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Surface properties of sulphur based surface modified n -Cu₂O thin films for enhanced liquefied petroleum gas sensing

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Abstract

The surface of electrodeposited n -Cu₂O thin films were modified by sulphidation using aqueous Na₂S followed by (NH₄)₂S vapor treatment. Compared to untreated thin films, the resultant films showed an enhanced response to liquefied petroleum (LP) gas at a relatively low operating temperature (~45 °C), one of the lowest reported for a cuprous oxide based material. X-ray diffraction spectra confirmed that the films were of single phase. Observed by contact angle measurements and energy dispersive x-ray spectroscopy, (NH₄)₂S vapor treatment converted the highly wetting sulphided films containing both Na and S to a partially wetting surface by forming sulphur on the film surface. This modification on the film surface, enabled the sensor response to recover to an ambient level after stoppage of LP gas flow, which sulphidation alone was inapt. Scanning electron micrographs complemented roughness measurements made by atomic force microscopy and showed a transformation of polycrystalline morphology of bare n -Cu₂O film to one having highly porous structures, which thereby increased the surface area of the surface modified films. Therefore, this work demonstrates that the surface of the n -type Cu₂O thin films modified by (NH₄)₂S vapor treatment and sulphidation can alter the surface wetting nature and increase the surface area to enhance LP gas sensing at a relatively low temperature.

Keywords: electrodeposition, gas sensor, liquefied petroleum gas, sulphidation, cuprous oxide, surface wetting

 Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

Solid state gas sensors are popular due to their low cost of production, compact size, portability and relative ease of fabrication. In particular, metal oxide thin film semiconducting materials such as ZnO, SnO₂, TiO₂, In₂O₃, WO₃, and CdO, have been widely used in effective gas sensing platforms [1]. In optimizing sensing performance, structural parameters such as grain size, porosity, texture, grain network and adhesiveness to target molecules play a significant role [2, 3]. While,

sensitivity, selectivity, speed and stability are all important, the ability of a material to detect a gas at an operating temperature close to room temperature is considered very important in simplifying the fabrication of the sensing device and minimizing the power requirement for operation [4, 5]. Synthesis of such materials has been reported previously [5], however, such research related to sensing of liquefied petroleum (LP) gas, a highly flammable gas and the main focus of the work presented in this paper has been limited. Room temperature sensing of LP gas by forming p -type polyaniline heterojunctions with

metal oxides (e.g. n -TiO₂, n -ZnO, n -CdSe and n -PbS) [6–9] has been reported, including work related to nanostructured nickel ferrite [10] and ferric oxide [11]. Several other materials have also been reported for LP gas sensing applications that operate optimally at a temperature well above room temperature [12–16]. Given the continued and extensive domestic and industrial usage of LP gas as an energy source, effective yet low cost sensing options continue to be pursued that will help to avoid hazards posed by leaking gas. Being earth abundant and environmentally friendly material, Cu₂O is a direct band gap semiconductor with a potential to be used as a green alternative for many applications, in particular for photovoltaics [17]. Capabilities of Cu₂O thin films in particular, have been explored and shown promise in the detection of gases [18–22]. Recent work on electrodeposited Cu₂O thin films doped with chlorine showed response to LP gas at relatively low operational temperatures [21], while shape controlled n -Cu₂O thin films with nano-cubic structures have demonstrated significantly better response to LP gas at lower concentrations compared to its microcrystalline counterpart [22]. Nevertheless, during all of the above attempts the optimal operating temperature of the sensing material had been well above room temperature. Also, previous work on the fabrication of copper sulphide thin films showing gas sensing properties using different techniques have demonstrated their ability to detect gases such as ammonia at room temperature [23–25]. Furthermore, the surface treatment of electrodeposited Cu₂O, in particular by sulphidation has shown improved electrical transport and photo-response properties through the reduction of surface defects [26]. Jayathilaka *et al* further demonstrated that (NH₄)₂S vapor treatment of electrodeposited p -Cu₂O films reduces resistivity by at least four orders of magnitude, while preserving structural integrity [27] and Jayathilaka *et al* also reported that (NH₄)₂S vapor treatment of sulphidated electrodeposited n -Cu₂O films improved photovoltaic efficiency from 0.11% to 0.54% [28]. Similar surface treated electrodeposited n -Cu₂O thin films have also shown improved LP gas sensing ability in our previous work [29]. Here it was observed that both an optimal treatment of the films with (NH₄)₂S vapor as well as having a minimum Cu₂O thin film thickness was critical in introducing optimal response at a relatively lower operating temperature (~45 °C) in the presence of LP gas, while being able to recover response to ambient level in the absence of LP gas. It is also worth noting that, while not optimal, the material also responded to LP gas even at temperatures close to room temperature (30 °C). In the work presented in this paper, further analysis of changes observed in the surface properties during the intermediate steps of the fabrication process is discussed. Thereby, insight on the role played by both sulphidation and (NH₄)₂S vapor treatment of n -Cu₂O microcrystalline thin films in the context of LP gas sensing is presented.

2. Experimental details

2.1. Fabrication of thin films

Titanium (Ti) plates were used to electrodeposit n -Cu₂O thin films. Before deposition, the substrates were cleaned

with detergent, dilute nitric acid, acetone and finally rinsed with distilled water. The n -Cu₂O thin films were potentiostatically electrodeposited at –200 mV versus the reference electrode in a three-electrode electrochemical cell (with a saturated calomel electrode (SCE) as the reference electrode, platinum plate as the counter electrode) that contained aqueous solutions of 0.1 M sodium acetate (Sigma-Aldrich, purity –99.0%) and 0.01 M cupric acetate (Sigma-Aldrich, purity –99.0%). Deposition time was varied as required with the temperature of the electrolyte maintained at 60 °C and with continuous stirring using a magnetic stirrer. An aqueous solution of 0.01 M Na₂S (Sigma-Aldrich, purity –98.0%) was used for the sulphidation of n -Cu₂O thin films. Drops of Na₂S were placed from a liquid droplet marker (volume per drop of approximately 0.15 ml) and spread across a 2 cm × 2 cm plate to form a thin layer. The films were heated at 200 °C for approximately 5 min. After sulphidation, films were thoroughly cleaned with distilled water and allowed to dry in air. Thereafter, the sulphidated films were further exposed to 50% vol. aqueous solution of (NH₄)₂S vapor at room temperature (27 °C).

