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THIN FILMS OF COPPER OXIDE NANOSTRUCTURED VIA RAPID THERMAL PROCESSING

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Abstract. Nanostructured copper oxide films were obtained by the method of chemical synthesis from solutions (SCS) and exposed to post-growth rapid thermal processing (RTP) in air at different temperatures to study the influence of annealing temperature on morphological, chemical, structural and sensing properties. Controlled modification of surface morphology, in the particular size of nanostructures, crystallinity and phase can be achieved by RTP, which is preferred due to saving of energy budget nowadays. Detailed physico-chemical analysis of the films was performed using the scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman and energy dispersive X-ray (EDX) techniques. Sensors based on the copper oxide nanostructured films after RTP for 30 s only were tested with 100 ppm hydrogen gas at an operating temperature range from 250 ºC to 350 ºC. The difference

in the response to 100 ppm hydrogen gas of the sensors based on thermally processed films at different temperatures was determined. We also noted that the change in the response of the sensing structure is correlated with its surface morphology controlled by RTP regime with a short duration. A detection mechanism to hydrogen gas has been proposed as well.

Keywords: *copper oxide, nanostructures, SCS, rapid thermal processing, DFT.*

Rezumat. Peliculele de oxid de cupru nanostructurat au fost obținute prin metoda sintezei chimice în soluții (SCS) și expuse după depunere la tratament termic rapid (RTP) în aer la diferite temperaturi pentru a studia influența temperaturii tratamentului termic asupra proprietăților morfologice, chimice, structurale și senzoriale. Modificarea controlată a morfologiei suprafeței, în particular a dimensiunii nanostructurilor, cristalinității și fazei au fost obținute cu ajutorul RTP, care este preferat datorită necesității consumului de energie în prezent. Analiza fizico-chimică detaliată a peliculelor a fost realizată cu ajutorul microscopului electronic de baleiaj (SEM), difracție cu raze X (XRD), Raman și tehnici pe baza dispersiei razelor X (EDX). Senzorii pe baza peliculelor de oxid de cupru nanostructurat după RTP numai de 30 s au fost testate la 100 ppm hidrogen la temperaturi de operare între 250 °C și 350 °C. Diferența în răspuns la 100 ppm hidrogen a senzorilor bazați pe peliculele tratate termic rapid la diferite temperaturi au fost determinate. Noi am observat că modificarea în răspuns a structurilor senzoriale corelează cu morfologia suprafeței controlată de regimul RTP cu durată foarte mică. De asemenea, un mecanism de detecție a hidrogenului a fost propus și confirmat prin calculele DFT.

Cuvinte cheie: o*xid de cupru, nanostructuri, SCS, tratament termic rapid, DFT.*

1. Introduction

Copper oxides are non-toxic and can be synthesized by various simple and low-cost methods. The low-dimensional structures of copper oxides (CuO and Cu_2O) with high surface-to-volume ratio have been used in various fields such as photovoltaics, gas sensing of volatile organic compounds and toxic gases, lithium-ion batteries, electrochromic devices, super-capacitors, field emission devices, non-enzymatic biosensors for glucose detection, antimicrobial applications, microfluids and photo catalysis [1, 2].

Copper oxide can have two oxidation states and three crystalline phases with distinct parameters: pure CuO or Cu (II) cupric oxide with monoclinic crystalline structure, pure Cu_2O or Cu (I) oxide with cubic crystalline structure oxide, and Cu_4O_3 paramelaconite, a mix of Cu (II) and Cu (I) with tetragonal crystalline structure. The more stable phases at relatively high temperature (up to 500 ºC, which is suitable for gas sensing applications) and ambient pressure are CuO and Cu_2O [1, 2].

Various methods for the growth of copper-based nano- and micro-oxide materials were developed, such as chemical based synthesis methods [3], thermal decomposition [1-3], thermal oxidation of Cu metal [4], etc. The controlled post-growth modification of surface morphology, in particular size of nanostructures, crystallinity and phase can be achieved by thermal processing at different temperatures and duration. Nowadays, rapid thermal processing is preferred due to energy efficiency nowadays. For example, by rapid thermal processing of Cu_2O films the non-planar CuO/Cu_2O with unique gas sensing properties heterostructures was reported [2,4]:

$$2Cu_2O + O_2 \rightarrow 4CuO \quad (1)$$

The choice of methods for obtaining the detector surface is an important step to realize the gas detectors with necessary properties. The morphology of the obtained surface determines the ratio of surface area to volume, which determines the amount of gas that reacts at a given time, which in turn determine the conductivity of the sensor with and without the gas atmosphere. The surface morphology significantly affects not only the sensitivity of the sensor, but also indicative characteristics such as the time-dependent response of the sensors, the long-term stability, the selectivity and the optimal operating temperature [5].

