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Factorial electrochemical design for tailoring of morphological and optical properties of Cu_2O

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Abstract

The electrodeposition of cuprous oxide (Cu_2O) onto FTO-coated glass substrate was studied by using a statistical approach in order to control the Cu2O morphology and optical properties. The factorial design considered four electrodeposition conditions at two representative levels as input variables (electrolyte temperature and pH, deposition potential and duration) and the deposition charge and morphology of obtained Cu2O as the output variables. The morphology analysis showed the highest influence on crystal shape was exhibited by electrolyte temperature and pH, reaching significance levels of 95 and 98%, respectively. Temperature as low as 35°C and pH 12.2 results in cubic morphology, while other parameters result in octahedron shape. The highest absorbance was exhibited by the Cu_2O with cubic morphology.

Key Words**: Electrodeposition, morphologies of Cu_2O, 2-level factorial design.**

1.- INTRODUCTION

Cuprous oxide, Cu_2O, also known as mineral cuprite, is a transition metal oxide, reddish grey in colour, with a density of 6 $gr.cm^{-3}$, that crystallizes in a face centered cubic lattice (fcc) with a lattice parameter of $4,267 \cdot 10^{-10}$ m [1].

This mineral occurs naturally, generally in the form of octahedral crystals, although cubic and dodecahedral crystals are by no means rare. On occasions it can also be found in the form of bright red fibrous crystals.

Due to its being a p-type semiconductor, it is used in thin layers for optical and optoelectronic applications. These applications are particularly based on the direct energy gap (2.0 eV a 300 K), have a high absorption coefficient in the visible region and an estimated theoretical solar conversion efficiency of approximately 12% [2, 3, 4].

Cuprous oxide of different morphologies (thin layers, cubes, octahedral, fibers, etc.) can be grown by a number of different deposition techniques, such as chemical vapor deposition (CVD), spray pyrolysis, thermal oxidation, sputtering, chemical oxidation and electrodeposition.

The techniques used to obtain semiconductors have evolved from the primitive fused salt electrolysis, used particularly in Si and Ge purification, up to the methods in current use, as mentioned above, of which electrodeposition is the most widely used.

Since most of these techniques produce films with a mix of Cu_2O and CuO, it is highly important to find the specific synthesis reaction parameters of pure Cu_2O.

In the present study we used the cathodic reduction method by applying electrodeposition (ELD) [5,6,7] to a glass substrate coated with a conductive layer of fluorine doped tin oxide (FTO). In previous studies we had experimentally determined the optimal parameters of temperature, potential, pH and electrodeposition time for film growth. Optical property spectra were also carried out at ambient temperature to study the evolution of optical emission properties of the different morphologies obtained.

2. EXPERIMENTAL PROCEDURE AND RESULTS

2.1 Experimental Procedure

Samples were obtained by electrodeposition (ELD) on a 1 x 3 cm^2 glass substrate coated with a thin layer of fluorine doped tin oxide (FTO).

For the control of applied potential, exposure time and temperature, a Model 263A potentiostat-galvanostat and its corresponding cell (EG&G DIVISION INSTRUMENTS, INC.) was used. The electrolyte was heated by a water bath.

The reference electrode used was Ag/AgCl in a saturated solution of KCl/AgCl and a Pt counterelectrode. Electrolyte was a solution of: SO_4Cu (0,4 M) + Lactic Ac. (3 M) + Na OH (4 M) + de-ionized water.

Previous to electrodeposition, potentiostatic voltammetry of +1 a –1 volts was performed to determine the range in which reduction processes would occur.

