



TEMPERATURE DEPENDENT ELECTRICAL AND GAS SENSING PROPERTIES OF Ce/CuO NANOSTRUCTURES

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CERTIFICATION

The undersigned certifies that he has read and hereby recommends for acceptance by the Faculty of Science a dissertation titled: **TEMPERATURE DEPENDENT ELECTRICAL AND GAS SENSING PROPERTIES OF Ce/CuO NANOSTRUCTURES**, in fulfilment of the requirements for the degree of Master of Science (*Physics*) of the Botswana International University of Science and Technology.

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DEDICATION

To my beloved parents, thank you for your enduring support.

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List of abbreviations and symbols

AFM	Atomic Force Microscopy
Ag	Silver
BET	Brunauer-Emmett-Teller
Ce	Cerium
CeO ₂	Cerium oxide
Co	Cobalt
Cr	Chromium
CSP	Chemical spray pyrolysis
Cu	Copper
CuO	Copper oxide
D	Crystallite size
DC	Direct Current
EDX	Energy Dispersive Spectroscopy
Fe	Iron
FTIR	Fourier Transform Infrared spectroscopy
h+	Hole
In ₂ O ₃	Indium oxide
K	Kelvin
La	Lanthanum
Mn	Manganese
MO	Metal oxide
Ni	Nickel
NiO	Nickel oxide
SEM	Scanning Electron microscopy
Tb	Terbium
TiO ₂	Titanium dioxide
Uv-Vis	Ultraviolet-Visible
W-H	Williamson-Hall
WO ₃	Tungsten oxide
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction
Zn	Zinc
δ	Dislocation density
ε	Microstrain

List of publications

Publication related to this thesis

1. **R. Bosigo**, L. M. Lepodise, A. Kuvarega, C. Muiva. Hydrothermal synthesis of CuO and CeO₂/CuO nanostructures: spectroscopic and temperature dependent electrical properties. J Mater Sci: Mater Electron 32, 7136-7152 (2021). **DOI: 10.1007/s10854-021-05423-6**
2. **R. Bosigo**, L. M. Lepodise, G. Chimowa, C. Muiva. Enhanced ethanol sensing response of nanostructured Ce-doped CuO thin films. Materials Chemistry and Physics 280 (2022) 125841. **DOI: 10.1016/j.matchemphys.2022.125841**

Other publications

1. L. M. Lepodise, **R. Bosigo**. Signatures of aromatic carbons in the infrared absorption spectra of soils. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, (2021). **DOI: 10.1016/j.saa.2021.120469**
2. C. Muiva, L. M. Lepodise, **R. Bosigo**, A. Juma. Structural analysis and temperature dependent conductivity of La_xCu_{1-x}O shrimp-like nanostructures synthesized via wet chemical precipitation. Materials Characterization 170, 110707 (2020). **DOI: 10.1016/j.matchar.2020.110707**
3. L. Lebogang, **R. Bosigo**, K. Lefatshe, C. Muiva. Ag₃PO₄/nanocellulose composite for effective sunlight driven photodegradation of organic dyes in wastewater. Materials Chemistry and Physics journal 236, 121756 (2019). **DOI: 10.1016/j.matchemphys.2019.121756**

Abstract

Research on semiconducting metal oxide (MO) nanostructures is a fascinating field that has received massive interest due to their significant physical and chemical properties which can be useful in the development of highly efficient nanodevices. Incorporating impurities such as metal elements into the MO matrix offers tailored properties for various applications. Doped MO nanostructures exhibit modified structural, optical, electrical and morphological properties rendering them useful for fabricating high-performance devices. This study focuses on the synthesis of Cerium-Copper Oxide (Ce/CuO) nanopowders and thin films using simple hydrothermal and spray pyrolysis methods that are both inexpensive and eco-friendly. Characterization techniques including X-ray diffraction (XRD), Raman spectroscopy, Fourier Transform Infrared spectroscopy (FTIR), Ultraviolet-Visible spectroscopy (Uv-Vis), Scanning Electron microscopy (SEM), Energy dispersive spectroscopy (EDX), Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) and two-point probe method were employed to gauge the characteristics of the synthesized samples. XRD analysis revealed formation of monoclinic phase of CuO with decreasing crystallinity of the samples as the Ce content increased. Analysis with EDX detected Cu, Ce, and O in the samples. A Raman peak corresponding to the CeO₂ phase was identified at higher Ce doping levels. SEM imaging revealed that Ce incorporation induces changes in nanostructure morphology. The optical bandgap (E_g) depicted a blue shift as the Ce content increased in the samples. The Ce/CuO samples exhibited enhanced temperature-controlled DC conductivity with the 4% Ce sample showing the lowest activation energy, lowest T_{max} and consequently the maximum conductivity peaking at a temperature of 503K. Ethanol sensing capabilities of Ce/CuO thin films were measured at different ethanol concentrations and working temperatures. Good stability and maximum response were observed for the 4 % Ce thin film. The sensor exhibited greater response to ethanol compared to methanol, acetone, acetonitrile, and ammonia. These results suggest that the Ce/CuO is a promising ethanol gas detector, with the Ce dopant playing a significant role in improving the electrical and sensing properties of CuO.

Chapter 1 Introduction

1.1 Overview

Nanotechnology is a multidisciplinary discipline of science that works with materials that have at least one dimension between 1 and 100 nanometers. Nowadays, nanotechnology has evolved into a frontline research area due to its vital applications which are instrumental in advancement of the human standard of living. Through miniaturization of materials, new and improved gadgets are developed making a huge contribution to the upgrade and ease of human life [1] [2] [3]. Materials developed at nanoscale have been attracting significant research attention owing to their distinct chemical and physical properties that differ from their bulk counterparts. The size confinement effects and higher surface to volume ratio of the nanostructures often give rise to altered properties that are not found in bulk materials. These materials are also cheap, exhibit enhanced functionality; require less energy to function and less material for fabrication [4] [5]. In depth study of these materials has led to development of novel high-strength materials which have the ability to mimic natural occurrences, and respond to stimuli applicable to numerous industrial applications [6] [7] [8].

1.2 Semiconducting metal oxides

Semiconducting metal oxides (MOs) are amongst the most studied classes of nanomaterials due to their indisputable applicability in various innovative multifunctional materials. They are the foundation of most modern ground-breaking devices owing to their remarkable properties useful for practical applications in many areas of health, education, and environmental sustainability [9] [10] [11]. The functional properties of MOs depend on a variety of characteristics such as structural defects, chemical composition, morphology, specific surface area and grain size. Altering any of these properties allows for manipulation of the material making them the most versatile class of materials with properties that cover most aspects of materials science including semiconductivity, superconductivity, ferroelectricity and magnetism. MOs find application in p-n junction devices such as solar

cells, LEDs, lasers, photodiodes, photoresistor, and supercapacitors, as well as catalysts, batteries, and supercapacitors [12] [13] [14]. To date, MOs composed of transition metals have been highly explored due to their novel and exciting properties. Over the years, numerous nanostructured MOs of varying morphologies, chemical compositions, particle sizes and structures have been studied extensively to broaden the understanding of their synthesis, characteristics and applications.

The study of the electrical properties of MO nanomaterials is critical for their application in sensors and electronic components. MOs are especially popular in the development of nanoelectronic devices due to their relatively better stability, extraordinary electrical performance, low-cost and large volume manufacturing [15]. They were first introduced to the field of electronics when they were used as interlayers in light emitting diodes. This has led to numerous studies on their use in a variety of high technological applications [16]. MOs are now being extensively used as functional components in computer hardware, display devices, high temperature superconductors, magnetic recording devices, gas sensors and audio devices [17].

MO semiconductors have been proven to be potential materials for development of solid-state gas sensors due to their simple manufacturing methods, stability in harsh conditions and high gas sensing response [18]. They were initially introduced as chemoresistive gas sensors decades ago when it was discovered that electrical properties of MOs were highly sensitive to the changes in their surrounding environment [19]. Studies showed that introduction of a gas to the surface of a MO semiconductor induced conductivity changes upon adsorption and desorption of the gas molecules. Since then, MO semiconductors have led the research on gas sensors due to their low cost and relative simplicity [20]. Numerous MOs have been reported to be useful in everyday life, increasingly in applications related to health and safety-related application areas such as food processing, medical diagnostics, detection of toxic/flammable/explosive gases and air-quality monitoring [21].

In order to improve properties of MO nanostructures, dopants are incorporated into the metal oxide matrix thereby manipulating its properties according to the scope of application

and research interest. Dopant addition is a powerful technique for improving performance of semiconducting MOs [22]. The features of a single phased MOs are modified through addition of a suitable metal ion thereby adjusting the morphology, energy band structure, creating lattice defects and vacancies thus improving performance in various applications leading to numerous new inventions [22] [23] [24]. Pure and doped MOs have been the subject of recent research for a variety of practical uses. This research on MOs has been growing at an exponential rate, resulting in the emergence of new scientific fields.

Copper Oxide (CuO) is amongst the MOs that has been widely studied due to its unique properties and possible applications. These properties include thermal superconductivity, photovoltaic properties, high stability, and antimicrobial activity [25]. At nanoscale, CuO has other unique and exciting properties making them candidates for applications in catalysis, thermal conductivity and lithium ion batteries. Furthermore, CuO nanostructures with variable morphologies can be easily synthesized via simple solution based techniques unlike many other semiconductors which require more complex procedures [26]. Investigations on nanostructured CuO have grown tremendously due to its penetration into electronics, paints and coatings, energy storage, sensors, catalysts and other novel applications. Recent studies have reported on the use of doping to modify the physio-chemical behavior of CuO nanomaterials. Dopants have been incorporated into the CuO to produce effective defects and create optimized compounds for promising performances in practical applications [27] [28] [29].

1.3 Statement of the problem

CuO nanostructures have been widely investigated because of their remarkable electrical and gas sensing properties. The low cost of production and non-toxic nature makes CuO technologically important for applications in sensing and electronic devices. However, CuO is amongst the many MOs that suffer from drawbacks such as poor selectivity, high temperature of operation and relatively low response which limit their use in electronic and sensing applications. Doping with metal ions has been reported as an efficient method of tuning the electrical and gas sensing properties of CuO to overcome its shortcomings. The

present work therefore focuses on synthesis of doped CuO nanostructures with improved electrical and gas sensing properties using simple economic synthesis methods.

1.4 General objective/Aim

The primary aim of this work is to study the effect of Ce dopant on the temperature dependent electrical and gas sensing properties of CuO-based nanostructures. The objectives of this work include the following:

- To study the effect of varying the Ce dopant on electrical properties of Ce/CuO nanostructures synthesized using a simple and eco-friendly hydrothermal method.
- To investigate the effect of Ce dopant variation on the gas sensing properties of Ce/CuO nanostructures deposited via chemical spray pyrolysis.
- To investigate the effect of doping on the vibrational, structural, optical, and morphological properties of Ce/CuO nanostructures synthesized through hydrothermal and chemical spray pyrolysis method.
- To measure the temperature dependent electrical and gas sensing properties of Ce/CuO nanostructures synthesized via hydrothermal and chemical spray pyrolysis.

1.5 Hypothesis

- Incorporation of Ce additive in CuO matrix will lead to improved properties of CuO nanostructures allowing for enhanced performance in various applications.

1.6 Significance of the study

Nanotechnology has been embraced worldwide and its fundamental processes have been adopted for the advancement of humanity. There has been enormous research output in this field especially in the category of MOs. Doping of MOs, such as CuO can modify the chemical and physical properties by introducing structural defects thus leading to development of unique properties and significantly enhanced performance compared to the pure MO [30]. Although there has been some success in this direction, there is still need for the ultimate understanding of CuO based nanostructures in terms of synthesis, properties

and applications. This requires a methodical knowledge in the subject which will allow synthesis of CuO based nanostructures with tailored properties and enhanced overall performance using simple fabrication techniques. The findings from the current study will add knowledge in CuO-based nanostructures which may indicate some suitable applications of these materials in electrical and optoelectronic devices.

Chapter 2 Literature review

MO nanostructures have significant role in the scientific field because of their distinctive properties. Their easy preparation, stability and remarkable applications have contributed to their popularity. CuO is amongst the MOs that have been investigated for many applications. Extensive research efforts have been focused on modifying CuO nanostructures by incorporation of dopants to develop tailored physical and chemical properties to improve performance in a variety of applications [22]. In this chapter the various fields where the CuO-based nanostructures are being used have been presented and several noteworthy aspects that were investigated previously have been reviewed.

2.1 CuO

CuO is one of the most important semiconductors and has been investigated since the last quarter of the last century. The continuously growing interest arises from their remarkable properties and the possibility to synthesize high quality CuO nanostructures at relatively low costs. It is amongst the most studied semiconducting transition metal oxide due to its remarkable structural, chemical, electrical, and optical properties [31] [32]. CuO nanostructures are known for their relatively high natural occurrence of precursor materials, easy processing, environmental safety, chemical stability, and higher thermal and electrical conductivities which endorse their practical usage [33]. Research work on CuO nanostructures has increased exponentially in recent years due to potential applications in gas sensors [34], microelectronics [32], batteries [35], catalysis, high-temperature superconductivity, photocatalysis, solar energy conversion and antimicrobial agents [36] [37]. CuO is a semiconducting material with a narrow energy bandgap of 1.21 eV at room temperature. It is a p-type semiconducting material which occurs in a monoclinic crystal structure having every copper atom bonded to four atoms of oxygen in a square co-planar geometry [38] [39].

CuO has been considered attractive for the development of solar thermal energy collectors due to its high solar absorption capabilities and low thermal emittance [40] [41] [42]. Owing

to their high thermal conductivity, CuO nanoparticles could be useful as fillers for improving heat transfer in nanofluid and lubricant systems [43] [44] [45]. CuO nanoparticles have successfully demonstrated excellent catalytic activity for numerous chemical reactions. It is particularly widely employed for direct decomposition of nitrogen oxide [46] [47] and boosting the ammonium perchlorate thermal decomposition reaction [48] [49] [50]. Due to excellent antimicrobial activity against a range of bacteria, CuO can be exploited as a substitute for gold and silver nanoparticles in the production of antimicrobial devices. Its nanostructures can be integrated with polymers used in hospitals for wound dressing and implant coating [37] [51]. The narrow band gap property of CuO nanostructures makes them important materials for photoconductive and photothermal applications [52] [53]. Furthermore, due to the high chemical stability, biosafety and sensitivity to changes of environment conditions, CuO have been successfully used for gas [34] and bio sensing [54] applications.

2.2 Dopants

Doping of MO semiconductors is a fundamental process for modifying the electrical, optical and structural properties of materials [22]. As evidenced in the literature, the controlled introduction of desired impurities into CuO has been widely investigated in order to improve properties and performance in various applications. Several doping elements such as chromium (Cr^{3+}), cerium (Ce), Cobalt (Co) and manganese (Mn) have been incorporated into the CuO matrix to develop high-quality nanostructures with enhanced chemical and physical properties in recent years [27] [28] [55] [56] [57]. The doping process modifies the parent material's structure by introducing extra energy levels into its band structure. It also inhibits charge recombination by capturing electrons and promotes excess charge carriers. Furthermore, dopant addition can transform the surface-to-volume ratio and morphology thereby generating multiple active sites through production of defects and vacancies within lattice [30] [55].

Ping Lu et al. [56] have reported on the effect of copper vacancies and structure distortion on ferromagnetism in CuO nanostructures with Cr^{3+} doping. They presented an account that

Cr^{3+} ions incorporate into the CuO lattice which induces generation of more Cu vacancies thus enhancing ferromagnetism in the Cr-doped CuO system. Co and Mn doping have also showed an effect on the magnetic properties of CuO. A superparamagnetic state was achieved for pure CuO which then converted to antiferromagnetic and spin glass state for Co- and Mn-doped CuO nanostructures, respectively [27]. Co doping has also been previously applied to improve antibacterial performance of CuO nanostructures [28]. Zinc (Zn) doping into CuO has been shown to improve the antibacterial activity of CuO. This was attributed to the creation of Zn^{2+} ions and Cu^{2+} ions on the surface of CuO, which resulted in the development of more reactive oxygen species (ROS), thereby significantly increasing the antibacterial activity of CuO [29] [58]. Other metal elements such as aluminum (Al) [59], terbium (Tb) [60], silver (Ag) [61], iron (Fe) [62] [63], nickel (Ni) [64] [65] and lanthanum (La) [66] have previously been used to modify CuO so as to improve electrical conductivity, thermal conductivity, catalytic performance, biosafety, gas sensing response and magnetic properties.

Previous studies have achieved incorporation of Ce into CuO showing improvements of overall performance for different applications. Studies on photocatalytic activity found that Ce doped CuO nanostructures exhibited enhanced photodegradation ability towards dyes including rhodamine B and methylene blue compared to the undoped CuO [67] [68]. The Ce additive introduced defects in the CuO which inhibited electron-hole recombination. It also narrowed down the optical bandgap thus improving the photon adsorption which resulted in the enhanced photocatalytic performance of up to 95 % and 99 % [68]. Ce doping of CuO has also revealed enhancements in antibacterial efficiency. Tariq Jan et al. [57] found that Ce doping induced the release of Ce^{4+} and Cu^{2+} ions, resulting in increased antibacterial activity of Ce doped CuO nanostructures. The enhanced antimicrobial activity of CuO nanostructures with Ce doping was also attributed to generation of more ROS. Further investigations revealed that Ce doped CuO nanostructures were biosafe and biocompatible [57]. In a study by Inderjeet Singh et al. [69], Ce doped CuO nanostructures showed better selectivity and response to methanol. Response was about 28 times towards methanol which was attributed to the shift in the oxygen defect concentration with Ce doping.

Ce is the element with the highest abundance in the lanthanide series. It is a rare earth metal that occurs in two stable states (Ce^{3+} and Ce^{4+}). Ce ions have attracted much interest because of their distinctive attributes that can be used in applications such as glass manufacturing, catalysis, fuel additives, and batteries [70]. Ce has the high oxygen storage capacity and relatively high mobility due its unique electron structure [71]. Several research studies have reported that Ce doping improves a variety of material properties. R. S. babu et al. [72] reported on cerium co-doped CdO:Zn films deposited by chemical spray pyrolysis with low electrical resistivity and enlarged carrier concentration. V. Kumar et al. [73] reported on the enhancement in electrical conductivity and magnetic properties of Ce-doped hematite samples than the pure hematite sample. Zhang et al. [74] and Zhu et al. [75] found that Ce doping improved gas sensor properties for both ZnO and NiO, respectively.

2.3 Review of fabrication methods

MOs exhibit chemical and physical properties that are influenced by parameters such as size distribution, morphology, grain size and composition which strongly rely on the technique of synthesis. Numerous methods that allows for alteration of different parameters have been developed to synthesize MO nanostructures using several chemical and physical strategies. CuO nanostructures of various shapes have been synthesized using biological, chemical and physical methods. Solution-based synthesis techniques including sol-gel [76] [77], hydrothermal [78] [79], co-precipitation [80] [81], Chemical spray pyrolysis [82] [83], and chemical bath deposition [84] are commonly employed for CuO fabrication due to simplicity and low cost. CuO nanostructures of various shapes including nanoflowers, nanospheres, nanodendrites, nanochips, and nanorods have been synthesized by solution-based methods [85] [86] [87] [88] [89]. Morphology affects performance of the nanostructures in various applications, that is, CuO nanostuctures with different shapes will not perform in the same capacity in the same application [90]. Generally, the use of growth regulators [91], different precursor salts with varying concentrations and different solvents also has the capability of influencing the CuO properties thus altering performance [92].