Homogeneous detection surfaces with a well-defined structure can be obtained by direct synthesis of the Cu_2O oxide phase, or by the temperature reduction reaction of Cu_2O to CuO. Copper oxide in the CuO phase is a semiconductor with a *p*-type electrical conductivity and a bandwidth of approximately 1.1-2.0 eV, which has been widely implicated in VOCs gas detection tasks [6]. In this context, single crystalline CuO nanowires demonstrated high performance for the detection of ethanol vapors, even at room temperature [7]. It is also known that copper oxide is an excellent catalyst for volatile organic compounds, and thus they were used for the detection of hydrogen, mainly by surface metallization, due to its very active surface [7]. The oxidative dehydrogenation process and mechanism of ethanol (C_2H_5OH) molecules and oxidation of acetaldehyde molecules were recommended and illustrated in previous work [8]. Experimental studies demonstrated that the morphology of the oxide surface affects the selectivity of the sensor. Thus, morphology control by post-deposition rapid thermal annealing (RTA) for a short duration is an interesting topic for research. Here, the hydrogen gas sensing properties of prepared structures based on CuO/Cu_2O films have been studied and presented in detail. Density Functional Theory (DFT) based calculations have presented insights into H_2 gas sensing on CuO surfaces.

2. Experimental

A. Synthesis of CuO/Cu_2O and Characterization

Copper oxide (Cu_2O) layers were synthesized on glass/quartz substrates by growth from chemical solutions, which was described in detail in a previous paper [8]. The growth solution is mixed on the basis of copper thiosulphate, as a cationic precursor, in which 1 M of Cu sulphate pentahydrate ($CuSO_4 \bullet 5H_2O$) and 1 M Na thiosulfate ($Na_2S_2O_3 \bullet 5H_2O$) were mixed. The complex solution is diluted to 0.1 M Cu ion using deionized water (DI). The complex anion solution consists of 2 M NaOH. Single SCS cycle of Cu_2O thin film deposition can be described as follows: immersion of the glass in anion solution for adsorption of hydroxyl groups, then immersion of the same glass in the Cu^+ ions solution for reaction with OH^- groups. An experimentally elaborated graph is used to control the film thickness. The optimal film thickness was determined to be 0.7 μm [8]. After chemical deposition of the nano-layers, rinsing in DI water takes place and finally exposed in a stream of hot air (~ 150 ^oC) for 1 min.

The rapid thermal processing (RTP) method is used to change the surface morphology and the crystal phase composition of the copper oxide nanostructured films. The samples were exposed for 30 s at different temperatures (650 ^oC, 700 ^oC and 750 ^oC) by using a high-intensity infrared emitting *lamp*s, followed by deposition of gold contacts for electrical connection and studies of gas sensing properties. This short period of RTP allows us to save

the thermal budget for technological processes significantly if compare with previous works [9, 10].

The electrical measurements of the sensors were carried out by the two-probe method in a homemade installation. The electric current as a function of the gas pulses applied to the surface of the nanostructured films was recorded using the Keithley 2400 sourcemeter. The electrical resistance was measured under the ambient atmosphere and under influence of the hydrogen gas at relative low concentration (100 ppm). The relative humidity was the same as in the ambient (40%), and was measured using an electronic hygrometer [9].

Hydrogen was chosen as a test gas with a flow rate of 500 sccm (ml/min), generated using a pre-calibrated mass flow controller [10] and the gas concentrations were controlled using the following expression [11, 12]:

$$C(ppm) = \frac{C_1 * F_{gas}}{F_{tot}}, \quad (2)$$

where: C is the necessarily gas concentration; C_1 is the initial concentration *(ppm)* of the tested gas; F_{gas} is the flow of the H_2 gas; and F_{tot} is the final flow of the mixed gases.

B. Computational Methodology

We used the Vienna ab initio simulation package (VASP) employing a plane-wave basis set [13-16], the projector augmented wave (PAW) method for depicting the ions and electrons interactions [17], and Perdew– Burke–Ernzerhof functionals [18, 19] to evaluate the nonlocal exchange -correlations. We used DFT+U method to treat strong correlations through the Hubbard model in the Dudarev formalism [20] for modelling copper oxides, as this was found to predict accurate structural, electronic magnetic as well as surface properties in our earlier works [21, 22]. Here, we used a more accurate method of dispersion corrections, i.e. DFT-D3 approach by Grimme [23], while all other details related to computations remain unchanged [21, 22].

3. Results and Discussion

A. Morphological characterization

After the post-deposition rapid thermal processing (RTP), the color of the deposited film has visually changed. Figure 1 shows the SEM image of RTP copper oxide films at 650 °C for 30 s. The scale bars on the SEM images are 200 nm. It can be demonstrated that the surface morphology of the film shows a conglomeration of interconnected nano-crystallites with random shape with a diameter of about 200 nm. It can be observed that in the SEM image of the nanostructured copper oxide film with RTP at 700 °C for 30 s, the nano-crystallites have the same structure in the environment, but locally agglomerations of nano-crystallites with a diameter of 100-150 nm are observed. The edge of nano-crystallites can be observed. In a previous work [24], it was demonstrated that the processing at a higher temperature than 700 °C with a treatment time of 60 s will lead to the formation of crystals highlighted more strongly, which achieve a defined form. Thus, we can assume that differentiation of the surface morphology is dependent on both the RTP temperature and time.

