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STRUCTURAL AND OPTICAL PROPERTIES OF COPPER OXIDE THIN FILMS PREPARED BY NOVEL "IN SITU CVD" METHOD

Thin films of copper oxides were obtained by novel "in situ CVD" method on glass substrates using copper monocloride as precursor. Films were synthesized both in the air atmosphere and in the air-argon atmosphere. The X-ray diffraction patterns showed a change in the phase composition of the films obtained in air during the synthesis. Phase transitions CuO-Cu2O-CuO are characteristic for samples synthesized at 400 °C. A sample of 1 min had a monophasic CuO structure. The first transition from the CuO to Cu_2O occurs in the narrow time interval between 1 and 2 minutes of pyrolysis. The second transition from the Cu_2O phase to the two-phase form of CuO + Cu_2O occured between 3 and 5 minutes of synthesis. On the sample 10 minutes only a small amount of Cu_2O was observed. And, finally, a sample synthesized in 20 minutes had a monophasic CuO structure. The phase restructuring is related to the kinetics of the film synthesis process and is determined by the ratio of the rates of supply of copper and oxygen atoms to the interface of the substrate-the growing layer. Films obtained under oxygen deficiency conditions were identified as monophasic Cu_2O at the synthesis time of up to 20 minutes. The increase in time led to the formation of mixed phases. The Cu_2O films obtained at 500 °C for 1 minute had high transparency with a transmission maximum of 80% at a wavelength of 600 nm. The FWHM values obtained from XRD patterns of the films indicates a high ordering of the crystal structure.

Key words: Copper oxide, XRD, Phase composition, CVD.

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«In situ CVD» жаңа әдісімен алынған оксид мысының құрылымдық және оптикалық қасиеттері

Прекурсор ретінде мыстың монохлориді қолдану арқылы шыны төсемде мыс оксидінің жұқа қабықшалары жаңа "in situ CVD" әдіспен алынған. Қабықшалар ауа атмосферасында және ауа-аргонды қоспада синтезделген. Синтез уақытын өзгерткен кезде ауада алынған қабықшалардың рентгенограммаларында фазалық құрамының өзгергені байқалды. 400°С кезінде синтезделген үлгілер үшін CuO-Cu_2O-CuO фазалық ауысуы тән. 1 мин ішінде алынған үлгі CuO монофазалық құрылмға ие болды. Екіфазалық CuO + Cu_2O түрге CuO-дан Cu_2O-ге дейін бірінші ауысу 3 және 5 минут синтез арасында өтті. 10 ішінде синтезделген үлгіде тек аз ғана Cu_2O саны байқалды. Және, соңында, 20минут аралығында синтезделген үлгі CuO монофазалық құрылымға ие болды. Мақалада қабықшаның фазалық қайта құрылу процесі қабықшаның синтездеу кинетикасымен және төсем мен үдемелі қабат аралығына шекара айырығына қарай мыс пен оттегі атомдарының өту жылдамдығымен анықталатыны көрсетілген. Синтез уақыты 20 минутқа дейін оттегі дефицит кезінде алынған қабықшалар монофазды Cu_2O ретінде қарастырылды. Уақытты асыру кезінде араласқан фазалар пайда болуына әкелді. Өткізуі максимумы 80% болғанда толқын ұзындығы 600 нм құрайтын 500 °С кезінде алынған Cu_2O қабықшалар 1 минут уақыт ішінде жоғары мөлдірлігіне ие болды. Қабықшалар рентгенограммаларынан алынған FWHM мәндері олардың кристалдық құрылымының жоғары реттілігін көрсетеді.

Түйін сөздер: мыс оксиді, рентген дифракциясы, фазалық құрам, CVD.