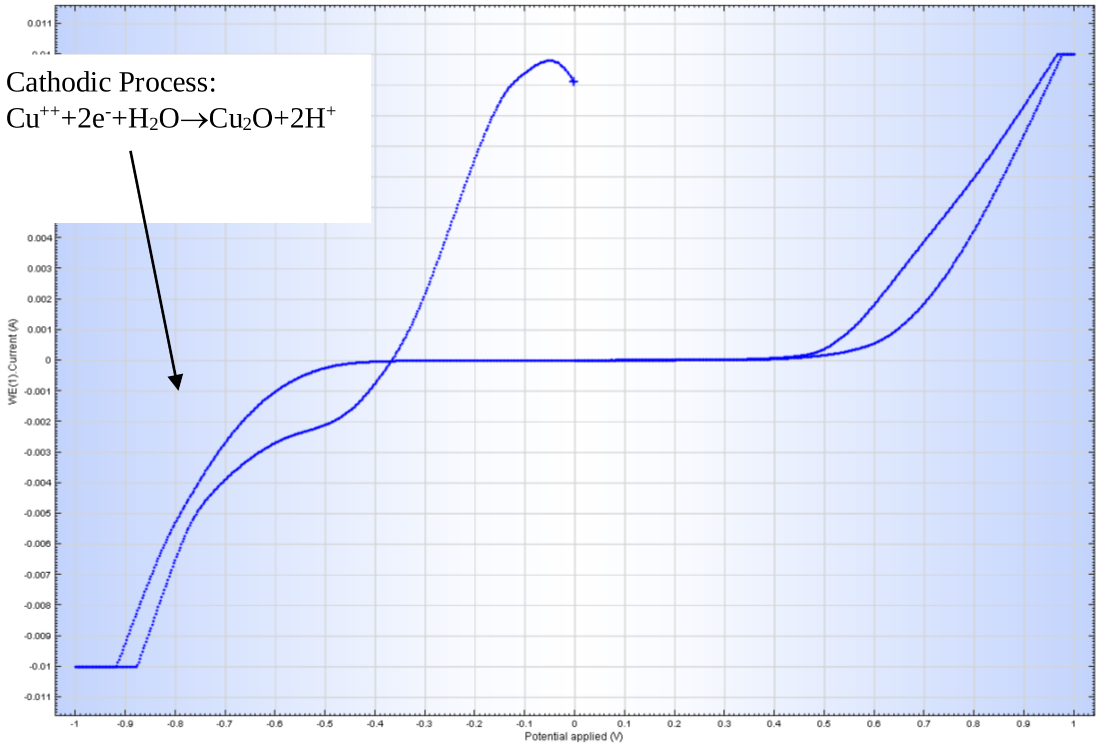
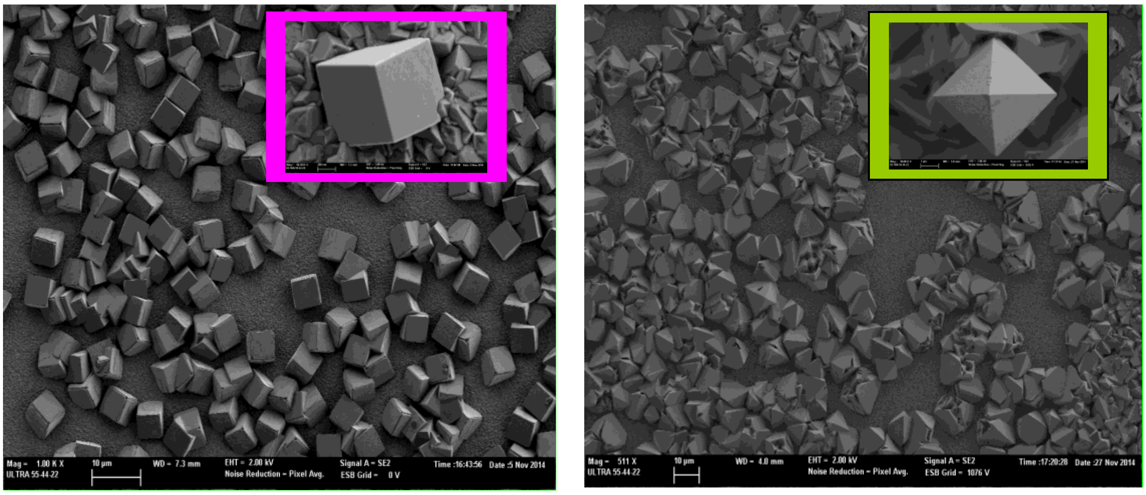

Cathodic Process:
$Cu^{++}+2e^{-}+H_2O \rightarrow Cu_2O+2H^{+}$

Figure 1.- Potentiostatic voltammetry

As can be seen in Figure 1, reduction processes took place within a potential range of – 0.5 V to -0.9 V, at 35 ºC and 60ºC with no apparent differences between these temperatures.

