INVESTIGATION OF GRAPHENE DOPANT CONCENTRATION ON Eu_2O_3 THICK FILM USING SCREEN-PRINTED METHOD FOR CO_2 GAS SENSING

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MASTER OF SCIENCE IN ELECTRICAL ENGINEERING

2025

Faculty of Electrical Technology and Engineering

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**A thesis submitted
in fulfillment of the requirements for the degree of
Master of Science in Electrical Engineering**

Faculty of Electrical Technology and Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2025

DECLARATION

I declare that this thesis entitled "Investigation of Graphene Dopant Concentration on Eu_2O_3 Thick Film Using Screen-Printed Method for CO_2 Gas Sensing" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :

Name : KUBERAHVENTHAN A/L SANMUGAVELAN

Date : 21.7.2025

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Electrical Engineering.

Signature :

Supervisor Name : Ts. Dr. Mohd Hafiz bin Jali

Date : 22.7.2025

DEDICATION

My parents have been a constant source of inspiration, support, and advice for me throughout my academic career, and I dedicate this thesis to them. They have taught me to stand out, be tenacious, have confidence in myself, and never give up. I am appreciative of their selfless love, sacrifices, and unshakable faith in me. This accomplishment would not have been feasible without their assistance. Next, I want to thank especially my main supervisor Ts. Dr. Mohd Hafiz Bin Jali and co-supervisor Ts. Dr. Siti Amaniah Binti Mohd Chachuli who helped me do this master project.

ABSTRACT

The development of gas sensing devices that operate effectively at room temperature is crucial for improving environmental monitoring systems, particularly the sensitive detection of carbon dioxide (CO_2). Europium oxide (Eu_2O_3) has potential as a sensing material but lacks sensitivity, stability, and response time at room temperature, making it unsuitable for real-world application. The objective of this research is to improve CO_2 detection capabilities under ambient conditions by systematically incorporating graphene dopants into Eu_2O_3 thick films. In addition to an undoped Eu_2O_3 gas sensor, thick film sensors with different graphene concentrations of 0.1%, 0.5%, 1%, 2%, and 5% by weight were fabricated using the screen-printing method on Kapton substrates. The gas sensors were characterised using Field Emission Scanning Electron Microscopy (FESEM) for morphological assessment, Energy Dispersive X-ray (EDX) for compositional analysis, Raman spectroscopy for structural evaluation, and X-ray Diffraction (XRD) for crystallographic analysis. Their performance was evaluated in a controlled laboratory environment, with CO_2 detection carried out at concentrations of 30, 50, and 70 sccm at room temperature. The aim of this study was to determine the optimum graphene concentration that maximises sensor response time, recovery characteristics, detection sensitivity, repeatability, hysteresis, and stability. Based on the experimental results, the 2% Eu_2O_3/Gr gas sensor exhibited the best performance, with a low resistance of 0.0874 GΩ and enhanced sensitivity towards CO_2 at concentrations of 30, 50, and 70 sccm, with values of 2.40, 2.37, and 2.34, respectively. The 2% Eu_2O_3/Gr sensor demonstrated a 2.1-fold gain in sensitivity (26.50 pA/sccm), a 4.5-fold improvement in resolution, and a 2.2-fold decrease in standard deviation, along with a linearity of 98.04% compared to the undoped Eu_2O_3 sensors. Graphene's large surface area and high conductivity facilitate CO_2 adsorption and charge transfer between Eu_2O_3 and CO_2 molecules, resulting in enhanced production of carbonate species through redox reactions with Eu^{3+} ions. The ideal graphene doping level was found to be 2%, which maintained the structural integrity of the Eu_2O_3 gas sensors while increasing conductivity. In summary, this research demonstrates that graphene-doped Eu_2O_3 thick films offer a viable approach for room-temperature CO_2 gas detection, with enhanced stability, sensitivity, and response times. Further research into graphene concentration and fabrication methods may provide deeper insight into the relationship between dopant concentration and sensing performance, supporting the development of effective CO_2 sensors for industrial and environmental applications.

