



ELSEVIER

Thin Solid Films 405 (2002) 23–28



www.elsevier.com/locate/tsf

# Chemical vapor deposition of $6\text{CuO}\cdot\text{Cu}_2\text{O}$ films on fiberglass

Jorge Medina-Valtierra<sup>a,\*</sup>, Jorge Ramírez-Ortiz<sup>b</sup>, Victor M. Arroyo-Rojas<sup>b</sup>, Pedro Bosch<sup>c</sup>,  
J.A. de los Reyes<sup>c</sup>

<sup>a</sup>Centro de Investigaciones en Óptica A.C., Unidad Aguascalientes, Prol. Constitución No. 607, Fracc. Reserva Loma Bonita, Aguascalientes 20200, Mexico

<sup>b</sup>Facultad de Ciencias Químicas, Universidad Autónoma de Zacatecas, Km. 1 Carr. A Cd. Cuauhtémoc, Guadalupe, Zac. 98600, Mexico

<sup>c</sup>Universidad A. Metropolitana-I, Av. Michoacán y La Purísima s/n, México City, D.F. 09340, Mexico

Received 8 December 2000; received in revised form 17 July 2001; accepted 17 July 2001

## Abstract

To coat fiberglass with copper oxides, in particular with the paramelaconite structure  $6\text{CuO}\cdot\text{Cu}_2\text{O}$ , we have used the chemical vapor deposition (CVD) procedure of a copper precursor. The deposition of copper oxides was done using a horizontal-flow reactor, 2,4-pentanedionate copper(II) as precursor and  $\text{O}_2$  as carrier-reactant gas at several deposition temperatures. In order to establish a correlation between experimental parameters and the resulting copper species, as well as film quality, the samples that were produced, were evaluated using techniques such as X-ray diffraction (XRD), visible spectrophotometry, scanning electronic microscopy (SEM) and atomic force microscopy (AFM). The most important result is that  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  thin films are obtained over a short range of deposition temperatures. The film growth of this copper phase occurred in the [202] and [004] directions. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Chemical vapor deposition; Fiberglass substrate;  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  films; Cuprous oxide

## 1. Introduction

Fiber-supported materials are widely used in a variety of applications including as catalysts. Notable examples include coated ceramic fibers that are used as macrocomposites [1], activated carbon fibers for the retention of  $\text{SO}_2$  [2], metal oxides supported on active carbon fibers to perform the catalytic reduction of  $\text{NO}_x$  [3], and fiber-supported perovskites to oxidize natural gas [4].

Copper oxides are compounds that can be used as electric conductors [5,6] or as catalytic species [7–9]. There are several examples over that last alternative. Oxidation of methanol is done on a surface of  $\text{Cu}^{1+}$ ,  $\text{Cu}^0/\text{ZnO}$  [7].  $\text{CuO}/\text{ZSM-48}$  catalyzes supercritical water oxidation of 2-chlorophenol [8].  $\text{Cu}_2\text{O}$  or a mixture of  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  promotes the  $\text{NO}_2$  dissociation [9].

Typically, three ways are used for preparing supported catalysts: impregnation, co-precipitation, and ion

exchange. More recently, novel methods have emerged to obtain monolayer dispersion of oxides on porous supports [10] or on metallic sheets [11].

Several techniques have been devised for the synthesis of metallic oxides films such as chemical deposition in a equilibrium solution [6], chemical vapor deposition (CVD) using metallorganic precursors [12], spin-coating [13], plasma spray deposition [11], and application of the sol-gel method [14].

The CVD process provides thin films with a high uniformity of chemical composition [15]. Another characteristic of this technique is that it enables one ability to coat any geometric shape with a deposit of crystalline nanoparticles [16]. One advantage of CVD over other methods, is the ability to selectively deposit films onto a particular substrate area [17].

The objective of this present work is to design an experimental procedure for obtaining different copper phases on commercial fiberglass. We stress the paramelaconite phase series, that is deposited over a short temperature range and that it has been shown to have an interesting catalytic activity in a previous work [18].

