Enhanced LPG Sensing Efficiency Through Electrodeposited Chlorine-Doped Cuprous Oxide Thin Films

A.H.M.N.N. Bandara, K.N.D. Bandara, G.K.R. Senadeera, V.P.S. Perera
Department of Physics, Faculty of Natural Sciences, The Open University of Sri Lanka
doneranji@gmail.com

1. ABSTRACT

The study involves comprehensive analyses of Cl-doped Cu_2O thin films deposited on FTO substrates, exploring their properties and gas-sensing efficiency. Contact angle measurements were conducted using the sessile drop method, indicating increased non-wetting behavior in Cl-doped films compared to undoped Cu_2O. Scanning electron microscopy images identified distinct grain distribution and surface features, with Energy Dispersive X-ray Spectroscopy confirming the presence of Cl atoms in the Cl-doped film. Mott-Schottky analysis revealed p-type conductivity in the deposited Cu_2O films, showcasing a higher acceptor concentration and lower valence band edge position for the Cl-doped film compared to undoped Cu_2O. Gas sensing efficiency was optimized for liquid petroleum gas (LPG), with Cl-doped Cu_2O exhibiting a high response (~13%) and fast identification (~20 s response, ~15 s recovery) at 70 ℃. Variations in LPG sensitivity were noted at different temperatures, with a maximum response (~20%) observed at 100 ℃ for Cl-doped films. The findings indicate successful enhancement of LPG sensing efficiency through Cl-doped surface modification of Cu_2O, demonstrating the potential for optimized gas sensing applications.

2. INTRODUCTION

Certain metal oxides, like titanium dioxide, are used in photocatalytic applications, breaking down organic pollutants under light exposure [1]. Meanwhile, Cu_2O exhibits semiconductor behavior with a narrow bandgap, making it suitable for optoelectronic applications [2]. It demonstrates interesting optical properties, especially in the visible spectrum, making it useful for photovoltaic and photocatalytic applications. Cu_2O thin films have been explored for solar cell applications, either as a standalone absorber layer or in heterojunction structures with other materials to harness solar energy effectively. These films are used in photocatalytic applications for degrading organic pollutants and splitting water molecules into hydrogen and oxygen under light irradiation. Metal oxide semiconductors are commonly used in gas sensors due to their sensitivity to gases like carbon monoxide, nitrogen oxides, and volatile organic compounds. Cu_2O thin films are utilized in gas sensors [3-6], particularly for detecting gases like carbon monoxide, LPG, etc. due to their sensitivity and conductivity changes in the presence of specific gases. Fabrication techniques include physical vapor deposition, chemical vapor deposition, sol-gel processes, and other methods [7] that allow the creation of thin films or nanostructured materials, optimizing their properties for specific applications. Specifically, Electrochemical methods involve the reduction of copper ions in a solution onto a conductive substrate under specific conditions to form Cu_2O films.

Cu_2O is prone to oxidation, limiting its stability in certain environments. Researchers are exploring methods to enhance its stability without compromising its properties. Ongoing research [4,6,8] focuses on improving the efficiency and properties of semiconductor metal oxides. Scientists explore new modifications to their structures and enhance their

functionalities for advanced applications in electronics, renewable energy, environmental sensing, and beyond [9,10]. Doping Cu_2O thin films involve intentionally introducing impurities or foreign atoms into the crystal lattice to alter its electrical, optical, or structural properties [11]. Chlorine doping, specifically, involves the introduction of chlorine atoms into the Cu_2O lattice to modify its characteristics. Chlorine doping [5,11] typically involves substituting oxygen (O) atoms in the Cu_2O lattice with chlorine (Cl) atoms. This substitution can alter the electronic structure by introducing new energy levels within the bandgap, affecting the conductivity and other properties such as carrier concentration, band structure, and optical properties of Cu_2O thin films [5,11]. The specific impact depends on the concentration of chlorine dopants and their arrangement within the crystal lattice. This research paper presents the electrodeposition method used to deposit undoped and Cl-doped Cu_2O thin films, on FTO substrates. It includes an extensive examination of the surface morphology and wettability of these Cu_2O films. Additionally, the electrical properties were investigated using Mott-Schottky analysis. The study highlights these characterizations to optimize the effectiveness of detecting liquid petroleum gas under different operating temperatures.

