentration produced the maximum sensitivity and response to acetone vapour.

2. MATERIALS AND METHODS

A 0.2 M solution of zinc acetate dihydrate ($Zn(C_3COO)_2 2H2O$) was made by dissolving 0.746 g of the substance in 20 ml of ethanol and stirring it until it was entirely dissolved. For the preparation of Cu-doped ZnO thin films, a 0.02 M solution of copper sulphate was made. This was accomplished by 0.026g of copper sulphate being thoroughly dissolved with 20 ml of ethanol under constant stirring using a magnetic stirrer. Diethanolamine was added drop by drop while the ZnO solution was continually stirred to bring the pH of the solution to 7. The appropriate amount of the copper sulphate solution was added to the ZnO solution to produce the required copper concentration for Cu-doped ZnO thin films. For instance, to prepare 3 at % Ag-doped ZnO, 17 ml of the ZnO solution was mixed with 3 ml of the silver nitrate solution. The resulting mixture was stirred regularly using a magnetic stirrer for an additional two hours to ensure proper mixing. The solution was aged for 24 hours.

We performed a series of 10-minute sonication on glass substrates in acetone, ethanol, and deionized water. After that, nitrogen gas was used to dry the substrates. An automated dip coating equipment was then used to dip these clean, dry substrates vertically into the solution and remove them at a rate of 5 mm/s. The coated substrates underwent a 10-minute drying operation at 100 °C to allow the solvent to evaporate. The coated substrates were then annealed in the air for two hours at 500 °C, resulting in the development of thin films of ZnO and Cu-doped ZnO.

3. RESULTS AND DISCUSSION

3.1. XRD analysis:

An X-ray diffractometer outfitted with a high-resolution detector and a Cu K radiation source was used for the XRD examination in order to assess the structural properties of the films. A range of 20° to 80°, the diffraction patterns were recorded with steps of 0.02°. The four unique samples of ZnO used in the investigation were pure ZnO, ZnO doped with 1% copper, ZnO doped with 3% copper, and ZnO doped with 5% copper. These samples were labelled as Pure ZnO, CuZ-1%, CuZ-3%, and CuZ-5%, respectively. It was found that each sample exhibited a hexagonal wurtzite crystal structure based on the XRD pattern shown in Figure 1.

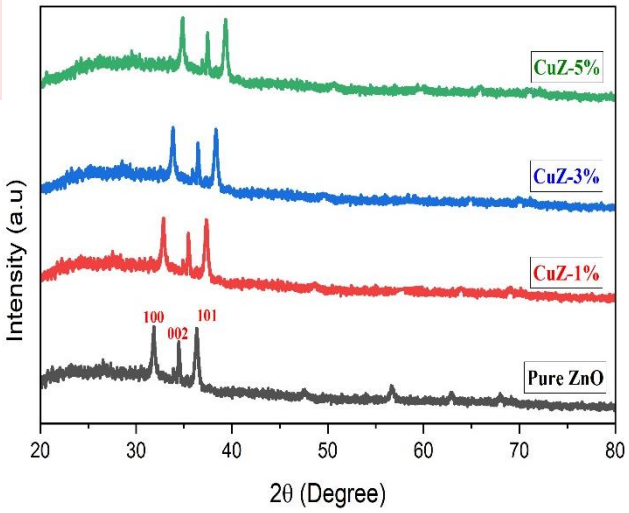

Fig.1.XRD pattern of Pure and Cu doped ZnO films

This was demonstrated by the prominent and well-defined diffraction peak that occurred at an angle of 2 = 34.42° and corresponds to the (002) crystal plane. The ZnO c- axis orientation is compatible with the peak alignment.