\* Corresponding author. Tel./fax: +52-4-976-0946.

E-mail address: jmedinav@cioags.com.mx (J. Medina-Valtierra).

Table 1  
Experimental conditions for the deposition of Cu<sub>2</sub>O and CuO films

Sample	Deposition temperature (°C)	Precursor flow (mol min <sup>-1</sup> ) × 10 <sup>-7</sup>	O <sub>2</sub> /Cu(acac) <sub>2</sub> (mole ratio) × 10 <sup>3</sup>
F-320	320	1.82	6.8
F-325	325	2.05	6.0
F-340	340	2.20	5.6

## 2. Experimental methods

Films composed of copper oxides were deposited over fiberglass by sublimation and transportation of (acac)<sub>2</sub>Cu(II) with a O<sub>2</sub> flow (oxidizing agent), resulting in the decomposition of the copper precursor, deposition of Cu<sup>0</sup> and Cu<sup>0</sup> oxidation on the fiberglass over a short range of deposition temperatures.

The copper precursor was purchased from Aldrich Chemical Co. (97%) and it was used without further purification. The substrate was a piece of a 8-μm fiberglass (weight 0.1 g) from Corning Inc. This was cleaned in an ultrasound bath with isopropyl alcohol and then dried in a stream of pure, hot air. Then it was placed in the reactor for the CVD process. All gasses used were from Infra Co and were of gas chromatograph grade.

The film growth experiments were carried out using a horizontal-flow, atmospheric-pressure CVD reactor, a Pyrex glass tube (2-cm i.d. × 30-cm long) with two sections each surrounded by a furnace. The furnace temperature, controlled by a digital temperature controller, was measured by a Fe-constantan thermocouple. At the left side of the furnace, the precursor was sublimated at 190 °C and transported to the right side of the furnace by an O<sub>2</sub> flow of 30 ml min<sup>-1</sup>. At the right side of the furnace, the deposition of Cu phases took place at different temperatures in a range between 320 and 340 °C.

In a previous publication [19], several depositions were made to establish suitable experimental parameters to warrant a deposit of either the Cu<sub>2</sub>O or CuO phase. The experimental conditions are summarized in Table 1. The molar flow rate was determined by measuring the total amount of the copper precursor sublimated during the deposition time (2.5 h).

Under a constant flow rate of O<sub>2</sub>, the chemical properties of the deposited films depend on the operation conditions, namely the deposition temperature ( $T_d$ ) and the O<sub>2</sub>/precursor mole ratio ( $R$ ). In fact, Condorelli et al. observed higher oxidation states for deposited copper when increasing both the temperature and the O<sub>2</sub>/Cu(acac)<sub>2</sub> mole ratio [20]. However they found that at a constant  $R$  value, both Cu<sub>2</sub>O and CuO were present at 420 °C while above 450 °C, a small difference of 30 °C, only CuO was present. On the other hand, when copper phases were deposited at 450 °C, films were made exclusively of CuO for  $R=10^3$ , and at  $R=10^2$ , a difference of ten orders of magnitude, both CuO and Cu<sub>2</sub>O were present. This is a clear indication that the deposition temperature plays a more important role in the deposition process. Copper films deposited become consistent with this perspective according to the data in Table 1. For instance,  $R$  values in the range from  $5.6 \times 10^3$  to  $6.8 \times 10^3$ , almost a constant value for  $R$ , a film of Cu<sub>2</sub>O is obtained at  $T_d=320$  °C; the CuO phase was obtained at  $T_d=340$  °C. However, at a temperature of 325 °C, it appeared an intermediate phase, 6CuO·Cu<sub>2</sub>O, which is called paramelaconite. To verify that the chemical deposition of this crystalline phase was indeed paramelaconite and not a Cu<sub>2</sub>O/CuO mixture, other experiments were made at deposition temperatures between 325 and 340 °C. The Experimental conditions for this series are summarized in Table 2.

