PREPARATION OF CUPROUS OXIDE THIN FILMS BY CHEMICAL DEPOSITION AND RAPID PHOTOTHERMAL PROCESSING

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INTRODUCTION

Thin films are well known for their applications as materials for different semiconductor devices manufacturing. Thin film technology is widely used to improve optical, electrical and mechanical proprieties, as well as to produce materials with proprieties that could not be obtained in bulk materials.

Cuprous oxide (Cu_2O) thin films that is a non-toxic material is potentially attractive for photovoltaic cells and sensor applications [1-3]. The present work report the formation of homogeneous conductive Cu_2O thin films by chemical bath deposition technique and improvement of their characteristics by rapid photothermal processing. Also a procedure that improves the efficiency by irradiating UV light during the chemical growth of the Cu_2O films is presented. Results of the investigations of the Cu_2O thin films and their gas sensing characteristics in the presence of sulfates and air pressure were evaluated.

1. CHEMICAL BATH DEPOSITION AND RAPID PHOTOTHERMAL PROCESSING

Cuprous oxide (Cu_2O) is a promising semiconductor material having the band gap of about 2.1eV (direct) so it is ideal for fabrication of photovoltaic devices and has been the subject of a number of intense basic research regarding its properties. Cu_2O thin films have been prepared by using different methods like chemical vapor deposition, thermal oxidation, anodic oxidation, reactive sputtering, electrodeposition, sol-gel, chemical deposition, etc [3-8]. Among them, chemical bath deposition (CBD) has attracted special interest for preparation of oxide thin films during the last years due to its simplicity and low cost, capability to achieve large area coatings, include simple and thus inexpensive equipment and low deposition temperatures which together result in low cost processes; reduced environmental impact; minimize undesirable interdiffusion of components in multilayer device structures. Chemical deposited Cu_2O films was preliminary investigated for gas sensors [9].

Annealing process is being guided largely by the requirements of removing the defects and electrical charges from oxide films. Recently, lamp-based rapid photothermal processing systems have been introduced as an alternative thermal annealing equipment solution. The interactions of photons with thin films provide thermal effects and quantum photo-effects. The performance of rapid thermal processing (RTP) techniques improved by the use of quantum photo-effects in thermal processing lead to reduced activation energy [10]. The quantum photo-effects dominated RTP is rapid photothermal processing (RPP). At lower temperatures (comparatively to RTP), thin films and semiconductor devices with better performance, reliability and yields can be processed by RPP.

The purpose of the present work is to develop a method to obtain Cu_2O thin films by CBD under UV light and investigate the impact of RPP on the electrical, structural, morphological and sensing properties and is expected to find out the optimum RPP condition to obtain high quality Cu_2O films for devices applications.

1.1. Chemical bath deposition of cuprous oxide

Chemical bath deposition is a possible alternative to vapour-phase and chemical-precursor techniques and has been used to produce a large variety of semiconductor materials, multicomponent films and single oxides. At the technological level, this method has also greatly succeeded in making CdS, Zn(O, OH, S), SiO_2, SnO_2, $CdSnO_4$ and Cu_2O [11,12]. CBD takes place by the generation of OH^- and then neutralization of cationic species on the electrode surface. This method is based on the controlled precipitation of the material to be prepared, in such a way to produce a film upon the substrate surface. Although, precipitation can be controlled by adjusting the experimental conditions (chemical composition and process temperature), nucleation in the solution and on the reactor walls

cannot be completely avoided. Hence, only a small part of the reagents in solution is used in the substrate film growth and a larger amount of material produces colloidal particles in the solution and a useless film upon the reactor walls. During CBD film growth, two processes can take place: a heterogeneous reaction upon the substrate surface occurring between adsorbed ionic species and those in the solution; and colloidal particles first nucleated in the solution can be adsorbed upon the substrate surface. The first process leads to compact and well-adhered films, constituting good prospects for electronic applications, but the second process yields porous and badly adhered films. Accordingly, there is a great interest in optimizing the efficiency of the CBD method, by minimizing both the deposition process upon the reactor walls and the homogeneous precipitation in the solution [9,12].