From a study of the Pourbaix diagram [8] of a $Cu\text{-}H_2O$ system with lactic acid at 25 ºC, it can be seen that the Cu^{++} stability area increases when lactic acid is added to the solution, thus raising the pH range, so that it is possible to have Cu^{++} without precipitating CuO. In other words, lactic acid is added to the solution as a complexing agent on Cu^{++} until it is reduced to Cu_2O..

Morphological characterization of the deposited structures was by Field Emission SEM. As can be seen in Figure 2, the predominant morphologies were cubes and octahedrons.



a) b)

Figure 2. Characteristic morphologies of Cu_2O: a) Cubes; b) Octahedrals.

The crystalline structure and coating were studied by X-ray diffraction (Rigaku ULTIMA IV diffractometer), with CuK radiation and 0.5° angle of incidence.

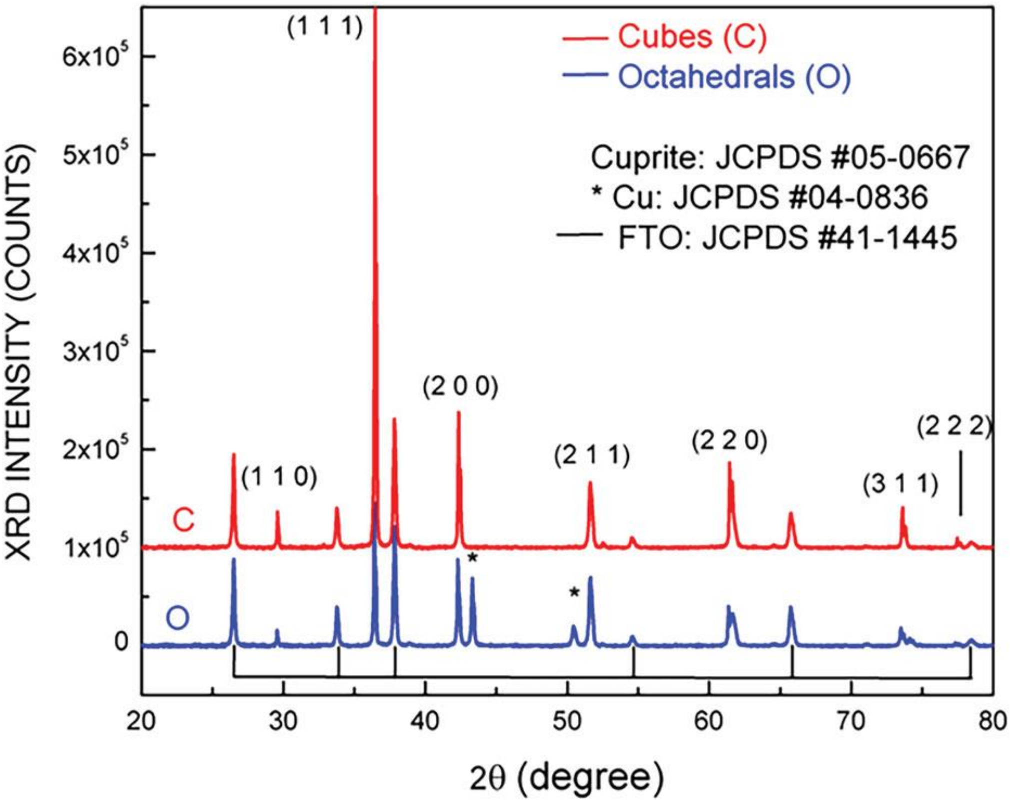


Figure 3. Diffractogram of Cu_2O deposited on FTO.

Figure 3 and Table 1 show the diffractogram of the m3 sample and the corresponding 2θ diffraction angles of Cu_2O and FTO.