The determined diffraction peak angles and related crystallographic planes for different doping concentrations are shown in detail in Table-1. The Joint Committee on Powder Diffraction Standards (JCPDS) card no. 36-1451 was used to identify these diffraction peaks. The XRD patterns showed a modest shift in the diffraction peaks towards higher angles as

Table-1: Doping concentration, crystallographic planes, and diffraction angles of thin films

Doping Concentration	Crystallographic Planes		
	(100)	(002)	(101)
Pure ZnO	31.87°	34.45°	36.33°
CuZ-1%	32.87°	35.46°	37.33°
CuZ-3%	33.87°	36.46°	38.33°
CuZ-5%	34.87°	37.46°	39.33°

the amount of Cu doping was increased. This change indicates that Cu ions have been incorporated into the ZnO lattice. Zn^{2+} (0.72 Å) and Cu^{3+} (0.54 Å) have different ionic radii, which causes lattice strain and a little decrease in the lattice constant of ZnO.

Consequently, there is a displacement of the diffraction peaks. The Scherrer equation, which relies on a full width at half maximum, was used to calculate the average crystallite size of the thin films.The indicated crystallite sizes for pure ZnO and Cu-doped ZnO were 29.1 to 34.5 nm and 22.3 to 32.1 nm, respectively. As the concentration of Cu doping increases, grain formation is inhibited by the addition of Cu ions, resulting in a reduction in crystallite size [25].

3.2. Sem analysis

The surface morphology images of the Cu-doped ZnO thin films are shown in Fig. 2. With the exception of pure ZnO, all films show grains of ZnO that resemble flowers within the plane. The size of ZnO grains gradually increases as Cu doping concentration rises. This demonstrates that Cu doping has a minimal impact on the formation of ZnO crystals, presumably as a result of the low concentration of Cu doping. There is currently conflicting information regarding the effects of Cu doping on ZnO crystal development. For instance, Drmosh, Qasem A., et al. [26] observed non-uniform grain sizes in Cu-doped ZnO thin films compared to pure ZnO thin films, while Othman, A. A., et al. [27] reported that Cu doping led to smaller ZnO grains. Agarwal, D. C., et al. [28] discovered that at low Cu doping concentrations, smaller ZnO grains were produced, whereas at higher Cu doping concentrations, Cu nanoparticles were produced.