2.4 Electrical properties of CuO-based nanostructures

It is critical to investigate the electrical behavior of CuO nanostructures prior to their use in the fabrication of nanodevices and nanoelectronics. CuO has found potential applications in sensors [93], solar cells [94], photo detectors [95], photocatalysts [96], nanofluids [97], field-emission devices [98], superhydrophobic surfaces [99], water treatment [100], magnetic storage [101], diodes [102], high temperature superconductors [103], antibacterial agents [104], rechargeable batteries and many more [33] [89] [105] [106] [107] [108]. Typically, the p-type nature of CuO found in the literature has been attributed to the excessive h^+ formation in the valence band effected by the intrinsic Cu vacancies in lattice structure. Generally, the concentration of the free h^+ is mainly determined by the cation vacancies and the excess oxygen within the material [109] [110].

Numerous studies of the DC electrical conductivity of CuO nanostructures have been carried out. Raj et al., reported on the temperature dependent conductivity of CuO samples under vacuum and air atmospheres. They found that the conductivity increased with an increase in crystalline size and that the mechanism of conductivity was defect-dependent with holes associated with Cu^{2+} vacancies as charge carriers [111]. Hafeezullah et al. [109] studied the semiconducting behaviour of CuO thin films synthesized by chemical spray pyrolysis where conductivity increases with temperature indicating a thermally activated mechanism of conductivity; the activation energy ranged between 0.311 eV and 0.293 eV [109]. CuO nanofibers with diameter of about 60 nm and length above 100 μm prepared by electrospinning technique recorded an electrical conductivity of $3 \times 10^{-3} \Omega^{-1} cm^{-1}$ because of generation of holes [112]. Collins et al. investigated the electrical conductivity of CuO at room temperature. They found that CuO pellets annealed at 923 K in oxygen and argon recorded conductivity values in order of 10^{-2} and $10^{-3} \Omega^{-1} cm^{-1}$ respectively [39]. Chen et al. reported on the electrical behavior of CuO nanoparticles in nitrogen, oxygen, dry and humid air at various temperatures and found that electrical conductivity increased due to adsorption of oxygen [113]. Literature has reported that Cu vacancies result in the generation of Cu^{3+} ions to retain charge neutrality, this contributes to the electrical

properties (p-type semiconducting behavior of CuO) associated with the cation vacancies [39] [113] [114].

2.5 Gas sensing properties of CuO-based nanostructures

Semiconducting MOs have been found to be the most suitable materials that could be applied in gas sensor measurements. MO semiconductor gas sensors also referred to as chemoresistive gas sensors, have a broad spectrum of applications such as air quality monitoring, the control of industrial and chemical processes, individual safety at home and the place of work, medical and automotive applications [115]. Chemoresistive sensors are devices which undergo changes in electrical resistance upon exposure to a gaseous chemical compound [116]. These sensors have been attracting attention of many users ever since 1962 when the first report on chemoresistive gas sensors came out. Seiyama et al. developed a gas detector using ZnO thin films based on the change in electrical conductivity of semiconductors upon adsorption and desorption of gases [19]. During exposure to a certain gas, the gas gains or loses electrons to the sensor thus changing the density of the charge carriers, resulting in changes in the surface resistance [19] [115]. This finding has triggered an interesting pathway toward the development of new gas sensors by various research groups. In the 1970s, the first chemoresistive gas sensor was invented and commercialized by Taguchi [117]. The sensor device was fabricated using tin dioxide (SnO_2) as the sensitive material for practical application as household gas sensors. Since then, considerable effort has been dedicated to the development of chemoresistive sensors to improve performance and simplify their use for the safety in the household and workplace [118] [119]. Owing to their low cost, relative simplicity and large number of detectable gases, semiconductor MOs [119] [120] including tungsten oxide (WO_3), ZnO, SnO_2 , titanium dioxide (TiO_2) and indium oxide (In_2O_3) have been extensively investigated [121] [122] [123] [124] [125] [126] [127]. They possess a variety of electronic, chemical, and physical properties that make them popular candidates for gas detection applications.

CuO is a promising material for the development of highly sensitive, but inexpensive sensors including optical, gas and bio sensors [127] [128] [129] [130] [131]. Various studies have

been focused on investigating the sensing properties of the CuO for different gases, including H₂S [132], H₂ [133], NO₂ [134] CO [135] and ethanol [136]. Electrical property studies of CuO have shown that its conductivity can be regulated by partial oxygen pressure during synthesis. This means that the nanostructures will be very sensitive to the presence of adsorbed molecules thus offering the possibility of chemical sensing. Generally, the sensing property of CuO is primarily based on the electron transfer occurring between the gas molecules and the CuO surface. For a reducing gas such as H₂S, the chemical reaction is initiated by the pre-adsorbed oxygen species (O₂, O⁻ and O₂⁻) on the CuO surface. The oxygen species will react with the gas leading to a decrease of the h⁺ density and electrical conductivity of CuO [132]. On the contrary, an oxidizing gas will promote trapping of electrons thus increasing the h⁺ density and electrical conductivity of CuO [134] [137].

Chapter 3 Methodology

A variety of fabrication methods for nanomaterials can be found in literature. These methods are the key component in creation of nanomaterials of desired composition and morphology. In this study, fabrication of Ce/CuO nanostructured powders and thin films were achieved using the hydrothermal and the spray pyrolysis methods, respectively. Different techniques including X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR), Ultraviolet-Visible spectroscopy (Uv-Vis), Scanning Electron microscopy (SEM), Energy dispersive spectroscopy (EDX), Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and Brunauer-Emmett-Teller (BET) were used for characterization of the synthesized nanostructures. The gas sensing and electrical properties of the nanostructures were also measured. This chapter gives a description of materials, experimental procedures and characterization techniques used in this study.

The reagents used were obtained from Sigma-Aldrich and were used in the synthesis processes without further purification.

3.1 Hydrothermal synthesis method

A simple hydrothermal synthesis technique was employed for the synthesis of Ce/CuO nanostructures. Hydrothermal method is widely used for fabrication of nanostructured materials with various morphologies. It refers to the synthesis by chemical reactions of substances in a sealed vessel heated above ambient temperatures and pressures. Crystal growth is typically performed in a vessel called an autoclave with the chemical reactions usually occurring in an aqueous solution [138]. The hydrothermal technique is conducive for growth of high-quality crystals with less defects and dislocations. With the use of this technique properties such as particle morphology, grain size, crystallite phase, ion additives and aging time are easily controllable.

3.2 Fabrication of CuO and Ce/CuO nanostructured powders

Initially, solutions of 82 mmol copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CAS: 10125-13-0) and 164 mmol sodium hydroxide (NaOH , CAS: 1310-73-0) were obtained by dissolving each salt in 100 ml and 40 ml of distilled water, respectively. Cerium acetate dihydrate solutions ($(\text{CH}_3\text{CO}_2)_3\text{Ce} \cdot 2\text{H}_2\text{O}$, CAS: 206996-60-3) were prepared by dissolving the 0.49, 0.65, 0.97, and 1.30 g masses in 60 ml of distilled water and then adding each to the prepared $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution to yield 3, 4, 6 and 8 % Ce, respectively. 16 ml of polyethylene glycol (PEG, MW: 340-420 g/mol) was then added to each mixture to act as a growth regulator. The solution was then continuously stirred for 10 minutes. Thereafter, 40 ml of NaOH was added while each mixture was magnetically stirred to produce a blue precipitate. The precipitate was loaded to an autoclave and kept at 120 °C for 3 hours before cooling to room temperature. The products were transferred to a beaker and washed using deionized water and then calcined at 500 °C for 3 hours. The same method of preparation was used for CuO without adding the $(\text{CH}_3\text{CO}_2)_3\text{Ce} \cdot 2\text{H}_2\text{O}$ solution. The prepared samples were denoted as Ce/CuO and CuO, respectively. An overview of the overall hydrothermal method of synthesis is illustrated in Figure 3.1.

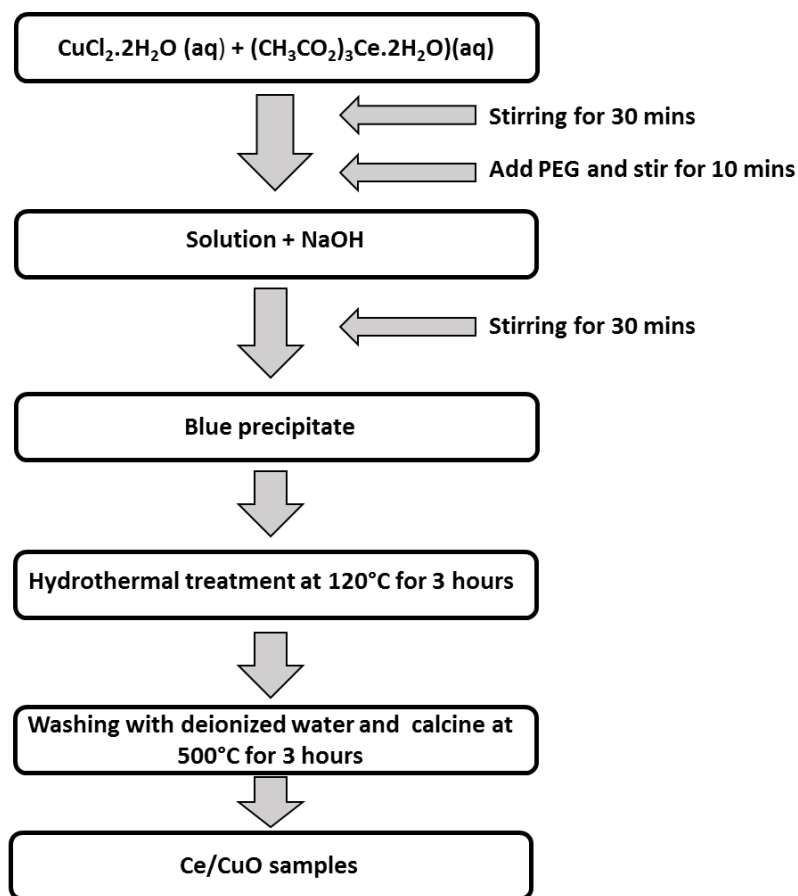


Figure 3.1: Schematic illustration of hydrothermal synthesis of CuO and Ce/CuO nanostructured powders.

3.3 Chemical Spray pyrolysis (CSP)

CSP is a thin film deposition process in which a solution is sprayed onto a heated surface such that the components of the precursor solutions react to produce a chemical compound. The chemical reactants deposited are chosen such that the unwanted compounds are volatile at deposition temperature so that only the desired chemical compound remains [139]. A typical CSP system consist of spray solution container, liquid flow meter, spray nozzle, compressed air for atomization and a heater. CSP is a simple and low-cost technique which offers advantages such as good reproducibility, moderate deposition temperatures, easy dopant addition and potential for large area deposition [140]. The scheme of the CSP method is illustrated in Figure 3.2.

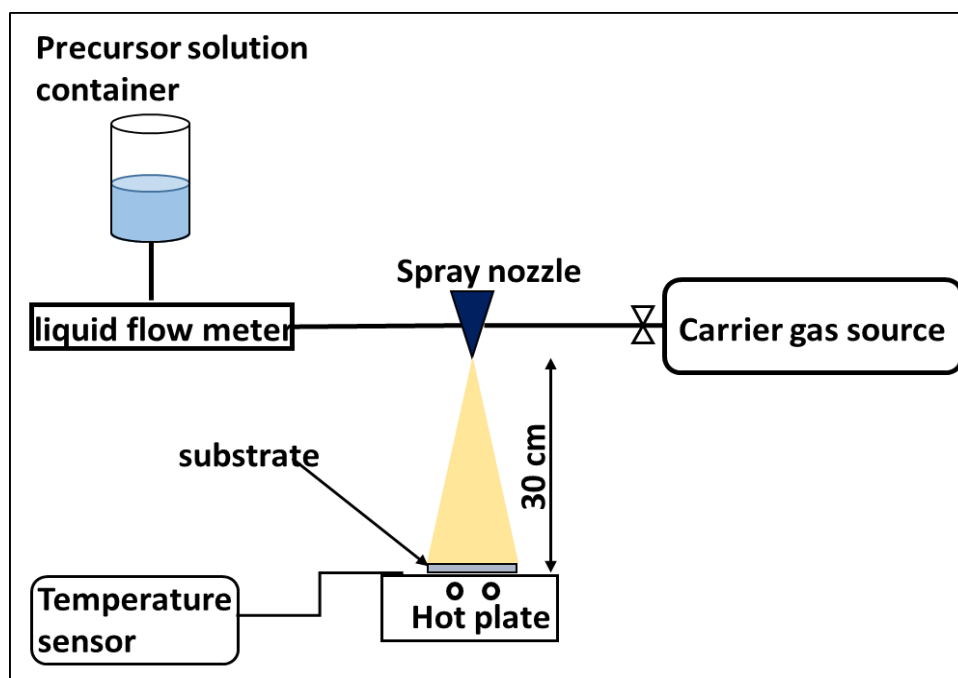


Figure 3.2: Schematic illustration of the chemical spray pyrolysis method.

3.3.1 Fabrication of Ce/CuO thin films

The Ce doped CuO thin films were formed on glass substrates using the chemical spray pyrolysis technique. Glass substrates were cleaned thoroughly by ultrasonic agitation in sulfuric acid solution, followed by acetone, and finally rinsed with deionized water. The undoped CuO solution was prepared by dissolving 0.004 mol of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 40 ml deionized water. For complete dissolution, the solution was magnetically stirred for 15 minutes. This solution was then loaded into a syringe and positioned in the spray setup. The cleaned glass substrates were placed on a hotplate 30 cm from the spray head. The operating temperature was maintained at 350 °C and flow rate was set to 1 ml/min with compressed air as the carrier medium. The solution was sprayed on the substrate for 10 mins to form a thin film. After the deposition process, the substrate was left on the hotplate for 30 minutes to evaporate residual water content. To improve crystal quality, the thin film was annealed at 400 °C for 2 hours. Ce doping was prepared by adding various mole percentages (2, 4, 6 and 8) of $(\text{CH}_3\text{CO}_2)_3\text{Ce} \cdot 2\text{H}_2\text{O}$ to the copper salt solution to obtain the Ce

doping as required. Figure 3.3 shows preparation procedure of Ce/CuO thin films by the CPS technique.

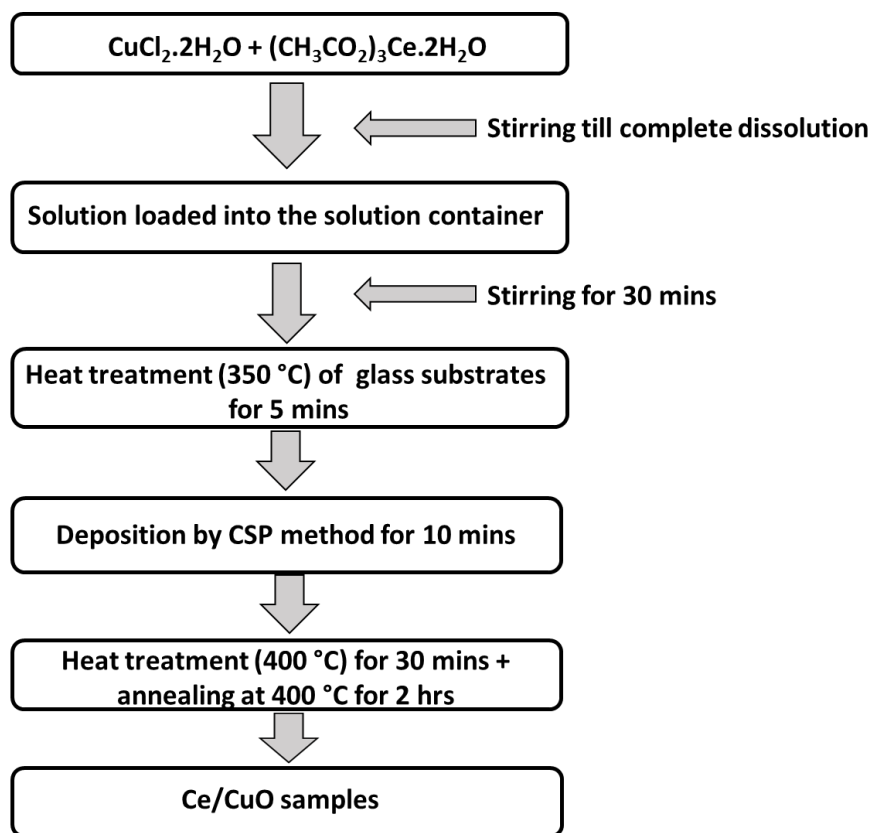


Figure 3.3: Flow diagram of the chemical spray pyrolysis synthesis procedure for Ce/CuO thin films.

3.4 Characterization techniques

3.4.1 X-ray based techniques

In this work, the crystal structure of the fabricated nanostructures was analyzed by an XRD diffractometer of model Bruker D8 Advance, Germany. The diffractometer is furnished with a 3-kW generator, Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) source and Lynx Eye XE energy dispersive strip detector. The samples were scanned over the range of $2\theta = 20 - 70^\circ$ with a voltage and current setting of 40 kV and 40 mA for the X-ray generator. The XRD data was used to determine the average crystallite size (D) through the renowned Scherrer expression [141];

$$D = \frac{0.9\lambda}{\beta_{hkl} \cos \theta} \quad (3.1)$$

In which, β_{hkl} is the full width at half maximum (FWHM). XRD data also yields information on structural parameters such as micro-strain (ϵ) [142] and dislocation density (δ). These parameters were estimated from,

$$\delta = \frac{1}{D^2} \quad (3.2)$$

$$\epsilon = \frac{d_{hkl} - d_{hkl(0)}}{d_{hkl(0)}} \quad (3.3)$$

Where d_{hkl} is the interplanar spacing of the prepared thin films and $d_{hkl(0)}$ is the interplanar spacing of a reference pattern for CuO according to PDF File No. 04-007-1375. Williamson-Hall states that the sum of the effects due to crystallite size (D) and the micro-strain (ϵ) in the sample yields the overall peak broadening which follows the expression [143];

$$\beta_{hkl} \cos \theta = \frac{0.9\lambda}{D} + 4\epsilon \sin \theta \quad (3.4)$$

identified as the Williamson-Hall (W-H) equation. The W-H plots of $\beta_{hkl} \cos \theta$ versus $4\sin \theta$ can be used to determine the average crystallite size and the micro strain of the samples under study.

The XPS characterization was used for analyzing the elemental composition of the nanostructures. Elemental composition of the samples was studied using a Sigma probe (ThermoVG, U.K.) with an aluminium radiation source. The X-ray power was set to 30 W, the beam diameter to 100 m, and the takeoff angle to 45 °. To prepare for characterization, the powdered samples were dispersed in ethanol and sonicated for 2 hours before being drop cast onto the surface of a clean silicon wafer. The samples were mounted onto a sample holder and then loaded into the XPS chamber.

3.4.2 Microscopy-based techniques

The surface morphology of the material was investigated using SEM analysis. SEM measurements were obtained with a JEOL 7100 field emission scanning electron microscope (FE-SEM) operating at 20.00 kV coupled with an energy dispersive X-ray spectroscopy (EDX). All the samples were mounted on the sample holders using a carbon tape adhesive and loaded into the sample compartment of the SEM instrument. The samples are also carbon coated to minimize the charging effect during characterization.