3. EXPERIMENTAL DETAILS

3.1 Fabrication of Cu_2O thin films

Before deposition, the FTO substrates underwent treatment by being exposed to an acetone bath and sonicated in distilled water for a few minutes to enhance the adhesion of the Cu_2O film to the FTO surface. Approximately a 1×1.5 cm^2 area of the FTO substrate was submerged in an electrolyte solution comprising 3.5 M lactic acid (Sigma–Aldrich, purity - 99.0%) and 0.45 M cupric sulfate $CuSO_4$ (Sigma–Aldrich, purity - 99.0%). The electrolyte's pH was adjusted to pH 10.5 using NaOH (Sigma–Aldrich, purity – 98.0%). The electrolyte was kept at a constant temperature of 60°C inside a water bath with continuous stirring. A 0.02 M $CuCl_2$ aqueous solution was added as the chlorine precursor of the lactate bath [5]. The Cu_2O thin films were electrochemically deposited potentiostatically in a three-electrode electrochemical cell using a platinum counter electrode and Ag/AgCl reference electrode. A constant potential of -450 mV was given across the Ag/AgCl reference and FTO substrate throughout a deposition period of 30 minutes [12]. Post-deposition, the films were thoroughly cleaned with distilled water and left to dry at room temperature in normal air.

3.2 Thin film characterization

Contact angle measurements were made using the sessile drop method with double distilled water. (Parts of 10 µl) The contacting surface was observed through a digital microscope (2MP 1000x 8 LED USB Digital Microscope Endoscope) and the angle of contact was determined using Image J software. Droplets were allowed to settle on the film surface for ~10 min before measurements and measured the average contact angle for three separate drops on each sample surface. The conductivity of deposited Cu_2O films was verified using Motts-Schottky plots which were conducted in a 0.1 M sodium acetate

(NaAc) electrolyte solution (pH 7.5) and the surface morphology studies of deposited Cu_2O thin films were observed using a Scanning Electron Microscope (SEM) (Zeiss EVO 15 LS). Energy Dispersive X-ray Spectroscopy (EDX) analysis of chlorine-doped Cu_2O thin film measurements was performed at 20 kV.

4. RESULTS AND DISCUSSION

4.1 Surface Wettability Through Contact Angle Measurements

Contact angle measurements were made using the sessile drop method with three separate double distilled water droplets placed on the fabricated film. Here, Fig. 1(a,b) illustrates the undoped and Cl-doped Cu_2O thin film average contact angle measurements respectively.

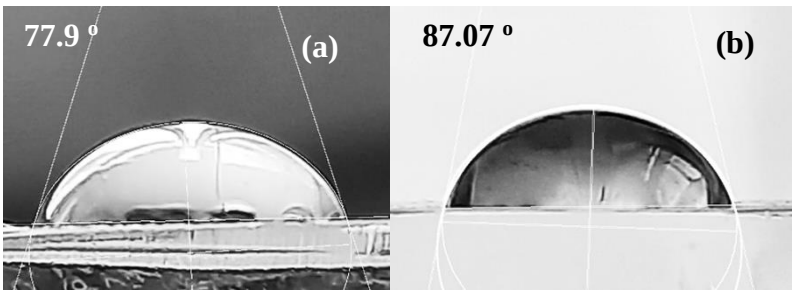

Figure 1: Average contact angle of electrodeposited (a) undoped (b) Cl-doped Cu_2O thin films grown on FTO Substrates.

Abiding the former studies [13] on contact angle variation and film wettability, the average contact angles measured for Cl-doped Cu_2O thin films deposited on FTO substrates have shown an increase in its non-wetting behavior due to the concentration of chlorine dopants and the structural change within the crystal lattice of the film relative to the undoped Cu_2O.