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Структурные и оптические свойства тонких пленок оксида меди, полученных новым методом «in situ CVD»

Тонкие пленки оксидов меди были получены новым методом «in situ CVD» на стеклянных подложках с использованием монохлорида меди в качестве прекурсора. Пленки синтезировали как в воздушной атмосфере, так и в воздушно-аргоновой смеси. На рентгенограммах наблюдалось изменение фазового состава пленок, полученных на воздухе при изменении времени синтеза. Для образцов, синтезированных при 400°C, характерны фазовые переходы CuO-Cu_2O-CuO. Образец, полученный за 1 мин имел монофазную структуру CuO. Первый переход от CuO к Cu_2O наблюдался в узком интервале времени между 1 и 2 минутами пиролиза. Второй переход от фазы Cu_2O к двухфазной форме CuO+Cu_2O происходил между 3 и 5 минутами синтеза. На образце, синтезированном в течение 10 минут наблюдалось только небольшое количество Cu_2O. И, наконец, образец, синтезированный за 20 минут, имел монофазную структуру CuO. Показано, что фазовая перестройка определяется кинетикой процесса синтеза пленки и отношением скоростей подхода атомов меди и кислорода к границе раздела между подложкой и растущим слоем. Пленки, полученные в условиях дефицита кислорода за время синтеза до 20 минут, были идентифицированы как монофазный Cu_2O. Увеличение времени приводило к образованию смешанных фаз. Пленки Cu_2O, полученные при 500 °C в течение 1 минуты, имели высокую прозрачность с максимумом пропускания 80% при длине волны 600 нм. Значения FWHM, полученные из рентгенограмм пленок, указывают на высокую упорядоченность их кристаллической структуры.

Ключевые слова: оксид меди, рентгеновская дифракция, фазовый состав, CVD.

Introduction

In recent years, a large number of publications devoted to the use of films of copper oxides to create a number of semiconductor devices: solar cells [1-4], various sensors

To date, the increased interest in obtaining copper oxide films is due to the prospects for using this semiconductor material for the environmentally friendly production of cheap solar cells [1-4], rectifying diodes [5], various sensors [6,7].

Various physical, chemical and electrochemical methods for the preparation of CuO and Cu_2O thin films have been proposed. Each of them has advantages and disadvantages. In most of the earlier studies, mixed phases consisting of Cu, CuO and Cu_2O were obtained, which is the main problem when using synthesized layers as an active component of solar cells [8]. In [9], the first results on the synthesis and study of CuO films obtained by a new method of catalytic decomposition of copper chloride using a powder source were presented and the possibility of obtaining monophase CuO films was demonstrated. This investigation is aimed at studying the conditions for the production of Cu_2O films and the accompanying phase transitions in the CuO-Cu_2O system.

Results and discussion

According to the technique described in [9] thin films in the CuO-Cu_2O system were obtained on glass substrates. The synthesis regimes were experimentally determined depending on the temperature, time and fractional composition of the copper chloride powder source, the thickness of which in all the experiments was 0.8 mm. The synthesis was carried out on substrates measuring 24x24 mm2 with a thickness of 0.15-0.17 mm. The thickness of the films was within the range of 0,1-3,0 μm and increased with increasing temperature and synthesis time. Optimum conditions were found under which layers of monophasic material were formed. The temperature interval for the synthesis of Cu_2O films was 400-500°C for powders of 200 mesh fraction and 450-550°C for powders of 100 mesh. In the first case, the time interval of monophasic growth of Cu_2O films was 2-4 min, whereas in the second case, 1.5 ± 3 min. Beyond these synthesis times, either two-phase Cu_2O-CuO layers or monophase CuO layers have grown.

Measurement of the films characteristics was carried out on analytical equipment: X-ray diffractometers “D8 ADVANCE”and “DRON-3”, Raman spectrometer “Solver Spectrum” and two-channel spectrometer “Shimadzu UV-3600”.

