Copper Sulfate Pentahydrate Target Behavior During Pulsed Laser Deposition to Produce Dichroic Coatings for Beam Splitters

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Abstract. Copper sulfate pentahydrate (CuSO₄·5H₂O) used as target in the pulsed laser deposition (PLD) process led to producing thin films with dichroic properties. The coatings were applied on glass slab and hemp fabrics. Investigation of CuSO₄·5H₂O transformation during ablation and deposition based on FTIR analysis showed that the thin film chemical composition is a mixture of different products resulted from CuSO₄·5H₂O dehydration and decomposition, followed by melting and vaporization of the CuO and recombination of the different species in the plasma of ablation. Simulation in COMSOL of the CuSO₄·5H₂O laser heating anticipates the processes and phenomena to be expected during PLD. Optical properties of the thin films are investigated in UV-Vis as reflecting properties and by laser induced fluorescence (LIF). Applications are considered for dichroic plate beamsplitters, as well as others. Dichroic beamsplitters have a large range of applications among which they are useful for combining / splitting laser beams of different color. When the chemical composition provides also electrical conductivity specific properties, the coating may bring more value to the new device or material. In order to ascertain whether a dichroic system can be produced one way or the other achieving at the same time specific characteristics, it is important to understand the physico – chemical processes behind that. With this study, we determine the method to produce dichroic coatings on glass and on hemp fabric, looking at the same time into the mechanism that leads to the result.

1. Introduction

The aim of this study is to investigate pentahydrate copper sulfate target behavior under laser irradiation expected being that chemical reactions that may occur, should lead to a dichroic beam splitter based on coatings of copper derivative compounds. COMSOL simulation was performed to provide information on thermal conditions developed on the target for preliminary estimations.

Previously reported depositions of copper derivative compounds have started from copper metallic target or copper oxide, being conducted in specific gaseous atmosphere to provide chemical elements or groups for the desired end product [1-5]. Different from that, herein we consider that the target itself can supply the elements and groups for the product without gaseous atmosphere in the deposition
chamber and without further preparation and processing needed neither before, nor during or after deposition.

Dichroic beamsplitters have a large range of applications among which they are useful for combining / splitting laser beams of different colors [6-8]. When the chemical composition provides also electrical conductivity specific properties, the coating may bring more value to the new device or material [9, 10] and for its possible applications in optoelectronics [5].

Recent researches have reported copper effects to inactivate coronavirus to less than 60 minutes [11], including new coronavirus SARS-CoV-2 responsible for Covid 19 disease [12], while the virus time life on other materials counts days. With regards to these studies, pulsed laser deposition of copper and copper derivatives may be used for producing coatings on materials for protection masks and other cloths used in medical and for day to day activities.

In order to ascertain whether a dichroic system or medical device can be produced one way or the other achieving at the same time specific characteristics, it is important to understand the physico – chemical processes behind that. With this study we determine the method to produce coatings on glass and on hemp fabric by PLD method that uses copper sulfate as target, looking at the same time into the mechanism that leads to the final result. Dichroic properties will be studied based on the UV-Vis properties of reflection and transmission.

2. Methods and materials
A target of pentahydrate copper sulfate was used for film deposition on substrates of glass and of hemp twill fabric. The deposition was perform by Pulsed Laser Deposition (PLD) with YG 981E/IR-10 laser system using the following parameters: \( \tau = 10 \) ns pulse width, \( \lambda = 532 \) nm wavelength, \( \alpha = 45^\circ \) incident angle, \( \nu = 10 \) Hz pulse repetition time, \( r = 336 \) \( \mu \)m spot radius, \( F = 25 \) J/cm2 fluence, \( d = 3.5 \) cm distance between target and support, pressure in the deposition chamber (Figure 1) \( 3 \times 10^{-2} \) Torr.

3. Results and discussions
3.1. COMSOL simulation
COMSOL simulation was conducted using the numerical model reported in [13, 14] to anticipate deposition results and to evaluate chemical species that are expected to form during PLD process.