The chemical deposition method was earlier used by M. Ristov et all. [8] but the characteristics was improved using UV light-assisted growth and RPP of films. By means of this procedure, the precipitation process occurs only upon the substrate and films are more homogeneous. Chemical bath deposition of cuprous oxide Cu_2O from aqueous solution system including copper sulphate pentahydrate CDA Reagent grade, thiosulphate and sodium hydroxide was used for electroless-chemical deposition of Cu_2O. The addition of dietanolamine enhanced the solubility and improved wettability of the solution to glass substrate used.

The glass substrates were cleaned, before deposition, by chloric acid followed by rinsing redistilled water and ethanol, than boiling in acetone and isopropanol respectively. Cu_2O depositions were carried out in an aqueous baths of thiosulphatocuprate (I). The growth mechanisms of Cu_2O in a CBD process is considered to be similar with that of CdS, which has been discussed in detail elsewhere [13]. The global reaction for Cu_2O chemical bath deposition:

$$CuSO_4 + Na_2S_2O_3 \rightarrow 3Cu_2S_2O_3 \cdot 2Na_2S_2O_3 . \qquad (1)$$

Comparison of equilibrium constants for the various reactions involved indicates that complex solution is not stable, thus the growth of Cu_2O films might be start with fresh solution.

Cuprous oxide deposition of different thickness was done from solutions containing 0.5÷1.5 M $CuSO_4$, 0.5÷1.5 M $Na_2S_2O_3$ and 1÷4 M NaOH with temperature ramped from 50÷85°C over 4÷5 s for one dipping cycle. Using equivalent conditions with $CuSO_4$ yielded negligible Cu_2O deposition. Therefore, new conditions were needed for the deposition of Cu_2O.

Cu_2O deposition was optimized by varying the concentrations of: 1) $CuSO_4$, from 0.5 M to 1.5 M; 2) $Na_2S_2O_3$ from 0.5 M to 1.5 M; and 3) NaOH from 1 M to 4 M. Substrates were dipped into baths after mixing the chemical solutions at room temperature according to (1) and heating the third solution to the bath set temperature in the range 50÷85°C. After Cu_2O deposition, the samples were washed in deionized water and dried by heating in air jet at 150°C for 5 min. Quartz slides were used as the substrates because they allow optical transmission up to 5 eV.

Was studied the deposition kinetics by variation of concentration of complex solution in the range 0.25÷1 M under UV irradiation of substrate. Composite solution was diluted by deionized water DI to respective concentration. The mechanisms scheme for the CBD process consists in next consecutive steps: the reaction of dissolved precursors of the halogen and the metal at the substrate surface (heterogeneous chemical), and then the deposition by diffusion of precipitates and clusters formed in solution.

The film thickness was determined gravimetrically by measuring the change in weight of the substrate due to film deposition. The medium thickness of the film d in Angstroms is determined according to the formula:

$$d = 100W / A \cdot \rho , \qquad (2)$$

were W - the change in weight, A – substrate area, ρ - density of cuprous oxide (6.1g/cm^3) [9]. For comparison the thickness also was measured by interferometric methods and scanning electron microscope (SEM).

The influence of RPP conditions on the physical structure of the films (composition and morphology) was studied by VEGA TS 5130MM scanning electron microscope (National Center for Materials Study and Testing). The structure of the Cu_2O films was investigated by Energy Dispersive X-ray (EDX) spectroscopy and was used to show the presence of Cu and O, and determine their atomic ratio. Depending on the concentration of the chemical bath, Cu_xO_y and/or Cu_2O oxide were detected on the as-deposited film by Energy Disperse X-ray spectroscopy.