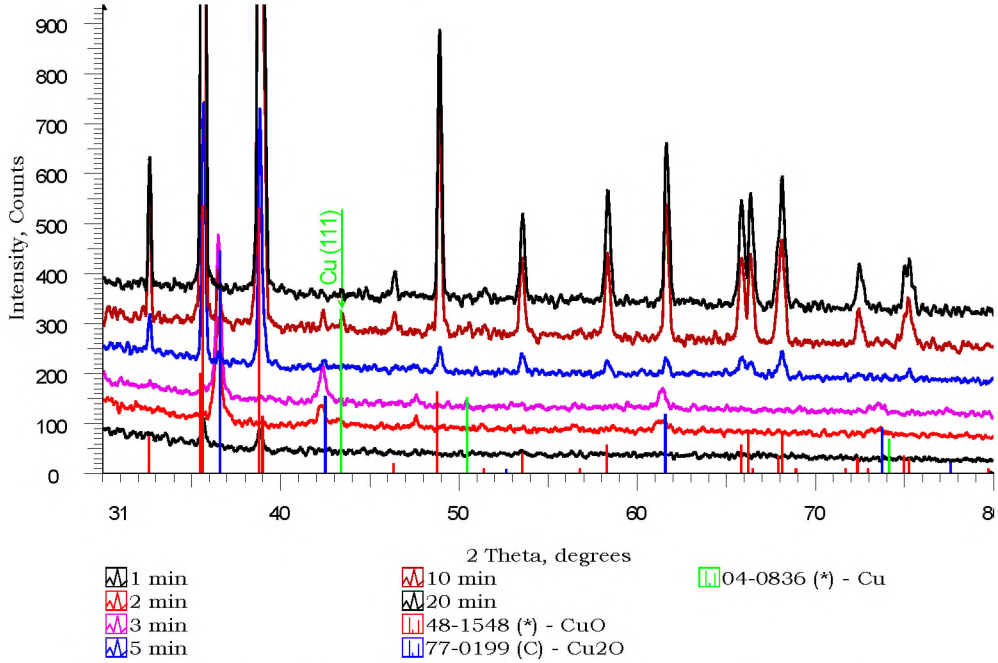


Figure 1 – Results of X-ray diffraction patterns of copper oxides films synthesized at 400C for different times in the air atmosphere

Figure 1 shows the diffractograms of films synthesized in air at different times. It can be seen that for the samples obtained after 2, 3 and 5 min, a phase transition is observed twice. The first transition from the CuO to Cu_2O occurs in the narrow time interval between 1 and 2 minutes of pyrolysis at 400°C. A sample of 1 min had a monophasic structure. It consisted of CuO phase only (the first two strongest doublets). For samples 2 and 3 min, four peaks of Cu_2O and traces (one peak) of CuCl are observed, which are related to insufficient cleaning of the film surface from the source powder residues. The second transition from the Cu_2O phase to the two-phase form of CuO + Cu_2O occured between 3 and 5 minutes of synthesis. On the sample 10 minutes only a small amount of Cu_2O was observed. And, finally, a sample synthesized in 20 minutes had a monophasic CuO structure. Fig. 2, obtained from the analysis of X-ray patterns, demonstrates the change in the phase composition of these films. An important result of X-ray spectra analysis is that in films grown for 2 and 3 minutes there was no CuO phase, in spite of the fact that all samples undergo a one-minute annealing step, on which a CuO phase is formed.

Our explanation of this phenomenon is based on the possibility of creating thermodynamic conditions for the transformation of copper (II) oxide into copper (I) oxide in the process of continuous layer growth under conditions of oxygen deficiency at the interface between the film and the powder source. In this case, oxygen atoms can be formed as a result of the decomposition of copper (II) oxide molecules by the reaction:

$$2CuO \Rightarrow Cu_2O + 1/2\ O_2.$$

Such a transformation is characteristic for synthesis from powders of 200 and 300 mesh, while at the same temperature for 100 mesh powders monophasic CuO films are formed at any synthesis times. The high rate of decomposition of copper chloride from a powder source and the insufficiently intensive diffusion of air oxygen into the reaction zone ensures the formation of Cu_2O layers at this temperature and short synthesis times. Further transition to a two-phase composition region and then to a single-phase CuO is explained by the depletion of the powder source by copper chloride, which leads to a decrease in the rate of formation of the oxide phase (as occurs at the initial stage of the synthesis within 1 minute). The amount of oxygen diffusing to the growth boundary becomes sufficient for the oxidation of the previously formed Cu_2O layer to CuO and for the further formation of CuO, until the source is completely depleted. According to the foregoing, copper oxide films at long growth times should be monophasic CuO, which is observed

experimentally. When the synthesis temperature increases, the Cu_2O phase forms in a shorter time.