In figure 2 (a) the SEM image of the copper oxide film with rapid thermal processing at 700 °C for 30 s is depicted, showing the morphology of the film. In figure 2 (b), the energy dispersive X-ray (EDX) mapping analysis of copper oxide was performed; showing roughly even distributed copper (Cu) and oxygen (O) atoms.

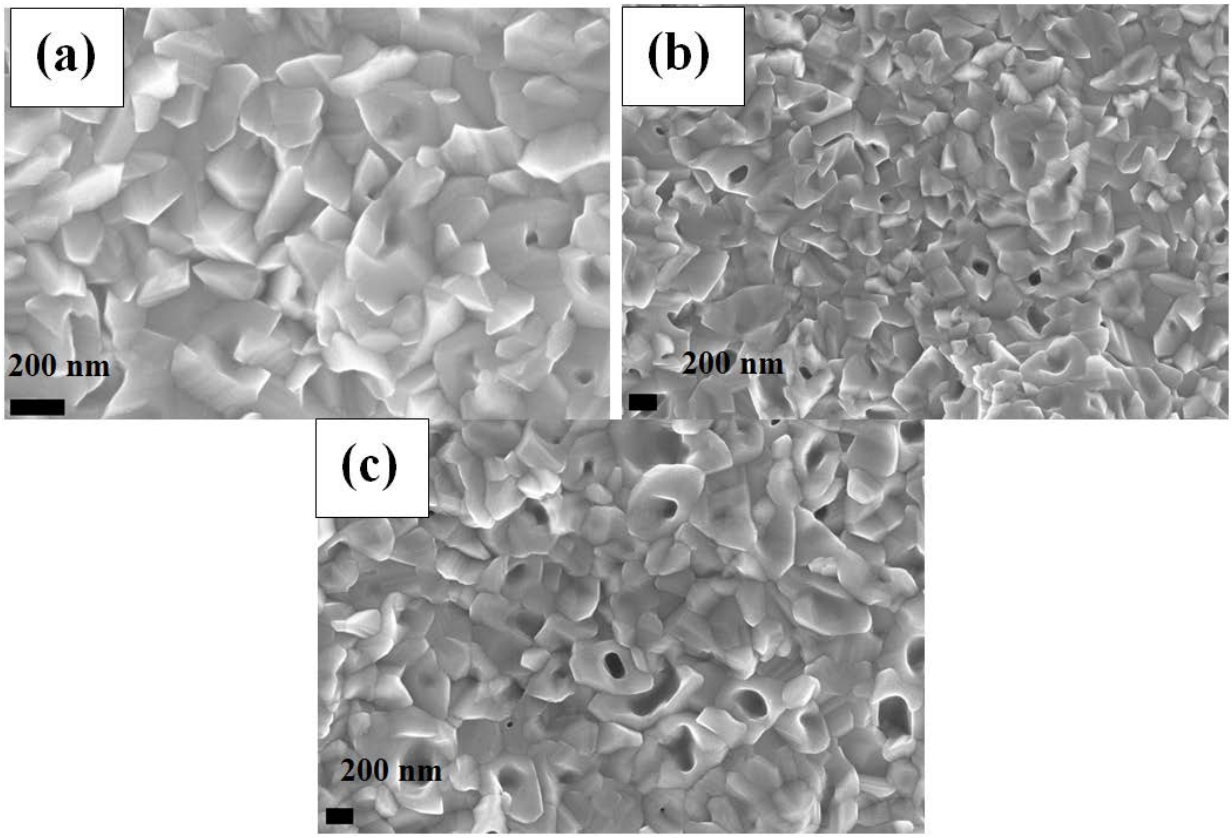

Figure 1. SEM image of Cu_2O/CuO thin nano-layers synthesized by SCS method and hermally processing after deposition at: (a) 650; (b) 700; (c) 750 °C by RTP method for 30 s.