AFM technique was used for surface profile imaging of the thin films. AFM measurements for this study were carried out with the Bruker Dimension Edge AFM system with a contact tapping mode over an area of $1 \times 1 \mu\text{m}$.

3.4.3 Optical radiation techniques

The Raman spectroscopy technique was employed to study of vibrational properties of molecular structures enabling identification of materials. The microstructure of the samples in this study was investigated using a Horiba LabRam High Resolution Evolution spectrometer, which used a 514 nm line of an argon ion laser with an excitation laser power of 17 nW in the wavenumber range $200\text{--}1800 \text{ cm}^{-1}$. A Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted at room temperature using a Bruker Vertex 70 FTIR in the wavenumber range of $4000 - 400 \text{ cm}^{-1}$.

The optical properties of various materials can be analyzed by measuring the transmittance/absorption/ reflectance in the UV-VIS wavelength range. For this study, the Evolution 201 UV-VIS spectrophotometer was used to analyze the optical properties of the prepared samples in the UV-Vis-NIR range (300-1100 nm). The measurements were conducted at room temperature. The powdered samples were scattered in deionized water and sonicated for 1.5 hrs to prepare them for characterization. They were loaded into quartz cuvettes and taken for UV-VIS measurements, whereas the thin film samples did not require any initial preparation. Transmission data was used to estimate the energy band gap of materials through the Tauc method. The Tauc's (Eq.(3.5)) equation was adopted to estimate the energy band gap of the films.

$$\alpha h\nu = B(h\nu - E_g)^n \quad (3.5)$$

In this formula, α is the absorption coefficient, $h\nu$ is the photon energy, B is a constant, E_g denotes the optical band gap energy in eV and n can either be equivalent to 1/2 for direct band gap transitions or 2 for indirect band gap transitions [144]. The n was taken to be 1/2 for evaluation of the direct band gap of the prepared samples. The absorption coefficient was determined from the expression in Eq. (3.6) [145].

$$\alpha = -\frac{1}{t} \ln\left(\frac{1}{T}\right) \quad (3.6)$$

The band gaps were estimated by plotting $(\alpha h\nu)^2$ vs $h\nu$ and extrapolating the linear part of the curves to the energy axis.

3.4.4 Other techniques

The BET method was used for surface area analysis of nanomaterials. Surface area analysis was performed on a Tristar II 3020 version 2.00 system by measuring the adsorption-desorption as a function of relative pressure using N₂ adsorption at liquid-nitrogen temperature. The samples were degassed for 12 hours at 180 °C using the micromeritics VacPrep 061 sample degas system.

3.4.5 Electrical Properties Analysis

Electrical characterization for nanostructures is widely carried out through the measurement of electrical resistivity (ρ) and conductivity (σ) of a material. Electrical resistivity is the measurement of the material resistance towards the flow of current whereas conductivity is a measure of the current carrying capability of a material. In this study, electrical measurements were performed under atmospheric air with pelletized samples of diameter 6 mm and thickness 2 mm. Each sample was heated from room temperature to 573 K and the bulk resistance measurements were taken at 10 K intervals using the two-point probe method illustrated in Figure 3.4. Resistivity was calculated from the expression,

$$\rho = \frac{RA}{L} \quad (3.7)$$

where L is the pellet thickness in meters (m), R is the sample resistance in ohms (Ω) at a particular temperature and A is the pellet cross sectional area in square meters (m^2). The electrical conductivity is obtained from,

$$\sigma = 1/\rho \quad (3.8)$$

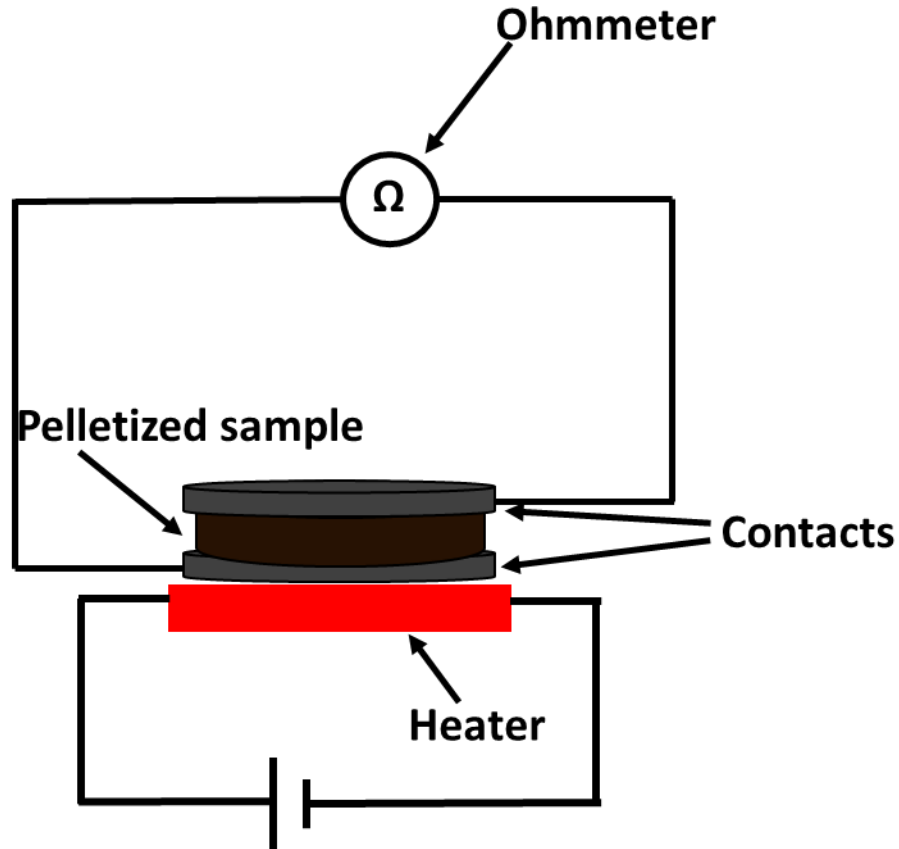


Figure 3.4: Schematic illustration of electrical resistivity measurement by two-point probe method.

Activation energy refers to the minimum energy amount that is required for a chemical reaction to occur. It can be estimated using the expression known as the Arrhenius equation (Eq.(3.9)). This equation relates the activation energy of a material to its electrical conductivity [146].

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (3.9)$$

where σ_0 is a pre-exponential factor, E_a is the activation energy, k_B is the Boltzmann's constant and T is the absolute temperature. Eq. (3.9) can also be expressed linearly as,

$$\ln \sigma = -\frac{E_a}{k_B T} + \ln \sigma_0 \quad (3.10)$$

$\ln \sigma$ against $1000/T$ was plotted from the electrical data and values of E_a were estimated from the slopes of the linear fitted graphs [147].

3.4.6 Gas sensing measurements

For gas sensor fabrication, two copper contacts were fixed on the thin film surface. Connecting wires made of copper were then attached to each contact using a solder. An illustration of the thin film sensor fabrication is displayed in Figure 3.5.

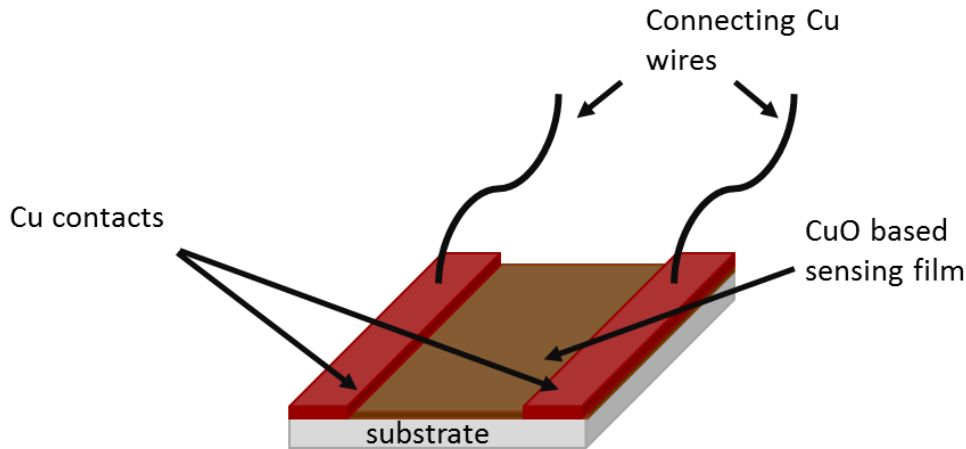


Figure 3.5: Schematic diagram of CuO-based thin film gas sensor.

The flow through measurement method was used to determine the gas sensing properties of the films in a laboratory-made gas sensing setup. In this method, the gas sensor response measurements are carried out under continuous flow of test gas. Concentration of the test gas is monitored by mixing with air using mass flow controllers. For recovery measurements, the mass flow controller of the test gas was turned off and the sensor recovers in air. The gas

sensing setup for this study is shown in Figure 3.6. Alicat's MC-series mass flow controllers were used to control the gas flow. Compressed air was kept flowing inside the chamber at 0.050 slpm to create ambient atmosphere. Compressed air was used as a carrier gas for gas sensing measurements. The target gas was introduced into the sensing chamber as a vapor. Compressed air was bubbled through the test gas solution to form the vapor. At room temperature (25°C), gas flow rates ranging from 0.070 to 0.090 slmp were measured using gas sensors. A digital LCR meter was used to measure the resistance change when the films were exposed to the target gas. The gas response was calculated as $R_{\text{air}}/R_{\text{gas}}$ using the thin film resistances in air (R_{air}) and in the presence of the target gas (R_{gas}). For measurement at elevated temperatures a mini heater was fixed under the sample.

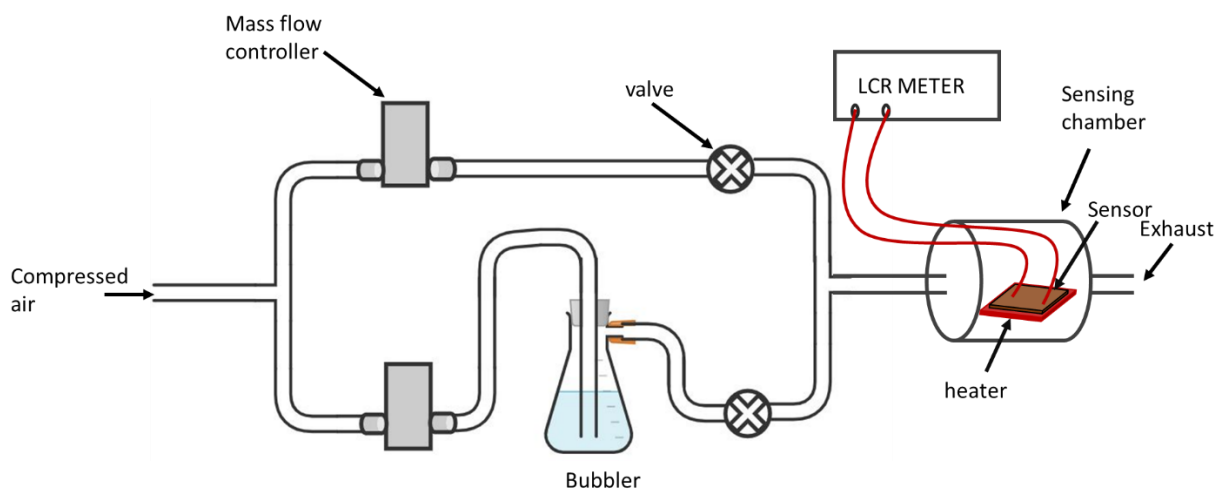


Figure 3.6: Gas sensor measurement setup.

Chapter 4 Results and discussions

A systematic study of Ce/CuO nanostructured powders and thin films is reported in this chapter. The effect of the Ce dopant on the morphological, structural and optical properties of CuO and Ce/CuO nanostructures with varying Ce/Cu mole ratios was investigated. The electrical conductivity studies and gas sensing ability of the nanostructures were also studied. Section 4.1 reports on characterization of CuO and Ce/CuO nanostructured powders prepared by the hydrothermal technique whereas Section 4.2 describes the characterizations of Ce/CuO thin films prepared by chemical spray pyrolysis method.

4.1 Structural, morphological, optical and temperature dependent electrical properties of CuO and Ce/CuO nanostructured powders

4.1.1 X-ray diffraction (XRD)

XRD patterns of the samples are displayed in Figure 4.1. All XRD plots showed peaks at $2\theta = 32.5, 35.6, 38.8, 48.8, 53.5, 58.3, 61.6, 66.1$ and 68.0° , which were indexed to the (110), (-111), (111), (-202), (020), (202), (-113), (321) and (220) lattice planes of monoclinic phase CuO (COD #90-16326). An additional peak was observed at $2\theta = 28.6^\circ$ corresponding to (111) diffraction plane of CeO_2 (COD #90-09008) for the mixed oxide samples (Figure 4.1 (b)). This peak was relatively weak and broadened which indicated that the CeO_2 was highly dispersed on the CuO lattice and that some of the cerium atoms may have been incorporated into CuO to form a solid solution [148]. This peak became more visible as the mol% concentration of Ce was increased which may indicate oxidation of Ce^{3+} to Ce^{4+} and formation of CeO_2 during sample synthesis [149]. From Figure 4.1 (a), it can be observed that the intensity of the CuO peaks decreased as the concentration of cerium increased in the sample. This decrease may be attributed to changes in crystal stability caused by the formation of defects in the CuO lattice system as a result of CeO_2 incorporation, which may segregate along grain

boundaries, interfering with CuO crystal aggregation [150] [151].

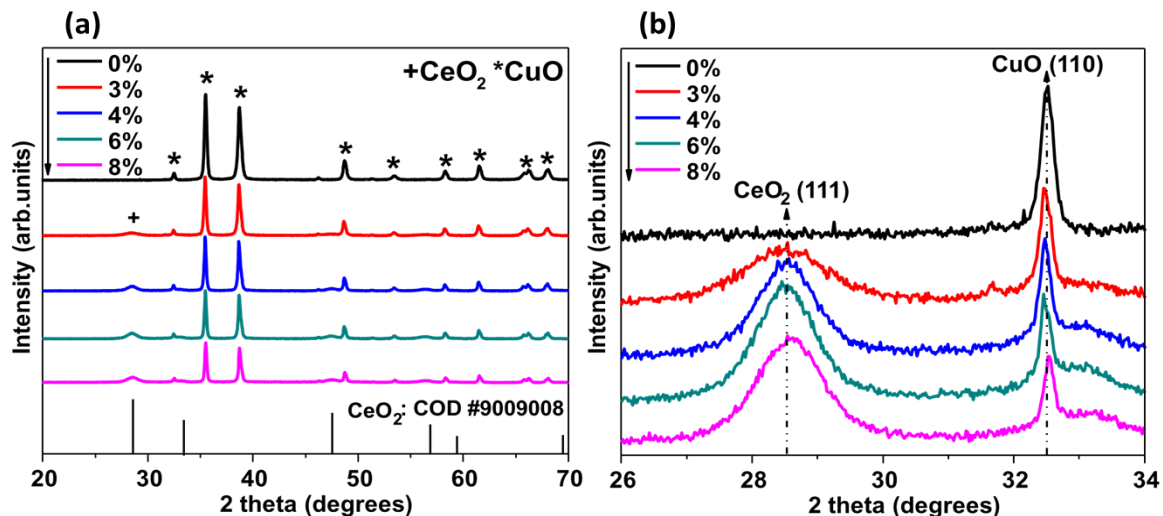


Figure 4.1: XRD plots of (a) CuO, Ce/CuO and CeO₂ reference pattern (black bars, COD #9009008); and (b) magnification from 26° to 34° to clearly show the CeO₂ peaks.

As the fraction of the Ce increased, the crystallite size increased suggesting an improvement of the crystallinity of the samples as shown in Table 4.1. It was further noticed that as crystallite size of the samples increased, the strain and dislocation density decreased. This indicates reduced lattice defects and better crystallization of the nanostructures. Figure 4.2 shows the W-H plots of $\beta_{hkl}\cos\theta$ against $4\sin\theta$ used to estimate the average crystallite size and the micro strain of the samples. Table 4.1 presents the estimated values obtained via the W-H and Scherrer methods. The values confirm the nanostructured nature of the samples.

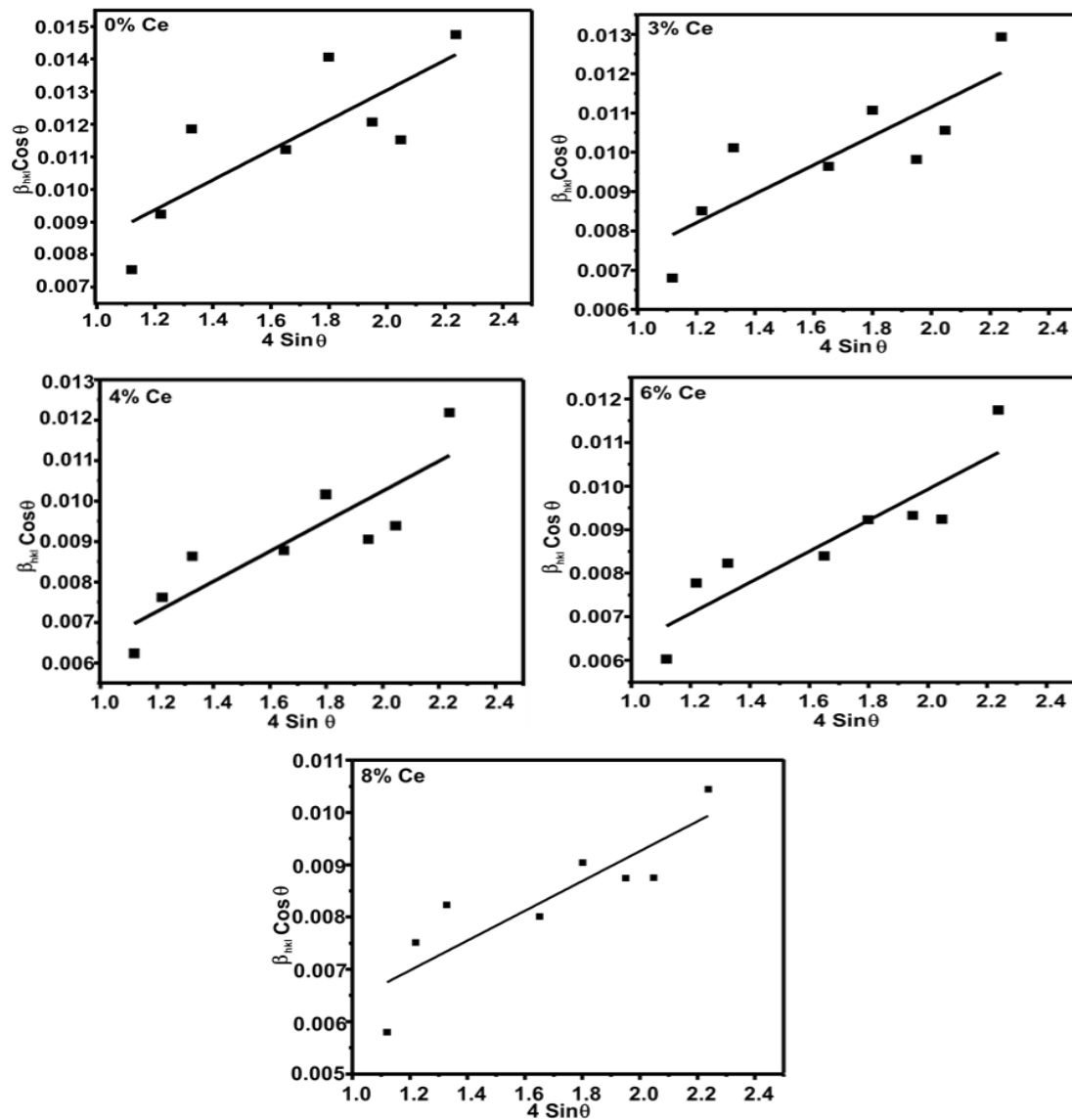


Figure 4.2: Williamson-Hall plots for CuO and Ce/CuO.