Reduction of the synthesis temperature to 350°C leads to the formation of monophasic CuO at any times of heat treatment, since at low temperatures the decomposition of copper chloride is less intense and the concentration of diffusing air oxygen becomes sufficient for complete oxidation of copper.

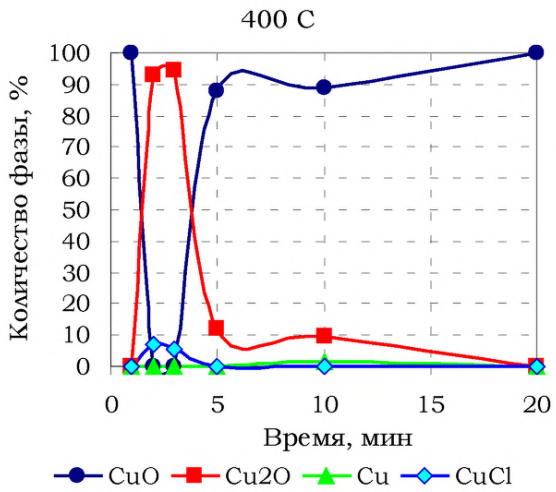


Figure 2 – Change in the phase composition of copper oxides films synthesized at 400C for different times in an air atmosphere

It is important to note that if at low times and low synthesis temperatures oxide phases are formed by surface reaction at the atomic level, then at high temperatures and long times the formation of copper (II) oxide occurs as a result of solid-phase reaction in the already formed copper (I) oxide film with transformation of a cubic structure of Cu_2O into a monoclinic structure of CuO. This process is not spontaneous in nature and can proceed for a sufficiently long period.

Based on the above-proposed phase transformation mechanism, a technique was developed for the production of Cu_2O films of optical quality with a thickness of 10 nm to 1 μm. Synthesis was carried out under conditions of oxygen deficiency. A flow quartz reactor was used for the experiments with an argon-air mixture (70 vol% Ar). The blowing rate was 4 cm^3/s. The growth kinetics of the films are shown in Fig. 3, where the rhombic markers show the film thickness as a function of the synthesis time for 500 μm powder source thickness of and square markers for 1 mm thickness. In both cases, the 100 mesh fraction powders were used, and the temperature was 400°C.

It is seen from Fig. 3 that with a smaller thickness of the powder source, the growth rate and the thickness of the films synthesized in the interval from 5 to 20 min are higher. This effect is explained by the fact that with a smaller source thickness, air oxygen diffusion to the substrate surface is faster and oxidation of copper ions is intensified. At synthesis times of 3-5 minutes, the thickness of Cu_2O films obtained from a thin source is only slightly higher than the value for a thicker source with the same slope of the curves, which is caused by transient processes associated with the initial heating of the source to a predetermined temperature and activation of the decomposition of copper chloride throughout thickness of the source. Figure 4 shows photographs of Cu_2O films synthesized at 400C on glass substrates measuring 24x24 mm^2 using the procedure described in [9]. The synthesis was carried out in an air atmosphere for 3 minutes from a 200 mesh зщцвук source (a) and in a flow system with reduced oxygen content for 8 minutes from a 100 mesh powder source (b). In the first case, the film thickness was 14 μm. It is characterized by a strong surface roughness indicating a high growth rate under these conditions. The film obtained in the second case showed high transparency, as evidenced by photo (b), where the inscription located under the substrate with the film has practically the same contrast with the uncovered areas. The film thickness in this case was 400 nm.