B. Energy dispersive X-ray characterization

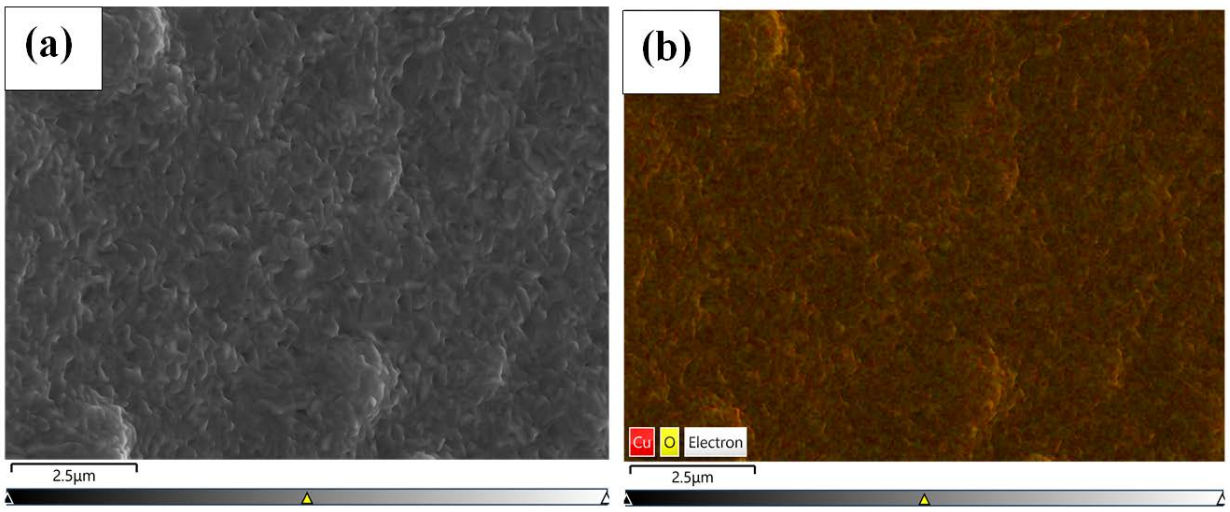

Figure 2. Energy dispersive X-ray (EDX) mapping analysis of copper oxide (CuO) film with rapid thermal processing at 700 °C (R700): (a) SEM image of the film for EDX mapping; (b) EDX mapping of the detected elements.

In figure 3, the individual EDX map of the detected elements copper and oxygen are presented, showing that these are distributed evenly on the surface. In figure S1, a line-scan EDX mapping of the copper oxide (CuO) film with RTP at 700 °C (R700), and results of the measurements are summarized in table 1, showing the atomic % of detected elements. On this film oxygen at% are slightly higher than the ones of copper.

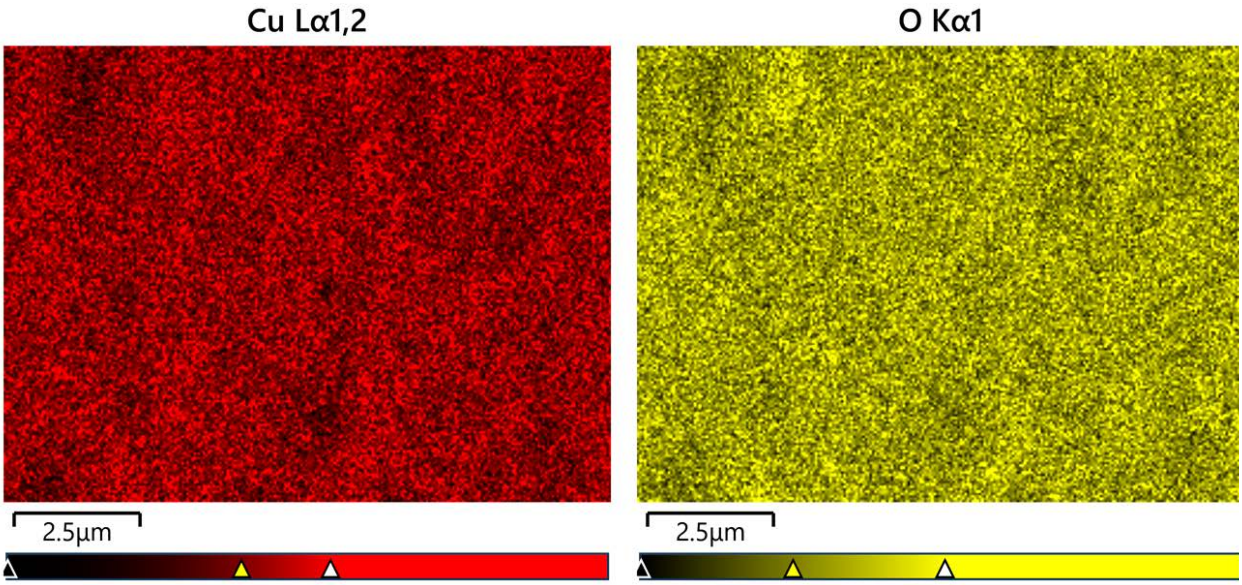

Figure 3. EDX mapping of individual elements on the copper oxide (CuO) film with rapid thermal processing at 700 °C (R700) for 30 s.

Table 1

Distribution of detected elements on the copper oxide (CuO) film with rapid thermal processing at 700 °C (R700 sample set)

Element	At%
O	54.72%
Cu	45.28%
Total	100%

C. XRD and Raman part characterization

X-ray diffraction (XRD) and micro-Raman spectra were used to analyze the crystal structure of copper oxide films at different rapid thermal processing temperatures. Figure 4 (a) shows the XRD patterns of CuO films with rapid thermal processing at 650 °C (curve 1), 700 °C (curve 2), and 750 °C (curve 3).