1.2. Rapid Photothermal Processing of Cu_2O films

Annealing is needed as one of the most important processes because the as-deposited polycrystalline films are generally too resistive and

have to be annealed to crystallize and to remove the electrical charges and defects from oxide films. Both furnace annealing and rapid photothermal processing were used in our experiments. Furnace annealing was performed in air in a quartz tube furnace at temperature 300°C for 1.5 h. RPP was performed in an IFO-6 system developed at the Department of Microelectronics and Semiconductor Devices, TUM. The set-up detailed described in [14]. RPP based on coherent light as a source of energy has emerged in recent years as an alternative of furnace processing. The lamp-based rapid photothermal processing RPP system provides short cycle time, reduced exposure and flexibility compared to batch-type furnaces. Allowable thermal budget has decreased as device dimensions. Strong demand in photothermal budget reduction and cycle time reduction made RPP become a very popular photothermal processing method in 21st century [10]. The photon-matter interaction is described by thermal effects and quantum effects. Photons increase the vibration amplitude of the atoms, raising the temperature of the film and the underlying substrate and thermal effects takes place. Also photons with lower wavelengths excite the atoms, molecules participating in thermal process and quantum effects take place. The efficiency increasing of material and energy by RPP makes it a key technique for the fabrication of the entire spectrum of advanced semiconductor devices. By combining this with advanced CBD methods, further optimization can be realized. It is shown that rapid photothermal processing not only allows green semiconductor manufacturing but also improves the performance and reliability over conventional methods. Therefore the results from RPP-treated samples are discussed in this paper, although measurements of furnace annealed samples are also presented for comparison. In this contents after deposition the samples were subjected to different temperature RPP using IFO–6 system. The cuprous oxide easily oxidized during the annealing process in the presence of oxygen. The as-deposited films were calcined at 200°C, 300°C, 350°C, 400°C for 5÷100 sec. The optimum duration of RPP was determined as 7 sec for Cu_2O films.

2. RESULTS AND DISCUSSION

2.1. Growth kinetics of Cu_2O thin films

First, the influence of concentrations of $CuSO_4$, $Na_2S_2O_3$ and NaOH on Cu_2O growth on glass, quartz, Si substrates was sequentially investigated. The deposition parameters, film and sample results are summarized in Table 1. Each row represents variation of a single component concentration. Appropriate amount of $CuSO_4$ and $Na_2S_2O_3$ were determined based on efficiency and used to fix the concentration for the next row. For the concentration ranges shown, NaOH (row C) had the greatest effect on the Cu_2O film deposition while $Na_2S_2O_3$ (row B) had the least. Decreasing the concentration of NaOH or increasing the concentration of $CuSO_4$ (row A) yielded thicker films, but resulted in an early start of colloidal growth. Colloidal growth is not desirable for device application. The films of Table 1 clearly constitute a narrow range of film thickness, limited to ~400 nm.

Therefore, in order to obtain thicker Cu_2O films and to avoid colloidal growth, concentrations of NaOH and $CuSO_4$ were varied together. This is conceptually presented in Figure 1. As growth rate is very sensitive to variations in $CuSO_4$ and NaOH concentrations at the lower concentration regime, Cu_2O deposition was investigated at higher $CuSO_4$ and NaOH concentrations. But later increasing of NaOH concentration induce films etching. For the indicated range of NaOH concentration (row C) it's observed the best effect on film deposition and on composition of obtained thin films.

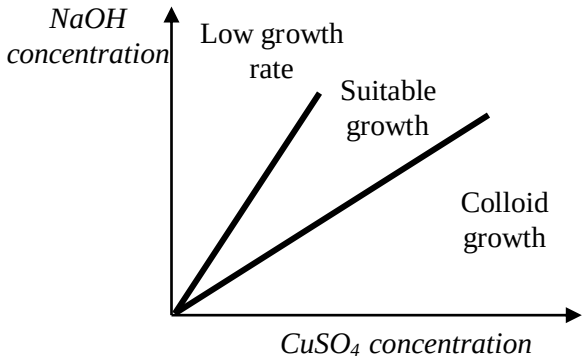


Figure 1. Schematic graph of the variation of Cu_2O growth with $CuSO_4$ and NaOH concentration based on the results of Table 1.

Decreasing of NaOH temperature conduce to Cu_xO_y films growth, but increasing above 85°C induce films etching and nonuniformity of films. These procedure is described in Table 1 and is shown in Fig. 1. Due to the growth rate sensibility to variation of copper sulphate and sodium hydroxide concentrations to low regime, Cu_2O deposition was studied for higher concentrations.