2.2. Thin film characterization

The n -type conductivity of the surface modified Cu₂O thin films has been studied previously where a positive photo current spectral response signal could be observed for n -type conductivity [26]. The n -type conductivity of deposited Cu₂O films with and without surface treatment was verified using photo current spectral response measurements (see figure S1) (stacks.iop.org/JPhysD/50/485304/mmedia) using a three electrode photo electrochemical cell containing a 0.1 M sodium acetate solution. The reference electrode was a saturated calomel electrode and a platinum plate was used as the counter electrode. The contact area of the Cu₂O film with the electrolyte solution was ~4 mm². Structural characterization was done using x-ray diffraction (XRD) analysis (Regaku Ultima-IV). Energy dispersive x-ray spectroscopy (EDX) (INCA 10 mm² SDD detector x-act) was performed to confirm the surface composition of the selected thin films. Scanning electron microscopy (SEM) (Zeiss EVO 15 LS) was used to observe the surface morphology of the deposited films, while topographic images and other surface specific roughness parameters were quantified using atomic force microscopy (AFM) (Park Systems XE-100). The AFM was operated in the non-contact mode with a cantilever having a tip radius of less than 10 nm and operated at a frequency of 0.5 Hz. The statistical parameters of roughness distribution (Peak-to-valley difference, root mean square roughness, average roughness, maximum peak height, skewness, and kurtosis) were measured along the diagonal for each of the AFM images from a sample area of 5 μm × 5 μm at 0.01 nm resolution. Wetting nature of fabricated thin film surfaces were characterized using the sessile drop method [30] with double distilled water. Water drops placed on the film surface were observed through a digital microscope (2 MP 1000 × 8 LED USB Digital Microscope Endoscope). The captured images were post processed using ImageJ software with splines constructed at the

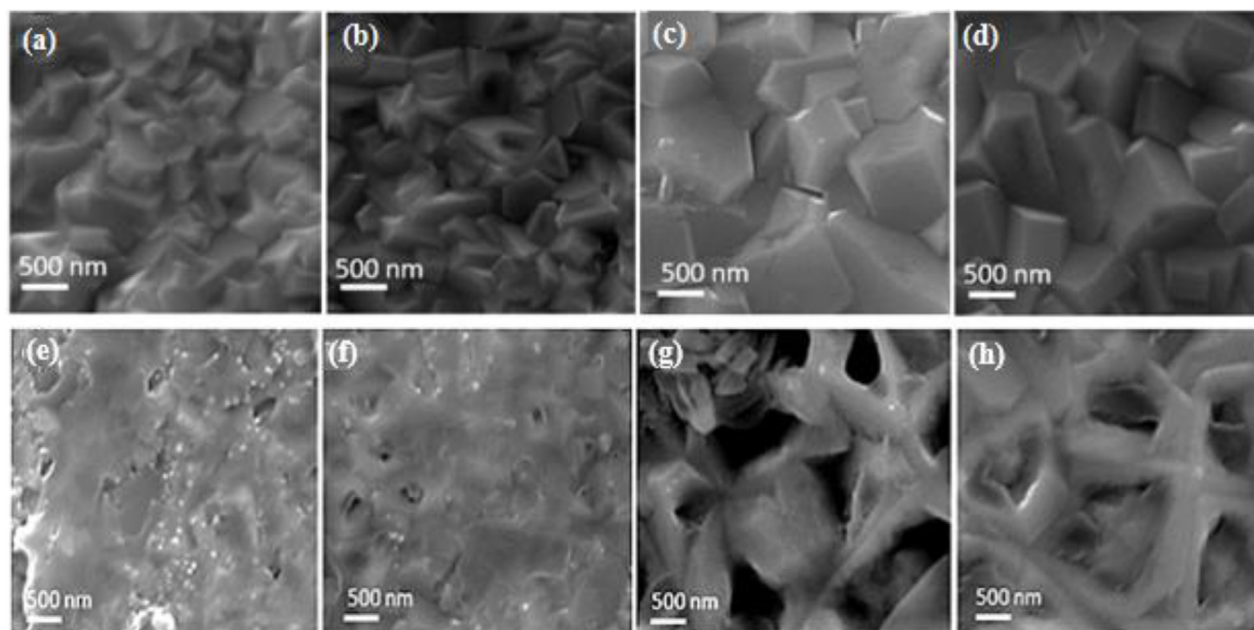


Figure 1. The scanning electron micrographs (SEM) show the morphological variations of an electrodeposited n -Cu₂O thin films with deposition times (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min (with calculated film thicknesses of 368 nm, 588 nm, 1395 nm and 1952 nm respectively) and (e)–(h) the corresponding thin films after sulphidation using three drops of 0.01 M Na₂S with exposure to 50 vol.% (NH₄)₂S vapor for 5 s at 27 °C.

liquid and film interface to determine the angle of contact. Droplets were allowed to settle on the film surface for ~15 min before measurements. An average contact angle was obtained by taking measurements for at least three separate drops on each sample surface.

2.3. LP gas sensing measurements

Contact probes were placed on the thin film for measuring resistance using a computer interfaced digital multimeter (Keithley, 2100). Thin film resistance variations were measured under ambient conditions and in the presence of LP gas by varying thin film surface temperatures (30 °C–150 °C). Temperature was varied using a heater with thin film surface temperature monitored and regulated using a type-K thermocouple. These measurements were made inside a custom made gas perfusion chamber (for details see supplementary methods and figure S2).

3. Results and discussion

3.1. Surface morphology and compositional analysis

Figures 1(a)–(d) shows the scanning electron micrographs (SEM) of n -Cu₂O thin films deposited for 15 min, 30 min, 45 min and 60 min respectively. Figures 1(a)–(d) clearly shows that with the increasing thickness, the average size of the polycrystalline grains have increased. However, beyond a deposition time of 45 min no significant increase in the average grain size is observed (compare grain sizes shown in figure 1(c) with figure 1(d)).