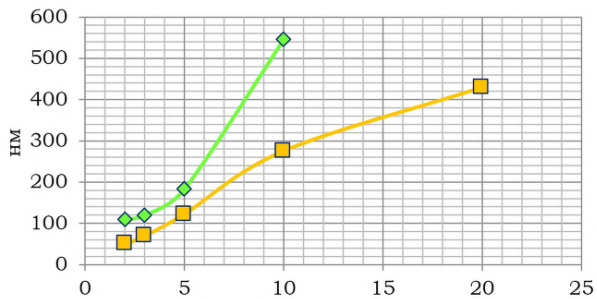


Figure 3 – Dependence of Cu_2O film thickness on the synthesis time

The obtained samples of optically transparent films were studied by X-ray phase analysis, Raman scattering and atomic force microscopy.

X-ray study of the films was performed on an automated diffractometer DRON-3 by using X-ray radiation tube with a Cu anode. Mode of operation

of the tube: 35 kV, 30 mA. Diffractograms were recorded in the range of angles 2θ = 4 – 80°, step 0,02°, with 1 s measurement time. Figures 5 and 6 show X-ray diffraction patterns obtained from films synthesized under conditions of oxygen deficiency at a temperature of 400°C for 2 and 4 minutes, respectively.

(а) (б)

Figure 4 – Samples of Cu_2O films synthesized in air (a) and in the argon-air atmosphere (b)

The spectra have a pronounced peak (111), stronger for 4 min of synthesis, over which the FWHM was calculated equal to 0.414° for 2 minutes and 0.419 for 4 minutes. These values of the FWHM indicate a high degree of ordering of the crystallites in the films. The cell parameters were determined to be 4.2868Å for 2 minutes of growth and 4.2892 Å for 4 minutes and the crystallite size was 21.089 nm and 15.895 nm for 2 and 4 minutes, respectively. According to the Cu_2O database, the card number 78-2076 (ASTM base) is a cubic cell with a parameter of 4.258Å. For both samples, the deviation from the standard is 0.0288 Å or 0.67% for 2 min. And at 0.0312Å or 0.73% for 4 minutes. Thus, the peak (111) is shifted in the diffractograms relative to the reference position, which indicates the existence of a solid solution containing a non-stoichiometric number of oxygen and copper atoms.

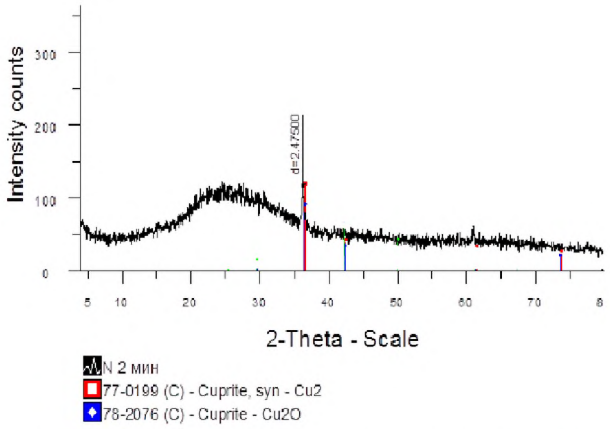


Figure 5 – XRD pattern of Cu_2O film synthesized in 2 min

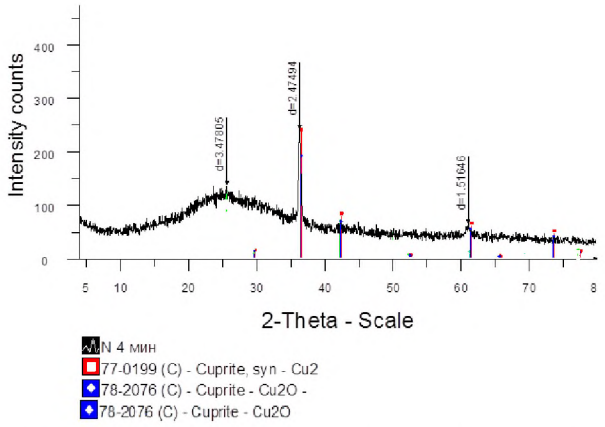


Figure 6 – XRD pattern of Cu_2O film synthesized in 4 min

Along with XRD studies, the phase composition of films synthesized in an argon-oxygen medium was identified by Raman scattering and atomic force microscopy. Figure 7 shows the Raman spectrum obtained from a film synthesized at 400°C for 10 min under oxygen deficiency conditions. This spectrum is identical to the spectrum of copper (I) oxide from the mineral database RRUFF [10].