However, high NaOH will give rise to high pH in the solution, which can result in high concentration of $Cu(OH)_2$ and unfavorable etching of cuprous oxide.

Table 1. Influence of chemical concentrations on film growth for Cu_2O deposition at 75°C for 20 dippings

	Deposition Parameters			Summary of Results
	$CuSO_4$ [M]	$Na_2S_2O_3$ [M]	NaOH [M]	
A	**0.5 - 1.5**	1	2	- Increasing $CuSO_4$ conc → onset of colloidal growth - Increasing $CuSO_4$ conc. → increasing thickness - Maximum thickness < 400 nm - Best thin film → at 1.1 M
B	1.1	**0.5-1.5**	2	- Decreasing $Na_2S_2O_3$ conc. → slight increase in thickness - Increasing $Na_2S_2O_3$ conc. → Cu_2O growth - Maximum thickness < 500 nm - Best thin film → at 1.1 M
C	1.1	1.1	**1.0-4.0**	- Decreasing NaOH conc. → onset of colloidal growth - Decreasing NaOH conc. → CuO growth - Increasing NaOH conc. → Cu_2O growth, lower resistivity - Maximum thickness < 500 nm - Increasing bath temperature > 85°C induce films etching - lowering bath temperature < 60°C induce Cu_xO_y films growth

As before, ideal conditions for Cu_2O deposition were determined based on sample characteristics and reproducible control of layer deposition (row C). The optimal concentrations of $CuSO_4$, $Na_2S_2O_3$ and NaOH carried out with deposition at 75°C. Under these conditions, the solution was clear and colorless until 25 successive dippings and then it started to become reddish-brown with immersion cycles.

The Cu_2O films deposited on Corning glass substrate under the above conditions were investigated. The variation of film thickness with deposition time is qualitative similar to that of Cu_2O deposition by CD.

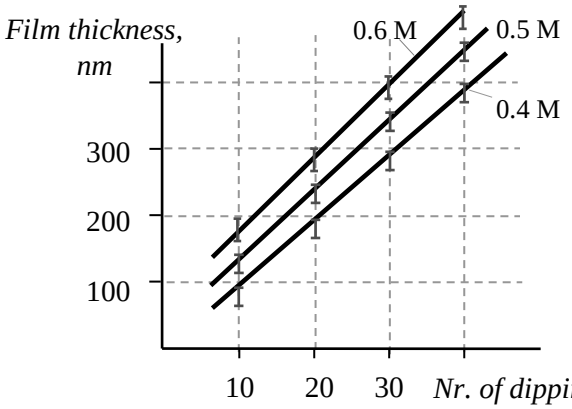


Figure 2. Thickness variation of Cu_2O films, deposited on Corning glass slides, vs. number of dipping. Bath temperature = 75°C.

Growth kinetics were studied by measuring dependence of film thickness versus number of successive dipping in sodium hydroxide beaker hold at 75°C and in complex solution bath hold at room temperature. Figure 2 shows the film thickness variation with the deposition time (number of dippings) for different concentrations of complex solution by diluting with DI water. In this case the deposition consists of three different phases. The first phase is the period for nucleation, which may vary depending on the substrate. Deposition on a polycrystalline Cu_2O layer with a textured morphology could greatly shorten the nucleation time and catalyze the Cu_2O growth by providing a high density of nucleation centers. The second phase with nearly linear growth corresponds to the heterogeneous ion-by-ion growth on the substrate based on reaction (1). The third phase is the adhesion of Cu_2O precipitates and larger particles. As described above, growth of Cu_2O in a CBD process goes from a heterogeneous phase of only depositing on the substrate to a homogeneous phase of precipitating in the solution. Heterogeneous growth yields a dense, conformal buffer layer, but the homogeneous growth deposits a layer with adherent Cu_2O precipitates.