The electrodeposited thin film thicknesses were also evaluated using equation (1) based on the Faraday's law of

electrolysis assuming that only single phase Cu₂O was deposited [31]:

$$d = \frac{QM}{neA\rho N_A} \quad (1)$$

where, Q , M , n , e , A , ρ and N_A represent the total charge passed during deposition, molecular weight of the deposit, number of electrons taking part in the reduction, charge of an electron, area of deposition (measured in cm²), bulk density of the deposit (measured in g cm⁻³) and Avogadro's number respectively. The calculated thickness variation of n -Cu₂O films deposited at -200 mV versus SCE for different deposition times, 15 min, 30 min, 45 min and 60 min, were 368 nm, 588 nm, 1395 nm and 1952 nm respectively.

Based on the previously reported work by Jayathilaka *et al* who measured the photocurrent variations of n -Cu₂O thin films and p -Cu₂O thin films as a function of exposure time of (NH₄)₂S [26, 27], these films were then subjected to sulphidation (by 0.01 M Na₂S (three drops) and heating at 200 °C) followed by (NH₄)₂S vapor treatment. The SEMs of the treated thus, surface modified films with corresponding deposition times discussed earlier are shown in figures 1(e)–(h). With the introduction of surface modification, it is evident that the porous structures are predominant on the surface of the Cu₂O film deposited for 45 min (see figure 1(g)).

The number of Na₂S drops placed on an n -Cu₂O thin film deposited for 45 min was also varied so that the atomic percentage of sulphur increased with the placed number of Na₂S drops. It was observed that the porous structure depended on the extent of sulphidation (see figure S2 in the supplementary material). This observation further indicates that the surface of the n -Cu₂O film can be modified by using an optimum Na₂S content during sulphidation. This behavior

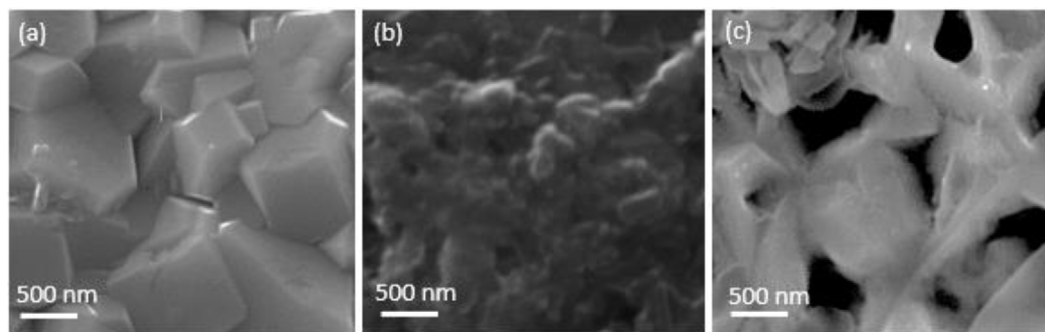


Figure 2. The scanning electron micrographs (SEM) of electrodeposited n -Cu₂O thin film structures. (a) n -Cu₂O thin film deposited for 45 min, (b) thin films after sulphidation by placing a thin layer of 0.01 M Na₂S at 200 °C and (c) sulphided thin film with exposure to 50 vol.% (NH₄)₂S vapor for 5 s at 27 °C.

is also consistent with the observations reported by Isac *et al* who deposited Cu_xS thin films using automatic spray pyrolysis technique at 275 °C–325 °C [32]. It has been reported that the variation of sulphur content during sulphidation of Cu₂O films affects the Cu concentration of the formed Cu_xS film and thus, the crystallinity and the morphology of the film [26–28]. Therefore, the observed pore density variation upon (NH₄)₂S vapor treatment may have been caused by the nature of the formed Cu_xS layer. Based on above evidence, n -Cu₂O thin films deposited for 45 min with sulphidation using three drops of Na₂S and (NH₄)₂S vapor treated for 5 s were considered optimal for the subsequent LP gas response measurements.

The scanning electron micrograph (SEM) in figure 2 further elaborates the introduced surface modifications at each treatment step starting from a n -Cu₂O thin film electrodeposited for 45 min (figure 2(a)) followed by sulphidation using Na₂S (figure 2(b)) and vapor treatment using (NH₄)₂S (figure 2(c)). It is noted that following sulphidation, the film morphology has undergone substantial changes due to the formation of a smooth and homogeneous Cu_xS thin film as shown in figure 2(b). Such surface morphological features due to the formation of a Cu_xS thin film have been reported in several other research studies [33–35]. It can be seen that the porosity of the film surface arises due to the exposure of the film to (NH₄)₂S vapor as shown in figure 2(c), and supported later by AFM measurements.

Figure 3 shows the x-ray diffraction patterns (XRD) of an n -Cu₂O thin film deposited for 45 min before sulphidation, after sulphidation using three drops of 0.01 M Na₂S and after exposing the sulphided thin film to 50 vol.% (NH₄)₂S vapor for 5 s at 27 °C. It can be clearly seen from figure 3(iii) that the film has maintained the identity in terms of its Cu₂O structure, while not showing any peaks due to the formation of Cu_xS phase on the surface of the film. It has been previously reported that due to the thinness of the Cu_xS phase formed on the film surface, Cu_xS, XRD peaks can only be seen by high energy x-ray diffraction (HEXRD) measurements [36]. The sharp peaks at 2θ angles, 29.54°, 36.19°, 42.18°, 61.10°, 73.11° and 77.38° corresponding to crystalline planes of (110), (111), (200), (220), (311) and (222) matched well with standard Cu₂O data (JCPDS card PDF file no.05-0667). Furthermore, any slight changes seen in the XRD spectral peaks related to

Cu₂O phases were not significant given the uncertainty level of the measurement.

Energy dispersive x-ray spectroscopy (EDAX) spectra obtained for sulphided and both sulphided and (NH₄)₂S vapor treated Cu₂O thin films are shown in figure 4. The inset tables provide the average elementwise weight and atomic percentages obtained from multiple EDAX spectra.

The EDX measurements confirm the presence of relatively high percentages of Na and considerable percentage of S upon sulphidation. Once the sulphided film is subjected to (NH₄)₂S vapor treatment, it can be seen that the Na content has reduced drastically and S content has increased in the film compared to sulphided Cu₂O thin film.