PENYIASATAN KEPEKATAN DOPAN GRAFENA PADA FILEM TEBAL Eu_2O_3 MENGGUNAKAN KAEDAH CETAKAN SKRIN UNTUK PENGESANAN GAS CO_2

ABSTRAK

Pembangunan peranti penderia gas yang beroperasi dengan berkesan pada suhu bilik adalah penting untuk menambah baik sistem pemantauan alam sekitar, terutamanya dalam pengesanan sensitif karbon dioksida (CO_2). Europium oksida (Eu_2O_3) berpotensi sebagai bahan penderiaan tetapi tidak mempunyai kepekaan, kestabilan dan masa tindak balas pada suhu bilik, menjadikannya tidak sesuai untuk aplikasi dunia sebenar. Objektif penyelidikan ini adalah untuk meningkatkan keupayaan pengesanan CO_2 di bawah keadaan ambien dengan memasukkan dopan grafena secara sistematik ke dalam filem tebal Eu_2O_3. Sebagai tambahan kepada penderia gas Eu_2O_3 yang tidak didop, penderia filem tebal dengan kepekatan grafena berbeza sebanyak 0.1%, 0.5%, 1%, 2% dan 5% mengikut berat telah direka menggunakan kaedah percetakan skrin pada substrat Kapton. Penderia gas dicirikan menggunakan Mikroskop Imbasan Medan Pancaran Emisi (FESEM) untuk penilaian morfologi, Spektroskopi Sinar-X Sebaran Tenaga (EDX) untuk analisis komposisi, spektroskopi Raman untuk penilaian struktur, dan Difraksi Sinar-X (XRD) untuk analisis kristalografi. Prestasi mereka dinilai dalam persekitaran makmal terkawal, dengan pengesanan CO_2 dijalankan pada kepekatan 30, 50, dan 70 sccm pada suhu bilik. Matlamat kajian ini adalah untuk menentukan kepekatan grafena optimum yang memaksimumkan masa tindak balas sensor, ciri pemulihan, kepekaan pengesanan, kebolehulangan, histeresis, dan kestabilan. Berdasarkan keputusan eksperimen, penderia gas 2% Eu_2O_3/Gr mempamerkan prestasi terbaik, dengan rintangan rendah 0.0874 GΩ dan kepekaan yang dipertingkatkan terhadap CO_2 pada kepekatan 30, 50, dan 70 sccm, dengan nilai masing-masing 2.40, 2.37, dan 2.34. Penderia 2% Eu_2O_3/Gr menunjukkan peningkatan 2.1 kali ganda dalam kepekaan (26.50 pA/sccm), peningkatan 4.5 kali ganda dalam resolusi, dan penurunan 2.2 kali ganda dalam sisihan piawai, bersama-sama dengan lineariti 98.04% berbanding dengan penderia Eu_2O_3 yang tidak didopkan. Luas permukaan grafena yang besar dan kekonduksian tinggi memudahkan penyerapan CO_2 dan pemindahan cas antara molekul Eu_2O_3 dan CO_2, menghasilkan peningkatan pengeluaran spesies karbonat melalui tindak balas redoks dengan ion Eu^{3+}. Tahap dopan grafena yang ideal didapati 2%, yang mengekalkan integriti struktur penderia gas Eu_2O_3 sambil meningkatkan kekonduksian. Secara ringkasnya, penyelidikan ini menunjukkan bahawa filem tebal Eu_2O_3 yang didopkan grafena menawarkan pendekatan yang berdaya maju untuk pengesanan gas CO_2 suhu bilik, dengan kestabilan, kepekaan dan masa tindak balas yang dipertingkatkan. Penyelidikan lanjut mengenai kepekatan grafena dan kaedah fabrikasi mungkin memberikan gambaran yang lebih mendalam tentang hubungan antara kepekatan dopan dan prestasi penderiaan, menyokong pembangunan penderia CO_2 yang berkesan untuk aplikasi industri dan alam sekitar.

ACKNOWLEDGEMENT

First and foremost, I would like to take this opportunity to express my sincere gratitude to my parents. I would like to extend my heartfelt thanks to numerous people and organizations for their invaluable support throughout the course of my master's project. First and foremost, I would specially like to thank Ts. Dr. Mohd Hafiz Bin Jali, my supervisor, and my co-supervisor Ts. Dr. Siti Amaniah Binti Mohd Chachuli, for all their excitement, patience, insightful remarks, helpful information, wise counsel, and never-ending ideas, all of which have been incredibly beneficial to me during my research and writing for my thesis. Their vast knowledge, extensive experience, and professional competence enabled me to effectively complete my project. I would not have been able to complete this work without their assistance and direction. I could not have asked for a better study supervisor.