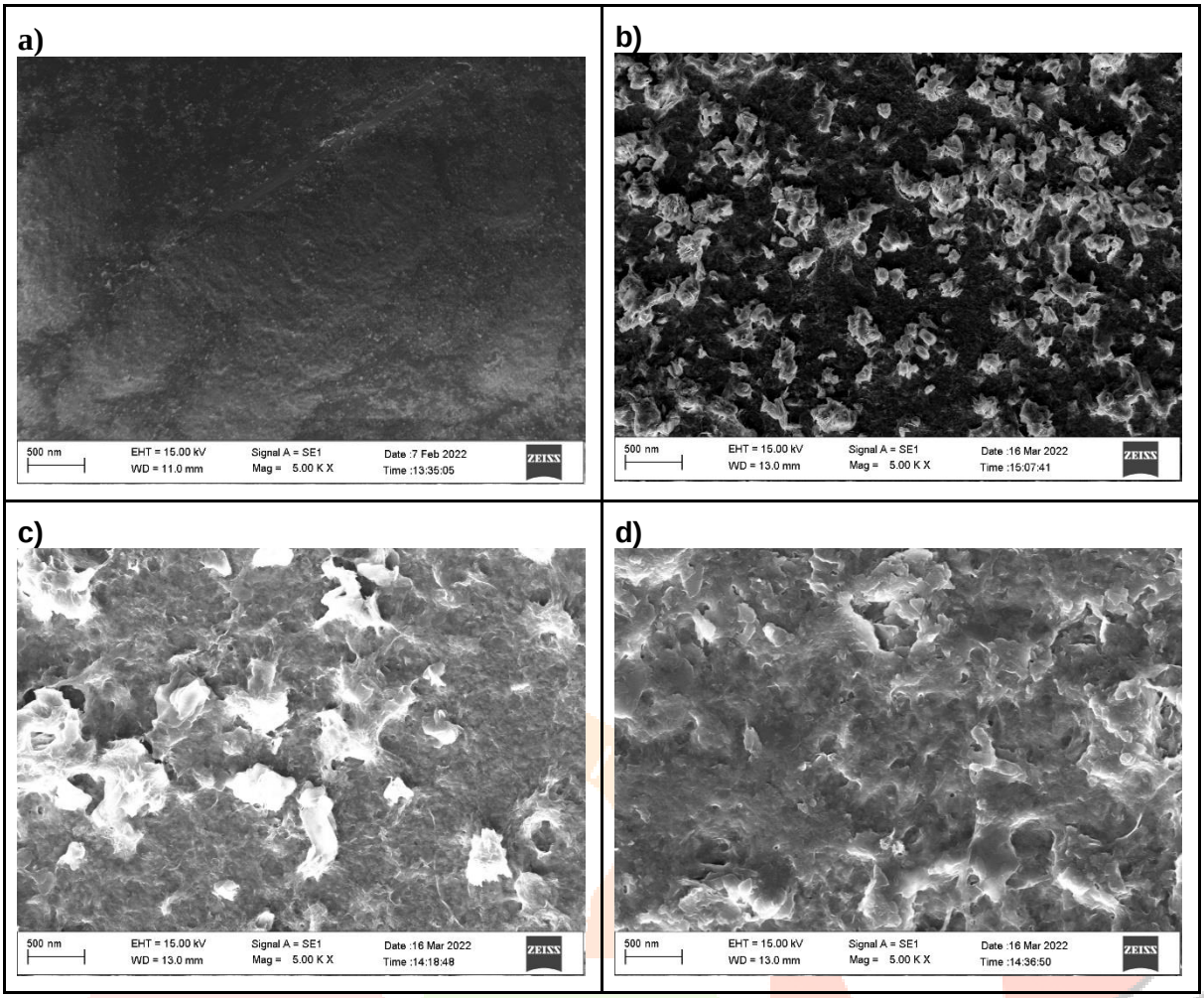

Fig.2. Fig.2. SEM images of (a) Pure ZnO (b) CuZ-1% (c) CuZ-3% (d) CuZ-5%

Surprisingly, the crystallinity of ZnO did not decrease despite the precipitation of Cu nanoparticles. On the other hand, as the amount of Cu nanoparticles rises, the ZnO grains enlarge. The variable lattice positions occupied by Cu in ZnO, which were influenced by diverse film deposition processes and annealing treatments, can be blamed for the observed variances in the effects of Cu doping on ZnO grain development. Our samples clearly show that Cu doping has no effect on the development of ZnO grains and does not cause appreciable nonuniformity in grain size. However, an increase in surface pores is seen in the case of sample CuZ-5 at%. The presence of more gasification substances within the film as a result of a higher dopant concentration may be the cause of this increase in pores. The sol-gel process of film deposition frequently results in the presence of pores. The SEM image shows particles with an estimated diameter of 27 nm, which indicates the existence of Cu nanoparticles.

3.3. UV Absorbance:

A UV-Vis spectrophotometer was used to perform UV-Vis spectroscopy, which covered the wavelength range of 200 to 800 nm. It was intended to evaluate the films and ascertain their band gap energy and absorption characteristics. There were significant UV absorption edges and transparent patches in both pure ZnO and Cu-doped ZnO thin films. The material's electrical transitions from the valence band to the conduction band are responsible for the absorption edge. The absorption edge of the films underwent a redshift (wavelength shift) as Cu dopant concentration was increased [29]. This suggests that the band gap energy