Different durations of immersions ranging from 3 s to 30 s were employed. It was found that durations longer than 15 s does not result in a higher film thickness. Hence 4-5 s in each of the solutions was chosen as the immersion period in the present work. Thus, growth of films is determined by several phases: nucleation period, which can vary depending on the substrate (nucleation centers), then linear growth which correspond to heterogene ion-ion on substrate as a result of chemical reaction and adhesion of Cu_2O and increase of particles.

Fig. 3 describes the growth kinetics of the Cu_2O films as a function of the immersion cycles for two different temperatures of sodium hydroxide solution. After 5 deposition cycles, the film appears silvery, corresponding to a film thickness of 50 nm, in all the different temperatures, ranging from 60–85°C, of the alkali solution.

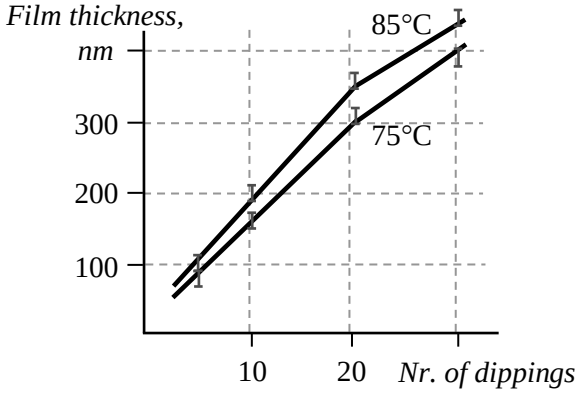


Figure 3. Film thickness vs. number of cycles of immersions for different temperatures of sodium hydroxide solution.

Progressively the film turns brassy, purple, bluish, etc, due to optical interference under daylight. Fig. 3 shows that the growth rate, typically 10-12 nm/cycle, slows down as the successive immersion cycle proceeds. In the case of deposition using the alkali solution at 85°C, the film growth slows down after 22 immersions, but the growth is faster at 75°C. This, however, does not lead to improvement in conductivity of the Cu_2O film.

The rinsing step employed between the dippings in the Successive Ionic Layer Adsorption and Reaction was ascribed to this chemical deposition technique. This process is meant to eliminate the transport of surface tension held solution layer to-and-fro the baths and hence avoids precipitation of semiconductor clusters and pigments in the bath. The reaction in such a case takes place only with the adsorbed ion layer leading to the deposition of thin films of relatively higher quality and also leads to lower deposition rate for the films than what is given in Figs. 2,3.

The cuprous oxide films growth rate is scaled linearly with complex solution of $3Cu_2S_2O_3 \cdot 2Na_2S_2O_3$ concentration. The linearity of deposition procedure ensures good control and reproducibility of cuprous oxide film thickness. For concentration greater than 0.6 M the deposition was non-uniform. As can be observed from investigations adherence of films is very sensible to concentrations changes, bath temperature and number of successive immersions.

2.2. Characterization of Cu_2O thin films

Was investigated the impact of rapid photothermal processing on the electrophysical and sensing characteristics of Cu_2O films with thickness 0.3 μm obtained by chemical deposition method on Corning glass substrates.

Figure 4 shows the temperature dependence of electrical resistivity in 300–480K range for cuprous oxide film after rapid photothermal processing at 250°C, 300°C, 350°C, 425°C with pulse duration of 7 s.

The electrical resistivity of samples without RPP shows similar values to those for cuprous oxide (IV) prepared by the sol-gel technique [7]. The resistivity of the electroless-chemical deposited films is of the order of 10^4–10^5 Ω·cm, which is very high compared to the 10^2–10^3 Ω·cm for the bulk Cu_2O. The high resistivity of the films are due to the copper vacancies (V_{Cu}) in the neutral (V_{Cu}^0) and -1(V_{Cu}^{-1}) charge states as the dominant point defects in cuprous oxide [15].