This observation can be thought to be a result of the decomposition of (NH₄)₂S into ammonia and hydrogen sulphide at room temperature. This could create a porous thin layer of sulphur on the oxide surface due to partially decomposed hydrogen sulphide. It has been reported that the decomposition of (NH₄)₂S into ammonia and hydrogen sulphide occurs at room temperature [37]. The polar nature of the film due to the presence of Na could be altered by deposited S, modifying the surface wettability of these films. This is evident from the contact angle measurements discussed in the next section.

3.2. Surface wettability through contact angle measurements

Contact angle measurements made using sessile drop method with double distilled water for the fabricated n -Cu₂O thin films are shown in figure 5. It is evident from literature that a surface is categorized as ‘wetting’ if contact angle made by the liquid is less than 30°. For contact angles between 30° and 89° it is said to be ‘partially wetting’ while, ‘non-wetting’ for 90° and above [38].

The average contact angles measured for bare n -Cu₂O thin films electrodeposited for 45 min, sulphided and subsequently (NH₄)₂S vapor treated were (89 ± 5), (26 ± 5)° and (40 ± 5)° respectively. Measurements therefore, indicate that sulphidation converts the n -Cu₂O thin films which are initially non-wetting into a wetting surface and that the subsequent (NH₄)₂S vapor treatment converts surface to partially wetting. Here the contact angle measurements can be correlated with the surface morphology, topography and the polar nature of the film

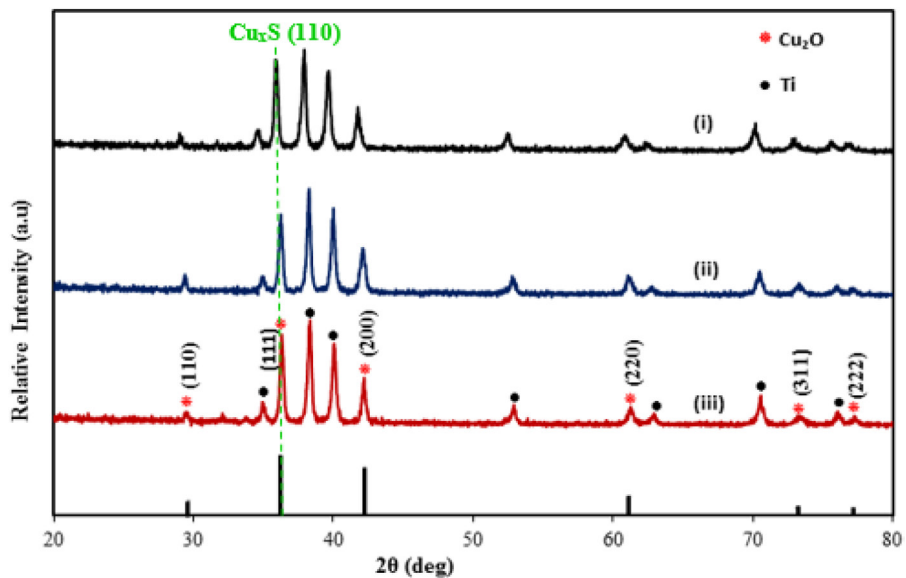


Figure 3. X-ray diffraction (XRD) spectra of *n*-Cu₂O thin film structures (electrodeposited for 45 min, (i) before sulphidation, (ii) after sulphidation by placing a thin layer of 0.01 M Na₂S at 200 °C and (iii) sulphidated thin film after exposing to 50 vol.% (NH₄)₂S vapor for 5 s at 27 °C, in comparison with the standard data for Cu₂O (JCPDS: 05-0667). The dashed line indicates the 2θ position corresponding to a Cu_xS (110) peak which can be seen only through high energy XRD measurements.

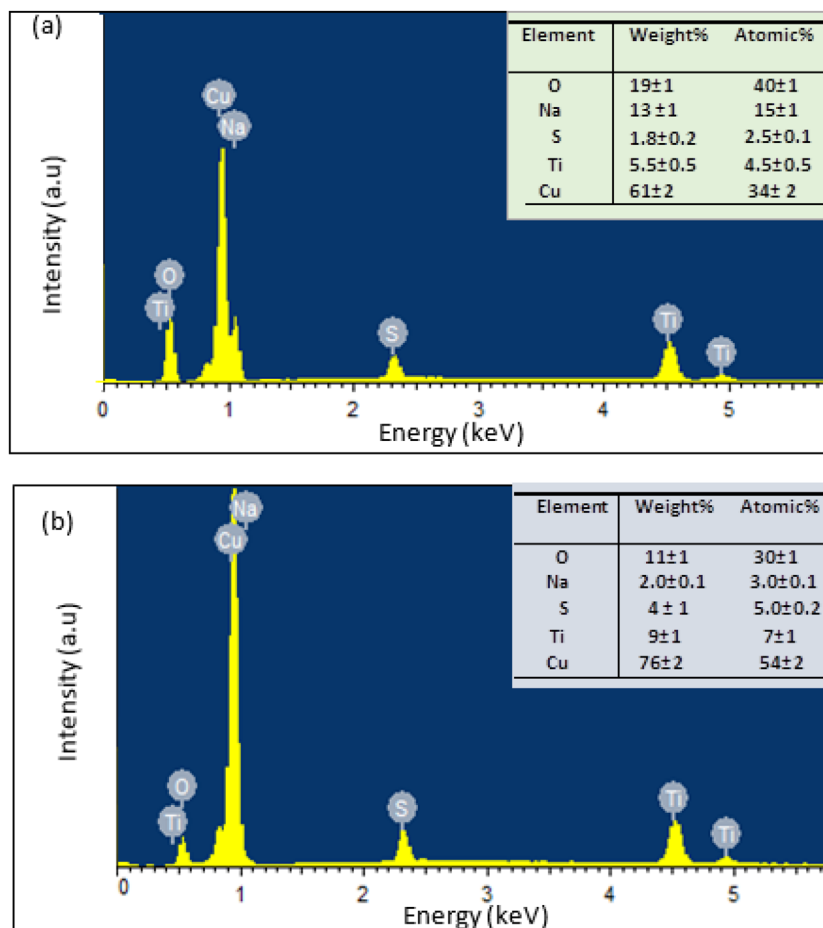


Figure 4. (a) EDAX spectra of sulphidated Cu₂O thin film (inset: table of average values of weight% and atomic% of elements of four spectrums) and (b) EDAX spectrum of sulphidated Cu₂O thin film with exposure of (NH₄)₂S vapor (inset: table of average values of weight% and atomic% of elements of four spectrums).