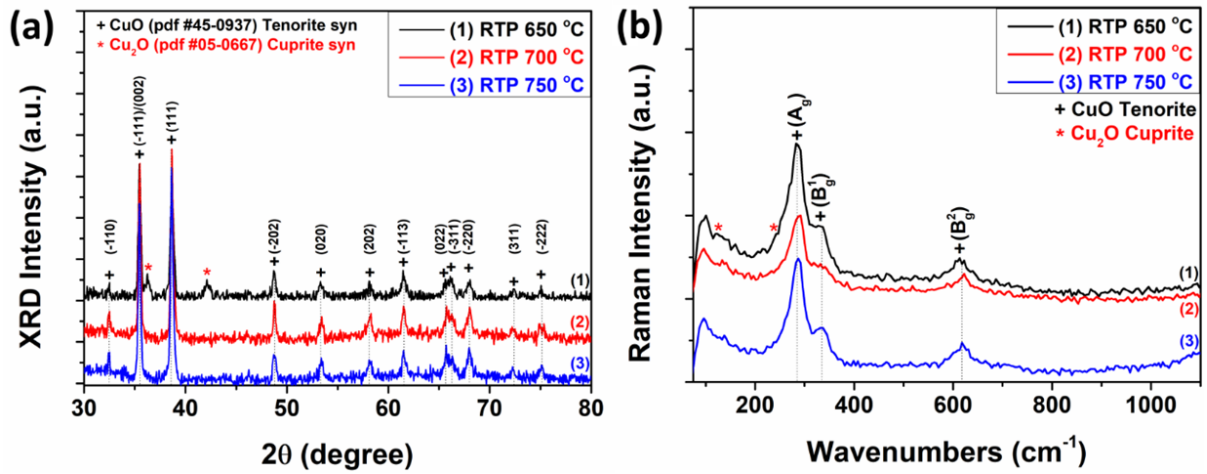

Figure 4. (a) XRD patterns and (b) micro-Raman spectra scanned of CuO films with rapid thermal processing of 650 °C (curve 1), 700 °C (curve 2), and 750 °C (curve 3).

From the Figure 4 (a) it can be seen that in the case of samples after RTP of 650 °C (curve 1), reflections at 2θ of 36.25° and 42.1° are assigned to the Cu_2O (Cuprite) phase, and at temperatures above of 700 °C (curve 2), and 750 °C (curve 3), these reflections disappear, which would mean the transition of the phase of Cu_2O (Cuprite) in CuO (Tenorite) phase. Cu_2O has a cubic crystalline structure with a space group $T_h^2 - Pn3[65W]$ or $O_h^4 - Pn3[72P]$, and the parameters of the unit cell are: *a* = 4.27 Å at *p*≈0 GPa, *a*= 4.18 Å at *p*≈10 GPa [82W], [10]. For all RTP regimes, the reflections (*hkl*) attributed to the CuO phase (Tenorite) were found, which correspond to the indices of the crystal lattice (-110), (-111)/(002), (111), (-202), (202), (-113), (022), (-311), (-220), (311), (-222) and (-131) Miller planes at 2θ values of 32.5°, 35.45°, 38.65°, 48.7°, 53.3°, 58.1°, 61.45°, 65.75°, 66.1°, 68.05°, 72.4° and 75.05°, respectively. CuO has a crystalline structure in monoclinic symmetry with the *C2/c* space group [10, 25] and lattice constants *a* = 4.684 Å, *b* = 3.423 Å, *c* = 5.129 Å, and β = 99.54° [10, 26].

To confirm XRD data, micro-Raman studies were performed. Figure 4 (b) shows a micro-Raman spectrum of CuO films with RTP at 650 °C (curve 1), 700 °C (curve 2) and 750 °C (curve 3). From Figure 4 (b) it can be seen that for samples with RTP at 650 °C (curve 1) five peaks are observed, where the three at the wavelength of about 287, 331 and 617 cm^{-1}, can be attributed to the CuO phase, and two peaks at the values of about 124 cm^{-1} and 242 cm^{-1} can be ascribed to the Cu_2O phase [10]. Also, from Figure 4 (b) it can be seen that at RTP of 700 °C (curve 2), and 750 °C (curve 3), the Cu_2O phase disappears, which would demonstrate the transition of the Cu_2O phase to the CuO crystal phase at temperatures higher than 650 °C for 30 s, which is in agreement with XRD data.

D. Gas sensing properties

For the investigation of the gas sensing properties of the CuO/Cu_2O nanostructured films, the meander-shaped gold contacts with an inter-distance of 0.9 mm were deposited on the surface of the samples. The response was investigated in atmospheric air towards 100 ppm of hydrogen gas at different temperatures. The response to gas was determined as the ratio of the sample electrical currents under exposure to ambient (I_{air}) and under exposure to hydrogen gas (I_{gas}):

$$S = \frac{I_{air}}{I_{gas}} \tag{3}$$

In figure 5 is compared hydrogen gas responses of the copper oxide sensors with different rapid thermal processing temperatures at different operating temperatures. The concentration of hydrogen gas is 100 ppm. The operating temperatures are 250 °C, 300 °C and 350 °C. At these three operating temperatures, all the investigated samples showed a high response to hydrogen gas after RTP regime. At lower operating temperatures the sensors show negligible responses to hydrogen gas, and therefore were not included.

At operating temperatures of 300 °C, the maximum response to the hydrogen atmosphere is observed for all three types of investigated sensor structures. Thus, at the indicated optimal operating temperature the samples with RTP at 650 °C, 700 °C, and 750 °C have a response of 3, 3.7, and 3.5, respectively.