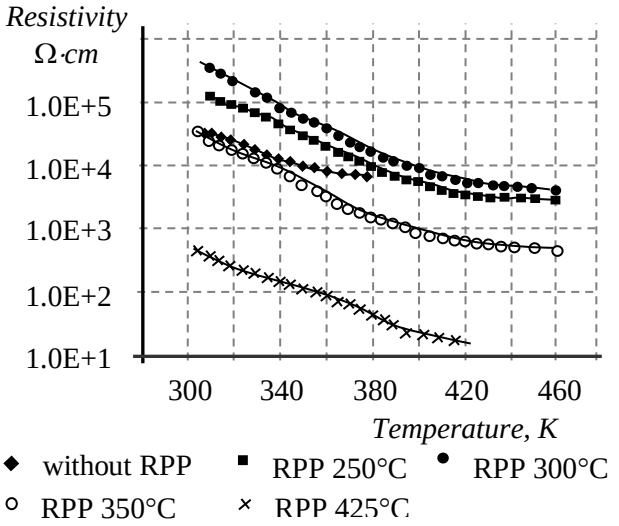


Figure 4. Temperature dependence of electrical resistivity of a cuprous oxide films after RPP.

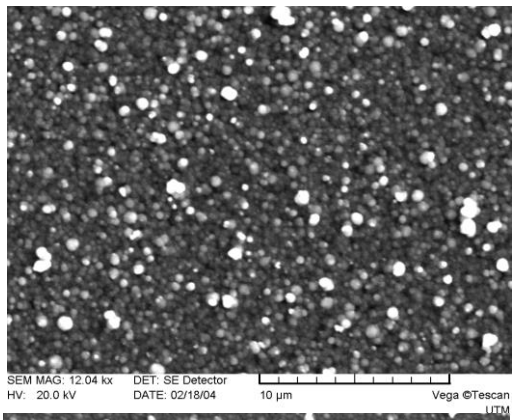
According to RPP with temperatures below 300°C increase of the resistivity with one order of magnitude. But RPP at temperatures higher than 300°C the resistivity decreased by a factor of 10÷100, also changing the color of films.

W. Siripala et al. [16] have reported that the resistivity of the electrodeposited Cu_2O films increased by a factor of 100 after conventional furnace annealing in air.

A comparison of SEM images of Cu_2O films grown on glass substrates by CBD method is shown in Fig. 5 (a) for as grown film; (b) RPP at

300°C for 7 s; (c) RPP at 400°C for 7 s; (d) conventional furnace annealing at 300°C for 1.5 h.

a)



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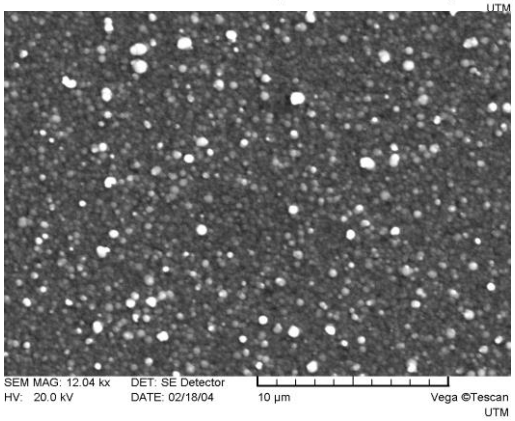

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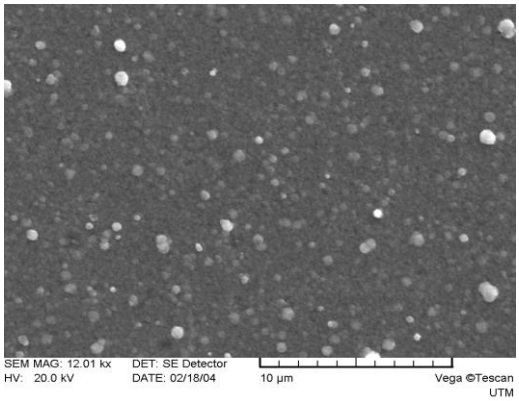