(a) 
(b)

**Figure 1.** Target phase change \( T(x) \): Temperature diagram on target irradiated spot area with maximum value (a); phase change based on CuSO\(_4\)·5H\(_2\)O dehydration and CuSO\(_4\) decomposition (b).

Based on COMSOL simulation results (Figure 1), decomposition steps of pentahydrated copper sulfate are noticed as being possible. In a first step, \( 383K < T < 923K \), CuSO\(_4\)·5H\(_2\)O loses water
molecules resulting into CuSO₄ anhydrous. Following that, in a second step CuSO₄ decomposes based on the chemical reaction described by equation (1).

\[
CuSO_4 \cdot 5H_2O \rightarrow CuO + SO_2 + O_2
\]  

(1)

The thin layer is expected to contain mainly CuO, but also CuSO₄ from ablation as clusters sourced in the dehydrated area, but also from recombination of the gas phase and ionic phase in the plasma plume of ablation.

![Figure 2](image.jpg)

**Figure 2.** Schematic representation of the target spot area affected by the laser irradiation during one pulse width.

\[ r_1 = 0.343 \text{ mm}; \ r_2 = 0.273 \text{ mm}. \]

\[
A_2 = \frac{\pi r_2^2}{2} = \frac{\pi (0.273)^2}{2} = 0.117069879 [mm^2]
\]

\[
A_1 = \frac{\pi r_1^2}{2} = \frac{\pi (0.273)^2}{2} = 0.184802617 [mm^2]
\]

\[
A_{ring} = A_1 - A_2 = \frac{\pi}{2} (r_1^2 - r_2^2) = \frac{\pi}{2} ((0.343)^2 - (0.273)^2) = 0.067732738 [mm^2]
\]

CuO (copper oxide) resulted in the thermal effect during laser beam interaction with the CuSO₄·5H₂O target, melts (M.P. = 1326°C = 1599K) and vaporizes (B.P. = 2000°C = 2273K). Plasma formation temperatures are even greater, 10⁴K order, leading to further breaking and recombination.

3.2. **Fourier transform infrared spectroscopy (FTIR)**

The chemical composition was analyzed with Fourier transform spectroscopy (FTIR) for both the target and the pulsed laser deposited film. The results evidenced by the changes in the spectra of Figure 3, show that different chemical species were obtained in the film, including copper sulfate, but also copper oxide and copper in metallic state as hydrogen sulfide adsorbed on the film indicates.

Based on the spectra of Figure 3, the chemical groups and vibrations for the target and thin film are identified and presented in Table 1 and Table 2, respectively.

Due to the conditions during ablation, the decomposition of pentahydrate copper sulfate takes place as per equation (1), followed by other interactions and recombination resulting in a mixed chemical composition of the thin film. FTIR analyses show difference between the target and thin film. The presence of the copper sulfate is shown on FTIR bands with wavenumbers of 1109 cm⁻¹; 874 cm⁻¹; 692 cm⁻¹; 983 cm⁻¹ for (SO₄)²⁻. Other compounds than those of the target are formed presumably due to recombination, such as free OH and H bonded noticed at 3435 cm⁻¹ wavenumber and H₂O recombined as 1648 cm⁻¹ band indicates.
Figure 3. FTIR compared spectra of copper sulfate target and thin films obtained by PLD method.

Table 1. Target of pentahydrate copper sulfate groups and IR vibrations.

| Wavenumber (cm\(^{-1}\)) | Vibration and groups | References |
|---------------------------|----------------------|------------|
| 3435                      | broad band – OH free and H bonded | [15] |
| 3300-3280                 | Cu-OH (OH from water) | [16, 17, 18] |
| 1648                      | H\(_2\)O bending vibrations (\(\delta\) H\(_2\)O within 1800-1300 cm\(^{-1}\) spectral region) | [15] |
| 1109                      | (SO\(_4\))\(^2-\) antisymmetric stretching modes | [15, 17, 18] |
| 874; 692                  | (SO\(_4\))\(^2-\) bending modes | [15, 17, 18] |
| 983                       | (SO\(_4\))\(^2-\) symmetric stretching modes | [15, 17, 18] |
| 3743; 3670; 3649          | OH free | [15, 18] |