No.	2-theta(deg)	d(ang.)	Height(cps)	Size(ang.)	Phase name	DB card number	Rel. height
1	26.4999	3.36075	56404.28	557.83	Cassiterite, syn(1,1,0)	00-041-1445	14.68
2	29.5818	3.01725	22073.54	1029.88	Cuprite, syn(1,1,0)	00-005-0667	5.74
3	33.7765	2.65152	24330.51	537.54	Cassiterite, syn(1,0,1)	00-041-1445	6.33
4	36.4415	2.46349	384298.34	928.57	Cuprite, syn(1,1,1)	00-005-0667	100
5	37.825	2.3761	75953.74	534.11	Cassiterite, syn(2,0,0)	00-041-1445	19.76
6	42.3234	2.13374	79274.29	910.33	Cuprite, syn(2,0,0)	00-005-0667	20.63
7	51.6221	1.76912	43811.36	419.37	Cassiterite, syn(2,1,1)	00-041-1445	11.4
8	52.4883	1.74194	3607.02	925.98	Cuprite, syn(2,1,1)	00-005-0667	0.94
9	54.5841	1.67991	5979.12	351	Cassiterite, syn(2,2,0)	00-041-1445	1.56
10	61.3915	1.50894	50673.93	818	Cuprite, syn(2,2,0)	00-005-0667	13.19
11	61.671	1.50277	21427.62	383.74	Cassiterite, syn(3,1,0)	00-041-1445	5.58
12	64.4371	1.44477	449.49	333.57	Cassiterite, syn(1,1,2)	00-041-1445	0.12
13	65.7262	1.41952	24502.53	393.61	Cassiterite, syn(3,0,1)	00-041-1445	6.38
14	73.5411	1.28678	27932.36	795.46	Cuprite, syn(3,1,1)	00-005-0667	7.27
15	77.4036	1.23192	6658.03	677.97	Cuprite, syn(2,2,2)	00-005-0667	1.73
16	78.4603	1.21796	3454.16	305.81	Cassiterite, syn(3,2,1)	00-041-1445	0.9

Table 1. Values of 2θ diffraction angles of Cu_2O and FTO.

To keep the number of experiments (prepared samples) to a minimum, a 2-level factorial design was adopted [9].

As there were four variables or factors to be considered at two levels, this approach involved 16 experiments (2x2x2x2 = 2^4).

Table 2 gives the values of the parameters in each experiment.

Table 2.Variables or control parameters and work levels.

Variable or factor	Codified Var.	Low level (-)	High level (+)
Temperature	A	35 ºC	60 ºC
Potential	B	-700 mV	-500 mV
ph	C	12.18	12.8
Time	D	35 minutes	75 minutes

Table 3. Design matrix, deposited charge aand morphologies (cubes and octahedrons)

Sample	A	B	C	D	% cubes and/or octahedrons	Deposited charge	Deposited charge C/cm^2
m1	-	-	-	-	80 % cubes	4.684	1.87
m2	+	-	-	-	100% octas.	6.64	2.66
m3	-	+	-	-	All cubes	2.43	0.97
m4	+	+	-	-	100 octas.	5.40	2.16
m5	-	-	+	-	100 octas.	2.12	0.85
m6	+	-	+	-	100 octas.	3.63	1.45
m7	-	+	+	-	100 octas.	0.038	0.015
m8	+	+	+	-	70 octas.	0.70	0.28
m9	-	-	-	+	100 % Cubes	10.55	4.22
m10	+	-	-	+	50 Cubes 50	8,317	3.32

					0ctas.		
m11	-	+	-	+	95 % cubes	5.32	2.13
m12	+	+	-	+	100 % octas.	12.76	5.10
m13	-	-	+	+	100 % octas.	1.70	0.68
m14	+	-	+	+	100 % octas.	3.57	1.48
m15	-	+	+	+	90 % octas.	0.17	0.068
m16	+	+	+	+	100 % octas.	0.583	0.2332

Table 3 gives the results obtained (deposited charge and morphology) by combining the two levels of the factors considered, as shown in Table 2:

Optical properties (transmittance) were determined by a spectrophotometer with integrating sphere and CCD detector optimized for the UV-VIS range. The spectra obtained are shown in Figure 4.