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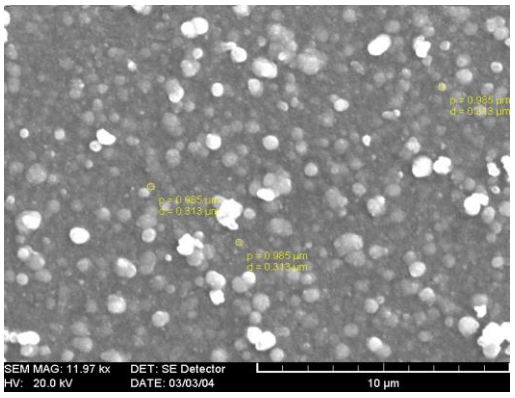

Figure 5. SEM images of as-grown Cu_2O (a); Cu_2O annealed at 300°C, 7 s (b); annealed at 400°C, 7 s (c) and furnace annealed at 300°C, 1.5 hours (d).

The comparison of Figs. 5 (a) - (d) found that the surface morphologies of the films have changed and represent different characteristics. The surface roughness of the films has changed. As can be seen the RPP improves surface roughness of Cu_2O thin films comparatively with conventional furnace annealing (CFA). Crystallites size decreased with RPP comparative to CFA at the same processing temperature.

The composition of films and the atomic ratio of Cu and O in the grown films is investigated by the EDX measurements made in the plan detection mode. The diameter of the focused electron beam in EDX analyses is about 4 µm and the beam is scanning the films surface area of (50µm×50µm). The penetrated depth of focused high-energy electron beam is about 2 µm. Fig. 6 illustrates the EDX pattern of Cu_2O sample. As can be seen, the peak at 1 keV corresponds to Cu. The average Cu content in Cu_2O film is calculated according to the integral intensity of the Cu peak with its ionization cross-section taken into account. The Cu:O ratio surveyed is 2:1 with an experimental error of about 10 % due to the small thickness of Cu_2O film compared with the high-energy electron beams penetration depth in EDX.

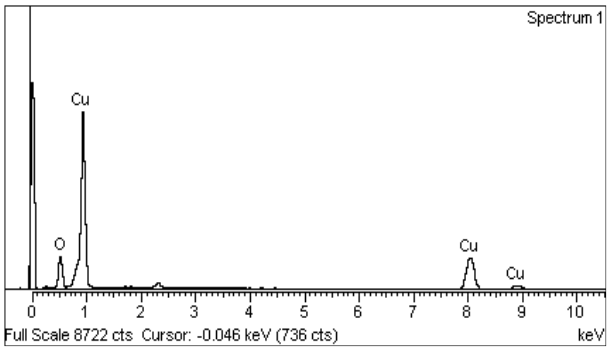

Figure 6. An EDX pattern of Cu_2O film onto glass.

EDX analysis shows that RPP at temperatures higher than 300°C lead to formation of Cu_xO_y and reduction of Cu:O ratio from 2:1 to 1:1 in dependence of processing regime.

In figure 7 is represented the sensing characteristics of cuprous oxide films during 10 min exposure to sulfates SO_4. As can be seen the RPP determine the stability of sensitivity of cuprous oxide films to sulfates, but at the same time reduce it for temperatures higher than 70°C.

Fig. 8 shows the resistance variation of Cu_2O thin films (0.2 µm thickness) with air pressure in VUP-5 system. It can be seen that the dependence is nonlinear for as-grown films. Therefore the resistance of films can be expressed

by $R_0+R_A \cdot P^n$, where n has values 0.25÷0.3. From experiments was observed that the values of R_0 and R_A decrease as the film thickness increases.

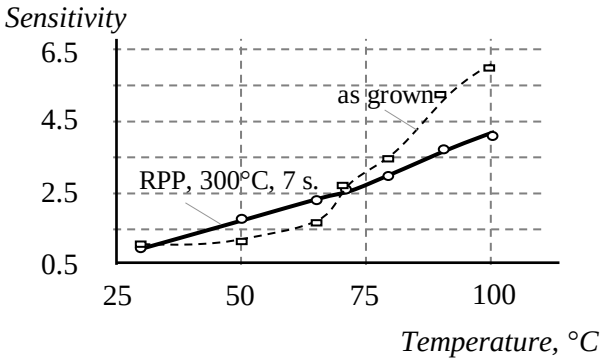

Figure 7. Dependence of sensitivity to sulfates with operation temperatures for cuprous oxide – based sensing devices.