I want to express my gratitude to the members of the Electrical and Electronics Engineering Department staff and the lab technicians for providing me with adequate resources to complete the project effectively.

Furthermore, I am deeply appreciative of my friends and well-wishers, whose recommendations and cooperation allowed me to finish the project. Once again, I would like to express my gratitude to my parents for their admirable patience and unwavering support throughout this journey.

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LIST OF ABBREVIATIONS

2D	-	Two-Dimensional
$BaTiO_3$	-	Barium Titanate
CeO_2	-	Cerium oxide
CO	-	Carbon Monoxide
CO_2	-	Carbon Dioxide
CO_3^{2-}	-	Carbonate Ions
CNTs	-	Carbon Nanotubes
EDX	-	Energy Dispersive X-Ray
FESEM	-	Field Emission Scanning Electron Microscopy
Eu_2O_3	-	Europium Oxide
Eu_2O_3/Gr	-	Eu_2o_3 Doped with Graphene
Eu^{3+}	-	Europium Ions
GO	-	Graphene Oxide
Gr	-	Graphene
In	-	Indium
MOS	-	Metal Oxide Semiconductors
NO_2	-	Nitrogen Dioxide
O^{2-}	-	Oxygen Ions
O_3	-	Ozone
PET	-	Polyethylene Terephthalate
Pd	-	Palladium
SnO_2	-	Tin (Iv) Oxide

TiO_2	-	Titanium Dioxide
WHO	-	World Health Organization
WO_3	-	Tungsten(Vi) Oxide
XRD	-	X-Ray Diffraction
Utem	-	Universiti Teknikal Malaysia Melaka

LIST OF SYMBOLS

%	-	Percentage
°C	-	Celcius
cm^{-1}	-	Reciprocal wavelength
GΩ	-	Giga ohm
g	-	Gram
ΔA	-	Output current
mg	-	Milligrams
mg/m^2	-	Milligrams per square metre
mm^2	-	Millimetre squared
nm	-	nanometre
pA	-	Pico Current
ppm	-	Parts-per-million
rpm	-	Revolutions per minute
sccm	-	Standard Cubic Centimetre per Minute
µm	-	micrometre
Wt%	-	Weight percentage

LIST OF PUBLICATIONS

The followings are the list of publications related to the work on this thesis:

Sanmugavelan, K., Mohd Chachuli, S.A., Jali, M.H., Harun, S.W., Thokchom S., 2024. Room Temperature Carbon Dioxide Gas Sensor based on Europium Oxide with a Kapton Film as a Flexible Substrate. *International Journal of Nanoelectronics and Materials (IJNeaM)*.

Sanmugavelan, K. 2025 “Europium Oxide Thick Films for CO_2 Gas Sensing”, *Journal of Advanced Research in Micro and Nano Engineering*, 36(1), pp. 47–57. doi: 10.37934/armne.36.1.4757.

Mohd Hafiz Jali, Siddharth Thokchom, Kuberahventhan Sanmugavelan, Mohd, A. and Harun, S.W. 2025. Investigation of Graphene Dopant Concentration on Eu_20_3 Thick Film for CO_2 Gas Sensing. doi: https://doi.org/10.2139/ssrn.5266442.

CHAPTER 1

INTRODUCTION

1.1 Background

Carbon dioxide (CO_2) is a natural greenhouse gas that plays a vital role in the carbon cycle on Earth. Respiration, volcanic activity, and organic matter degradation all contribute to its ongoing release of CO_2 (Ivankin, 2022). Human activities like burning fossil fuels and deforestation contribute to excessive CO_2 levels in the atmosphere, which are dangerous for the environment and human health (Yurak and Fedorov, 2025). In small or poorly ventilated spaces, CO_2 may be extremely dangerous. Notably, a 2021 CO_2 leak at a poultry facility in Georgia, USA, killed six people and hospitalized over a dozen others due to asphyxiation (Bielka et al., 2024). These cases indicate CO_2 particularly harmful since it is odourless, colourless, and can induce unconsciousness or death at high quantities (Saadi, 2019). Gas sensors are essential in a variety of applications, including environmental monitoring, industrial safety, and air quality control. (Rezk, Sharma and Gartia, 2020). Traditional CO_2 sensors that use infrared absorption techniques work well, but they have drawbacks such decreased sensitivity at lower gas concentrations, high power consumption, and high cost (Zhou et al., 2020).