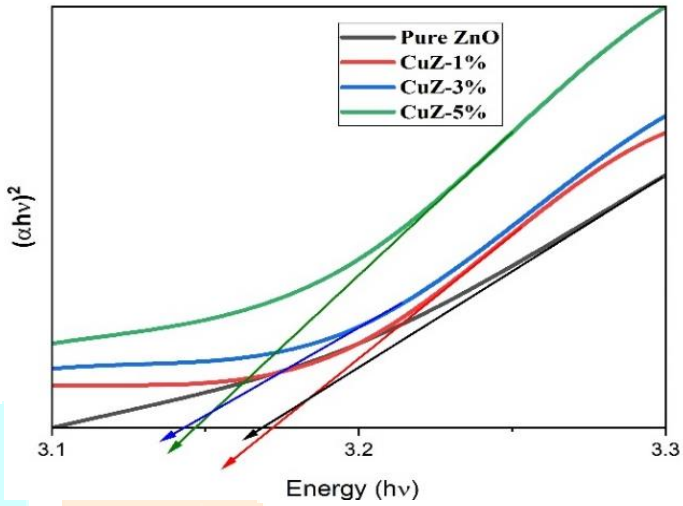

Fig.3. UV– Vis absorption spectra of pure and Cu doped ZnO thin films

of the films was decreased as a result of the insertion of Cu ions into the ZnO lattice [30]. The observed redshift was brought on by the presence of Cu dopants, which produced intermediate energy levels within the bandgap. The bandgap energies and optical absorption properties are very important for the thin film gas sensing applications.

Due to their capacity to offer greater sensitivity within the necessary wavelength range, Cu-doped ZnO thin films in particular are well-suited for acetone gas sensing. This is made possible by Cu doping's capacity to tune the bandgap energy and the absorption edge's redshift. In Fig. 3, the absorbance graph is displayed.

3.4. Band gap

The Tauc plot method was employed to determine the bandgap energy (Eg) for the films. The Tauc figure compares the photon energy (h)2 and the absorption coefficient (), where h is the photon energy and is the absorption coefficient. The bandgap energy can be calculated by locating the point where the energy axis and the linear region of the Tauc plot intersect.

The pure ZnO thin film's computed band gap energy in this investigation was 3.146 eV. The bandgap energy decreased with an increase in Cu doping concentration.

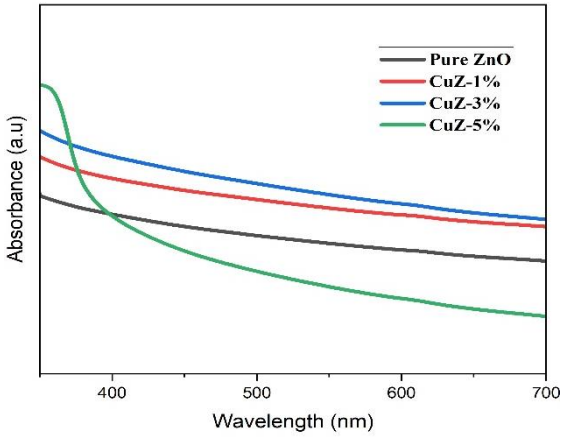

Fig.4.Band gap variation of pure and Cu doped ZnO thin films

Bandgap energies and Cu concentrations for Cu-doped ZnO thin films are listed (Table 2). With increasing Cu doping concentration, the bandgap energy decreased, which points to the production of an alloyed ZnO:Cu material. Comparing the CuZ-5% sample to other samples, it was discovered that the band gap had slightly increased. As a result, of all the samples, the CuZ-3% sample showed the greatest response. The band gap graph, shown in Fig. 4, shows the correlation between photon energy (hυ) and $(\alpha h\upsilon)^2$

Table-2: Band gap energy of various doping concentration

Doping Concentration	Band gap Energy(eV)
Pure ZnO	3.170
CuZ-1%	3.172
CuZ-3%	3.142
CuZ-5%	3.146

3.5. Acetone gas sensing and response

When subjected to various concentrations of acetone gas (pure, 1 at%, 3 at%, and 5 at%), the electrical resistance of both pure and Cu-doped ZnO thin films was evaluated. The outcomes clearly showed the considerable influence of Cu doping on the films' capability to detect acetone gas. Fig.5 shows the sensing capabilities of the pure and Cu doped (3 at %) ZnO thin films at various acetone gas concentrations.