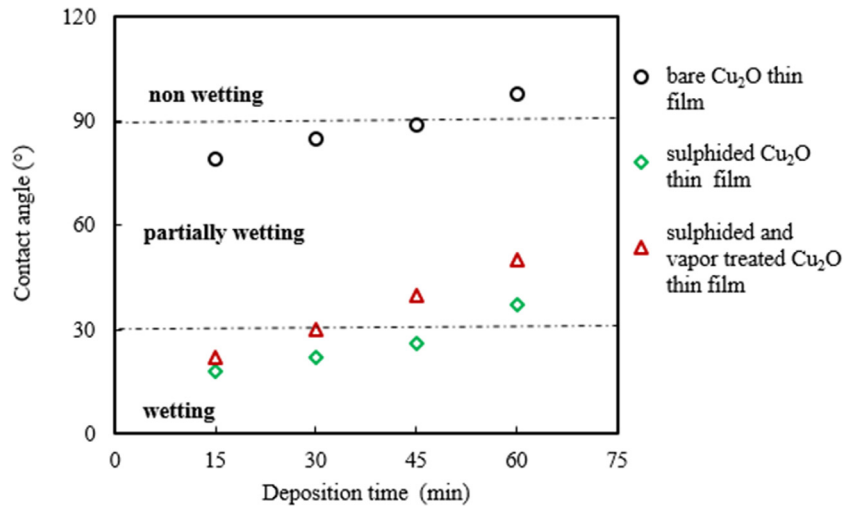


Figure 5. Contact angle variation of *n*-Cu₂O bare thin films, sulphided *n*-Cu₂O films and sulphided *n*-Cu₂O thin films with (NH₄)₂S vapor treatment under the deposition time durations 15 min, 30 min, 45 min and 60 min. The measurement uncertainty was $\pm 0.5^\circ$.

surface. It was noticed from both SEM and AFM measurements (later presented AFM roughness measurements) that the bare *n*-Cu₂O film surface was rough in nature, which enables air to be trapped in these structures. The trapped air pushes on any liquid placed on the surface making the surface highly non-wetting as confirmed by contact angle measurement shown in figure 5. However, as soon as these films were sulphided, the SEMs confirm that the surface becomes smoother, while laying a surface layer containing Na (confirmed by EDAX measurements) making the surface polar. This modification makes the surface wetting or gives rise to low contact angles. Interestingly, once these sulphided films were treated with (NH₄)₂S vapor the underlying porous structures reemerge and especially, decreasing Na content and the increased sulphur content cause the film surface to become less polar. The roughness emerged less polar surface now becomes partially-wetting.

3.3. Surface roughness analysis

Figure 6 shows the AFM images of an *n*-Cu₂O thin film deposited for 45 min (a) before sulphidation (b) after sulphidation using Na₂S drops and (c) sulphided thin film with exposure to 50 vol.% (NH₄)₂S vapor for 5 s at 27 °C. The 3D images of the AFM measurements shown in the figure indicate the change in surface morphology under the above three stages (a), (b) and (c). The line profiles taken along the diagonal of each AFM image and the corresponding histogram depicts the changes in surface roughness at each stage.

Initially, the bare sample shows a significant surface roughness which has been reduced due to the sulphidation process. Subsequently, the exposure of the sulphided surface to (NH₄)₂S vapor has given rise to an increased surface roughness. It can also be seen from the 3D AFM image shown in figure 6(c) (iii), that the porous nature of the surface has been increased by the (NH₄)₂S vapor treatment. The statistical parameters of roughness distribution measured along the diagonal for each of the AFM images shown in figures 6(a)(i)–(c)(i) are given in table 1.

In order to analyze the surface morphology, skewness (R_{sk}) values (as the third moment of profile amplitude probability density function) and the values of kurtosis (R_{ku}) (as the fourth moment of profile amplitude probability function) were used. The profiles corresponding to the sign of R_{sk} and R_{ku} are shown in figures S4(a) and (b) respectively [39]. Comparison of R_{sk} values in table 1 along with figure S4(a) indicates that the samples show a negative skewness which has increased due to (NH₄)₂S vapor treatment. Simultaneously, the sharpness of films reflected by R_{ku} values given in table 1 and the profiles shown in figure S4(b) indicate an increased sharpness of the film due to the (NH₄)₂S vapor treatment. In other words, the smoother nature of the surface ($R_{ku} < 3$, Platykurtic) of the film after sulphidation has changed into a surface having a Gaussian type amplitude distribution ($R_{ku} = 3$, Mesokurtic) arising from the increased roughness upon exposure of *n*-Cu₂O thin film surface after sulphidation to (NH₄)₂S vapor treatment [40]. Consequently, the (NH₄)₂S vapor treatment has increased the effective surface area for the adsorption of gas molecules.

3.4. Sensor response measurements

The resistance between the contact probes placed on the fabricated thin films was measured with and without LP gas. The bare *n*-Cu₂O thin films showed a resistance of ~ 1 M Ω which reduced after sulphidation (few hundreds of k Ω). As expected, following (NH₄)₂S vapor treatment the resistance further reduced (< 100 k Ω). The fractional change in the resistance or response (S) (given by equation (2)) was found by exposing films to 100% LP gas.

$$S = \left| \frac{R_{LPG} - R_{Air}}{R_{Air}} \right| \times 100, \quad R_{LPG} > R_{Air}, \quad (2)$$

where, R_{LPG} is the resistance of the film upon exposure to LP gas and R_{Air} is the resistance of the film under ambient atmospheric conditions.