The crystallite size values observed from the W-H are higher than the values obtained from the Scherrer equation. The difference may be attributed to the averaging within the particle size distribution. It can be observed that the largest crystallite sizes correspond to the lowest dislocation densities which are accounted for by the inverse square of proportionality [152]. The crystallinity corresponds to the fraction of the crystallite phase in the studied volume of the powdered sample.

Table 4.1: Crystallite sizes, micro-strain and dislocation density of CuO and Ce/CuO nanostructures

Sample	Crystallite size (nm)			Micro-strain	Dislocation density (nm ⁻²)	Degree of crystallinity
	W-H	Scherrer	Average			
0 % Ce	30.3	29.1	29.7	4.94×10 ⁻³	1.18×10 ⁻³	0.36
3 % Ce	51.4	31.8	41.6	4.17×10 ⁻⁴	9.89×10 ⁻⁴	0.51
4 % Ce	65.4	37.1	51.3	4.02×10 ⁻⁴	7.27×10 ⁻⁴	0.65
6 % Ce	55.5	38.0	46.8	3.57×10 ⁻⁴	6.93×10 ⁻⁴	0.76
8 % Ce	44.7	37.6	41.2	3.37×10 ⁻⁴	7.07×10 ⁻⁴	0.83

4.1.2 Raman spectroscopy

The Raman spectra of CuO and Ce/CuO are shown in Figure 4.3. CuO has a monoclinic structure and is a member of the C2h6 space group, which has two molecules for every primitive cell [33]. There are twelve zone-centre optical-phonon modes that can be represented by,

$$\Gamma = 4A_u + 5B_u + A_g + 2B_g \quad (4.1)$$

where Γ represents the degree of vibrational freedom, A_u and B_u denote the IR modes and A_g and B_g denote the Raman modes. There are normally six infrared active modes ($3A_u + 3B_u$), three acoustic modes ($A_u + 2B_u$) and three Raman active modes ($A_g + 2B_g$) [153]. Figure 4.3 shows vibration bands belonging to CuO at 279 cm⁻¹, 327cm⁻¹ and 614 cm⁻¹, corresponding to the A_g (296 cm⁻¹), B_g (346 cm⁻¹) and B_g (631 cm⁻¹) modes reported previously [154]. Another CuO broad peak appearing at 1104 cm⁻¹ is assigned to multi-phonon transition [155]. The vibration band at 454 cm⁻¹ is linked with F_{2g} Raman active mode CeO₂. This corroborates with other studies showing symmetric vibration modes of Ce-O. CeO₂ is generally known to have a fluorite structure and six optical phonon modes that give three band frequencies at 272, 465 and 595 cm⁻¹ [156]. However, the other characteristic bands of CeO₂ at 272 cm⁻¹ and 595 cm⁻¹ were not observable because they may have

blended in with the more intense CuO bands found at 279 cm^{-1} and 614 cm^{-1} . The position of the peak red shifted to lower frequencies attributed to energy lost as the phonon interacts with the vibrational modes of the samples. The significant intensities of the peaks for vibration bands indicate the high crystallinity of the nanostructures [157] [158]. The absence of additional peaks not belonging to the synthesized nanostructures indicates that the samples did not have any impurities. The Raman analysis agrees with the XRD data analysis.

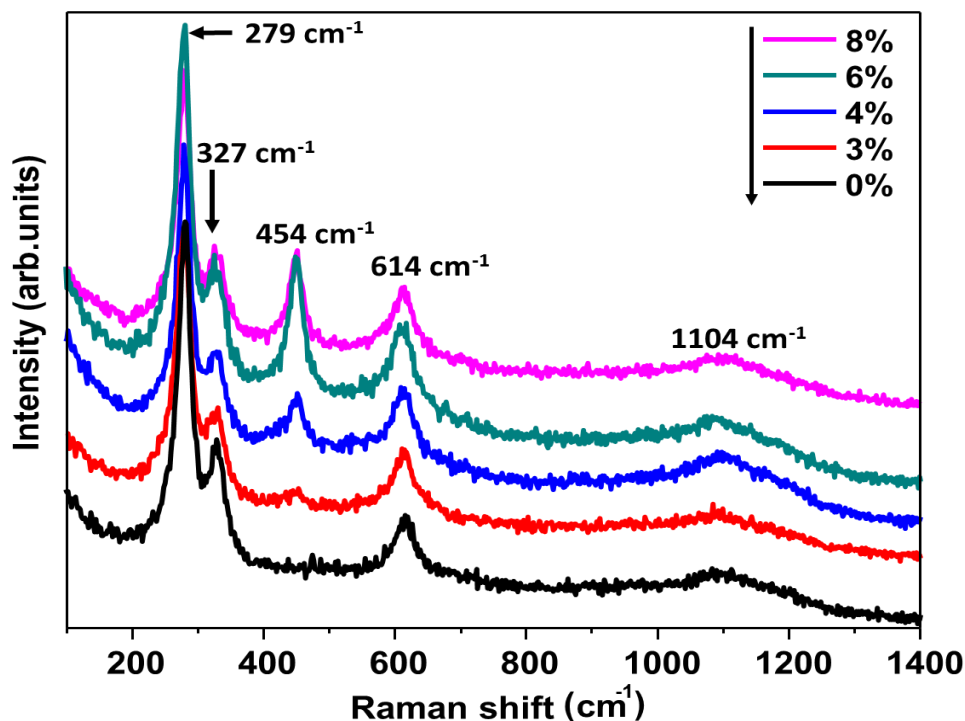


Figure 4.3: Raman spectra of CuO and Ce/CuO.

4.1.3 FTIR

FTIR was used to study the presence of organic and inorganic materials as well as polymeric substances in the synthesized samples. Figure 4.4 presents the infrared spectra of CuO and CeO_2/CuO with Ce concentrations of 0, 3, 4, 6 and 8 %. The spectra have bands at 3449 cm^{-1} and 3344 cm^{-1} that can be assigned to stretching vibrations due to the $-\text{OH}$ which points to the existence of moisture on the samples [159]. The peaks detected at 596 cm^{-1} and 538 cm^{-1} correspond to Cu-O stretching vibrations. [160]. Other absorption bands detected at 2197 cm^{-1} and 2027 cm^{-1} can be attributed to CO_2 on the surface of the samples [161].

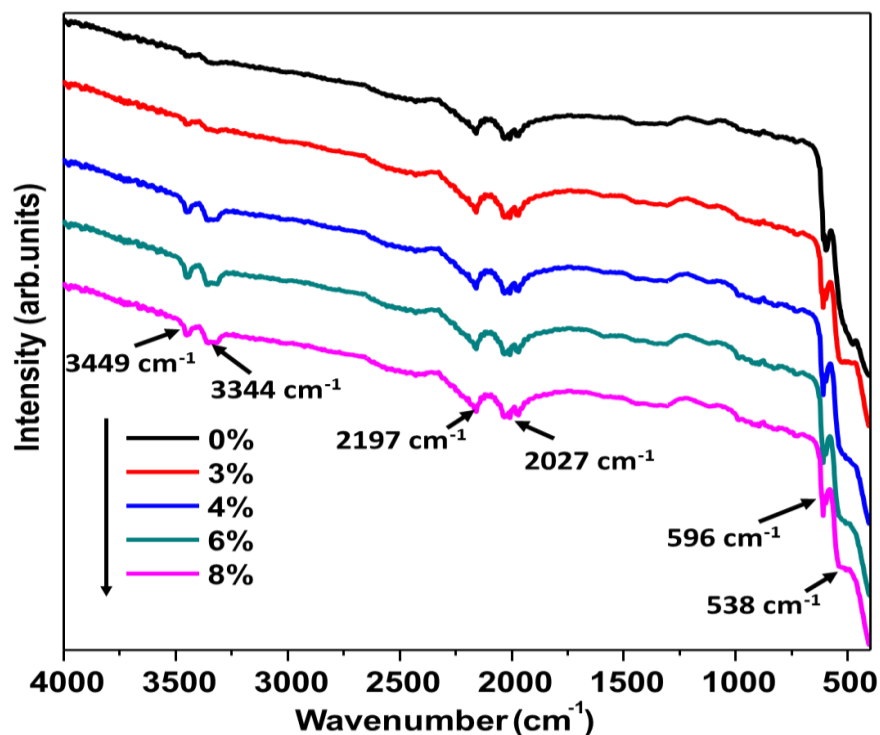


Figure 4.4: FTIR spectra CuO and Ce/CuO.

4.1.4 UV-visible transmission spectroscopy

UV-visible transmission spectroscopy was used to investigate the optical properties of the nanomaterials. Transmission measurements were taken at room temperature in the wavelength range of 300 nm to 1000 nm. It can be observed from Figure 4.5 that optical transmittance increases as the wavelength values widen in the near-infrared (NIR) region of the spectra for all the samples. This shows that the samples were darker for small wavelength values but became transparent as the wavelength increased. The 3 % sample showed the highest values of transmittance in this region.

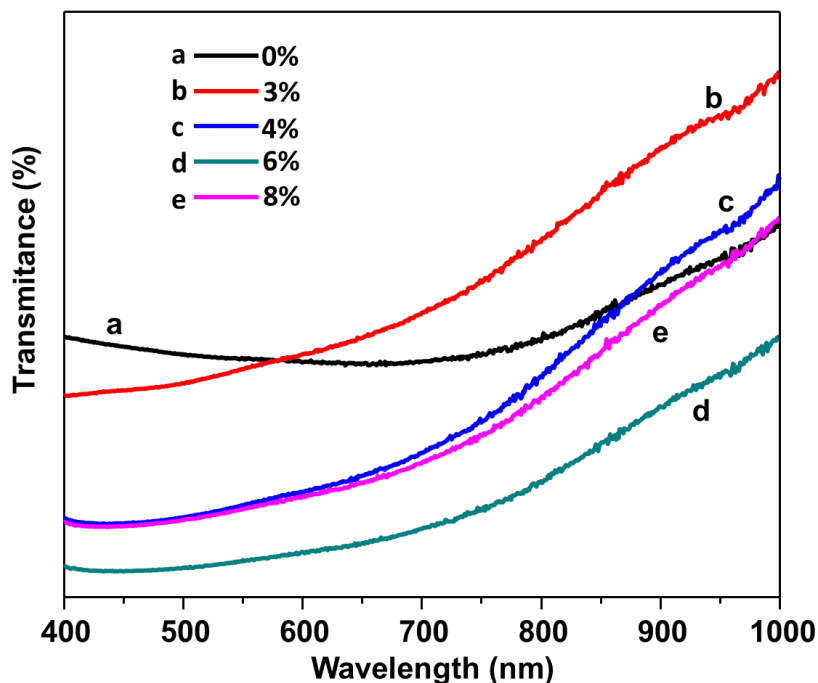


Figure 4.5: UV-Vis transmission spectra of a) 0 %, b) 3 %, 4 %, 6 % and 8 % Ce/CuO.

As shown in Figure 4.6, the band gaps were calculated by plotting $(\alpha h\nu)^2$ vs $h\nu$ and extrapolating the linear part of the curves to the energy axis. The direct energy bandgap of CuO was estimated to be 2.0 eV, which is significantly greater than the value of standard bulk CuO (1.2 eV); however, our results corroborate the findings of Kaur et al. [162]. This may be due to the strain in the nanostructures and the size effects at nanoscale [25]. This has also been attributed to the quantum confinement effect apparent in nanostructured materials [163]. A single cut-off energy was observed for the CuO and 3 % Ce sample showing bandgap values of 1.97 and 2.24 eV, respectively. Two bandgap values were deduced from the observed well defined cut-off energies in the Tauc's plot of higher Ce content samples (4 % - 8 %). It is clear that there is a single cut-off edge for lower doped samples (0 and 3 at%) and two distinct cut-off edges in the higher Ce doped samples, one yielding a bandgap in the range of 1.97 eV – 2.55 eV consistent with CuO and the other 3.00 eV – 3.49 eV which was attributed to the contribution of (CeO₂) with a wider known bandgap of (3.2 eV) [164]. The existence of some significant amount of CeO₂ to yield this result is evident from XRD and Raman spectroscopy. Similar results have been reported previously,

showing two main energy bandgaps for binary $(\text{CuO})_{0.6}(\text{CeO}_2)_{0.4}$ nanoparticles [165]. Furthermore, as the Ce content was increased from 3 % to 6 %, the bandgap energies of the samples increased. Further increase of Ce content to 8 % resulted in a decrease of the energy band gap. The shift in bandgap values confirmed the formation of defects in the CuO lattice, which was also supported by the XRD results.

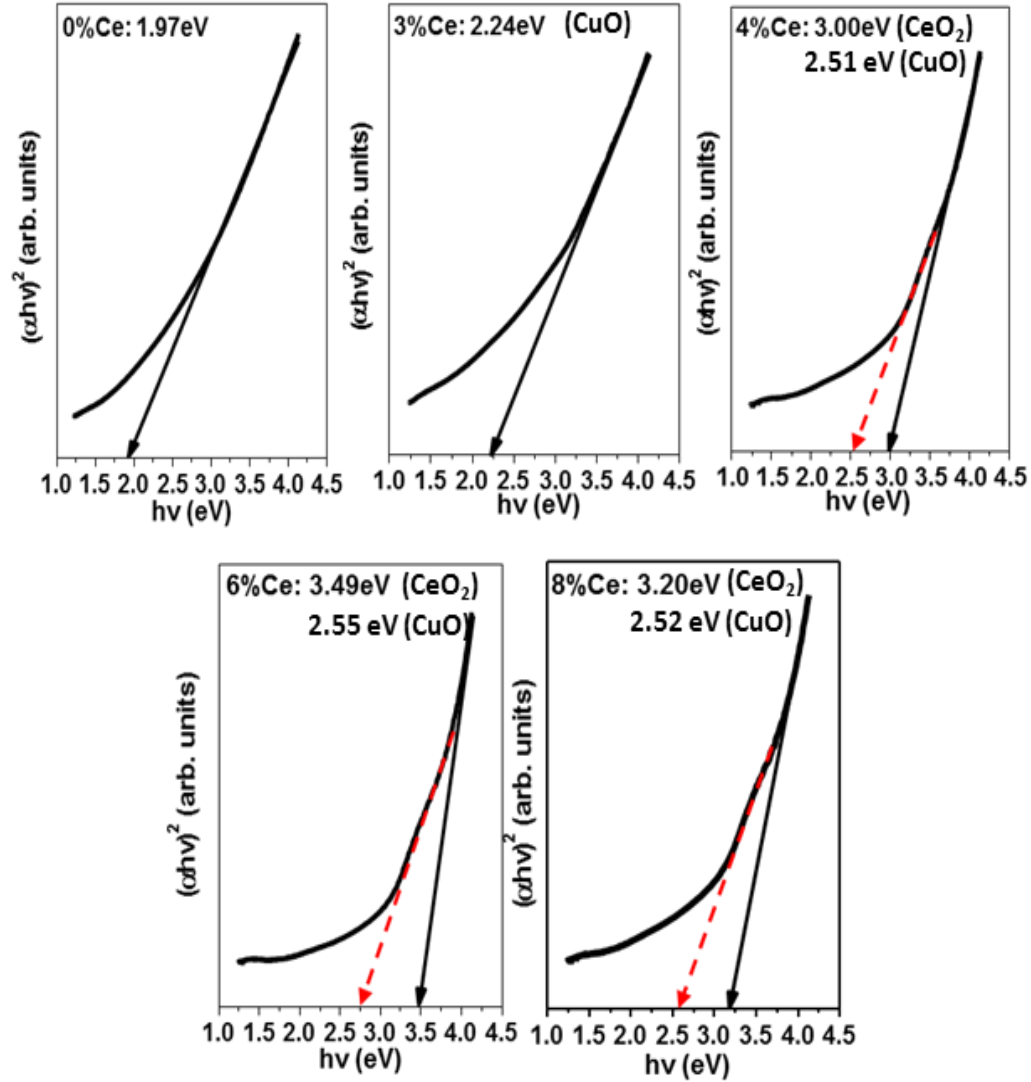


Figure 4.6: Tauc plots of CuO and Ce/CuO.

4.1.5 SEM

The top views of the CuO and Ce/CuO SEM images are shown in Figure 4.7. As shown in Figure 4.7 (a), agglomerated CuO particles of spherical shape were found on the entire surface. As the Ce content increased from 3 % to 8 %, the shape and morphology of the CuO nanoparticles was observed to be changing. Morphologies of the Ce/CuO samples showed the formation of nano-rods and nano-chips which were also agglomerated as the Ce content was increased. Similar findings were reported by Ponnar et al. [160] where the formation of highly agglomerated nano-rods and nano-flakes was observed and articulated to be due to small particles overlapping. A mixture of nano-rods and nano-spheres was observed for the 3 % to 6 % whereas the 8 % shows nano-chips formation only.

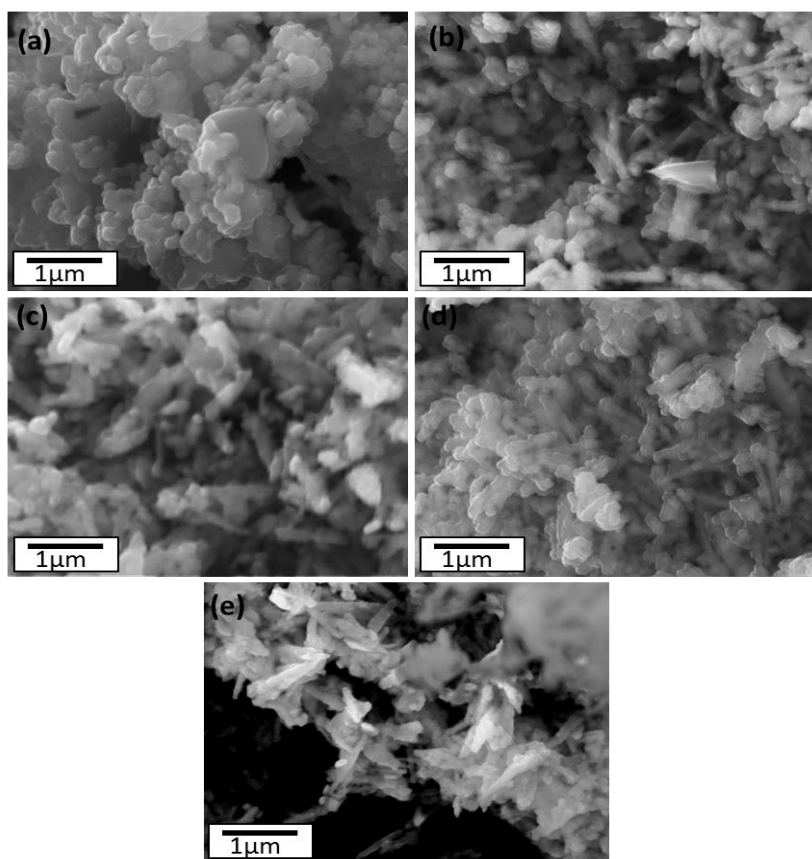


Figure 4.7: SEM images of (a) 0%, (b) 3%, (c) 4%, (d) 6% and (e) 8% Ce/CuO.