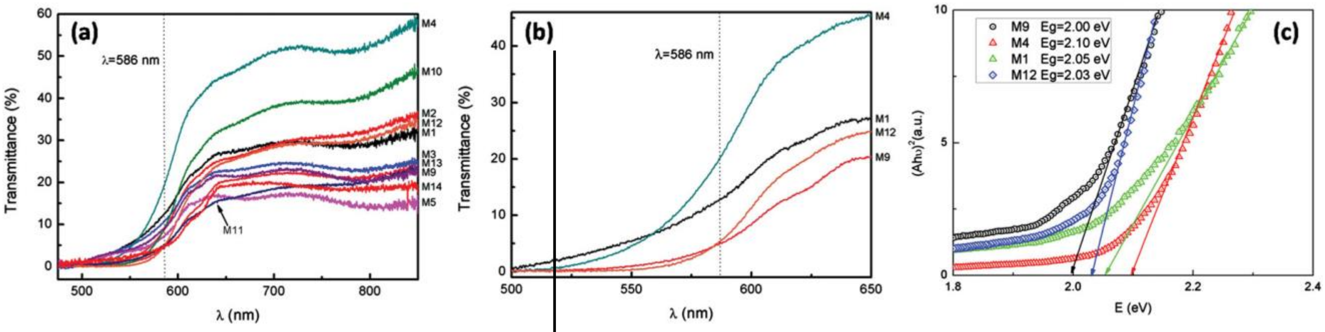


Figure 4. Optical transmission spectra of samples (m_1 to m_{16}) of Cu_2O.

2.2 Analysis of results

In this study we analyzed designs in which each variable or factor occurred only at two levels, identified as lower (-) and higher (+). General factorial designs and 2-level designs are important since few experiments are required for each factor, and, in spite of not being able to exhaustively explore a large region of the factor space, they can point to tendencies and so indicate a promising line for future studies. An additional advantage is that the results can be interpreted to a large extent by means of common sense and simple arithmetic.

The response variables, deposited charge and morphology were analyzed by a standard Yates algorithm on STRATGRAPHICS software [10].

2.3 Interpretation of results

The values of the response variables, deposited charge (C/cm^2) and percentage of cubes or octahedrons were analyzed by a Yates algorithm, for which the experiments were placed in the standard order, as seen in Table 3 (STATGRAPHICS Plus. Version 5.0 software was used).

For the deposited charge response variable, the analysis is:

Average = 1.71789 +/- 0.202731
A:Factor_A = 0.735025 +/- 0.405462
B:Factor_B = -0.696725 +/- 0.405462
C:Factor_C = -2.17172 +/- 0.405462
D:Factor_D = 0.872025 +/- 0.405462
AB = 0.412525 +/- 0.405462
AC = -0.277475 +/- 0.405462
AD = 0.023775 +/- 0.405462
BC = -0.269225 +/- 0.405462
BD = 0.154525 +/- 0.405462
CD = -0.905475 +/- 0.405462

The effect of a factor is understood to be a change in the response of the factor from level (-) to (+).

There is an interaction between two factors if the effect of one of them is modified on changing the considered levels of another factor.

The interpretation of the process development data indicates that the mean value of deposited charge is 1.71789 (C/cm^2) for the 16 cases studied.

The effects of some factors and interactions of two factors are also seen to be significant.

Thus, factor A (process temperature) causes the response variable (deposited charge) to rise by 0.735025 on moving from low level 35º C (-) to high level 60º C (+) in the process for all conditions of other factors.

Similarly, factor C (pH) is the most significant and lowers the response variable by 2.17172 units on changing from 12.18 (-) to 12.80 (+).

A more powerful analysis can be carried out with Analysis of Variance (ANOVA) (Table 4), which studies the effect of one or more factors on the mean of the response variable. We used STATGRAPHICS Plus Version 5.0 for these calculations.