Initially, the gas response measurements were taken for sulphided *n*-Cu₂O thin films under different operating

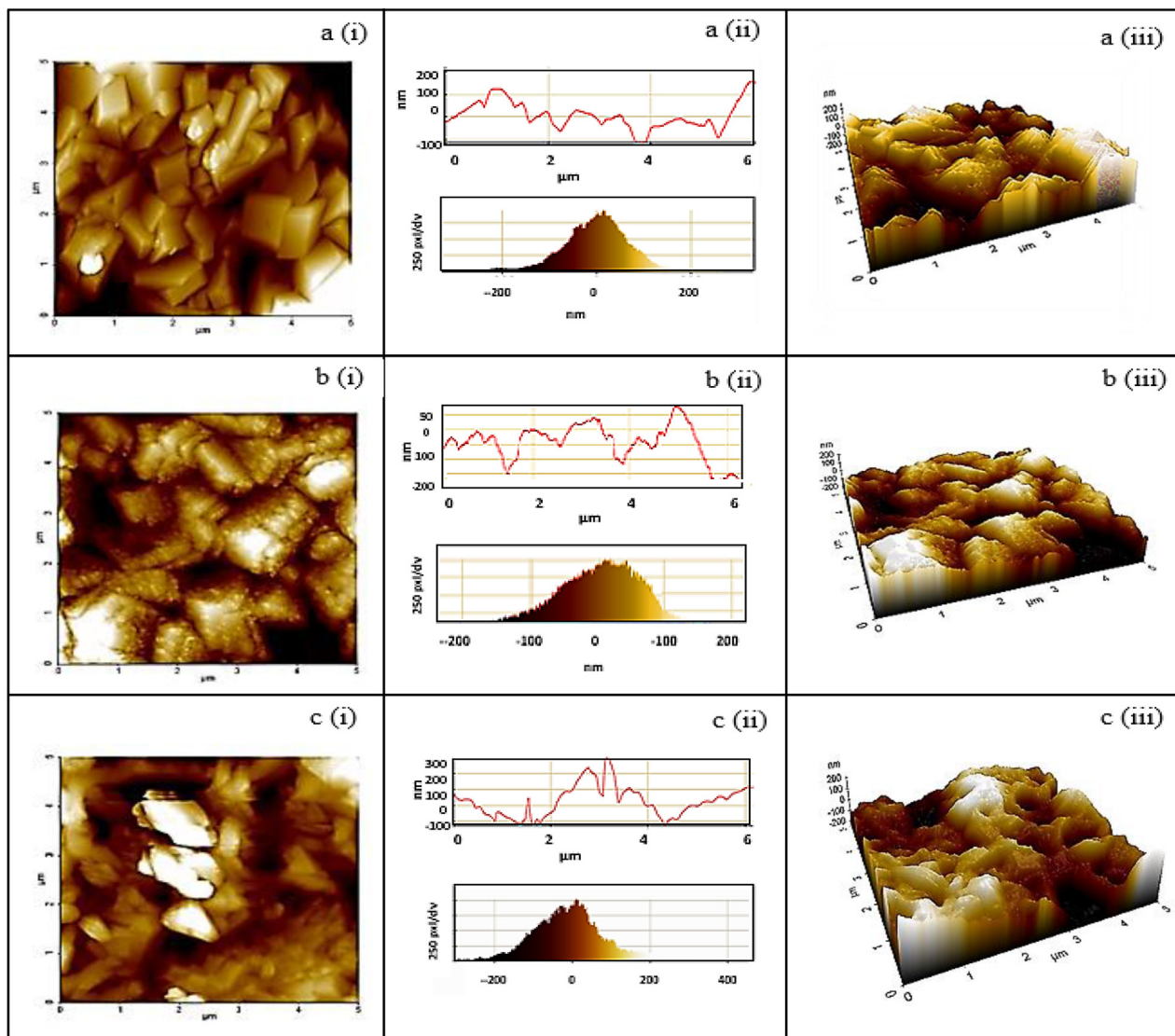


Figure 6. AFM images of a $5 \times 5 \mu\text{m}^2$ region of $n\text{-Cu}_2\text{O}$ thin films electrodeposited for 45 min (a) before sulphidation, (b) after sulphidation by placing a thin layer of 0.01 M Na_2S at 200°C and (c) sulphidation followed by film treatment to 50 vol.% $(\text{NH}_4)_2\text{S}$ vapor for 5 s at 27°C .

Table 1. Peak-to-valley R_{pv} , root mean square roughness R_q , average roughness R_a and maximum peak height R_z , skewness R_{sk} , kurtosis R_{ku} values of Cu_2O thin films with and without surface treatments.

Sample type	Roughness parameter					
	R_{pv} (nm)	R_q (nm)	R_a (nm)	R_z (nm)	R_{sk}	R_{ku}
Bare Cu_2O thin film	374	90	75	259	-0.441	2.55
Sulphided Cu_2O thin film	263	69	60	191	-0.236	1.99
Sulphided and $(\text{NH}_4)_2\text{S}$ vapor treated Cu_2O thin film	427	96	77	287	-0.637	3.00

temperatures. Figure 7 shows the response measurements of sulphided $n\text{-Cu}_2\text{O}$ thin films obtained as a function of operating temperature (45°C – 100°C). It is seen that the response increases with temperature yet does not recover upon stoppage of LP gas flow.

Figure 8(a) shows the reproducible response obtained for sulphided and $(\text{NH}_4)_2\text{S}$ vapor treated $n\text{-Cu}_2\text{O}$ thin films for repeated LP gas on/off cycles. Measurements were made at 45°C with a maximum response of $(48 \pm 2)\%$. Figure 8(b)

shows the response during a single LP gas on/off cycle as a function of operating temperature (30°C – 120°C) it is seen that the response maximizes at 45°C . It is also worth noting that the thin films also showed response at temperatures near room temperature (30°C). The measured response and recovery times were approximately 60 s and 40 s respectively. These times are comparatively lower compared to most of the other metal oxide LP gas sensing platforms reported. The lowest response time of 15 s was reported for Pd doped ZnO