4.1.6 EDX

Figure 4.8 depicts the EDX elemental mapping and spectra of CuO and 8 % Ce/CuO samples. Figure 4.8 (a) demonstrates that the Cu and O elements are evenly distributed confirming the homogeneity of the sample. Figure 4.8 (b) also presents an even distribution of Cu, O and Ce elements for the 8 % Ce sample. EDX spectrum of the undoped sample shown in Figure 4.8 (c) confirmed the presence of Cu and O without any other impurities. Figure 4.8 (d) shows EDX spectrum with peaks of Cu, Ce and O elements belonging to Ce/CuO. The other peaks that belong to Au and C appearing on both spectra emanates from the gold coat and carbon tape that was used to enable imaging.

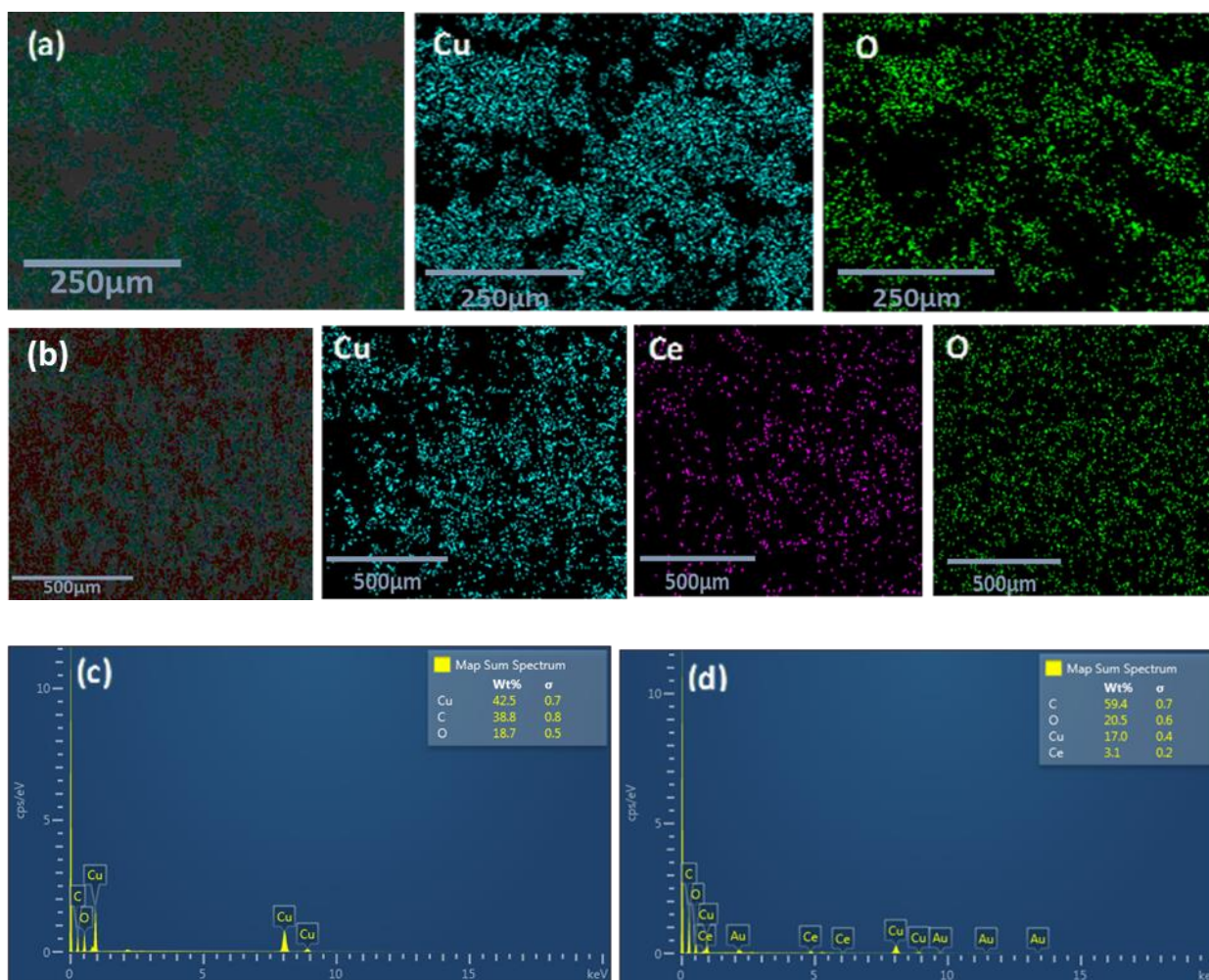


Figure 4.8: EDX mapping of (a) CuO, (b) 8 % Ce/CuO and EDX spectra of (c) CuO and (d) 8 % Ce/CuO.

4.1.7 XPS

Figure 4.9 and Figure 4.10 show the XPS spectra of CuO and 8 % Ce/CuO, respectively. The presence of Cu and O in the sample is indicated by the complete spectra of CuO shown in Figure 4.9 (a). Figure 4.10 (a) depicts an 8 % Ce/CuO spectrum, suggesting the existence of Cu, Ce, and O in the sample. The C detected on both samples was used as the reference. The XPS spectra of Cu 2p for the CuO sample is presented in Figure 4.9 (b). Peaks centered at 932.8 eV and 952.8 eV were ascribed to Cu 2p_{3/2} and Cu 2p_{1/2} of CuO, separately. The Cu 2p peaks shifted to lower values of 931.8 eV (Cu 2p_{3/2}) and 951.9 eV (Cu 2p_{1/2}) for the 8 % Ce/CuO shown in Figure 4.10 (b). The shift indicates that the electron density of Cu²⁺ is increased when Ce is added which results in the decrease of its binding energy [166]. From Figure 4.9 (b) and Figure 4.10 (b), the Cu 2p XPS results provide evidence of Cu²⁺ within the sample indicated by the distinctive satellite peaks at around 941.6 eV to 939.2 eV and 961.8 eV. These strong satellite peaks can be ascribed to electronic shake-up and are well known for indicating presence of Cu²⁺ species in the sample [167]. Figure 4.10 (c) shows four characteristics peaks; Ce⁴⁺ peaks positioned at 914.0 eV and 896.0 eV, and Ce³⁺ peaks found at 905.3 eV and 880.4 eV. These indicate a mixed valence on the surface of CeO₂ which is responsible for creation of oxygen vacancies and other useful characteristics of CeO₂ [168] [169]. The O 1s spectrum in Figure 4.9 (c) and Figure 4.10 (d) are representative of CuO and 8 % Ce/CuO respectively. The spectra were deconvoluted into 2 similar peaks centered at 529.0 eV and 531.8 eV for the CuO and 529.0 eV and 531.7 eV for the 8 % Ce sample. The 529.0 eV peak was attributed to the oxygen species bound to copper in the Cu-O bond [170]; whereas the peak positioned at 531.7 eV indicated the oxygen chemisorbed by the material as a carbonate or hydroxyl group [171]. An extra peak was observed for the 8 % Ce sample. This peak was detected at a lower binding energy value of 527.2 eV. Since this binding energy value was lower than that of CuO and CeO₂, it was attributed to the subsurface oxygen species that may have been formed due to Ce addition thus creating charge imbalance on the sample and modifying the electron density on CuO [172].

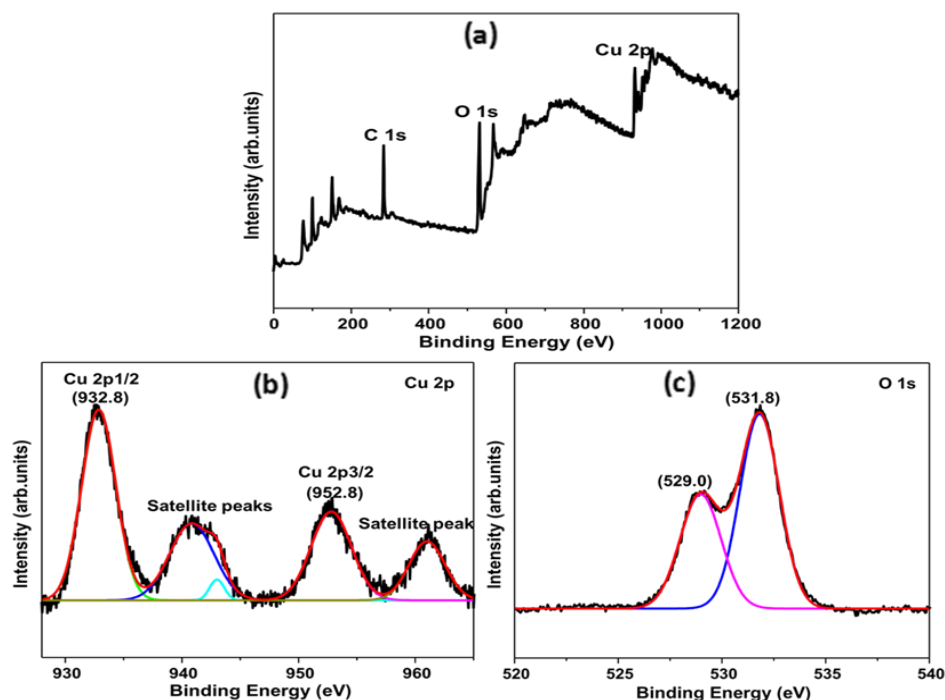


Figure 4.9: XPS showing profiles of the (a) wide scan of CuO, (b) Cu 2p and (c) O 1s for CuO.

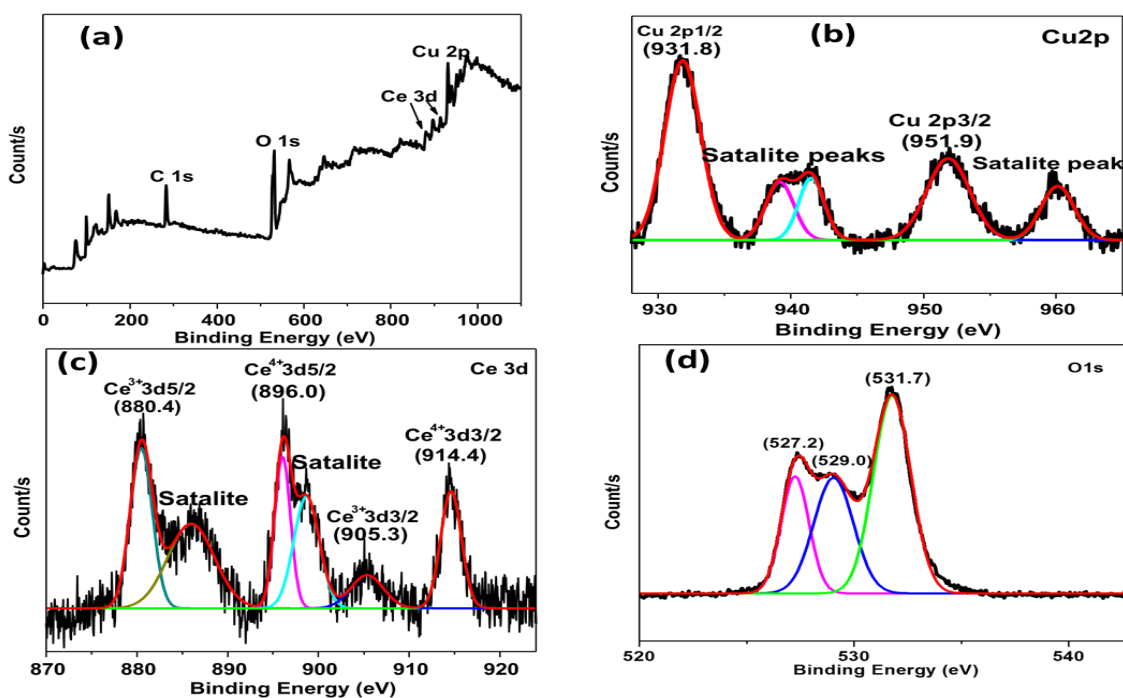


Figure 4.10: XPS showing profiles of the (a) wide scan of Ce/CuO, (b) Cu 2p, Ce 3d and (d) O 1s for 8 % Ce/CuO.

4.1.8 BET

N₂ sorption measurements were conducted to examine the pore structure of the samples. The N₂ adsorption-desorption isotherms of CuO and 8 % Ce/CuO samples are shown in Figure 4.11 (a) and (b). The plots depict hysteresis loops with relative pressures ranging from 0.6 to 1.0. This can be assigned to the filling and emptying of the pores in the sample by condensation indicating the porosity of the samples [173]. Figure 4.11 shows the graphs displaying characteristic type II isotherms according to IUPAC categorization [174]. The isotherms indicate that the adsorption of N₂ molecules occurs from the monolayer to the multilayer of the samples, which suggests that the samples have a continuous pore system with pore diameters varying from molecular to macro level. Hysteresis loops of H3 category were observed in Figure 4.11 indicating presence of slit-like pores [174] of variable sizes formed due to particle aggregation which is consistent with the SEM results. The pore size distribution estimated by the Barret-Joyner-Halenda (BJH) method shows a wide pore size distribution for the samples ranging from 1.7 nm to 238 nm, with an average pore width of 6.7 nm for CuO and 12.4 nm for 8 % Ce/CuO. The BET method calculated specific surface areas of 10 m²/g and 18 m²/g for CuO and 8 % Ce/CuO, respectively, and pore volumes of 0.018 cm³/g and 0.063 cm³/g. As Ce was incorporated into CuO, the surface area and pore volume increased. This was attributed to the contribution of the nano-chip morphology formed with Ce loading that was revealed by SEM analysis for the 8 % Ce sample, which has higher specific surface area compared to the nano-sphere morphology formed in the undoped sample. The higher surface area of the nanostructures suggests higher surface activities which is advantageous for numerous applications.

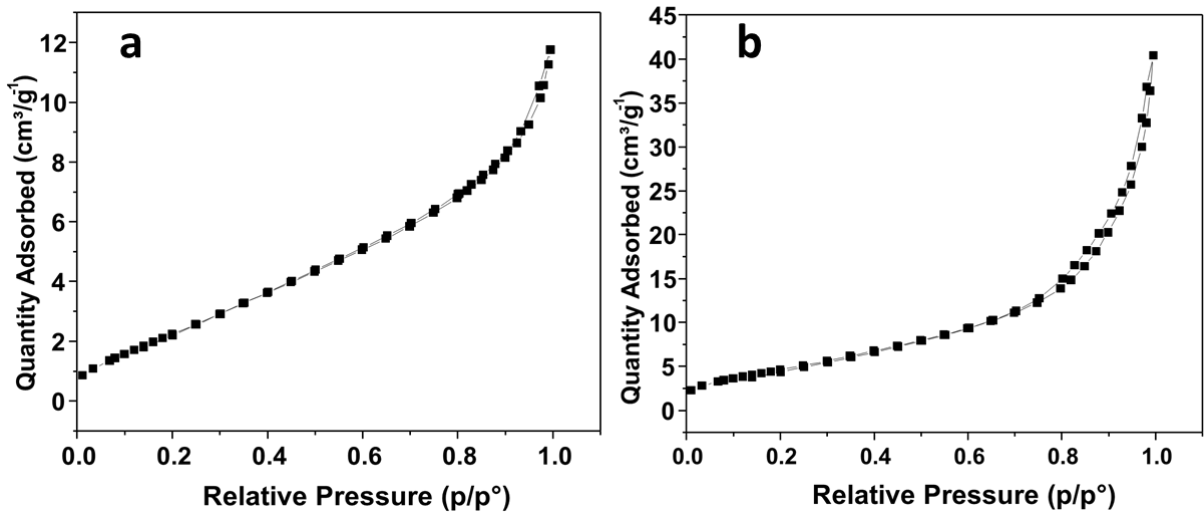


Figure 4.11: BET nitrogen adsorption–desorption isotherm for (a) CuO and (b) 8 % Ce/CuO.

4.1.9 Electrical properties

The electrical conductivity is obtained from Eq. (3.8). Figure 4.12 (a) demonstrates the change of electrical conductivity with temperature for the CuO and Ce/CuO nanostructures. It can be noted that as the sample temperature was raised, the conductivity of the samples increased showing a distinctive semiconductor quality brought about by increase in thermal energy which prompts more carrier generation [175]. The reported values of conductivity for the CuO single crystals at 333 K are of the order $10^{-5} \Omega^{-1} \text{ cm}^{-1}$ [176]. The least conductive sample (0 % Ce) in the present study recorded a conductivity of $3.6 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ at 333 K. This is approximately two orders of magnitude lower than the value for CuO single crystals. For the 4 % Ce doped sample, the recorded value was $4.8 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$, which is only one order of magnitude less than that of the CuO single crystals. From the plots, it is evident that Ce/CuO samples showed enhanced conductivity compared to the CuO. The sample with cerium concentration of 4 % showed the maximum conductivity peaking at a value of $4.29 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$ at a temperature of 503 K whereas the undoped CuO sample had the minimum conductivity of $1.96 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$. The conductivity of the samples with values of 0, 3, 4, and 6 % Ce increases until a certain temperature region and then decreases, indicating that the properties change with increasing temperature from those of non-degenerate semiconductors to those of metal-like materials. The 8 % sample, on the contrary, does not

exhibit the same trend, with conductivity values increasing throughout the temperature range measured. This is due to thermal excitation of charge carriers, for which a certain temperature is required for the sample to transition to metal-like behavior [177].

CuO is a p-type semiconductor, and the majority of charge carriers in the valence band are h^+ s. The conductivity arises mainly due to the deviation from stoichiometry arising from excess oxygen interstitials or copper metal vacancies [178]. In addition, multiple oxidation states of Cu may also play a role in enhancing this nonstoichiometry. The increased conductivity after doping may be ascribed to the production of charge carriers brought about by incorporation of Ce^{4+} into the positions of Cu^{2+} . When Ce dopants were incorporated into CuO lattice up to 4 % doping, the conductivity increased because of an increase in h^+ . The 6 % Ce sample showed decreased conductivity compared to the 4% Ce sample. The decrease indicates the possibility of neutralization of excess charge carriers due to enhanced lattice defects as well as increased scattering [178] emanating from the Ce^{4+} ions, which result in reduction of the mobility. Besides, the 4 % Ce sample recorded the highest mean crystallite size and the higher value of conductivity may be attributed to the minimised crystallite boundary scattering resulting from less dislocations.