Table 2. The thin film groups and IR vibrations.

| Wavenumber (cm\(^{-1}\)) | Vibration and groups | References |
|---------------------------|----------------------|------------|
| 3435                      | broad band – OH free and H bonded | [15] |
| 3300-3280                 | Cu-OH (OH from water) | [16, 17] |
| 1648                      | H\(_2\)O bending vibrations (\(\delta\) H\(_2\)O within 1800-1300 cm\(^{-1}\) spectral region) | [15] |
| 1109                      | (SO\(_4\))\(^2-\) antisymmetric stretching modes | [15, 17, 18] |
| 874; 692                  | (SO\(_4\))\(^2-\) bending modes | [15, 17, 18] |
| 983                       | (SO\(_4\))\(^2-\) symmetric stretching modes | [15, 17, 18] |
| 3743; 3670; 3649          | OH free | [15, 18] |
| 2459                      | H\(_2\)S adsorbed on copper (2500-2600) | [15, 16] |

Also the H\(_2\)S adsorbed on copper is indicated by the 2459 cm\(^{-1}\) band which confirms the existence of copper in metallic state. Copper oxide is confirmed by OO stretching vibration at 1105 cm\(^{-1}\) [19].
3.3. UV-Vis thin films spectra

For the same thin film deposited on glass, three UV-Vis measurements in three different spots of the same film were performed, namely PLD CuSO4/glass, PLD CuSO4/glass -edge 1, PLD CuSO4/glass -edge 2, and for the film deposited on hemp, two measurements in two different spots of the same film were performed, namely PLD CuSO4/hemp 1, PLD CuSO4/hemp 2. The UV-Vis spectra in Figure 4 (a) show reflection at the same wavelengths of 480 nm, 575 nm, 633 nm, 665 nm, 696 nm in visible and 930 nm, 967 nm in near infrared (NIR), which shows same chemical species have been deposited, but different rates of reflected wavelengths prove different quantities of each species. Transmittance spectra performed on PLD CuSO4/glass, PLD CuSO4/glass -edge 1, show maximum in NIR region at 1037 nm and 1021 nm, respectively. If deconvolution is analyzed, two spectra could be components of the main registered spectrum, with peaks at (727 nm, 996 nm) and (710 nm, 981 nm) for each of the two spots (Figure 4 b). The thin films show dichroic properties as evidenced by UV-Vis measurements (Figure 4 and Table 3), properties that are induced by the film chemical composition as a mixture of different chemical species, as it had already been evidenced by the FTIR spectra (Figure 3) and SEM-EDS mapping elemental distribution (Figure 7 a-f), as well as elemental composition of the thin films (Table 4). Another characteristic of the thin film that determine dichroic property is the granular morphology of the thin film as SEM images of Figure 6 a, b show.

| Table 3. Reflection intensities (%) |
|-----------------------------------|
| \( \lambda \) (nm) | PLD CuSO4/ glass -edge 1 | PLD CuSO4/ glass -edge 2 | PLD CuSO4/ glass | PLD CuSO4/ hemp 1 | PLD CuSO4/ hemp 2 |
|-----------------|----------------|----------------|----------------|----------------|----------------|
| 480             | 17.77          | 16.08          | 14.85          | 17.63          | 20.15          |
| 575             | 38.85          | 40.17          | 39.65          | 42.81          | 49.29          |
| 633             | 38.37          | 39.88          | 38.3           | 42.53          | 48.2           |
| 665             | 46.42          | 37.43          | 36.96          | 46.76          | 54.47          |
| 696             | 42.94          | 28.71          | 32.98          | 46.76          | 53.93          |
| 930             | 7.26           | 3.57           | 5.85           | 8.01           | 8.97           |
| 967             | 3.99           | 1.46           | 3.74           | 4.53           | 5.55           |

(a)

(b)