In order to observe the structural transition from single phase Cu<sub>2</sub>O to mixed phase Cu<sub>2</sub>O/CuO and to discuss it on the basis of X-ray diffraction, the deposited film of Cu<sub>2</sub>O was calcined at temperatures of 300 and 350 °C in an air atmospheric 3 h. Calcination was done in a temperature controlled oven at a pressure of 1 atm.

The adherence of the copper oxide films was tested by immersing the covered fiber into warm ethanol

Table 2  
Experimental conditions for the deposition of 6CuO·Cu<sub>2</sub>O films

Sample	Deposition temperature (°C)	Precursor flow (mol min <sup>-1</sup> ) × 10 <sup>-7</sup>	O <sub>2</sub> /Cu(acac) <sub>2</sub> (mole ratio) × 10 <sup>3</sup>
F-330	330	1.07	11.59
F-332	332	1.52	8.15
F-333	333	1.54	8.02
F-336	336	1.59	7.80
F-338	338	2.05	6.00
F-339	339	2.28	5.43

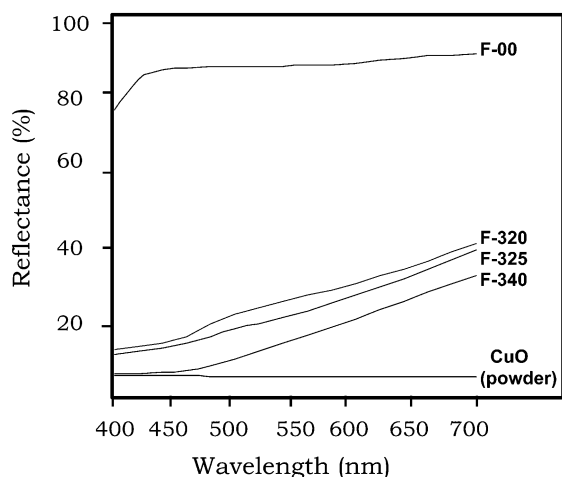


Fig. 1. Specular reflectance (%) spectra of the  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  films deposited on fiberglass at different temperatures. The fiberglass and  $\text{CuO}$  powder were included as references.

(50 °C) with stirring for 1 h. However, for planar surfaces, adherence can easily be tested applying a scotch tape and then removing it abruptly [21].

The copper oxide films on the fiberglass were examined using several techniques. X-ray diffraction patterns (XRD) were obtained with a Siemens D500 X-ray diffractometer using  $\text{Cu-K}\alpha$  radiation. Mean crystallite size in the  $[h k l]$  direction was obtained from the corresponding peak broadening with the Debye Scherrer equation. Preferred orientations were determined by comparing the experimental relative intensities with those reported in the JCPDS cards (International Centre for Diffraction Data). A scanning electron microscope (SEM) model JEOL 1100 was used to observe the film surface morphology. A visible spectrophotometer Macbeth model 7000 with a resolution of 0.1 nm was used to get the spectra, to define colors of the films and to determine the color parameters in each sample.

AFM observations of paramelaconite films were carried out at room temperature using a Nanoscope III manufactured by Digital Instruments. Surface areas of the original fiberglass and of the fibers with coating were determined from the  $\text{N}_2$  adsorption data using an Accusorb 2100-E instrument.

### 3. Results and discussion

The influence of substrate temperature on the nature of the product was examined at the same position in the hot zone. Generally, the films formed on fiberglass showed three different colors; light brown, dark brown and gray when  $\text{Cu}_2\text{O}$ ,  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  or  $\text{CuO}$ , respectively, were present. In the series where the fiberglass was coated with the paramelaconite phase, the difference in color of the crystalline layers was negligible.

Fig. 1 shows the visible reflectance spectra of samples of the first series including as references the original fiberglass (F-00) and  $\text{CuO}$  powder. The shape of the curves indicates that the films deposited on the fiberglass are smooth and homogeneous. These spectra, for films deposited at different temperatures and consequently with a characteristic copper phase, show a gradual change of color in the coating with respect to the deposition temperature. The films deposited at 320 and 340 °C show this color variation clearly (from light brown to gray) due to a change in the structure from  $\text{Cu}_2\text{O}$  to  $\text{CuO}$ .