Figure 4.12 (b) shows the temperature response ($d\sigma/dT$) of the samples, which may be defined as the change in conductivity with temperature change. It is clear that ($d\sigma/dT$) increases up to a maximum value, ($d\sigma/dT$)_{max} at a specific temperature (T_{max}) and then decreases indicating that after the (T_{max}) point there is diminishing change of conductivity with temperature. Both charge carrier concentration and lattice scattering increase in the samples with an increase of temperature [179]. At T_{max} , opposing effect of the increasing carrier concentration and lattice scattering yields ($d\sigma/dT$)_{max}. Prior to T_{max} , the effect of increasing carrier concentration is more significant than that of the lattice scattering. As the temperature exceeds T_{max} , the lattice scattering becomes dominant thus hindering charge carrier mobility and decreasing conductivity [179]. This point defined by ($d\sigma/dT$)_{max} and (T_{max}) is important in designing devices where conductivity is a factor since it indicates the useful temperature range in which the sample can be applied. The ($d\sigma/dT$)_{max} ($\Omega.cm.K$)⁻¹ (T_{max}) for the samples were 1.9×10^{-7} (483K), 2.2×10^{-7} (453K), 3.25×10^{-7} (393K), 2.1×10^{-7}

(473K) and 3.5×10^{-7} (483K) for the 0, 3, 4, 6 and 8 %, respectively. It is clear that between 0 and 4 %, there was a trade-off between $(d\sigma/dT)_{\max}$ and $(T_{\max})$.

Figure 4.12 (c) shows the Arrhenius plots used to estimate the activation energies of the CuO and Ce/CuO samples. This estimation was performed using the Arrhenius equation (Eq. (3.9)). $\ln \sigma$ against $1000/T$ was plotted from the electrical data and values of E_a were estimated from the slopes of the linear fitted graphs. It was noted that all the graphs were approximately linear which indicated that the samples had a characteristic extrinsic semiconductor material behavior with a single activation energy [180] [181].

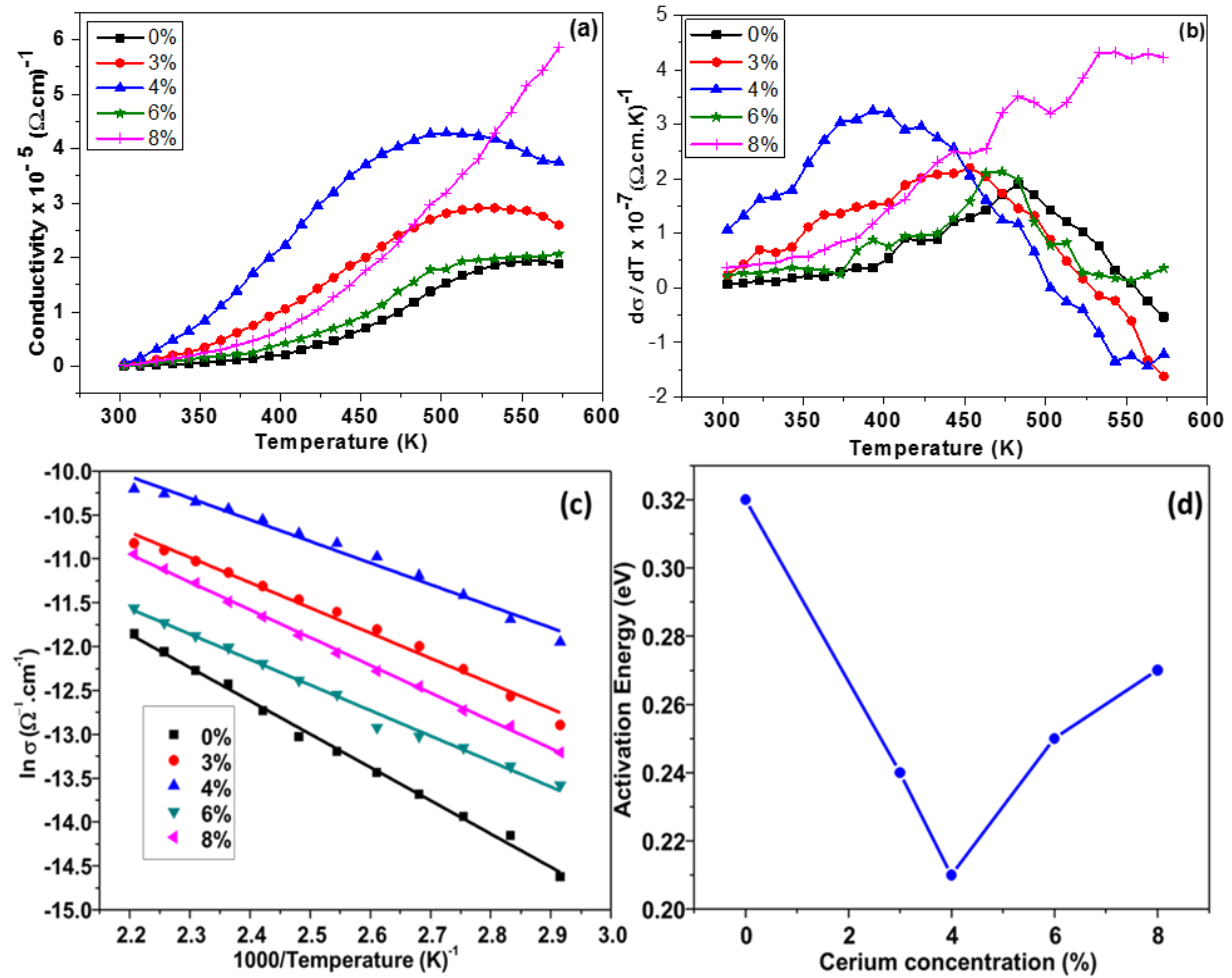


Figure 4.12: Electrical analysis plots for CuO and Ce/CuO: (a) Conductivity (σ) vs temperature (T), (b) Temperature derivative of conductivity ($d\sigma/dT$), (c) $\ln \sigma$ vs $1000/T$ and (d) Activation Energy (E_a) vs Ce concentration.

From Figure 4.12 (d), it can be noted that the highest value of E_a was recorded for the CuO sample. The obtained E_a values were 0.32, 0.24, 0.21, 0.25 and 0.27 for 0 %, 3 %, 4 %, 6 % and 8 % Ce, respectively. These values fitted well in the range of 0.11 – 0.7 eV usually reported [111] for CuO nanostructures. E_a decreased with increasing Ce concentration up to the 4 % Ce then increased again. The 4 % sample showed the lowest activation energy and the highest overall conductivity. This implies that the 4 % Ce was the optimum concentration for the Ce/CuO system. This was also the sample with the largest crystallite sizes as averaged from the W-H and Scherer methods. The activation energies were in the range of 0.21 to 0.32 eV and at these high temperature ranges, this low activation energy value points to conductivity via the nearest neighbour hopping of carriers. Consequently, increasing the temperature improves drift mobility by providing energy for charge carriers to hop from one site to another [182]. In addition, the trend of activation energy is similar to that of (T_{max}) implying that reduced activation energy also reduces (T_{max}). From the observations, it can be deduced that ramped addition of Ce into CuO alters the useful properties of the obtained Ce/CuO nanostructures and has potential to expand its applications in optoelectronic devices.

4.2 Structural, morphological, optical and gas sensing properties of nanostructured Ce-doped CuO thin films

4.2.1 XRD

X-ray diffraction measurements were conducted to identify the phases and the crystallinity of the CuO and Ce doped CuO thin films. Figure 4.13 illustrates the obtained XRD plots of thin films with varying concentrations of Ce. The strong peaks indexed at 35.5° and 38.7° demonstrated the polycrystalline nature of the films which corresponds to the monoclinic CuO phase according to the PDF file (04-007-1375). These XRD peaks were assigned to the CuO planes (002) and (111), respectively. There were no other peaks detected from impurities or secondary phases, indicating that the Ce ions were successfully incorporated into CuO. It should be noted that the dopant had no effect on the host matrix's crystal structure, thus the monoclinic structure of CuO was preserved in all samples.

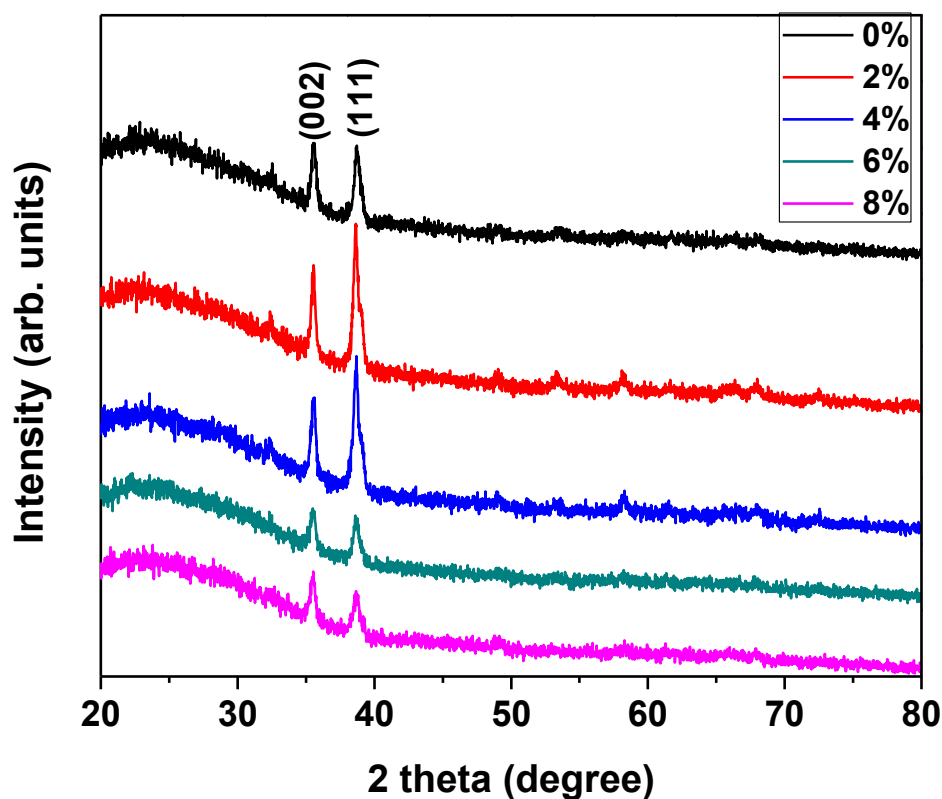


Figure 4.13 : XRD patterns of CuO thin films with different Ce concentrations.

Dopant addition has an effect on the intensity of the diffraction peak. It is clear that as the concentration of Ce doping increases, the diffraction peaks become broader and less intense. This indicates that Ce doping initiates small alterations in crystal symmetry, which results in the development of defects and vacancies at lattice sites [150]. Table 4.2 shows that the crystallite size was influenced by the Ce doping concentration, with calculated crystallite sizes ranging from 19.0 nm to 23.7 nm. The largest average crystallite size was obtained for the 2 % Ce doped CuO sample, then the crystallite size decreased as Ce doping was increased from 4 % to 8 % in agreement with the peak broadening. Initially, Ce ion incorporation resulted in cancellation of existing Cu^{2+} vacancies in the CuO crystal structure hence bigger crystals were formed for the 2 % Ce sample [183]. Crystallite size reduction observed with further doping was attributed to strain in the lattice of CuO that was brought about by the dopant ion incorporation hence inhibiting growth of crystals [184].

The dislocation density and lattice strain values are displayed in Table 4.2. The Ce doped thin films showed increased internal strain as compared to undoped CuO thin films indicating that Ce incorporation induced strain in crystal structure of CuO.

Table 4.2: Structural parameters of Ce/CuO films.

Sample	FWHM	D (nm)	δ ($\times 10^{15} \text{ m}^{-2}$)	ϵ ($\times 10^{-3}$)
0 % Ce	0.492	19.0	2.77	0.49
2 % Ce	0.394	23.8	1.77	2.66
4 % Ce	0.423	22.1	2.05	1.99
6 % Ce	0.413	22.7	1.94	3.22
8 % Ce	0.489	19.1	2.74	2.29

4.2.2 Raman Spectroscopy

Figure 4.14 illustrates the Raman spectra of Ce/CuO thin films. According to the group theory, CuO belongs to the $C2/c$ space group and has 12 vibration modes, only three of

which are Raman active. The Raman spectra revealed peaks positioned at 270.6 cm^{-1} , 319.3 cm^{-1} and 597.0 cm^{-1} for all the samples. These peaks were attributed to the Raman active modes of bulk CuO crystals, which corresponded to the Ag, Bg⁽¹⁾, and Bg⁽²⁾ modes [185]. This corroborates the XRD results thus confirming presence of monoclinic structured CuO in all the samples. The 4 % Ce doped film produced an additional peak at 443.5 cm^{-1} . This peak was assigned to the triply degenerate Raman active optical phonon mode (F_{2g}) of a CeO₂ [186]. The formation of a secondary phase in the samples beyond 2 % Ce doping was attributed to local precipitation of CeO₂ when Ce ions were no longer soluble in CuO [65]. This phase was not revealed by the XRD suggesting that it was formed in very small amounts such that it was below the XRD detection limit. However, the decreased crystallinity observed in XRD may be attributed to steric hindrance leading to discontinuities in the CuO lattice brought about by diffusion of these small amounts of CeO₂ to grain boundaries. Raman peak intensity changes were observed as the dopant concentration was varied, the 2 % Ce doped sample showed narrower and more intense peaks indicating high crystallinity of the sample which was uniform with XRD analysis.

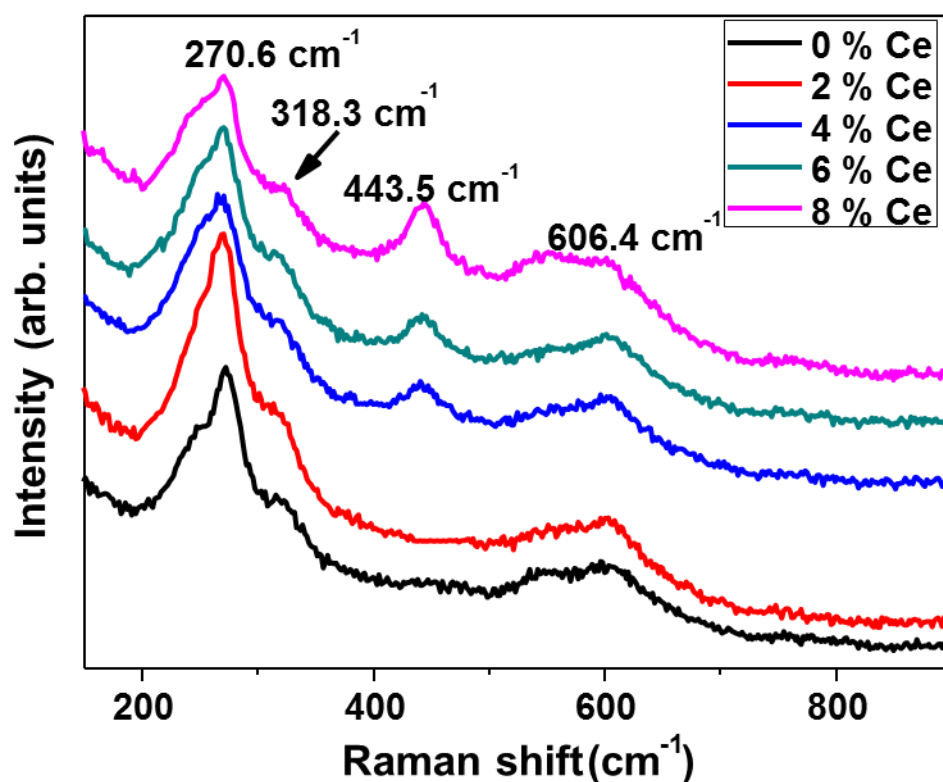


Figure 4.14: Raman spectra of Ce/CuO thin films.

4.2.3 SEM

Figure 4.15 shows SEM micrographs depicting the surface morphology of the Ce/CuO thin films. The SEM images displayed grain formation that appears to be dependent on %Ce concentration. From SEM images, all the samples show nanoparticles with different shapes, sizes, compactness and density. Irregular shaped nanoflakes with size ranging between 30 nm and 300 nm were observed to be randomly distributed. For the 0 % Ce and 2 % Ce sample ((a) and (b)), the films are composed of relatively uniform and adherent nanoflakes with size ranging from 30 nm to 180 nm. At 4 % Ce doping (Figure 4.15 (c)), the particles are agglomerated and appear to be stacked unevenly thus forming a rough surface. The grain size increased to the range of (80-280 nm). Grain size decreased for the 6 % Ce film (Figure 4.15 (d)) to the range of 50 to 200 nm, irregular randomly shaped grains were also observed. The uniform distribution of the particles observed from Figure 4.15 (e) suggest homogenous

nucleation across the substrate which formed a smooth film without cracks or holes. Table 4.3 shows the elemental composition of Ce doped CuO thin films. The presence of Cu and Ce elements in the deposited thin films was confirmed by EDX analysis. The amount of Ce incorporation in the thin films was comparable to that in the starting solution.

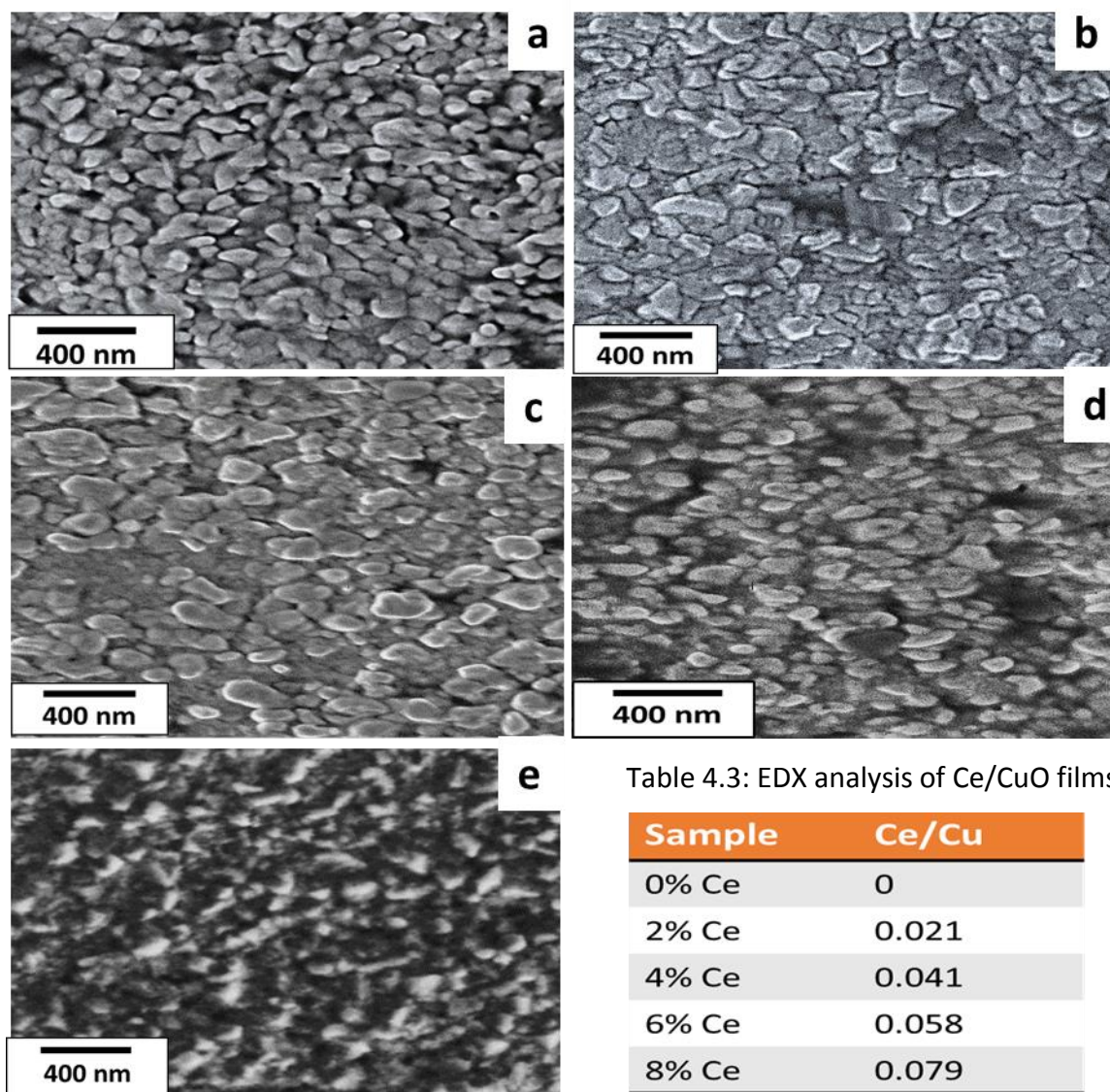


Figure 4.15: SEM micrograph of (a) 0 %, (b) 2 %, (c) 4 %, (d) 6 % and (e) 8 % Ce/CuO thin films.