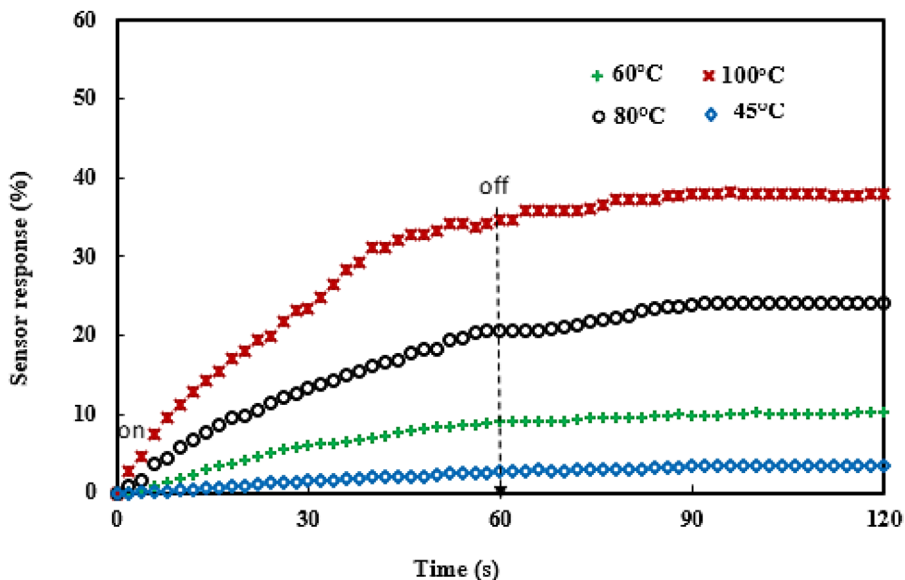


Figure 7. Sensor response (%) variation of an *n*-Cu₂O thin film after sulphidation (45 min deposited and by placing by placing a thin layer of 0.01 M Na₂S at 200 °C) at different sensor operating temperatures. Gas is turned off after 60 s.

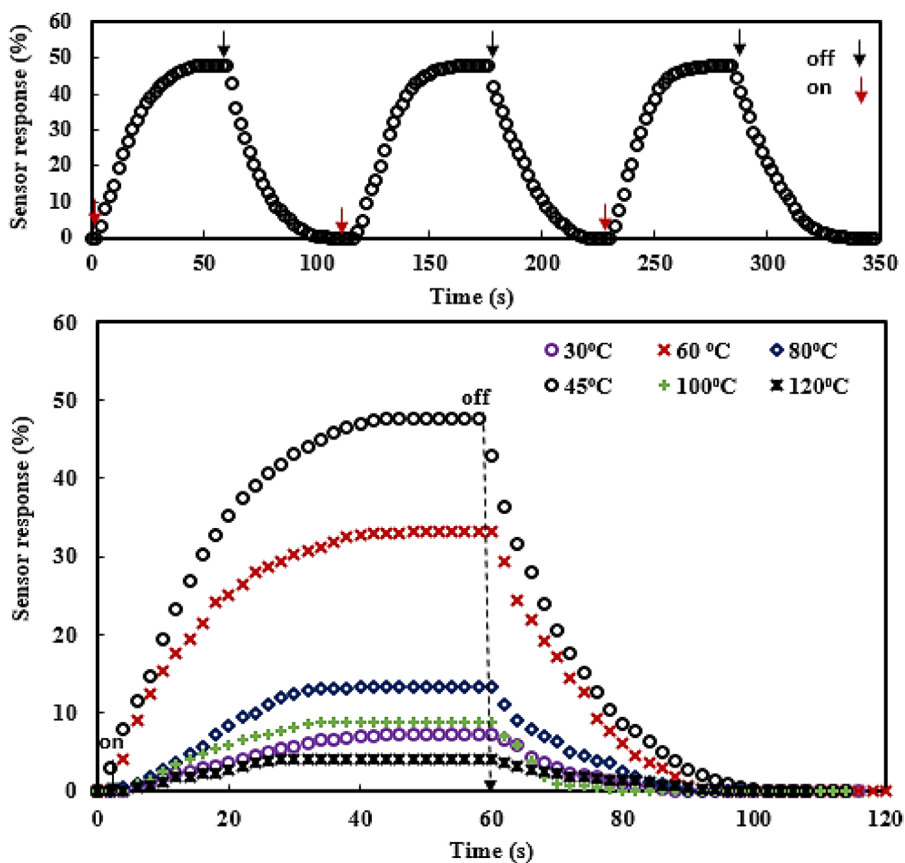


Figure 8. (a) Repeated cycles of maximum sensor response (%) variation of an *n*-Cu₂O thin film after sulphidation and (NH₄)₂S vapor treatment (45 min deposited and by placing three drops of 0.01 M Na₂S at 200 °C and with 5 s exposure time of (NH₄)₂S vapor) at different sensor operating temperatures measured at 45 °C, the temperature that corresponds to the maximum response of 48%. (b) Sensor response measurements as a function of sensing temperature of the thin film structure, the arrows indicate the time at which the gas supply was turned OFF.

[16]. While the highest reported response time is as much as 8 min for ZnO nanosheets of size 20–60 nm [41]. The typical response/recovery times in the order of ~100 s has been commonly reported for materials such as, *n*-Cu₂O microcrystalline (~1 μm) and *n*-Cu₂O nano-cubes (~150–300 nm) [22], TiO₂ interconnected web-like structures [42], CdO nanorods with thickness ~30–50 nm [43] and SnO₂ spherical grains of minimum crystallite size ~14 nm [44].