**Figure 4.** Optical properties of thin films obtained from CuSO4 using PLD method: Reflection spectra (a); Transmittance spectra of thin film PLD CuSO4/glass (b).
3.4. Laser induced fluorescence (LIF)

LIF spectroscopy was conducted with YG 981E/IR-10 laser system as for PLD process, but using 355 nm wavelength laser irradiation, 10 ns pulse width, 10 Hz repetition and 150 mJ energy. The LIF spectra of Figure 5 show the presence of both copper oxide and copper sulfate. The curvature going up in 400 nm region could be assessed to the emission of sulfur dioxide (from copper sulfate), reported by Syty et al. as fluorescence emission in the range 290 - 310 nm [20-24]. The emission band at 699 nm may be assessed to the peak that goes up to 750 nm representing copper fluorescence [22, 27, 28]. Tower bands in the ranges of 482 nm – 508 nm and 587 nm – 627 nm of the spectrum are consistent with hydroxyl radical formation, according to Cocean et al. [25, 26]. The hydroxyl groups denote either molecular water in the thin film or copper hydroxyl produced under PLD process.

| Table 4. Elemental composition of the thin films. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Element         | Mass [\%]      | Atom [\%]      | Mass [\%]      | Atom [\%]      |
| Oxygen          | 66.56417       | 51.3498        | 86.41754       | 58.17554       |
| Carbon          | 25.16761       | 21.43479       | 8.268215       | 32.34785       |
| Copper          | 8.268215       | 6.119176       | 5.355894       | 6.017582       |
| Sulfur          | 100            | 100            | 100            | 100            |

![Fluorescence Intensity vs. Wavelength](image)

**Figure 5.** Laser Induced Fluorescence spectra of the pulsed laser deposited thin films.

The mitigation of intensity for the deposition on hemp fabric compared with the deposition on silica glass slab is being considered due to water sorption phenomena into the fibers, and due to the diffusion of the deposited particles among the hemp fibers from the structure of the fabric.
3.5. **Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS)**

SEM images show the granularly structure of the film. This structure is present on both the glass substrate and the hemp substrate with large dispersion of the grains. Such morphological aspect of the thin film has an important role in their reflection properties, as already iterated herein.

![SEM images](image)

**Figure 6.** SEM images of thin films PLD CuSO$_4$/glass (a) and PLD CuSO$_4$/hemp (b).

![Elemental composition maps](image)

**Figure 7.** Elemental composition map for PLD-CuSO$_4$/glass: copper (a); oxygen (b); sulfur (c) and for PLD CuSO$_4$/hemp: copper (d); oxygen (e); sulfur (f).
Deposited particles variety in dimension, noticed in the SEM images, contributes to the optical properties as well. In addition to the optical properties of the deposited thin films, their important content in copper (25% in the film PLD CuSO₄/glass and 21% in the film PLD CuSO₄/hemp) makes them suitable for uses where copper is required to be added on different materials, such as textiles, in producing composites designed for masks and other equipment-ware for medicine, copper virucide properties being already proven [11, 12].

A uniform distribution appears on the elemental map as the elements superimpose over each other proving that most of them are combined in either by chemical bonds or in physical interactions, such as Van der Waals. The elements shown on map are present in the compounds found in FTIR and UV-Vis, with the mention that carbon is from the hemp substrate.

4. Conclusion and perspectives

A dichroic beam splitter has been achieved using copper sulfate. The film structure and different species deposited on substrate give it those properties. In addition, the possibility to deposit complex chemical species using PLD without special gas atmosphere in the deposition chamber is evidenced. The thermal decomposition under laser irradiation provides chemical components that can be anticipated when simulated the process in COMSOL. With careful changes of laser parameters, films can be tuned to specific needs. Such coatings find a large number of applications from optics, electronics, to medical and composite materials for protection equipment. With further studies, films with more complex behavior can be achieved.