4.2.4 AFM

Figure 4.16 shows two (2)- and three (3)-dimensional (D) AFM images of Ce doped CuO thin films with a scan area of $1\ \mu\text{m}^2$. In Figure 4.16 (a, a1), the surface of the 0 % Ce doped thin film consisted of spheroid grains that were uniformly dispersed over the scan area. The RMS roughness of this film was determined to be 8.36 nm. Surface morphology transformation was observed under the influence of Ce doping. The films reveal formation of randomly distributed irregular particles as seen in Figure 4.16 (b, b1). At 4 % Ce doping (Figure 4.16 (c, c1)), film particles were agglomerated on the surface and formed a mixture of large and small grains. Table 4.4 summarizes the behavior of surface roughness for the synthesized thin films. The obtained average roughness (R_a) increased from 8.36 nm to 20.50 nm, with an average roughness of 8.36 nm for 0 % and a maximum of 20.50 nm for the 4 % Ce film. The root mean square roughness (R_q) also increased from 6.74 nm for 0 % to 16.50 nm for the 4 % Ce thin film. The increase in surface roughness could be attributed to surface defects caused by the doping of CuO thin film with Ce. It might also have been attributed to grain stacking on the thin film surface, as observed through SEM analysis.

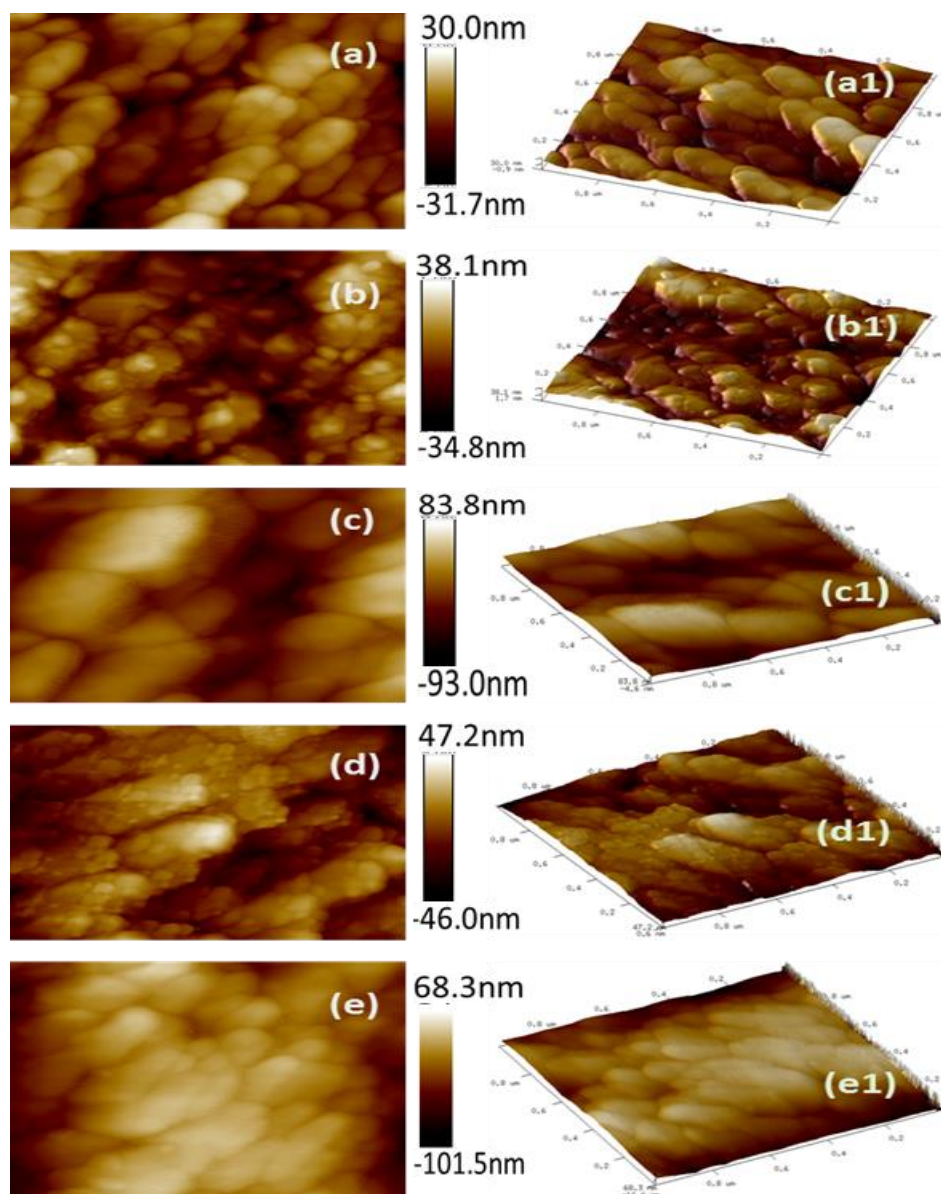


Figure 4.16: 2D and 3D images obtained from AFM analysis; (a, a1) 0 % Ce, (b, b1) 2 % Ce, (c, c1) 4 % Ce, (d, d1) 6 % Ce and (e, e1) 8 % Ce.

Table 4.4: Roughness parameters of Ce doped CuO thin films including R_a , R_q , and height of maximum roughness (R_{max}) and maximum roughness depth (R_v).

Sample	R_a (nm)	R_q (nm)	R_{max} (nm)	R_v (nm)
0 % Ce	6.74	8.36	57.40	33.40
2 % Ce	6.91	8.67	62.00	33.40
4 % Ce	16.50	20.50	110.00	1730.00
6 % Ce	7.53	9.58	67.90	219.00
8 % Ce	7.63	10.10	84.60	63.30

4.2.5 UV-Vis spectroscopy analysis

The optical properties of Ce doped CuO thin films were investigated in order to determine the effect of doping on the samples' energy band gap. Figure 4.17 (a) displays the transmission spectra of CuO for various Ce doping concentrations. The transmission profiles depict the usual behaviour of CuO with higher transmission in the NIR region. The optical bandgap energies of CuO with different Ce dopant concentration are illustrated in Figure 4.17 (b-f). The calculated energy band gaps were 1.70, 1.72, 1.75, 1.85 and 1.78 eV for 0 %, 2 %, 4 %, 6 % and 8 % Ce doped CuO, respectively. Similar results were reported by Baturay [187] for the Sb doped CuO thin films, the author attributed this behaviour to band tailing effect. Das et al. [188] also reported similar results for Ni doped CuO thin films. This effect was ascribed to increased carrier density due to dopant ions entering the host matrix. Such E_g effect may indicate that 6 % is the saturation point of Ce doping in CuO and Ce ions were no longer replacing Cu ions in the lattice sites beyond this point.

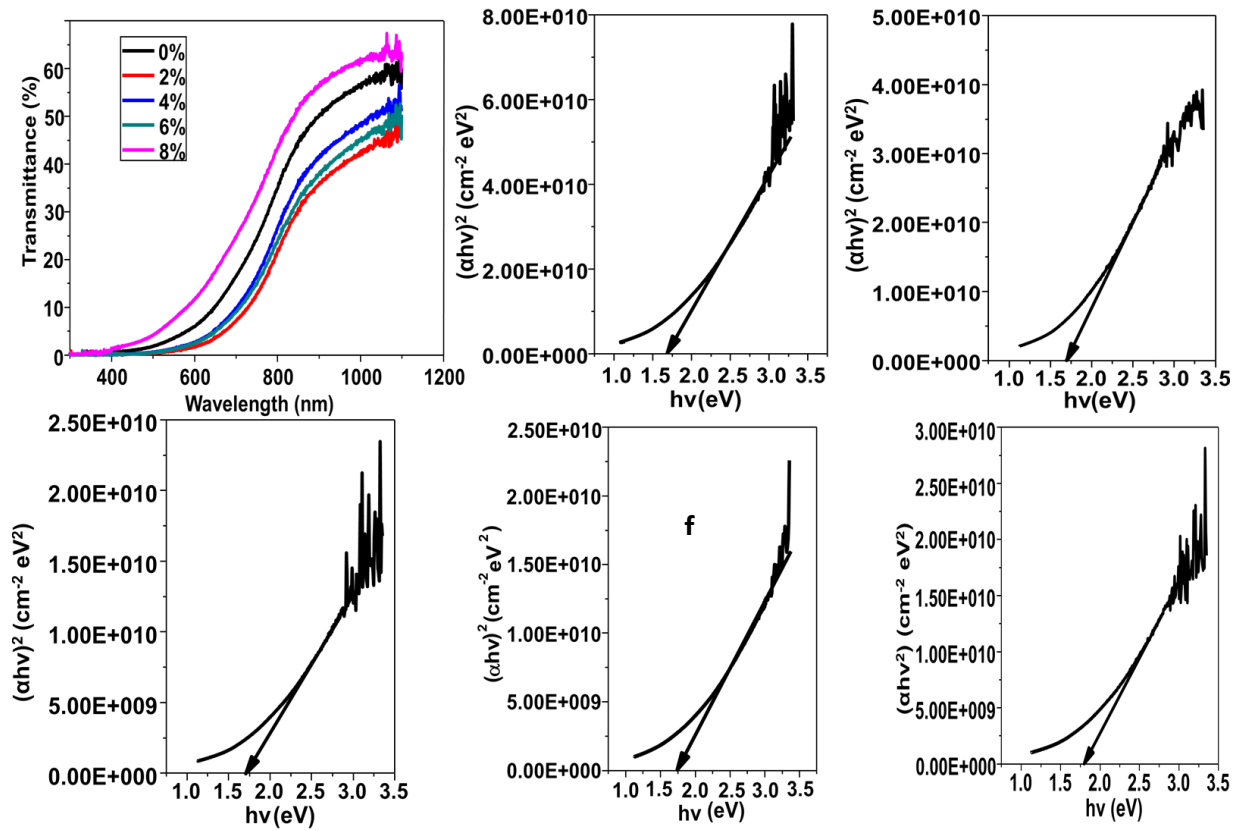


Figure 4.17: Transmittance spectra of 0, 2, 4, 6 and 8 % Ce doped CuO (a); $(\alpha h\nu)^2$ Vs photon energy of 0 % Ce (b), 2 % Ce (c), 4 % Ce (d), 6 % Ce (e) and 8 % Ce (f) doped CuO.

4.2.6 Gas sensing measurements

The ethanol sensing performance of Ce doped CuO thin films was investigated by measuring the resistance change upon stimulant gas exposure. Figure 4.18 (a-e) depicts the typical sensing response of the films at room temperature to different concentrations of ethanol (0.07, 0.08, and 0.09 slpm). Figure 4.18 (a,b) depict the experimental data analysis of the gas concentration dependent sensor response as a function of time. The observed results clearly indicate that all the samples were responsive towards ethanol. When the Ce-doped CuO thin films were exposed to ethanol gas, the response increased, and then restored to baseline when the gas was removed from the test chamber. This demonstrates the reversibility of the sensors, suggesting that the surface reactions are able to be reversed such that the sensors

return to their original state. The profiles exhibited an increasing sensor response as the target gas concentration was increased by changing the flow rate from 0.070 slpm to 0.090 slpm. This may be attributed to increased surface reactions due to larger coverage of the film surface by the gas molecules. The Ce doped CuO films showed enhanced response to ethanol compared to the undoped CuO film as observed in Figure 4.18 (c-d). In Figure 4.18 (e) response towards ethanol initially rises as the dopant concentration was increased from 2 % Ce to 4 % Ce, then a response decrease was observed for 6 % and 8 % Ce doped films. The 4 % Ce doped film shows the best response towards the various ethanol concentrations. The sensors exhibit gas response dependence to dopant concentration in which the 4 % Ce emerged as the optimum doping level since it gave the maximum sensor response in all the measurements. Response values obtained for 0.070, 0.080 and 0.090 slpm were 2.17, 2.34 and 2.55 for the 4 % Ce doped thin film. Enhanced response to ethanol vapour of the 4 % Ce doped CuO film was attributed to its high surface roughness revealed by the AFM analysis, the rough surface provided more active sites for oxygen species adsorption [189]. A decrease in sensor response observed beyond 4 % Ce doping may be due to excess dopant ions clustering at the surface of the films thus increasing the resistance.

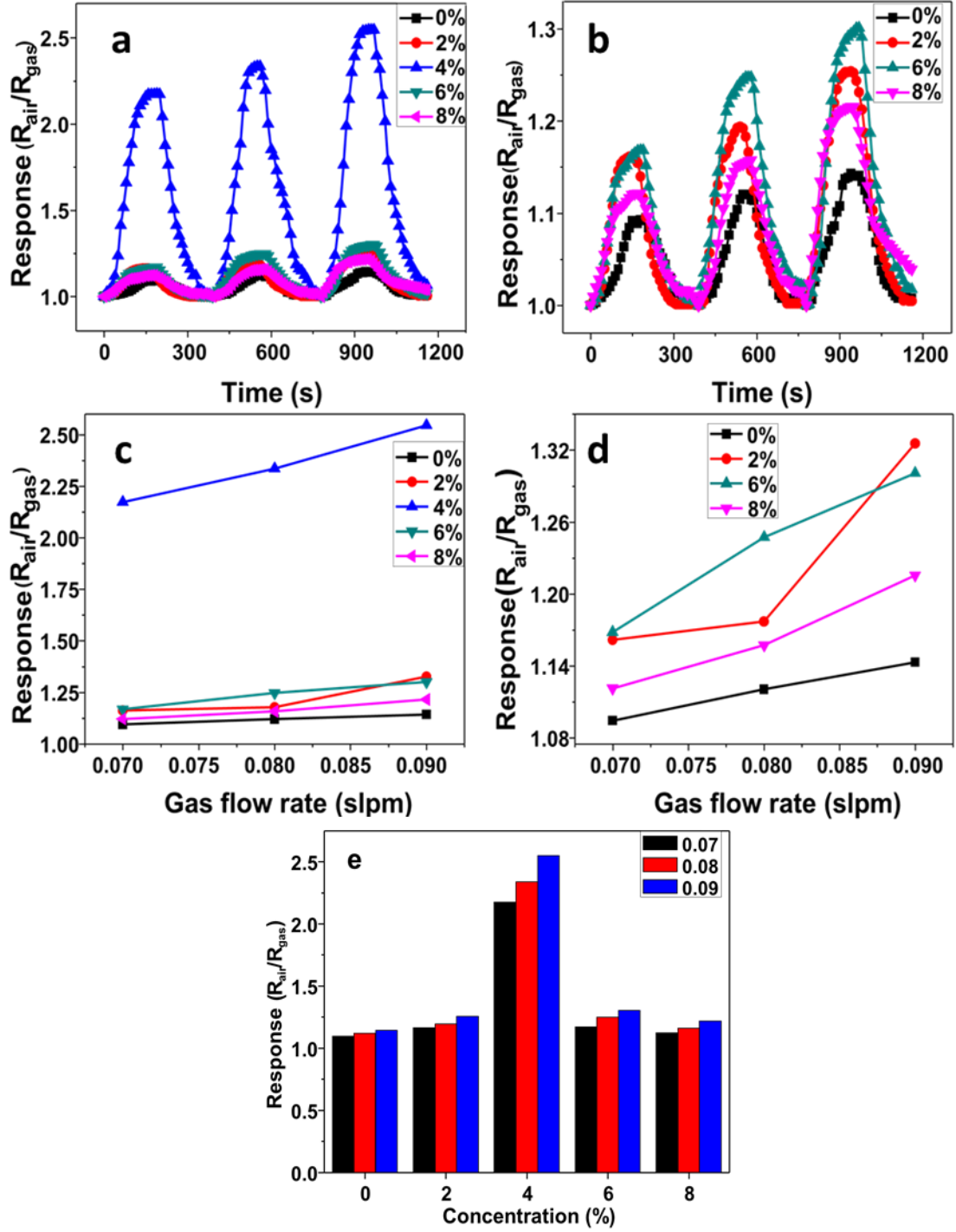


Figure 4.18: (a, b) Sensor response vs time graph, (c, d) sensor response vs flow rate and (e) sensor response vs Ce doping concentration of Ce doped CuO thin film sensors at room temperature.

The operating temperature influence to gas response was investigated by measuring sensing performance under operating temperatures of 25 °C, 100 °C and 150 °C. Figure 4.19 (a-c) shows the gas response vs operating temperature plots for different sensors with varying gas concentration. An increase in sensor response was observed as operating temperature was raised and the maximum response value was obtained at 150 °C for all the sensors. When the operating temperature was raised, thermal energy speeds up the gas sensing reactions and promotes overcoming of the activation energy barriers hence increasing the gas sensor response [190].