The dependence of the gas sensitivity on the RTP temperature and the operating temperature (OPT) is obvious. From Figure 5 we can conclude that, in the case of H_2 measurement, the highest response demonstrates the thin films subjected to RTP at 700 °C and OPT 300 °C.

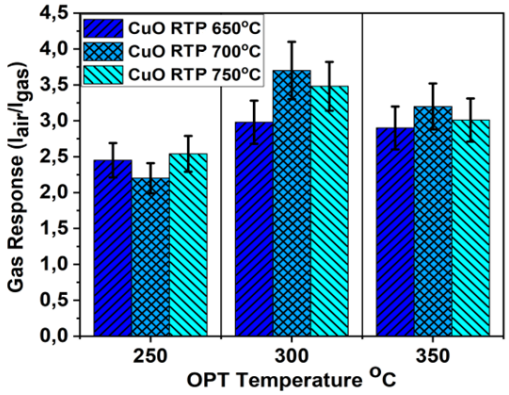

Figure 5. Responses of copper oxide nanostructured films with RTP at 650 °C, 700 °C and 750 °C in air to 100 ppm of H_2 gas versus operating temperature.

The higher gas response for samples with RTP of 700 °C can be attributed to the transition from Cu_2O phase to CuO phase in the RTP temperature range of 650 °C–700 °C by controlling the thickness ratio between CuO and Cu_2O layers, demonstrated by Lupan et al. [8].

Figure 6 shows the dynamic H_2 response of Cu_2O/CuO nanostructured films with RTP at 700 °C at an OPT of 300 °C. Two pulses of H_2 gas were applied to verify the repeatability of the device structures. All pulses indicate a response of ~ 3.7 with an error rate of no more than 10%. The response time from the application of the gas atmosphere to the gas response of 3.3 is ~ 14 s. Recovery of the sample from the maximum value up to the ratio of 1.37 takes place in 20 s.

It was also noted that the response curve does not return to the unit ratio in a reasonable time, probably due to the adsorption/desorption of gas species that takes place slowly on the surface of the films during hydrogen exposure.

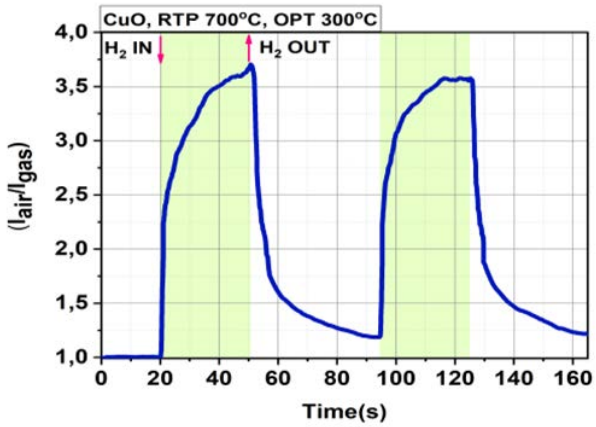

Figure 6. Dynamic hydrogen gas response of Cu_2O/CuO nanostructured films with rapid thermal processing at 700 °C for 30 s and working temperature OPT of 300 °C.

E. Proposed Hydrogen Gas Sensing Mechanism

The value of the response of CuO is mainly dependent on the type of surface vacancies, morphology and different impurities formed on the top of the nanostructured film [27]. Thus, we can say that surface phenomena play a critical role in the gas detection mechanism for the semiconductor metal oxides with *p*-type conductivity, like CuO.

Oxygen species at the crystal facets are absorbed in molecular form O_2^- or in atomic form O^-/O^{2-}. At temperatures below 200 °C, the majority species on the oxide surface are O_2^- [28]:

$$O_{2(g)} \rightarrow O_{2(ad)} \quad (4)$$

$$O_{2(ad)} \rightarrow O^{-}_{2(ad)} + h^{+}_{(lattice)} \quad (5)$$

At the same time, for OPT above 200 °C, the dominant species are O^- or O_2^- [28]:

$$\frac{1}{2}O_{2(ad)} \rightarrow O^{-}_{(ad)} + h^{+}_{(lattice)} \quad (6)$$

Adsorbed O^- or O_2^- generates the surface states with acceptor effect and captures electrons (e^-) from the valence band, and as a result the concentration of the holes (h^+) increases and the electrical resistivity decreases. For *p-type* semiconducting metal oxides at the surface, the holes accumulation layer is generated. The thickness of this region is directly proportional to the Debye length (λ_D) [8]. The conduction of electrical current takes place through the region of the accumulation layer, while the internal site of the oxides have a higher electrical resistance. The following reactions occur when semiconductor oxide is applied to the atmosphere with hydrogen (we assume that $h^+ + e^- = Null$) [28]:

$$H_{2(g)} + O^{-}_{(ads)} + h^{+} \rightarrow H_2O_{(g)} + Null \quad (7)$$

After placing the *p-type* semiconductor oxides in the atmosphere with the presence of H_2 gas, the electrical and chemical interaction between the O^- species and the hydrogen will take place. With the release of e^-, the e^- recombines with the surface h^+, which leads to the decrease in the holes accumulation layer and accordingly to lower electric current flowing through the crystallites.