4.2 Surface Morphology and Compositional Analysis

Figures 2(a) and 2(b) show the SEM images of undoped and Cl-doped Cu_2O thin films electrodeposited under the same fabrication conditions in 200 nm scale. As can be seen in the SEM images, each film has shown a unique grain distribution and visible roughness variations which resulted in the differences in contact angle and surface wetting behaviors observed in Fig. 1. Moreover, it was identified that the perfectly homogeneous clear cubical structure of undoped Cu_2O (Fig. 2a) has taken rods-like form with spots evenly distributed on the crystals. These foreign surface features were tested using Energy Dispersive X-ray Spectroscopy (EDX) analysis to observe the presence of Cl atoms in the deposited film. As evident in Fig. 2(c), a 1.16% atomic percentage of Cl was identified as contributing to a film surface modification.

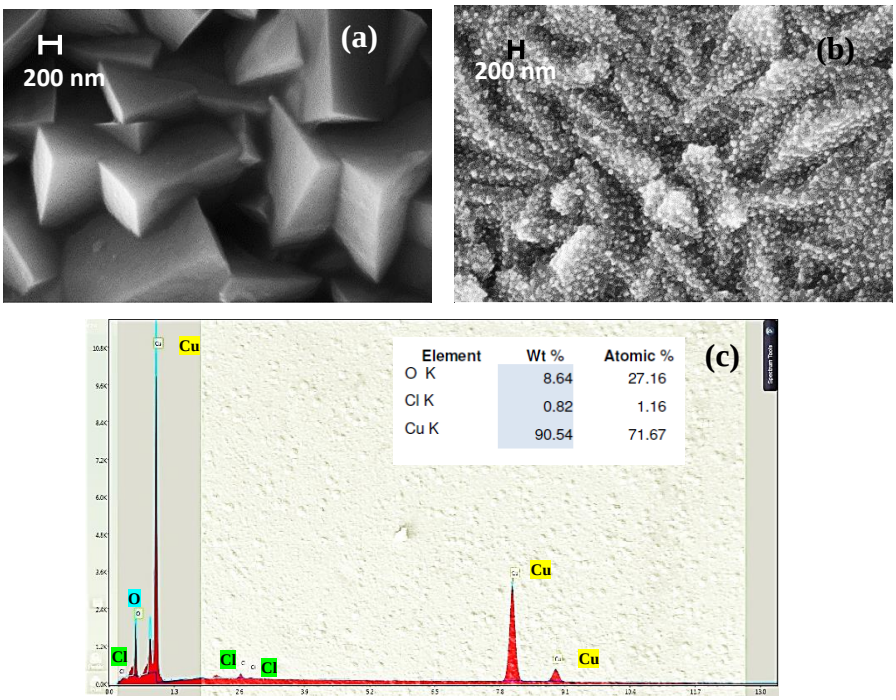

Figure 2: SEM morphological variations of electrodeposited (a) undoped (b) Cl-doped Cu_2O thin films grown on FTO substrates and (c) EDX analysis of chlorine-doped Cu_2O thin film measurements revealing the elemental composition of Cu, O, and Cl.

4.3 Electrical Analysis

Mott-Schottky analysis was primarily applied to characterize the properties of the space charge region and the electrical double layer at the interface between the semiconductor and the electrolyte. By following the Mott-Schottky relationship (Eq.1) where, $C, e, \epsilon_0, \epsilon_r, N_D, A, V_{FB}, k,$ and T denote the space charge layer capacitance of the film at potential V, the electron charge (1.602×10^{-19} C), the permittivity of the vacuum (8.854×10^{-12} F m^{-1}), the relative permittivity of Cu_2O [14], the free carrier concentration of the semiconductor, contacting film area, flat band potential, Boltzmann constant, and absolute temperature respectively, the resulting Mott-Schottky plot typically showed a relationship with linear regions having negative slopes, that confirmed the deposited Cu_2O films to have p-type conductivity [5] as depicted in Fig.3.