Table 4. Analysis of Variance

Source	**Sum of Squares**	**Gl**	**Mean square**	**F-Ratio**	**P-Value**
A: Factor A	2.16105	1	2.16105	3.29	0.1296
B: Factor B	1.9417	1	1.9417	2.95	0.1464
C: Factor C	18.8656	1	18.8656	28.69	**0.0030**

D: Factor D	3.04171	1	3.04171	4.63	**0.0842**
AB	0.680708	1	0.680708	1.04	0.3556
AC	0.30797	1	0.30797	0.47	0.5242
AD	0.002261	1	0.002261	0.00	0.9555
BC	0.289928	1	0.289928	0.44	0.5361
BD	0.0955119	1	0.0955119	0.15	0.7188
CD	3.27954	1	3.27954	4.99	**0.0759**
Total error	3.288	5	0.657599		
Total (corr.)		15			
Total (corr.)	33.9539	15			

The interpretation of the results indicates that the pH factor (coded C) is significant to a level of 99.7%, time (coded D) to 91,6% and the CD interaction to 92.41%, i.e. they influence the response variable by either raising or lowering it by the calculated value (Table II). The other factors and interactions are not significant at this level.

For the deposited morphology response variable (cube formation) the analysis is:

Mean = 29.0625 +/- 3.98483

A:Factor_A = -38.125 +/- 7.96967

B:Factor_B = 0.625 +/- 7.96967

C:Factor_C = -48.125 +/- 7.96967

D:Factor_D = 5.625 +/- 7.96967

AB = -5.625 +/- 7.96967

AC = 43.125 +/- 7.96967

AD = -0.625 +/- 7.96967

BC = 9.375 +/- 7.96967

BD = -11.875 +/- 7.96967

CD = -10.625 +/- 7.96967

The interpretation of the process development data indicates that the mean value of cube formation is 29.0625 for the 16 cases studied. The most significant factors are: temperature (factor A), pH (factor C), and AC interaction (factors A and C considered jointly). This information is confirmed by the variance analysis in Table 5.

Table 5. Analysis of Variance

Source	**Sum of Squares**	**Gl**	**Mean square**	**F-Ratio**	**P-Value**
A: Factor A	5814.06	1	5814.06	22.88	**0.0050**
B: Factor B	1.5625	1	1.5625	0.01	0.9405
C: Factor C	9264.06	1	9264.06	36.46	**0.0018**
D: Factor D	126.563		126.563	0.50	0.5118
AB	126.563		126.563	0.50	0.5118

AC	7439.06	1	7439.06	29.28	**0.0029**
AD	1.5625	1	1.5625	0.01	0.9405
BC	351.563	1	351.563	1.38	0.2924
BD	564.063	1	564.063	2.22	0.1964
CD	451.563		451.563	1.78	0.2400
Total error	1270.31	5	254.063		
Total (corr.)		15			

Total (corr.) 25410.9 15

This analysis confirms that temperature (factor A) is significant to 99.5% (P-value 0.005), pH (factor C) to 99.99% (P-value 0.0018) and AC interaction also to 99.99%.

Also, according to Figure 4, considering that the Cu_2O bandgap (2 eV) limits usable wavelengths ≤ 586 nm, it can be seen that the highest absorbances are found in samples m_1, m_2, m_3, m_4, m_5, m_9, m_{10}, m_{11}, m_{12} and m_{13}. It can also be seen that for equal deposited charges the samples with cubic morphology have greater absorption than those with octahedral morphology (e.g. m_3 and m_5 or m_1 and m_6). This is undoubtedly due to the External Surface/Volume ratio of the cubic samples being greater than that of the octahedral samples. As can be seen in Figure 2 and for the observed parameter of the edge of cube = $1.333 \cdot 10^{-6}$ m compared to = $5.1 \cdot 10^{-6}$ m, the S/V ratio of the cube is 3.2 times greater than that of the octahedron.

Conclusions

The factorial design of Cu2O electrodeposition indicated the deposition charge can be controlled by electrolyte pH (significance 99.7%) and deposition duration (significance 91.6%). For specific shaped Cu2O crystals, electrolyte temperature and pH showed the most significant effects, reaching levels of 95 and 98%, respectively (when temperature increased from 35 to 60 ºC and pH from 12.2 to 12.8), that is predominant cubicmorphology can be obtained at 35ÅãC and pH 12.2. The Cu2O films with predominantly cubic morphology exhibited the lowest transmittance. This work highlights the importance of combined electrodeposition conditions in order to tailor both morphological and optical properties of Cu2O films for optoelectronic applications.

Acknowledgements

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