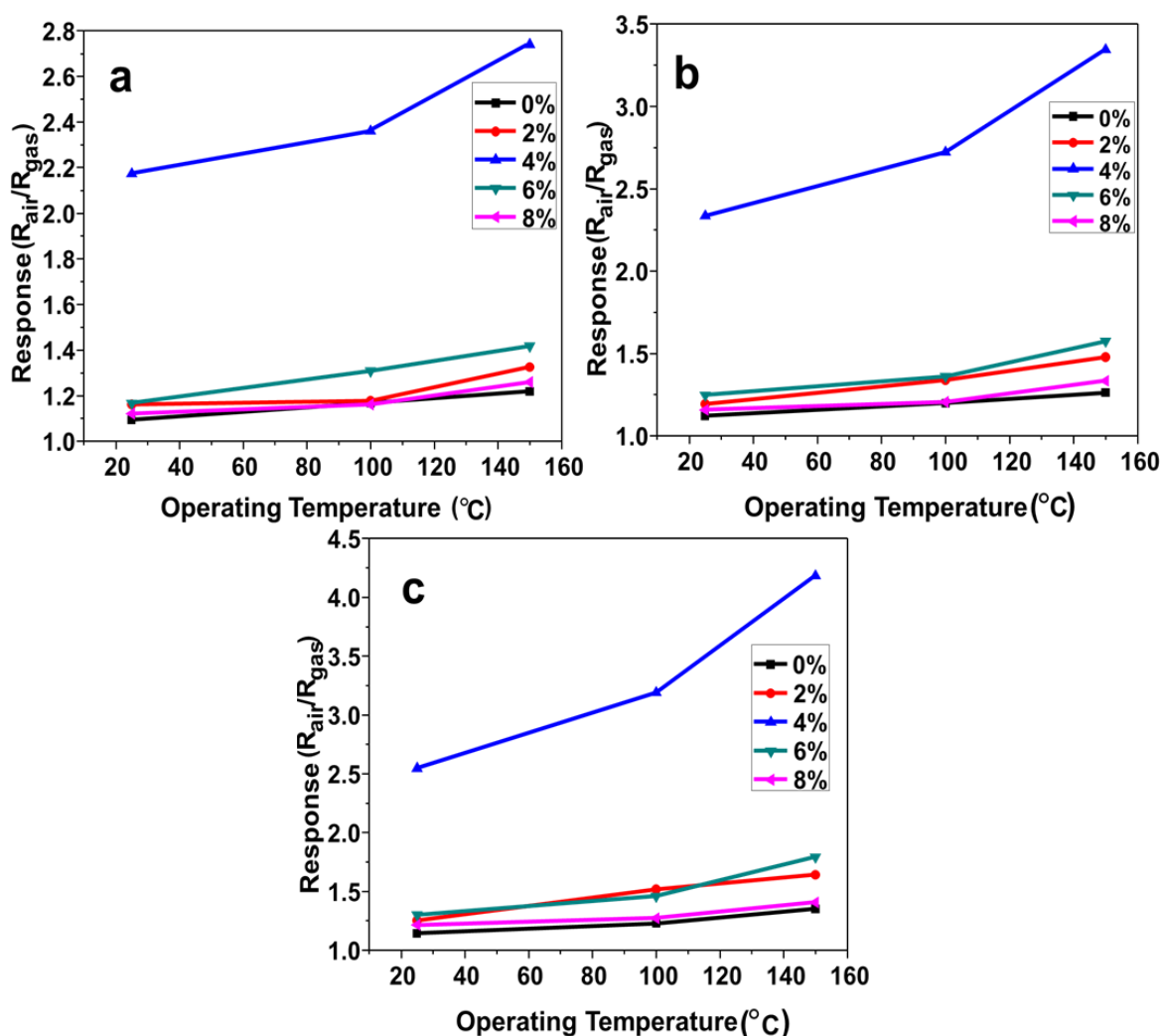


Figure 4.19: Gas sensor response measurements at different operating temperatures for a) 0.070 slpm, b) 0.080 slpm and c) 0.090 slpm

Gas sensing performance is mainly attributed to the change in electrical resistance initiated by adsorption/desorption process when a metal oxide is exposed to a target gas [191]. When the metal oxide film surface is exposed to air, oxygen molecules adsorb onto the surface forming O_2^- , O^{2-} and O^- species by extracting free electrons from the conduction band of the metal oxide depending on the operating temperature. The ionosorption process can be described by equation (4.2) - (4.5) [192];



In case of CuO based gas sensors, the process of adsorption leads to formation of a h^+ concentrated layer as shown in Figure 4.20 (a). The adsorbed oxygen species serve as active reaction sites for the targeted gas. When introduced to a gas, the oxygen species react with the gas molecules, releasing electrons back to the conduction band and decreasing the h^+ concentration in the surface layer (Figure 4.20 (b)) leading to increased resistance. The gas response of the CuO thin film is dependent on the change of h^+ concentration in the surface layer and the adsorbed oxygen species [193]. During ethanol detection, the chemical reaction typically occurring at the CuO surface may be presented as [192];

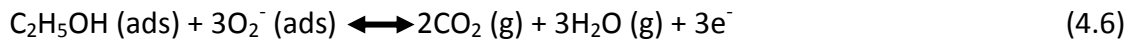


Figure 4.20 (c) and (d) presents the possible sensor response mechanism of the Ce-doped CuO thin films. The enhanced ethanol sensing response of the films suggests that the Ce^{4+} doping creates oxygen vacancies in the CuO lattice thereby facilitating adsorption of oxygen molecules. Ce^{4+} dopant ions within the CuO matrix stimulate charge transfer for the adsorbed oxygen molecules thus promoting adsorption of oxygen ions [69]. This promotes interaction between the sensor material and the target gas leading to higher resistance variations thus enhancing the sensor response.

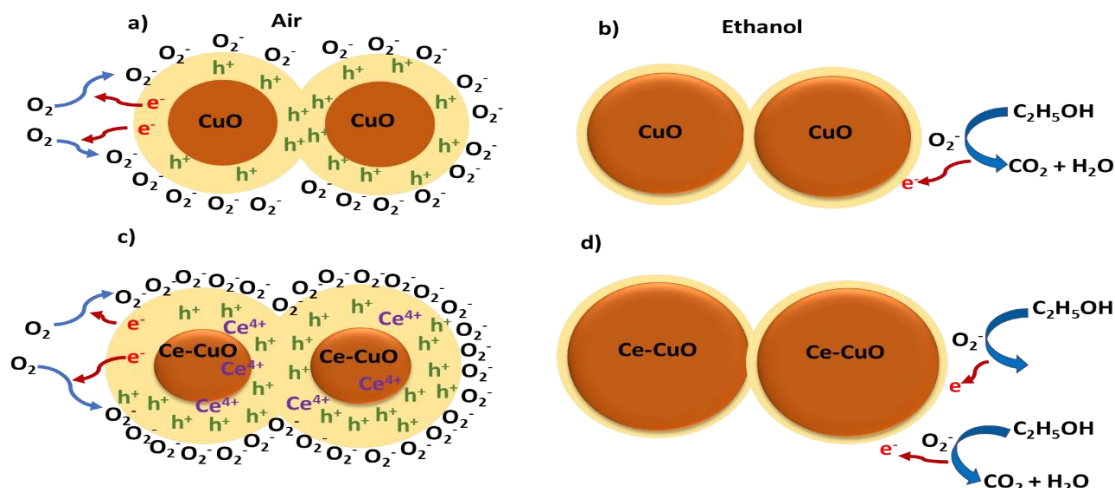


Figure 4.20: Schematic illustration of the gas sensing mechanism of CuO and Ce-doped CuO.

Selectivity is an essential parameter for gas sensors in practical applications. The gas response of the undoped and the 4 % Ce doped thin films was tested under various target gases at a temperature of 150 °C for the 0.09 slpm flow rate. It is worth mentioning that the sample with 4 % Ce was chosen since it was the sample that showed the best response both at room and elevated temperatures. The undoped CuO sample (0 % Ce) was included for comparison. Figure 4.21 displays the sensor response of the films under exposure to different gases namely acetone, ethanol, acetonitrile, methanol and ammonia. The 0 % and 4 % Ce doped films exhibited higher sensor response towards ethanol compared to other target gases. According to the obtained results, the highest response values were 1.5 and 4.2 for 0 % and 4 % Ce, respectively. The sensors' responses to acetone, acetonitrile, methanol, and ammonia were all less than 1.5, which is very low in comparison to their response to ethanol, which was 4.2, indicating that the thin films are more selective towards ethanol vapor.

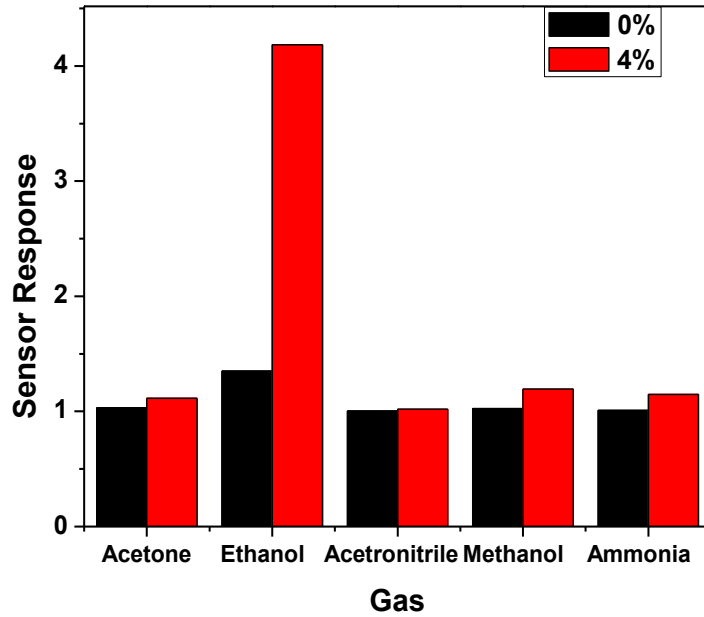


Figure 4.21: Response of CuO and 4 % Ce doped CuO under different target gas vapours.

The response of the 4 % Ce doped CuO film was evaluated several days after the initial gas sensing measurement to investigate the gas sensor's long-term stability. The measurements were taken at a flow rate of 0.090 slpm and an operating temperature of 150 °C. For these measurements, 4 % Ce doped film was selected because it had showed better sensor response compared to the other films. Figure 4.22 illustrates the sensor stability measurements taken over a period of two weeks. It can clearly be observed that the sensor shows excellent stability towards ethanol, the sensor response decreased from 4.053 to 4.013 over the duration of two weeks. The slight gas sensor response decrease may be due to development of moisture or an oxide layer on the thin film surface.

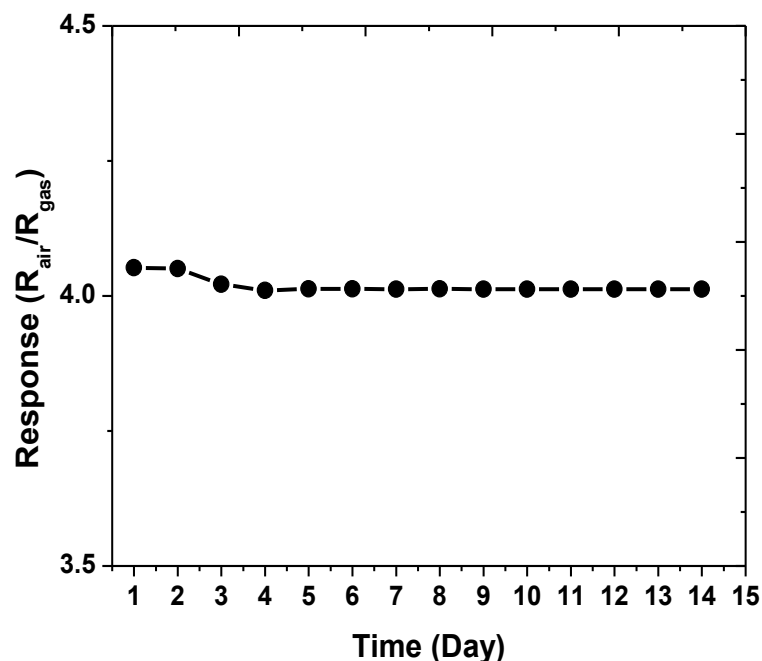


Figure 4.22: Long term stability of 4 % Ce doped CuO thin film to 0.09 slpm ethanol at 150 °C.

In the present study, the prepared sensors were responsive towards ethanol at room temperature which means sensible devices based on the material can be used at low energy consumption. The Ce-doped CuO thin films showed better sensing response towards ethanol compared to the undoped CuO. Ce^{4+} dopant ions are known for promoting charge transfer for the surface adsorbed oxygen molecules. This further increases the number of adsorbed oxygen ions. As a result, the surface sensing reactions are effectively accelerated thereby enhancing the sensor response. The sensors possess good reversibility. The 4 % Ce-doped CuO showed good stability and high selectivity towards ethanol gas. These findings suggest that Ce-doped CuO is a promising ethanol gas detector, and that the Ce dopant plays an important role in improving CuO's sensing properties.

Chapter 5 : Conclusion and recommendations

5.1 Conclusion

A systematic investigation of Ce doping on CuO nanostructures was carried out in this study. The first part of this work studied the effect of Ce incorporation on CuO nanostructured powders synthesised through hydrothermal synthesis. Sample characterization was performed to analyse the effects of Ce content on the structural, morphological, optical and electrical properties of CuO. XRD analysis verified formation of monoclinic structures for the CuO and Ce/CuO samples. An additional peak from CeO₂ was also identified for the Ce/CuO samples. SEM images showed morphological change from spheres to chips in the nanostructures with Ce doping. EDX analysis verified the Cu/Ce ratios and presence of Cu, Ce and O in the samples whereas the EDX elemental mapping confirmed the homogeneity of the samples. Optical transmittance analysis in conjunction with Tauc's law calculations indicated widening of the energy band gap with increasing Ce content. Raman spectra revealed vibration bands belonging to CuO and CeO₂ thus supporting the XRD results. The BET results showed higher surface area for the Ce/CuO sample indicating an improvement in the porosity. The electrical properties studies confirmed the semiconducting nature of the CuO and Ce/CuO samples through the temperature-dependent electrical conductivity measurements. They also uncovered enhanced conductivity for the Ce/CuO samples. The electrical conductivity showed a maximum value corresponding to 4 % Ce doping thus indicating optimum Ce⁴⁺ ion incorporation into the CuO lattice. At higher % Ce concentration, enhanced lattice defects as well as increased scattering result in a decrease in conductivity.

On the second part of this study, spray pyrolysis method was used to successfully synthesize Ce-doped CuO. The effect of Ce doping on various properties of CuO thin films was studied. XRD analysis identified formation of single phased monoclinic CuO for all the thin films. Raman spectroscopy confirmed presence of CuO in the films; formation of CeO₂ was also detected for the 4 %, 6 % and 8 % Ce doped thin films, supporting the XRD results. SEM and

AFM investigations confirmed morphology transformation of the films with Ce doping. The energy band gap was observed to increase with increasing doping concentration from 1.70-1.85 eV for the films 0 % - 6 % Ce doping then decreased for the 8 % sample. The gas sensing measurements revealed that the Ce-doped CuO films were significantly more responsive to ethanol than the undoped CuO film. The magnitude of sensor response was influenced by dopant concentration, operating temperature and ethanol concentration. Of all the Ce-doped films, the 4 % Ce doped film showed the maximum response value of 4.18 at 150 °C to ethanol flowing at 0.090 slpm. For the 0 % Ce sample, the response value of 1.14 was obtained at the same conditions. The enhanced ethanol sensing property of the 4 % Ce doped CuO film was attributed to formation of an increased number of active sites that was facilitated by Ce^{4+} ion incorporation into CuO. The 4 % Ce doped CuO film also exhibited long term stability and selectivity to ethanol therefore could be applicable in sensor applications. Based on the findings from this study, Ce doping proved to be an effective method of enhancing the properties of CuO nanostructures. In conclusion, an optimum doping of 4 % Ce was found to exhibit better electrical and gas sensing properties.

5.2 Recommendations

Even though the aims of the current research work were carried out successfully, there are several recommendations that can be considered for future work

- Gas sensing measurements for the Ce/CuO samples synthesized by hydrothermal method.
- Carry out gas sensing measurements over a wide temperature range to find the optimum temperature for the sensors and determine the concentration detection threshold.
- Perform gas sensing measurements with other common gases.
- Compare the thin films to the powder and determine whether the method of synthesis has any effect on the properties of the samples.

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Appendix

Contributing articles

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Hydrothermal synthesis of CuO and CeO₂/CuO nanostructures: spectroscopic and temperature dependent electrical properties

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ABSTRACT

In this study, CuO and CeO₂/CuO nanostructures were successfully synthesized via a hydrothermal route. The structure, morphology, composition and optical properties of these nanostructures have been studied using various techniques. X-ray diffraction (XRD) analysis showed the formation of monoclinic crystalline phase of CuO with a decrease in the crystallinity of the samples as the Ce content increased. Scanning electron microscopy (SEM) acquired images showing that increased Ce incorporation induces transformation of morphology from spherical to rod-like nanostructures. Energy-dispersive X-ray spectroscopy (EDS) mapping showed that Ce was homogeneously distributed onto the CuO matrix. UV/Vis/NIR spectrophotometer measurements depicted a blue shift in the bandgap from 2.0 to 3.5 eV for 0%–6% Ce and then 3.2 eV for 8% Ce. Brunauer Emmett Teller (BET) analysis revealed enhanced porosity with the incorporation of cerium. Raman spectroscopy results confirmed the presence of the $A_g(296\text{ cm}^{-1})$, $B_g(346\text{ cm}^{-1})$ and $B_g(631\text{ cm}^{-1})$ modes belonging to CuO. The F_{2g} Raman active mode observed at 454 cm^{-1} belongs to CeO₂. Fourier transform infra-red (FTIR) measurements showed stretching vibrations of Cu–O. The CeO₂/CuO samples exhibited enhanced temperature-controlled Dc conductivity with the 4% Ce sample showing the lowest activation energy, lowest $T_{\max}$ (peak value of $(d\sigma/dT)$) and consequently the maximum conductivity peaking at a temperature of 503 K. The nature of conductivity was elucidated on the basis of the carrier hopping model.

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Enhanced ethanol sensing response of nanostructured Ce-doped CuO thin films

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HIGHLIGHTS

- Ce-doped CuO thin films were synthesized by simple chemical spray pyrolysis route.
- Ce doping has an influence in the CuO sensing performance.
- Sensitivity at relatively low temperatures achieved.
- The sensing mechanism was ascribed to the oxygen vacancies induced by dopant.

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ABSTRACT

CuO based thin films doped with Ce concentrations varying from 0 to 8 mol% were prepared by chemical spray pyrolysis. X-ray diffraction analysis revealed bandgap modulation which is dependent on Ce doping and also showed preservation of the single phased monoclinic CuO structure for all the films after doping indicating successful substitution of Ce^{4+} ions in host matrix. SEM and AFM microscopy showed changes in morphology as Ce doping was increased. And this appeared to have a significant role on the ethanol sensing capabilities of the thin films which were measured at different working temperatures. Good gas sensing stability and maximum response was observed for the 4% Ce thin film. The sensing device was found to be more responsive towards ethanol than other common volatile organic compounds such as methanol, acetone, acetonitrile, and acetone. The response and recovery times for the sensing suggest a chemisorption mechanism.

1. Introduction

Metal oxides in general have served as the foundation of the majority of commercial gas sensors to date [1]. This is primarily due to their high response, high signal-to-noise ratio, and relatively fast response times. Their major drawbacks, however, have been high operating temperatures and poor selectivity. To address these shortcomings, a variety of techniques, including metal doping and surface morphology manipulation, have been adopted. Many applications, particularly those involving volatile gases, benefit from room temperature or low temperature sensing [2]. Cupric oxide (CuO), a monoclinic p-type semiconductor, has recently been recommended as a chemical gas sensor [3]. Its narrow bandgap, which ranges from 1.2 to 1.9 eV, makes it an excellent candidate for gas sensors that operate at lower temperatures. It is also inexpensive to produce and environmentally friendly, making it an ideal material for green economies and environments [4]. Highly selective

and sensitive gas sensors are required in a variety of industries for early detection of flammable and toxic air pollutants. Numerous studies have demonstrated that CuO can be extremely useful in monitoring hazardous and combustible gases [5–8].

To fully exploit the good properties of CuO, it has been doped with various metal ions in an effort to develop high quality nanostructures with excellent chemical and physical properties [9]. Dopants can be incorporated into the CuO matrix to modify its morphology, energy band structure, and create lattice defects or vacancies. This improves performance in applications such as gas sensing, optoelectronics, and spintronics [10–13]. Doping with rare earth elements has been shown to improve properties such as surface activity, ion mobility, and catalytic ability. Ce has attracted considerable attention because of its ability to form the redox couple Ce^{3+}/Ce^{4+} , which will ultimately result in modification of sensing properties in terms of sensitivity and selectivity [14]. Furthermore this doping will alter the operating temperature of

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