With respect to XRD results (Fig. 2), it is noted that at a deposition temperature of 320 °C two clear peaks are observed at  $2\theta$  values of 36.4 and 42.3° that correspond to the  $\text{Cu}_2\text{O}$  directions [111] and [200]. These data show that the film deposited under these conditions is composed of cuprite,  $\text{Cu}_2\text{O}$  with a cubic phase (JCPDS card 5-0667). However, if the temperature was higher (325 °C) the diffraction pattern changes

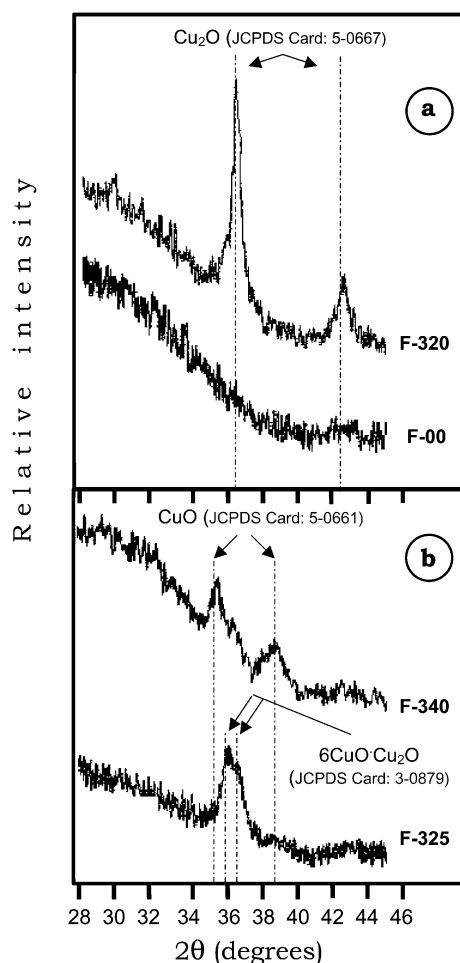


Fig. 2. XRD patterns of the original fiber and of copper films deposited on fiberglass at different temperatures. (a)  $\text{Cu}_2\text{O}$  film, (b)  $\text{CuO}$  and  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  films.

Table 3  
XRD results for  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  films on fiberglass

Sample	Deposition temperature (°C)	Reflection	$2\theta$ (°)	Phase and characteristics of the copper compounds
F-320	320	111	36.4	{Clearly defined peaks of $\text{Cu}_2\text{O}$ , crystallite size of 83 Å}
		200	42.3	
F-325	325	202	35.9	{Small peaks of $6\text{CuO}\cdot\text{Cu}_2\text{O}$ , crystallite size of 70 Å}
		004	36.3	
F-340	340	$\bar{1}11$	35.6	{Clearly defined peaks of $\text{CuO}$ , crystallite size of 79 Å}
		111	38.7	

notably, showing two nearly and broad peaks for the 202 y 004 reflections ( $2\theta=35.9^\circ$  and  $2\theta=36.3^\circ$ ) attributed to the paramelaconite structure (tetragonal) which is a mixed oxide,  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  (JCPDS card 3-0879). Nevertheless, the diffractogram of the F-325 sample shows an additional peak at about  $2\theta=43^\circ$  around the position of the 200 reflection of  $\text{Cu}_2\text{O}$ . This probably indicates a low content of  $\text{Cu}_2\text{O}$ . For the film deposited at 340 °C, the XRD pattern shows the presence of two new peaks close to  $2\theta=35.6$  and  $38.7^\circ$  which correspond to the  $\bar{1}11$  and 111 reflections of the tenorite with

a monoclinic structure,  $\text{CuO}$  (JCPDS card 5-0661). However, it is not possible to know if are preferential these orientations, because it should be regarded that both the  $[\bar{1}11]$  and  $[111]$  directions of  $\text{CuO}$  overlap with other  $\text{CuO}$  reflections, 002 and 200, respectively. Table 3 shows the XRD results for the different samples of the first series.