In Fig. 8 shown scans of 2x2 μm of the surface area of the film synthesized at a temperature of 400°C for 10 minutes. The height of the relief (a) in this case was about 50 nm with uniformly distributed clusters of the order of 200 nm, which makes it possible to obtain optically transparent films of this material.

The size of the clusters determined from the AFM measurements is much greater than that calculated from the X-ray spectra using the Scherrer formula, the applicability of which has a dimensional limitation. Therefore, the results obtained by the AFM method should be considered reliable, especially since they agree with the results of electron microscopic research. On the scan (b) is shown the image of the same surface area in the phase contrast mode. The presence of decoration at the boundaries of clusters may indicate the presence in the intercluster space of another phase, in particular, of amorphous copper oxide.

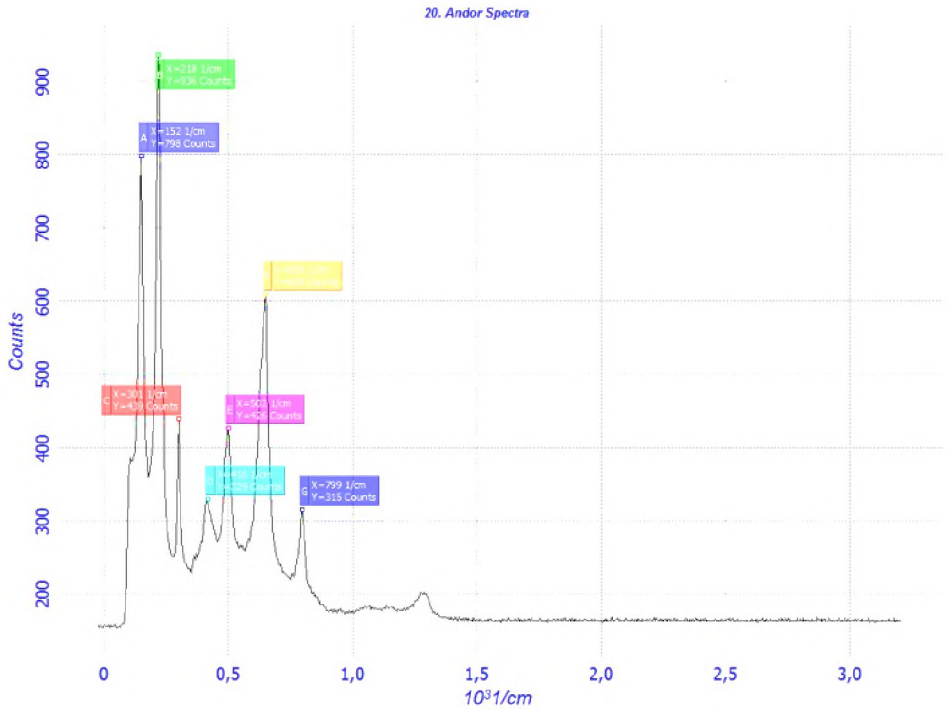
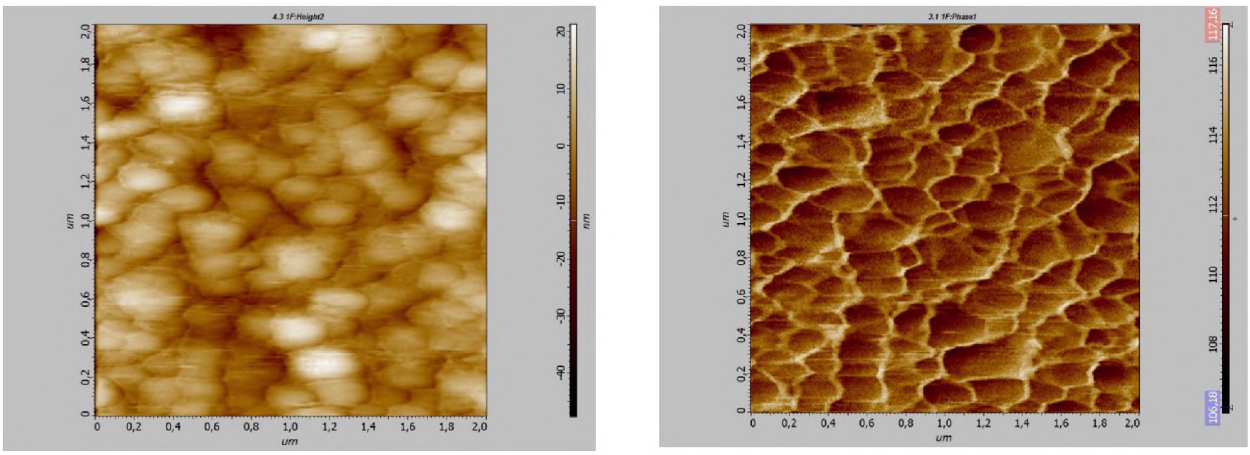