5. References

[1] Kassim A, Min H S, Haron M J and Nagalingam S 2011 Int. J. of Pharm. & Life Sci. (IJPLS) 2(11) 1190-1194
[2] Aravinda C L, Mayanna S M and Muralidharan V S 2000 Proc. Indian Acad. Sci. (Chem. Sci.) 112(5) 543–550
[3] Zhang Y, Aslan K and Previte M J R 2007 Appl. Phys. Lett. 90 173116
[4] Seiler W, Millon E, Perriere J, Benzeraga R and Boulmer-Leborgne C 2009 Journal of Crystal Growth 311 3352–3358
[5] Umesh Chandra Bind U C, Dutta R K, Sekhon G K, Yadav K L, Krishna J B M, Menon R and Nabhiraj P Y 2015 Superlattices and Microstructures Volume 84 24-35
[6] Xu Q, Tao J, Sun C, Zhao J, Wang Z, Du L, Niu C, Li X, Huang W 2020 Optics Communications, 454 124424
[7] Yang H, Ou K, Cao G, Shang X, Liu Y and Deng Y 2019 Optics Communications 443 104 – 109
[8] Fedaoouchea A, Badouia H A and Abri M 2018 Optik 157 1300-1305
[9] Zhou R, Huang T, Chen L, Chen S, Lin S and Zhuo Y 2017 JLMN-Journal of Laser Micro/Nanoengineering 12(2) 2017
[10] Floegel-Delur U, Riedel T, Wippich D, Goebel B, Rothfeld R, Schirmeister P, Werfel F N, Usoskin A and Rutt A 2011 IEEE Transactions on Applied Superconductivity 21(3) 2984-2987
[11] Warnes S L, Little Z R and Keevil C W 2015 mBio 6(6) e01697-15
[12] van Doremalen N, et al. 2020 The New England Journal of Medicine 2004973
[13] Cocean A, Cocean I, Gurlui S, Iacomi F 2017 U.P.B. Sci. Bull., Series A 79(2)
[14] Cocean A, Pelin V, M M, Cocean I, Sandu I, Gurlui S and Iacomi F 2017 Applied Surface Science 424 324–329
[15] Pretch E, Büllmann P and Badertscher M 2009 Structure Determination Of Organic Compounds.Tables Of Spectral Data, Fourth, Revised and Enlarged Edition, Springer – Verlag Berlin Heidelberg 2009, ISBN 978 – 3 – 540 – 93810 – 1, doi 10.1007/978-3-540-93810-1
[16] Miller F A and Wilkins C H 1952 Anal. Chem. 24 (8) 1253–1294
[17] Frost R L, Jagannadha R B and Keeffe E C 2010 Journal of Molecular Structure 977(1-3) 90-99
[18] Etalo A S 1988 CAN. I. CHEM. 66
[19] Chertihih GV andrews L and Bauschlicher CW Jr. 1997 J. Phys. Chem. A 101(22) 4026
[20] Augusta Syty 1973 Anal. Chem. 45(9) 1744-1747
[21] Burduhos-Nergis D-P, Vizureanu P, Sandu A V and Bejinariu C 2020 Applied Sciences 10(8) 2753 doi:10.3390/app10082753
[22] Zohora N, Kandjani A E, Orth A, Brown H M, Hutchinson M R and Gibson B C 2017 Sci Rep 7 16905
[23] Vizureanu P, Perju MC, Galusca DG, Nejneru C and Agop M 2010 Metalurgia international 15(12) 59-64
[24] Sharma S and Uttam K N 2017 Vibrational Spectroscopy 92 135-150
[25] Cocean I, Cocean A, Postolachi C, Pohoata V, Cimpoesu N, Bulai G, Iacomi F and Gurlui S 2019 Applied Surface Science 488 418–426
[26] Tsuboi Y, Kimoto N, Kabeshita M and Itaya A 2001 J. Photochem. Photobiol. A Chem. 145 209–214
[27] Ionescu D, Mătăsaru D, Radu V 2013 UPB Scientific Bulletin Series A-Applied Mathematics and Physics 75(4) 265-274
[28] Irimiciuc S A, Agop M, Nica P, Gurlui S, Mihaileanu D, Toma S and Focsa C 2014 Japanese Journal Of Applied Physics 53(11) 173-179