The SEM image of the surface morphology of samples constituting the first series is shown in Fig. 3. The copper phases deposited, completely covers the substrate. The film appears to be thin and continuous; its surface is an aggregate of separate small grains with diameters smaller than one micrometer. The size of these particles, measured by SEM and reported in a prior publication, ranged between 0.1 and 0.2  $\mu\text{m}$  [18].

Visible spectra for films of the second series, those deposited on a stretch range of temperatures, are shown in Fig. 4. They did not indicate a notable change of the spectral reflectance due possibly to a similar composition. The spectrum of the F-340 sample ( $\text{CuO}$  film) was included as reference.

XRD patterns in the second series are shown in Fig. 5. They are very similar and confirm the diffractogram

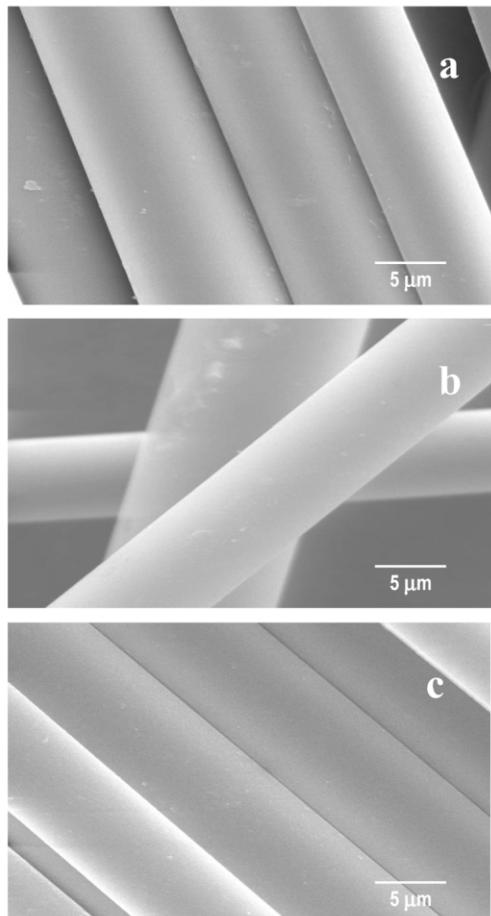


Fig. 3. SEM images of the copper oxide films deposited on fiberglass. (a)  $\text{Cu}_2\text{O}$  at 320 °C, (b)  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  at 325 °C, (c)  $\text{CuO}$  at 340 °C.

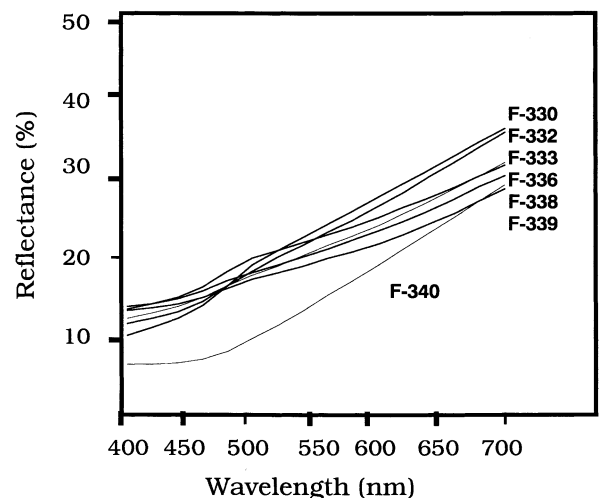


Fig. 4. Specular reflectance (%) spectra of the  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  films deposited on fiberglass at different temperatures. The F-340 sample is included as reference.