$$\frac{1}{C^2} = \left(\frac{2}{e\epsilon_0\epsilon_r N_D A^2}\right)\left(V - V_{FB} - \frac{kT}{e}\right) \quad (1)$$

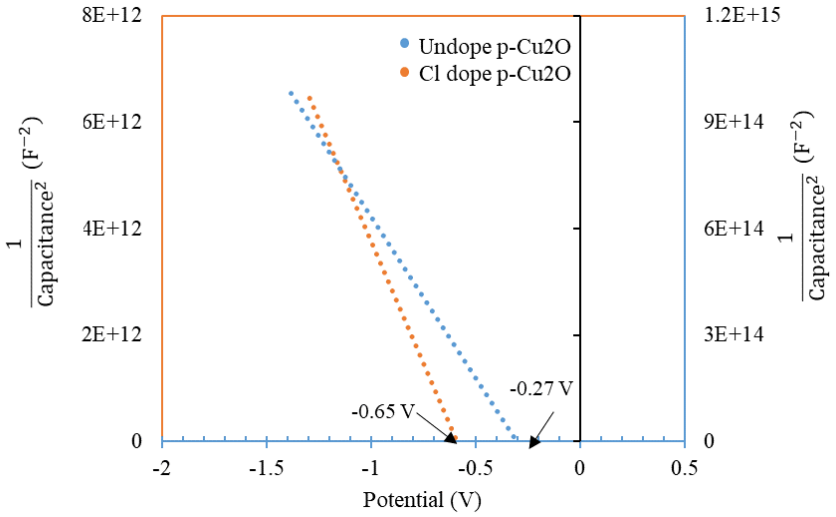

Figure 3: Mott-Schottky analysis of electrochemically deposited undoped and Cl-doped Cu_2O thin films grown on FTO substrates.

Based on the slope and intercept of the Mott-Schottky plot, carrier density N_D (Eq. 2) [6] and the flat band potential V_{FB} against normal hydrogen electrode (NHE) (Eq. 3) were calculated, where $E_{Ag/AgCl} = 0.197\ V$ [15]. The calculations are listed in Table 1.

$$N_D = \left(\frac{2}{e\epsilon_0\epsilon_r A^2\ (slope)}\right) \quad (2)$$

$$E_{FB\ (vs\ NHE)} = E_{FB\ (pH\ vs\ Ag/AgCl)} + E_{Ag/AgCl} + 0.059 \times pH \quad (3)$$

Table 1: Flat band potentials (vs. NHE) and carrier density variations of undoped and Cl-doped Cu_2O thin films deposited on FTO glass substrates.

Measurement	undoped Cu_2O	Cl doped Cu_2O
Flat Band Potential vs NHE (V)	0.363	-0.011
Carrier Density (m^{-2})	2.48×10^{22}	2.48×10^{24}

In comparison to the undoped Cu_2O, Cl-doped film has shown a consistent p-type conductivity with a higher carrier concentration of 2.48×10^{24} and a lower valance band edge position with respect to 0V of NHE. It is expected that this increase in electrical conductivity is observed due to the Cl introduced additional charge carriers (electrons and holes) which results in a shift of band edges.

4.4 Liquid petroleum gas sensing

Optimization of LPG sensing efficiency via chlorine-doped electrodeposited cuprous oxide thin films was investigated using a 5 cc min^{-1} flow rate of liquid petroleum (LP) gas injected into a sealed chamber containing the deposited film. Followed by a continuous 0.1 l min^{-1} compressed air flow flushing out the LPG, two gold spring probes placed 1 cm distance apart on the film measured the film surface resistance variation. The film's resistance in the air (R_a) and when exposed to LP gas (R_g) were measured [16]. Before entering the chamber, the gas underwent filtration through a silica background to eliminate water molecules. The sensor's response time and recovery time were determined by recording the duration taken to achieve 90% of the maximum resistance change (ΔR) induced by LPG and the time needed to return to 90% of the initial resistance during airflow, respectively. When the films were flushed with compressed air at a certain temperature, the film resistance decreased and stabilized with time due to the ionosorption of oxygen molecules on the Cu_2O surface [17,18]. Upon the injection of a reducing gas like LPG, it interacts with the ionosorbed oxygen as given in Eq. (4) and increases the resistance.