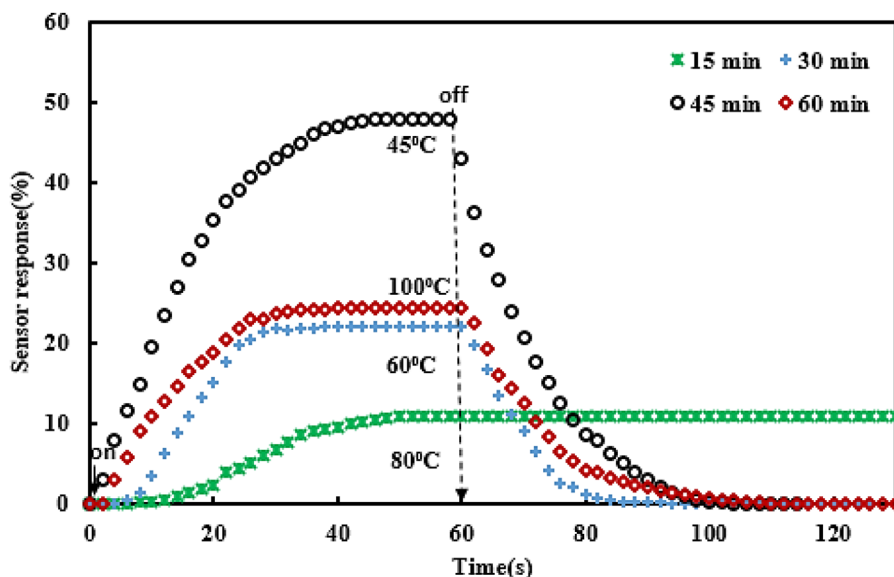


Figure 9. Sensor response (%) for sulphided and vapor treated (by placing a three drops of 0.01 M Na₂S at 200 °C and followed by exposure to 50 vol.% (NH₄)₂S vapor for 5 s at 27 °C) *n*-Cu₂O thin film structure showing LP gas sensing properties, with different *n*-Cu₂O deposition times.

Importantly, (NH₄)₂S vapor treatment has enabled the films to recover upon stoppage of the LP gas flow. Furthermore, these films are able to produce maximum response at a relatively low operating temperature. The results suggests that the partial wetting nature introduced by (NH₄)₂S vapor treatment had facilitated the recovery. It may be possible that desorption of adsorbed LP gas molecules becomes higher with increasing temperatures. This means that even though the gas response initially increases with temperature, upon reaching a maximum it decreases. This is a remarkable improvement compared to the bare *n*-Cu₂O thin films which were non-wetting and that had a response of only 4% at 85 °C in the presence of LP gas [21]

It is also worth observing the response curves for *n*-Cu₂O thin films grown using different deposition times (different film thicknesses) where, it is seen (in figure 9) that except for the film deposited for 15 min all the other films were able to recover to ambient resistance after the stoppage of LP gas flow.

Examination of the angle of contact measurements (see figure 5 or table S1) shows that the angle of contact for sulphided and (NH₄)₂S vapor treated *n*-Cu₂O thin film fabricated for 15 min, is 22° (<30°), which corresponds to a wetting surface. On the other hand the angle of contact measurements of sulphided and (NH₄)₂S vapor treated *n*-Cu₂O thin films fabricated for 30 min, 40 min and 60 min respectively have yielded values ≥30° and hence, partially wetting surfaces that enables effective desorption of H₂O produced during the sensing step resulting in good recovery characteristics.

The reaction mechanism of LP gas with the film surface has been discussed in detail elsewhere [22]. Initially, when the films are exposed to atmosphere, adsorption of oxygen causes film resistance to change and eventually to equilibrate. Physisorbed H₂O is eliminated from the surface and surface hydroxide groups are converted to oxygen species such as O₂, O₂²⁻, O⁻ and O²⁻. While the formation of such

polar molecular species on the surface would be regulated by the underlying surface atomic structure, surface wettability modifies the strength of adsorption of such polar molecular species on the surface. The gas response originates due to the reaction of LP gas molecules with the above surface oxygen species. Subsequently, the reaction of hydrocarbons with surface oxygen species causes the depletion of surface oxygen species and widening of the depletion layer leading to an increase in the film resistance. In such a system, the rates of adsorption/desorption for LP gas molecules and the products formed during sensing will be influenced by both the surface wettability and the kinetic energy (dependent on temperature) of the LP gas molecules [45, 46].

Therefore, results are consistent with the fact that the alteration of surface wettability by the (NH₄)₂S vapor treatment facilitates the desorption of surface reaction products (C_nH_{2n}-O, H₂O, CO₂) and releasing back of electrons [21, 22] from the film surface to enable the sensor to efficiently recover in the absence of LP gas flow. Thus, it can be seen that the maximum response observed around 45 °C is controlled by the wetting nature of the film surface which affects the adsorption and desorption kinetics of LP gas at different temperatures. While, the increasing temperature encourages absorption of LP gas molecules to the film surface, partially wetting nature of the surface facilitates the desorption which becomes increasingly significant at higher temperatures. As a result, even though the gas response initially increases with temperature, upon reaching a maximum it decreases. It is also worth mentioning that in the previously reported [28] work on LP gas sensing using sulphidation and (NH₄)₂S treatment, the sensing mechanism was proposed with the possible interaction of the underlying heterostructure, Cu_xS/Cu₂O. However, with our improved understanding about the surface properties through angle of contact and AFM roughness measurements, it is now possible to propose a simpler sensing mechanism as explained above, which only involves interactions occurring on the surface of the film.

4. Conclusions

The effect of surface modification through sulphidation (with Na₂S) followed by (NH₄)₂S vapor treatment of electrodeposited *n*-type cuprous oxide (*n*-Cu₂O) thin films on Ti substrates were investigated and films were successfully used for the detection of LP gas. XRD measurements confirmed that the films were of single phase. After (NH₄)₂S treatment, a thin layer of S was formed on the film surface. The observed wetting nature (low contact angles <30°) of sulphided films is correlated with the availability of high amount of Na (leads to high polar interactions) on the surface. Though, sulphided films showed a higher response in the presence of LP gas compared to bare *n*-Cu₂O, it lacked the ability to recover the response in the absence of LP gas. However, the subsequent (NH₄)₂S vapor treatment of sulphided thin films altered the thin film surface to a partially wetting surface (contact angles, 30°–89°) by forming a thin layer of S and resulted in its all-important ability to recover. Roughness measurements made using AFM and SEM studies revealed the enhancement of surface porosity (thus surface area) upon (NH₄)₂S vapor treatment. As a result, the thin film when exposed to LP gas, recorded a maximum response (fractional change of resistance) of 48% at a relatively low sensing temperature of 45 °C (while responsive at 30 °C), in comparison, bare *n*-Cu₂O films had maximized response to 4% when operated at 85 °C. Therefore, S based surface modifications not only can be efficiently used to improve *n*-Cu₂O light harvesting and electrical transport properties as previously demonstrated, but also allows modulation of surface wettability that affects the adsorption/desorption kinetics of surface interacting species as well as increases the surface area to improve overall response in LP gas sensing at temperatures close to room temperature.

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