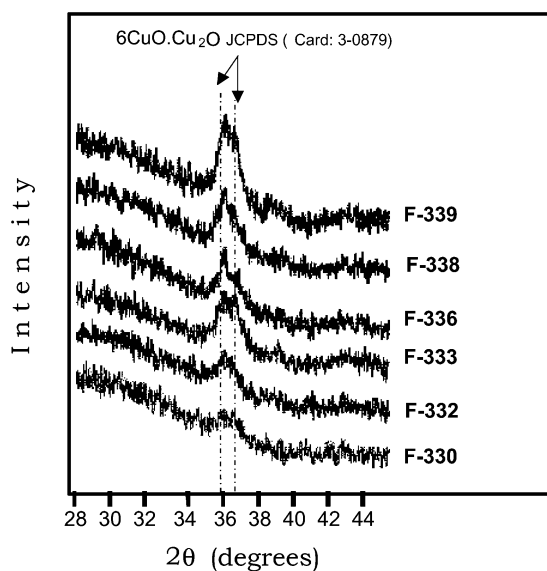


Fig. 5. XRD patterns of the  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  films deposited at different temperatures.

obtained at  $325^\circ\text{C}$ . Again, two clear peaks are seen in  $2\theta=35.9^\circ$  and  $2\theta=36.3^\circ$  for the paramelaconite structure. Reflections of the tenorite or cuprite structure are not clearly observed in these patterns. The corresponding diffractogram of the deposited film at  $330^\circ\text{C}$  shows that weak peaks can be observed. At higher temperatures, the films deposited on fiberglass show clearly the paramelaconite structure by the two characteristic peaks that correspond to the (202) and (004) planes. However, the diffractogram of the F-339 sample barely shows a new small peak in  $2\theta=38.7^\circ$  that corresponds to the preferential position of the 111 reflection of CuO. This indicates the presence of some of the CuO phase due to deposition temperatures near  $340^\circ\text{C}$ . Table 4 summarizes the XRD results from the samples of the paramelaconite series.

The SEM image of these samples are not shown since the surface morphology is the same as the first series

Table 4  
XRD results for  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  films on fiberglass

Sample	Deposition temperature ( $^\circ\text{C}$ )	Reflection	$2\theta$	Phase and characteristics of the copper compounds
F-330	330	202	35.9	{Small peaks of $6\text{CuO}\cdot\text{Cu}_2\text{O}$ , crystallite size of $65\text{ \AA}$ }
		004	36.3	
F-332	332	202	35.9	{Small peaks of $6\text{CuO}\cdot\text{Cu}_2\text{O}$ , crystallite size of $69\text{ \AA}$ }
		004	36.3	
F-333	333	202	35.9	{Defined peaks of $6\text{CuO}\cdot\text{Cu}_2\text{O}$ , crystallite size of $83\text{ \AA}$ }
		004	36.3	
F-336	336	202	35.9	{Defined peaks of $6\text{CuO}\cdot\text{Cu}_2\text{O}$ , crystallite size of $89\text{ \AA}$ }
F-338	338	202	35.9	{Defined peaks of $6\text{CuO}\cdot\text{Cu}_2\text{O}$ , crystallite size of $278\text{ \AA}$ }
		004	36.3	
F-339	339	202	35.9	{Defined peaks of $6\text{CuO}\cdot\text{Cu}_2\text{O}$ , crystallite size of $269\text{ \AA}$ }
		004	36.3	

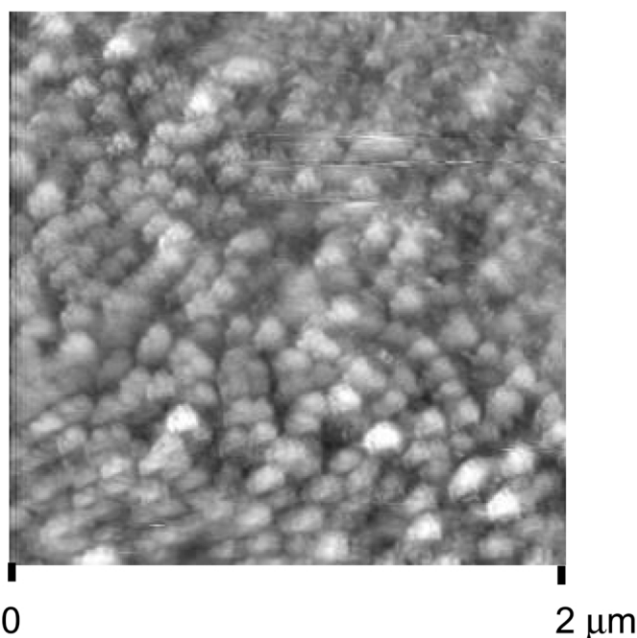


Fig. 6. AFM image of a  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  film grown at a temperature of  $332^\circ\text{C}$ .