$$O^{2-} + C_nH_{2n+2} \rightarrow CO_2 + H_2O + 2e^- \qquad (4)$$

The percentage change in the gas response compared to sensor resistance at ambient state (R_a) is given by Eq. (5). For p-type Cu_2O films $R_g > R_a$.

$$S = \left[\frac{(R_g - R_a)}{R_a}\right] \times 100\% \qquad (5)$$

At a chosen optimal temperature of 70 ℃ [5,10], Cl-doped Cu_2O maintained a maximum response of ~13% which was almost twice as undoped Cu_2O. This could be attributed to the Cl increased oxygen vacancies which ultimately increased the response percentage due to excessively increased conductivity [19]. With shorter response and recovery times of approximately 20 s and 15 s respectively the Cl-doped Cu_2O films presented a promising quick identification of LPG at low temperatures.

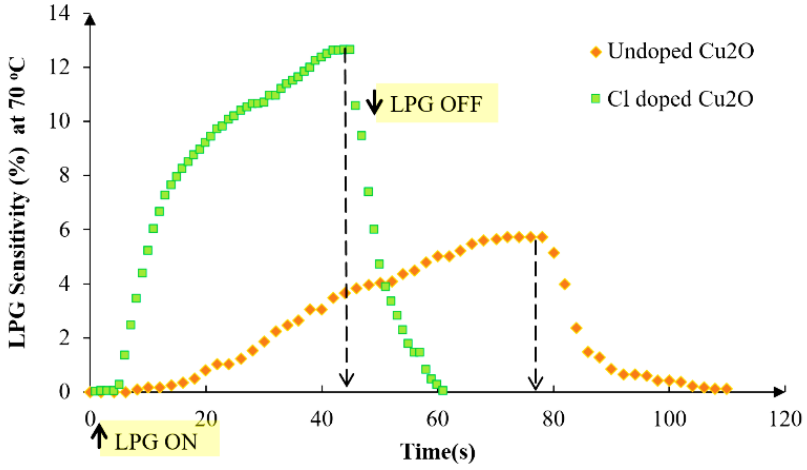

Figure 4: LP gas response measurements of undoped and Cl-doped Cu_2O thin films grown on FTO substrates.

To investigate the optimal operating temperature of the two doping conditions, the sensing chamber was maintained at different temperatures ranging from 60℃ to 120℃ through the LPG sensing process. However, the undoped Cu_2O films did not show a promising efficient gas response besides the 70℃ - 90℃ range. According to the LPG sensitivity variation of Cl-doped Cu_2O thin films at different temperatures shown in Fig. 5, a significant temperature dependence of sensitivity was identified possibly due to the thermal stability facilitated by apparent reduced particle size in the nanoscale. A maximum gas response of ~20% was observed at 100℃, which reduced gradually with lower and higher temperatures. Altogether, the gas sensing characterization of Cu_2O showed a successful optimization of LPG sensing with Cl-dope surface modification.