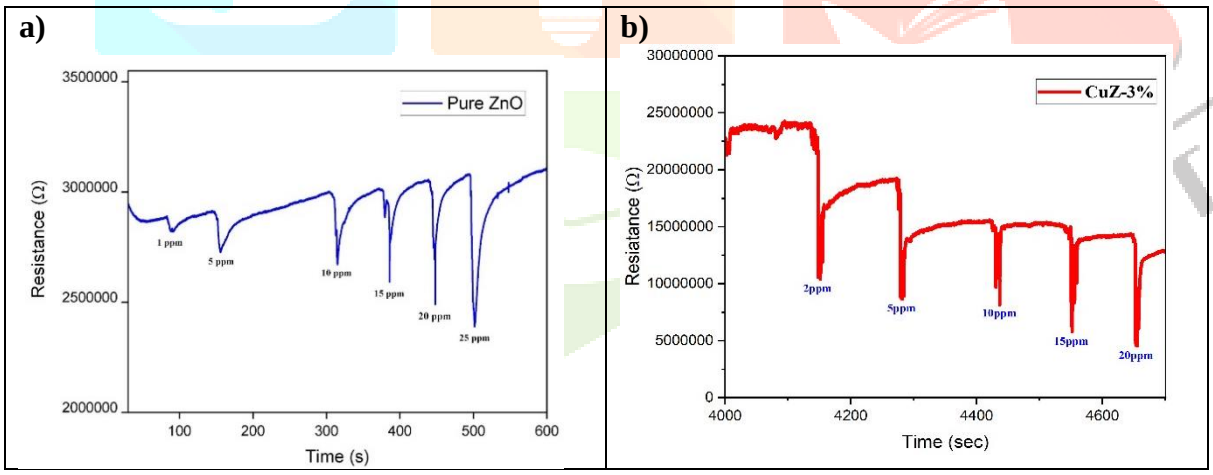

Fig.5.Acetone gas sensing**: a)** pure and **b)** Cu doped (3 at %) ZnO

The electrical resistance of the films significantly lowered after exposure to acetone gas, showing an increase in conductivity brought on by the interaction of acetone molecules with the film surface. The charge transfer mechanisms and surface reactions that take place when acetone molecules are adsorbed onto the film surface are responsible for this change in resistance [31].

Among all the samples, the 3 at % Cu-doped ZnO thin film demonstrated the highest response, displaying a much lower resistance than both the pure ZnO film and the other Cu-doped films. Fig 5(b) illustrates how the CuZ-3 at% thin film detects different concentrations of acetone gas. Defects are introduced and the amount of acetone molecule adsorption sites rises as a result of the integration of Cu ions into the ZnO lattice.

This improved reaction was assessed by computing the percentage change in resistance using the formula below, which provides evaluation of the thin films' acetone gas sensitivity:

$$\text{Response} = [(R_0 - R_{gas}) / R_0] \times 100\%$$

Where, the film's resistance in the presence of acetone gas is measured as R_{gas}, while its initial resistance is measured as R_0. The maximum sensitivity to acetone gas was demonstrated by the 3 at% Cu-doped ZnO thin film, which responded with a response of 46% when exposed to 10 ppm of acetone at ambient temperature. This demonstrates the film's great sensitivity and capacity for detecting acetone gas at low quantities. The thin films were tested against a variety of interfering gases, including ammonia, methanol, ethanol, and isopropanol, in order to determine their selectivity towards acetone. As a result of their low sensitivity to the interfering gases, the films showed good selectivity for acetone in the results. This selectivity is essential in real-world applications where it is necessary to detect and distinguish between particular target gases. In Fig. 6, the selectivity graph is shown.