The generated temperature at the surface of the films is one of the most important conditions of its work, it ensures the activation of adsorption-desorption processes that take place on the surface of the sensitive film of metal oxide. The operating temperature largely determines the selectivity and sensitivity of the *p-type* semiconducting metal oxides to a certain gas. This is dependent on the different activation energies of the adsorption processes for various gas species.

At an operating temperature lower than the optimal operating temperature, the desorption of the resultant reaction elements between the oxygen adsorbed on the surface and the reducing gas will be slower or will be absent at all, so that the surface will not recover for the subsequent adsorption of the gas. At a temperature higher than the optimal OPT, the gas does not absorb on the surface of the semiconductor oxide. Vacancies in the structure of the crystal facets of oxide have gas adsorption centers that allow changing in the response.

Another method of controlling the sensitive and selective properties is to change the surface morphology. It modulates the response according to the surface/volume principle. This approach is effective for both types of conductivities [8].

Post-growth thermal process at different temperatures allows the formation of various morphologies with the formation of crystallites with different dimensions and shapes that affect and permits control on the sensing mechanism.

Furthermore, it has been determined that the morphology with a smaller diameter of crystallites has better gas detection properties [28, 29]. The smaller diameter of the crystallites has a higher surface-to-volume ratio which results in the concomitant reaction of a larger number of *oxygen* species, which ultimately leads to improved gas detection properties [28].

F. DFT Calculations: H_2 gas molecule interaction with copper oxides

The exact oxidation state of copper oxide is challenging to determine as it consists of mixed phases of Cu_2O and CuO. The (111) plane has been found to be the most dominant plane in Cu_2O as well as in CuO morphologies [21, 22]. In our recent works based on DFT+U Hubbard parameter approach simulations, we found that U_{eff} = 7 eV value is appropriate to model both phases of copper oxide. Here, we used the same methodology to model the copper oxide surfaces, where we kept 3 top layers fixed to their bulk positions in 5 layers model of Cu_2O, while top two layers were fixed in 4 layers model of CuO (111) surface.

The Cu_2O (111) top surface consists of saturated and coordinatively unsaturated copper atoms, where most of the surface reactions take place at these coordinatively unsaturated copper atoms, acting as Lewis acid sites [30]. Here, H_2 molecule interacts with the surface through this copper atom as shown in figure 7, with interaction energy of -51.4 kJ/mol, making bonds of about 1.61 Å with the surface.

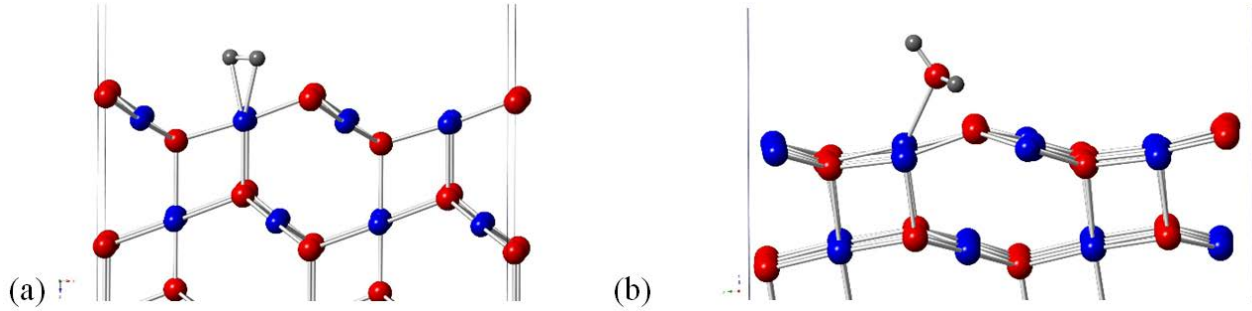

Figure 7. (a) H_2 molecule interaction with (a) Cu_2O (111) surface and (b) CuO (111) surface. Red and blue color balls indicate O and Cu atoms, while H atoms are represented by small grey color balls.

We next investigate the behaviour of H_2 gas molecule over CuO (111) surface, consisting of 3- and 4-coordinated copper and oxygen atoms in the top surface layer. As soon as H_2 gas molecule comes in contact with most exposed surface oxygen atoms, it forms molecularly adsorbed water molecule over the surface as shown in figure 7b. Here, H_2 molecule exhibits interaction energy of -55.3 kJ/mol, resulting in the reduction of the copper oxide surface.

We found that H_2 gas molecule interacts with both copper oxides with almost the same binding energy, whereas water molecules are expected to be formed as a result of H_2 gas molecule interaction with pristine CuO phases, resulting in the reduction of copper oxides.

4. Conclusions

Hydrogen is extensively used in research laboratories, biomedical systems, and auto transportation areas. In this work, the copper oxide nanostructured films were developed and investigated as hydrogen gas sensors. The aspect of controlling the response of the sensor structure by modifying the operating temperature of the film in the range of 250-350 °C and changing the post-deposition RTP temperature in the range of 650-750 °C for only 30 s has been demonstrated.