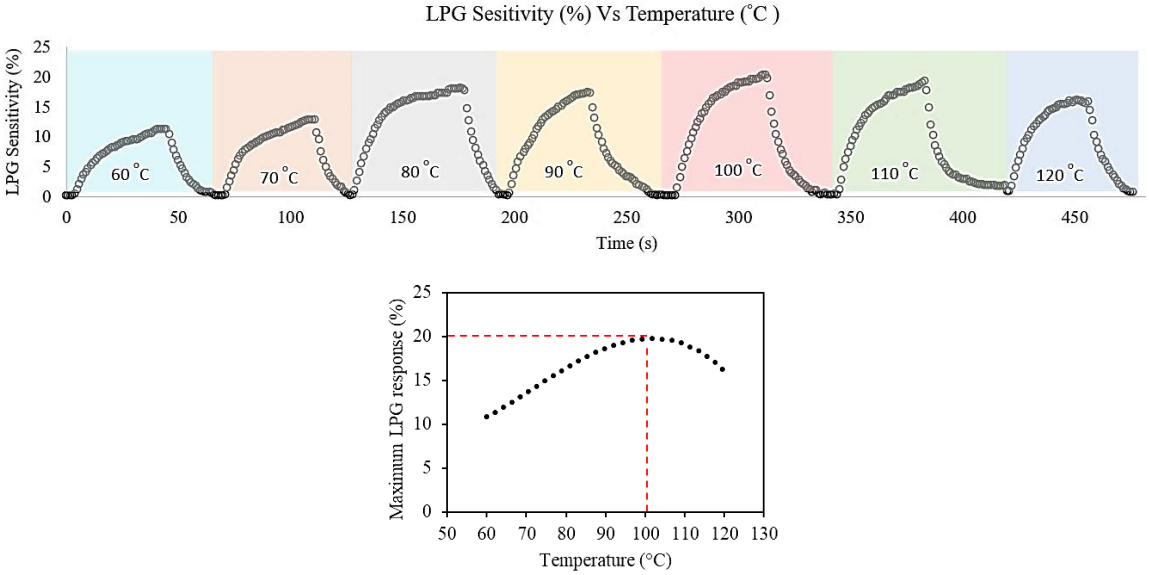

Figure 5: LP gas response measurements of Cl-doped Cu_2O thin films grown on FTO substrates at different operating temperatures.

5 CONCLUSION

The investigation was focused on elucidating the properties and optimization of liquid petroleum gas (LPG) sensing via chlorine-doped electrodeposited cuprous oxide (Cu_2O) thin films on FTO substrates. The contact angle measurements revealed an increased non-wetting behavior in chlorine-doped Cu_2O films compared to undoped Cu_2O, attributed to the dopants' concentration and structural alterations within the crystal lattice. Surface analysis through SEM imaging displayed distinct grain distribution and surface variations, influencing contact angles and wetting behaviors. EDX spectroscopy confirmed the presence of Cl atoms in the doped film. Mott-Schottky analysis indicated a p-type conductivity in deposited Cu_2O films, showcasing a higher acceptor concentration and lower valance band edge position for Cl-doped films compared to undoped Cu_2O. Gas sensing efficiency optimization for LPG involved meticulous investigations at varying temperatures. Cl-doped Cu_2O films demonstrated a substantial LPG response (~13%) at 70 ℃, with rapid identification capabilities. Temperature sensitivity analyses highlighted a temperature-dependent variation in LPG sensitivity, with a maximum response of ~20% observed at 100 ℃ for Cl-doped films. In contrast, undoped Cu_2O films exhibited limited gas response efficiency except within the 70 ℃ to

90 ℃ range. Overall, the gas sensing characterization indicated successful optimization of LPG sensing through Cl-doped surface modification of Cu_2O, signifying potential advancements in gas sensing applications.

6. REFERENCES

[1] Fujishima, A., & Zhang, X. *Titanium dioxide photocatalysis: present situation and future approaches*, Comptes Rendus Chimie. 9 (2006) 750-760.

[2] Alberola-Borràs, S., et al. *Cuprous Oxide as a Semiconductor Material in Photovoltaic Applications: Fabrication, Properties, and Devices*, Energies, 14 (2021) 973.

[3] Chithambararaj, et al. *Cuprous oxide (Cu2O) thin films for LPG gas sensor application by spray pyrolysis technique*, Mater. Today: Proceedings, 5 (2018) 378-384.

[4] Bandara, A.H.M.N.N., Perera, V.P.S., Senadeera, G.K.R. and Bandara, K.N.D., *Substrate Effect on Liquid Petroleum Gas Sensors of Cuprous Oxide Thin Films Electrodeposited in Acetate Bath*, ECS J. Solid State Sci. Technol., 11 (2022) p.107002.