(Fig. 3). The typical surface morphology of these films is smooth with splashed particles.

A typical example of a  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  film is illustrated in Fig. 6. From this AFM record one can note that a smooth and regular surfaces is obtained when this copper phase grows on commercial fiberglass. The size of the particles on the surface again ranged, between 0.1 and  $0.2\text{ }\mu\text{m}$ .

The surface area calculated for the original fiberglass was of  $0.2\text{ m}^2\text{ g}^{-1}$  and for the fibers with coatings was between 0.2 and  $1\text{ m}^2\text{ g}^{-1}$ , but not in a well defined order. However, the surface area of all fibers was comparable with aluminosilicate fibers of smaller diameters [3].

The adhesion of the copper oxide films to the fiberglass measured by our washing method indicated good

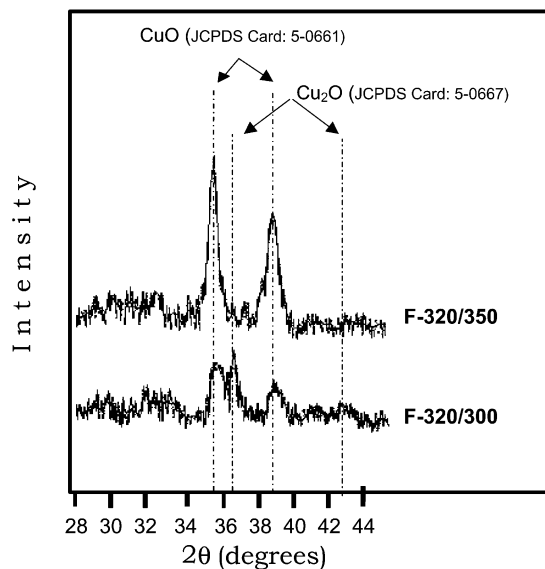


Fig. 7. XRD patterns of the  $\text{Cu}_2\text{O}$  film calcined at 300 and 350 °C.

results. In all samples, the film coating did not exhibit any peeling after washing with warm ethanol (as checked with an optical microscope); therefore, the covered fiberglass passed this adhesion test.

Complementary results are the diffractograms in Fig. 7 that correspond to the film deposited at 320 °C ( $\text{Cu}_2\text{O}$ ) after calcination at 300 and 350 °C, respectively. When the  $\text{Cu}_2\text{O}$  film is calcined at 300 °C, the obtained material is a  $\text{Cu}_2\text{O}/\text{CuO}$  mixture. The corresponding diffractogram shows both the  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  reflections as indicated. Reflections from the paramelaconite structure are not seen in this pattern. With a calcination at higher temperature (350 °C), the deposited film has the tenorite structure,  $\text{CuO}$ , as indicated in this figure by the presence of peaks at  $2\theta=35.6^\circ$  and  $38.7^\circ$ . In these experiments it is observed that when the  $\text{Cu}_2\text{O}$  film is thermally treated, this copper specie is converted directly to  $\text{CuO}$  and at 350 °C it completely crystallizes into the tenorite phase.

This indicates, first, that the best process for producing a  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  film is by its direct deposition and, secondly, that the optimal temperature range is between 332 and 338 °C as shown in Fig. 5.

#### 4. Conclusions

Copper oxides as thin films were obtained by chemical vapor deposition on fiberglass substrates. Experimental conditions that lead to the formation either the

$\text{Cu}_2\text{O}$  phase or  $\text{CuO}$  oxide have been discussed previously. However, it was interesting to see a continuous film when the  $6\text{CuO}\cdot\text{Cu}_2\text{O}$  phase was deposited directly and at a relatively low temperature.