Resistivity-to-pressure measurements were performed for the Cu_2O films deposited in different conditions according to Table 1. The largest variation in the resistance was exhibited by the film grown in 1M NaOH at 60˚C.

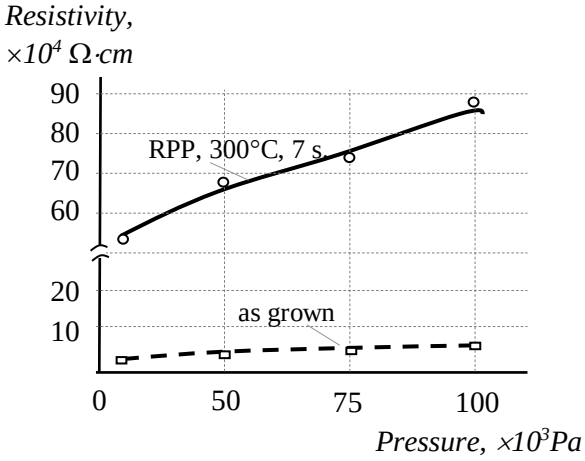

Figure 8. Variation in the resistivity of Cu_2O thin films (0.2 μm as grown and RPP) with pressure.

Examination by SEM microscopy and EDX revealed that chemical deposited Cu_2O films contain microcrystals surrounded by an amorphous phase. The crystalline-to-amorphous phase ratio increased with the temperature increase and the concentration of sodium hydroxide bath. From this and from resistance-to-pressure measurements one can conclude that this behavior results due the amorphous and polycrystalline phases of cuprous oxide. The microcrystals have a high conductivity and can be doped by absorbed oxygen, but the amorphous phase has low conductivity and it cannot be doped. In this order, a barrier potential is set up at the interface between the microcrystals and the amorphous phase and resistance is increased.

Cu_2O thin films can be prepared easily, the raw material is abundant, less expensive and available everywhere. Reliable ohmic contacts can be made to the Cu_2O without much difficulty.

3. CONCLUSIONS

Cu_2O thin films were deposited by a CBD method from an aqueous solution of thiosulphatocuprate. Were investigated various aspects of Cu_2O thin films: the effect of varying the growth parameters such as bath compositions (0.4M, 0.5M and 0.6M) and temperature (50÷85°C), UV-assistance during the film deposition on the properties of thin film; was determined the maximal optimal concentration (0.6M) and temperature 75°C to growth homogeneous Cu_2O thin films. The deposition rate of films is in the range 0.01 μm/min÷0.2 μm/min and depends on concentration and temperature of solution, slows down as the successive immersion cycle proceeds after 22 immersions in the case of deposition using the alkali solution at 85°C, but the growth rate is faster at 75°C. This, however, does not lead to improvement in conductivity of the Cu_2O thin film. Was determined that low temperatures (60°C-85°C) allow growth upon a glass substrates and is easily adapted to large area; thickness of the deposited layers may be readily controlled by variation of the number of immersions in the range 0.01÷0.5 μm.

From the SEM and EDX investigations performed could be conclude that Cu_2O thin film are polycrystalline with grain sizes 0.4÷0.6 μm and the morphology variation, crystallite size and Cu:O atomic ration is depending on the RPP temperatures. No apparent changes have been observed during RPP (7-15s) at temperatures below 300°C, but processing above this temperature produce darker films.

Under RPP at temperatures below 300°C the resistivity was increased with one order of magnitude, but RPP at temperatures higher than 300°C determine decreasing of the resistivity by a factor of 10÷100 comparatively with 1.5 h of conventional heat treatment.

Also by rapid photothermal processing was stabilized the sensitivity of cuprous oxide-based sensors to sulfates and at the same time was decreased at temperatures of measurement higher than 70°C. In this manner was controlled the

selectivity of sensors to different atmospheres. The largest variation in the resistance with air pressure was exhibited by the Cu_2O film (0.2 μm thickness) prepared from 1 M NaOH at 60˚C.

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