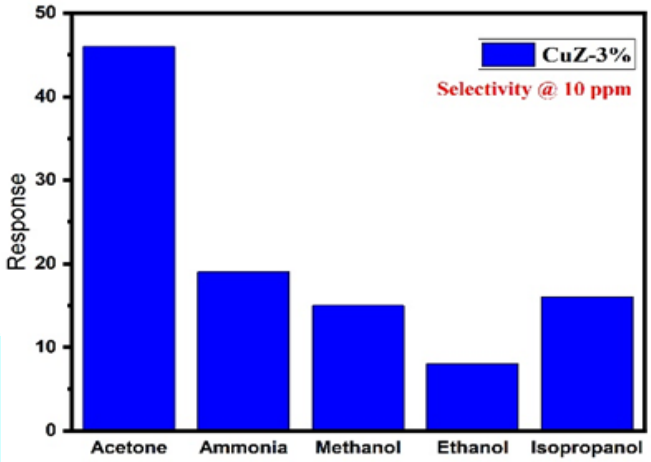

Fig.6. Response of Cu doped ZnO (3 at %) towards 10 ppm of various interfering gases

Table 3: Comparative Analysis of Acetone Detection Findings - Current Study vs. Other Research

Material	Temperature (°C)	Method	Acetone (ppm)	Response time (s)	Recovery time (s)	Reference
ZnO:Cu	RT*	Sol-gel	1	31	66	This work
ZnO:Al	500	Hydrothermal	1	147	181	32
ZnO:Al	500	Hydrothermal	0.5	78	113	32
ZnO:Al	500	Hydrothermal	0.1	44	70	32
ZnO:Al	450	Hydrothermal	10	3	-	33
ZnO:Al:Pt	450	Magnetron Sputtering	10	2.9	-	34
ZnO:CuO	310	Sol-gel	0.2	7	10	35
ZnO:Au	300	Wet-chemical	0.1	6	24	36
ZnO	RT	Sol-gel	5	12	7	37

*RT – Room Temperature

Analysing the response and recovery times of the thin films allowed us to assess their dynamic performance. The recovery time shows how long it takes for the resistance to return to its initial value once the acetone gas has been withdrawn, whereas the response time shows how long it takes for the resistance to stabilise after exposure to the gas.The thin ZnO film with 3% Cu doping had a quick response time of 31 seconds, demonstrating its capability to quickly detect changes in acetone concentration. It also showed a recovery time

of 66 seconds, which suggests that once the acetone gas was removed, it quickly returned to its initial state. The 3% Ag-doped ZnO thin film demonstrates remarkable dynamic performance based on these response and recovery durations, making it a possible candidate for real-time acetone gas sensing applications. A comparison of the acetone detection results from the current investigation with those from other studies is shown in Table -3

4. CONCLUSION

The increased acetone sensing capabilities of copper-doped zinc oxide (Cu-ZnO) thin films for non-invasive diabetes detection through breath analysis are thoroughly explored in this study report, which concludes. The thin films were prepared using the sol-gel dip coating process in the study, and their structural, morphological, optical, and gas sensing features were examined using a variety of characterisation techniques. Both undoped and Cu-doped ZnO thin films formed a highly crystalline wurtzite structure, according to X-ray diffraction analyses, with the latter exhibiting a shift in the XRD peaks as a result of the successful incorporation of copper into the ZnO lattice. Increased grain size and decreased surface roughness were discovered by scanning electron microscopy, which resulted in smoother film surfaces with improved optical transparency as detected by UV-visible spectrophotometry.

Acetone sensing, a biomarker linked to diabetes, was carefully considered when evaluating the thin films' gas sensing capabilities. The improved acetone sensing response of the Cu-doped ZnO thin films when compared to the undoped films suggests their potential for diabetes diagnosis. The study also revealed that the highest sensitivity to acetone vapour was achieved at a doping concentration of 3 at. % Cu, with response and recovery times of 31 sec and 66 sec, respectively.

The study highlights the potential of Cu-ZnO thin films produced by the sol-gel dip coating method as a promising platform for future applications in breath analysis and medical diagnostics, providing important insights into the development of enhanced sensing materials for non-invasive diabetes detection.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

Author contributions

C.Rajan conducted the initial materials selection and contributed to the characterization process. J.Gobinath provided support in materials selection. R. Murugesan collaborated in drafting and revising the manuscript. All authors participated in in-depth discussions and provided valuable insights into the crucial scientific aspects addressed in the paper. N.Pasupathy oversaw and guided the entire project as the project supervisor.

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