X-ray diffraction results show that the paramelaconite structure does not occur as an intermediate phase when  $\text{Cu}_2\text{O}$  is converted to  $\text{CuO}$  after a post-deposition calcination. It can be obtained directly by a chemical deposition process. It appears that the microtopography and the homogeneity of the films do not depend on the copper phase, exhibiting in all cases nanometric features that modify the optical properties as color variations and spectral reflectance.

#### References

- [1] R.S. Hay, J.R. Welch, M.K. Cinibulk, *Thin Solid Films* 308–309 (1997) 389.
- [2] J. Muñiz, J.E. Herrero, A.B. Fuertes, *Appl. Catal. B: Environ.* 18 (1998) 171.
- [3] M. Yoshikawa, A. Yasutake, I. Mochida, *Appl. Catal. A: Gen.* 173 (1998) 239.
- [4] D. Klvana, J. Kirchnerová, J. Chaouki, J. Delval, W. Yaici, *Catal. Today* 47 (1999) 115.
- [5] R.N. Briskman, *Sol. Energy Mater. Sol. Cells* 27 (1992) 361.
- [6] M.T.S. Nair, L. Guerrero, O.L. Arenas, P.K. Nair, *Appl. Surf. Sci.* 150 (1999) 143.
- [7] K.R. Harikumar, C.N.R. Rao, *Catal. Lett.* 47 (1997) 265.
- [8] K.S. Lin, H.P. Wang, *Appl. Catal. B: Environ.* 22 (1999) 261.
- [9] A.B. Gurevich, B.E. Bent, A.V. Teplyakov, J.G. Chen, *Surf. Sci.* 442 (1999) L971.
- [10] H. Chu, L. Lei, X. Hu, P. Yue, *Energy Fuels* 12 (1998) 1108.
- [11] L. Pranevicius, L.L. Pranevicius, P. Valatkevicius, V. Valincius, *Surf. Coat. Technol.* 123 (2000) 122.
- [12] G.G. Condorelli, G. Malandrino, I. Fragala, *Chem. Vapor Dep.* 5 (1) (1995) 21.
- [13] G.E. Buono-Core, M. Trejo, J. Lara, F. Aros, R.H. Hill, *Mater. Res. Bull.* 34 (14/15) (1999) 2333.
- [14] L.L. Díaz, J.J. Pérez-Bueno, Y.V. Vorobiev, J.R. Martínez, F. Ruíz, F. Pérez-Robles, J. González-Hernández, *Mater. Lett.* 42 (2000) 25.
- [15] S.S. Moon, J.S. Lee, S.W. Han, J.W. Park, T.H. Lee, S.K. Yang, H.H. Park, *J. Mater. Sci.* 29 (1994) 1545.
- [16] M.J. Hampden-Smith, T. Kodas, *Chem. Vapor Dep.* 1 (1995) 8.
- [17] M.J. Hampden-Smith, T. Kodas, *Chem. Vapor Dep.* 2 (1995) 39.
- [18] J. Ramírez-Ortíz, T. Ogura, J. Medina-Valtierra, S.E. Acosta-Ortíz, P. Bosch, J.A. de los Reyes, V.H. Lara, *Appl. Surf. Sci.* 174 (3–4) (2001) 177–184.
- [19] J. Ramírez-Ortíz, T. Ogura, J. Medina-Valtierra, S.E. Acosta-Ortíz, P. Bosch, J.A. de los Reyes, V.H. Lara, *Rev. Soc. Quím. Méx.* 44 (3) (2000) 215.
- [20] G.G. Condorelli, G. Malandrino, I. Fragala, *Chem. Mater.* 6 (1994) 1861.
- [21] H. Shin, R.J. Collins, M.R. Cruire, A.H. Heuer, C.N. Suenik, *J. Mater. Res.* 10 (1995) 692.