It was established that for the detection of relative low concentrations of hydrogen (100 ppm), the most optimal rapid thermal processing is at a temperature of 700 °C for 30 s. In this case, the structure showed a gas response of 3.7 at the operating temperature of 300 °C with the response and recovery times of about 14 s and 20 s, respectively.

It was observed that the film sensitivity is changed depending on its surface morphology, determined by the RTP temperature and time. EDX, XRD and Micro-Raman investigations demonstrated the transition of the film from the tenorite-cuprite mixed phases structure to the film with a surface tenorite structure at 700 °C for 30 s. Compared to the conventional thermal processing of CuO films in furnace described in [31], there is a significant enhancement in hydrogen sensitivity and an enormous energy budget saving. The proposed gas detection mechanism of oxides has been expressed. DFT found that H_2 gas molecule interacts with both copper oxides with almost the same binding energy. We consider that these results will be of a big interest for the elaboration of nanotechnology for low-energy-budget-oxide based detectors by a cost-effective approach and to develop a sensing mechanism.

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Conflicts of Interest: The authors declare no conflict of interest.

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Supporting Information

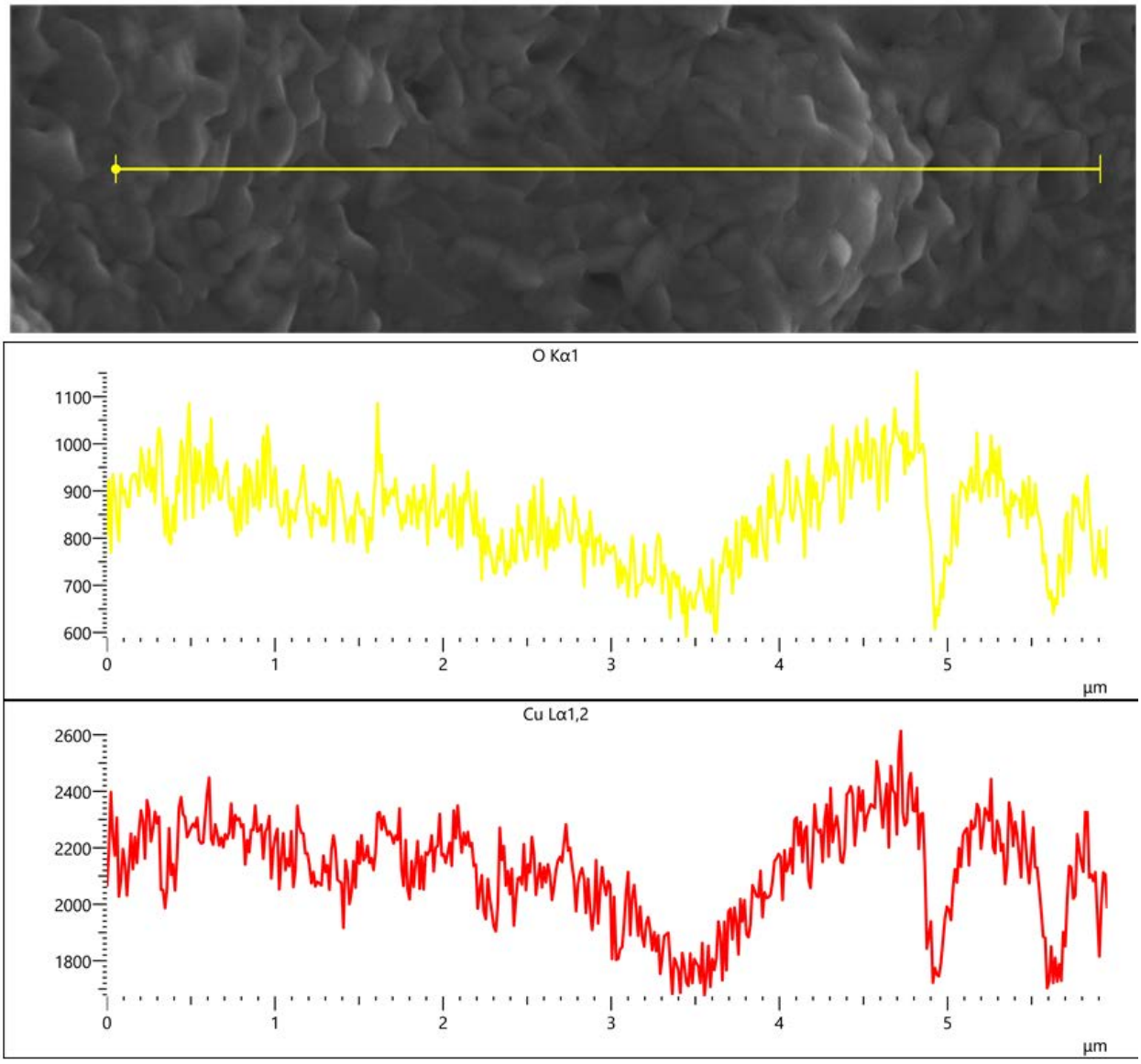

Figure S1. Linescan EDX mapping of the copper oxide (CuO) film with rapid thermal processing at 700 °C (R700).