Advanced materials which were metal oxide semiconductors such as zinc oxide (ZnO) and titanium oxide (TiO_2) and nanomaterials like carbon nanotubes (CNTs) and graphene have been investigated by researchers to overcome these difficulties. Metal oxide semiconductors are commonly utilized due to their ability to change electrical conductivity when exposed to gases, although they frequently require high temperature for operation and have low sensitivity and stability (Pandhi et al., 2020). In contrast, graphene, a two-dimensional material with high electrical conductivity, enormous surface area, and thermal stability, has shown considerable promise in gas sensing applications. Its integration with other materials increases gas adsorption, sensor responsiveness, and energy efficiency (Kauffman and Star, 2010a).

Current research identifies gaps in enhancing material characteristics for certain gases, such as CO_2. Europium Oxide (Eu_2O_3) is renowned for its thermal stability and electrochemical characteristics, but its effectiveness as a CO_2 sensor is yet underexplored. According to studies, doping Eu_2O_3 with graphene may improve gas adsorption and charge transfer, improving sensitivity (Amarnath and Gurunathan, 2021a). However, the effects varying graphene concentrations on Eu_2O_3 sensing capability have yet to be thoroughly explored.

In order to fill these gaps, the present research utilizes a screen-printing method to fabricate graphene doped Eu_2O_3 based CO_2 sensors. This method enables the cost effective and scalable fabricate of thick films, making it excellent for practical applications. This research intends to enhance the sensitivity, stability, and reaction times of sensors with varying graphene concentrations, leading to the advancement of effective CO_2 detection systems. Notably, this study provides a detailed evaluation of CO_2 sensing behaviour using thick Eu_2O_3 films enhanced with graphene doping, which, to the best of our knowledge, is reported here for the first time.

1.2 Problem Statement

Air quality and environmental monitoring have grown in importance as people become more concerned about industrial emissions, climate change, and public health. CO_2, a naturally occurring gas, plays a significant role in global warming. Elevated CO_2 levels in enclosed or industrial settings can pose health risks, despite being necessary for photosynthesis and respiration. Exposure to 100 sccm of CO_2 impairs cognitive function, whereas concentrations exceeding 500 sccm of CO_2 can cause dizziness, headaches, respiratory distress, and unconsciousness (Rezk, Sharma and Gartia, 2020). These highlights the urgent need for precise, affordable, real-time CO_2 gas sensors.

CO_2's non-polar molecular structure and low chemical reactivity make it difficult to detect at low concentrations and room temperatures (Wang et al., 2024). Current CO_2 detection technologies, such as non-dispersive infrared (NDIR) sensors, offer high accuracy but suffer from drawbacks including high cost, complex instrumentation, and high power requirements (Akhter et al., 2021). These limitations restrict its application in portable, low-power, large-scale environmental monitoring systems.

Metal oxide semiconductors (MOS) such as ZnO, SnO_2, and TiO_2 are commonly used in gas sensors due to their conductivity changes with gas exposure. However, these materials require high operating temperatures of 300–500 °C, which leads to increased power consumption, sintering, grain growth, and reduces sensor stability (Kumar, Prakash and Singh, 2015a). This study explores Eu_2O_3, a rare-earth metal oxide with higher thermal and electrochemical stability than ZnO or TiO_2 due to its ability to improve charge transport and lower internal resistance (Majumder et al., 2017). However, Eu_2O_3 suffers from low intrinsic conductivity and poor gas adsorption, leading to limited CO_2 sensitivity and low surface activity (Zito et al., 2020).

These limitations can be improved by incorporating graphene. Graphene is a two-dimensional carbon nanomaterial known for its high conductivity, large surface area, and chemical stability (Kumar et al., 2025). When integrated with Eu_2O_3, graphene enhances gas adsorption and charge transfer, improving sensitivity and lowering operating temperatures. It significantly increases sensitivity to reducing gases such as hydrogen and ammonia at 100–200 °C (Schedin et al., 2007; Chang et al., 2014). Graphene also prevents sintering and grain growth while maintaining surface area and porosity (Wu et al., 2013; Pargoletti et al., 2020). The integration of graphene into Eu_2O_3 gas sensors enhances long-term operational stability, mechanical strength, and thermal conductivity, thereby significantly improving overall sensor performance.