[5] Bandara, K.N.D. *Application of Electrodeposited Nano/Micro Structured Metal Oxide Thin Films for Liquefied Petroleum Gas Sensing*, PhD diss., Faculty of Science, University of Colombo, 2018.

[6] Bandara, A.H.M.N.N., Perera, V.P.S., Senadeera, G.R. and Bandara, K.D., *Performances of Nano-Structured Cu2O Thin Films Electrochemically Deposited on ITO Substrates in Lactate Bath as Liquid Petroleum Gas Sensors*, ECS Adv., 2 (2023) p.046501.

[7] Minami, T. *Transparent conducting oxide semiconductors for transparent electrodes*, Semicond. Sci. Technol., 20 (2005) S35-S44.

[8] Khan, et al. *The stability of cuprous oxide: A critical review and identification of the determining parameters*, Prog. Mater. Sci., 111 (2020) 100639.

[9] Chen, S., et al. *Recent Advances in the Application of Semiconductor Metal Oxides as Gas Sensing Materials: A Review,* Rev. Adv. Mater. Sci., 48 (2016) 336-352.

[10] Bandara, K.N.D., Jayathilaka K. M. D. C., Gunewardene M. S., Dissanayake D. P., and Jayanetti J. K. D. S., *Surface properties of sulphur based surface modified n-Cu2O thin films for enhanced liquefied petroleum gas sensing*, J. Phys. D: Appl. Phys., 50 (2017) 485304.

[11] Chen, L., et al. *Chlorine Doping Induced Improvement in Cu2O Thin Film Transistor Performance*, ACS Appl. Mater. Interfaces, 8 (2016) 9204-9211.

[12] Kafi, F.S.B, Jayathileka, K.M.D.C, Wijesundera, R.P, & Siripala, W, *Effect of Bath pH on Interfacial Properties of Electrodeposited n-Cu2O Films*, Phys. Status Solidi B 255 (2018).

[13] Liu, Y.L., Liu, Y.C., Mu, R., Yang, H., Shao, C.L., Zhang, J.Y., Lu, Y.M., Shen, D.Z. and Fan, X.W., *The structural and optical properties of Cu2O films electrodeposited on different substrates*, Semicond. Sci. Technol., 20 (2004) p.44.

[14] Sawicka-Chudy, P., Sibiński, M., Wisz, G., Rybak-Wilusz, E. and Cholewa, M., *Numerical analysis and optimization of Cu2O/TiO2, CuO/TiO2, heterojunction solar cells using SCAPS*, in J. Phys.: Conference Series 1033 (2018) p. 012002 IOP Publishing.

[15] Wickramasinghe, G.C., Perera, V.P.S., & Senthilnithy, R. *Exploration of Electrical and Optical Characteristics of Cuprous Oxide Synthesized Using Benedict's Reagent*, in Proc. SLIIT Int. Conf. Adv. Sci. Humanities, Colombo, (2021) 21-26.

[16] Siripala, W., & Kumara, K.P., *A photoelectrochemical investigation of the n-and p-type semiconducting behaviour of copper (I) oxide films*. Semicond. Sci. Technol., 4, (1989) 465.

[17] Wang, X.F., Song, X.Z., Sun, K.M., Cheng, L. and Ma, W., *MOFs-derived porous nanomaterials for gas sensing*, Polyhedron 152 (2018) pp.155-163.

[18] Wang, P., Zhan, S., Xia, Y., Ma, S., Zhou, Q. and Li, Y., *The fundamental role and mechanism of reduced graphene oxide in rGO/Pt-TiO2 nanocomposite for high-performance photocatalytic water splitting*, Appl. Catal. B Environ., 207 (2017) pp.335-346.

[19] Bandara, K.N.D., Jayathilaka, K.M.D.C., Disanayaka, D.P., Siripala, W. and Jayanetti, J.K.D.S., *Effect of Chlorine Doping on Gas Sensing Properties of Electrodeposited n-type Cuprous Oxide Thin Films*. In Proceedings of the Technical Sessions 30 (2014) pp. 11-16.