Figure 7 – Raman spectrum of a sample of copper oxide synthesized in argon-air medium



(а) (б)

Figure 8 – AFM scan of the Cu_2O film obtained at 400C for 10 min
(A) – relief, (b) – phase

An investigation of the optical transmission spectra of samples synthesized using a 100 mesh powder source under different temperature-time regimes also showed that their composition corresponds to copper (I) oxide. Figure 9 shows the transmission spectra of Cu_2O films characterized by high transmission in the visible and near infrared regions of the spectrum (samples 1-3). The increase in the growth time leads to a decrease in transmission, mainly due to the growth of light scattering on the surface relief (sample 4). The transmission spectra, along with reflection spectra (not shown) were used to determine the width of the forbidden band by a film.

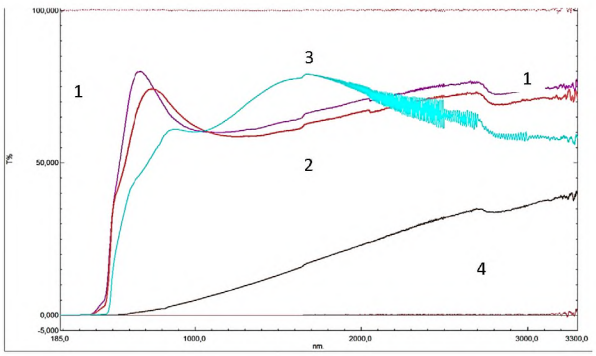


Figure 9 – Transmission spectra of copper oxide samples taken in the range from 185 to 3300 nm
1-500°C, 1 minute; 2 450°C, 2 min; 3-450°C, 5 minutes; 4 450°C, 20 min

For the films in Fig. 8, the values of the forbidden band width were obtained: 1 min -3.00 eV, 2 min – 3.00 eV, 5 min – 2.52 eV, 20 min – 2.54 eV. A slight increase in the Eg of the last film may be due to the partial post-oxidation of Cu_2O at large synthesis intervals. The Eg values for films obtained in 5 and 20 minutes are consistent with the literature data [11]. At the same time, for 1 and 2 minutes of growth, Eg had an abnormally high value, which can be due to a violation of stoichiometry, as follows from x-ray measurements.

Conclusions

A new method for obtaining thin copper oxide films using an air or an argon-air atmosphere, called "in situ CVD", is proposed.

The performed studies have shown the possibilities of the developed method for the synthesis of copper oxide films over a wide range of thicknesses using a copper chloride powdered source at relatively low temperatures.

A mechanism is proposed for a mutual transition from copper oxide (I) to copper (II) oxide and back, taking into account the kinetics of copper chloride decomposition processes and oxygen diffusion to the substrate-growing interface.

The results obtained can be used in the development of various sensors and optical filters.

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