The specific influence of graphene doping concentration on the CO_2 sensing capability of Eu_2O_3-based thick-film sensors unexplored despite its critical role in enhancing performance by modifying the film's electrical conductivity and structural characteristics. For example, nitrogen-doped graphene exhibits a shift from p-type to n-type conductivity and greater electron-hole transport asymmetry at higher doping levels (Sreedharan et al., 2015). Screen printing is a promising method for fabricating these films due to its low cost, scalability, and ability to produce uniform thick films, however it is less precise than methods such as chemical vapour deposition or hydrothermal method (Somalu et al., 2017)

Thus, there is a significant research gap in the development of low-temperature, low-cost, and sensitive CO_2 gas sensors based on graphene-Eu_2O_3 nanocomposites. The influence of graphene concentration on the sensing characteristics of Eu_2O_3 thick films, especially when fabricated by screen-printing method, remains unexplored. Addressing this gap is crucial for designing practical, high-performance CO_2 sensors for environmental and industrial applications.

1.3 Research Question

Based on prior work showing graphene ability to enhance the gas sensing properties of metal oxides, it is hypothesized that doping Eu_2O_3 with graphene will improve the CO_2 sensing capabilities of screen-printed Eu_2O_3 thick films. Specifically, it is expected that increasing graphene dopant concentration in Eu_2O_3 up to an optimal level will increase the sensor films conductivity, gas response, and operating temperature range for CO_2 detection. This should allow the Eu_2O_3 doped by graphene sensors to achieve higher sensitivity, faster response times, improved stability, and lower operating temperatures compared to undoped Eu_2O_3 (Busacca et al., 2020; Yan et al., 2021). A graphene doping concentration of 2 - 3 wt% is projected to yield the greatest enhancement in CO_2 response based on precedents with similar metal oxide-graphene composites (Wang et al., 2021; Yuan, Yang and Meng, 2021). However, the optimal graphene content may varies depend on synthesis method, film thickness, testing conditions, and other factors. This hypothesis will be tested by systematically evaluating the CO_2 sensing performance of screen-printed Eu_2O_3/Gr nanocomposite films fabricated with different graphene dopant levels from 0 to 5% concentrations.

i) What is the optimal concentration of graphene dopant for Eu_2O_3 thick film CO_2 gas sensors prepared by screen-printing method?

ii) How does variation in graphene dopant concentration affect the sensing mechanism, and consequently influence the sensitivity, response/recovery times, and stability of Eu_2O_3 thick film CO_2 gas sensors?

1.4 Research Objective

The main objective of this work is to investigate the optimum Eu_2O_3 doped graphene concentrations on thick film substrates for sensitivity enhancement. The following sub-objectives have to be met:

i) To fabricate graphene-doped Eu_2O_3 thick films using the screen-printing technique.

ii) To investigate the effect of varying graphene doping levels on sensing performance by analysing the morphological characteristics and electrical resistance under different CO_2 concentration levels.

iii) To experimentally evaluate the performance parameters of the proposed CO_2 gas sensors by comparing undoped Eu_2O_3 and optimized Eu_2O_3/graphene sensors in terms of repeatability, hysteresis, stability, response time, and linearity.

1.5 Scope of Research

This study investigates the influence of graphene dopant concentration on the gas sensing capabilities of Eu_2O_3 thick films fabricated by screen-printing method. The films were prepared with one undoped Eu_2O_3 and varying graphene concentration non-linearly from 0.1%, 0.5%, 1%, 2%, and 5% and screen-printed onto Kapton film to form thick film sensors. Lower concentrations of 0.1% and 0.5% improve conductivity without significantly altering the materials structure, but intermediate values of 1% and 2% increase sensitivity and response time. Higher concentrations of 5% graphene may increase conductivity, but too much graphene might cause clumping, reducing the sensors efficiency. This variance aids in the determination of the optimal concentration for sensor performance (Jiang et al., 2021). The graphene was expected to improve the conductivity and gas sensitivity of Eu_2O_3,