



HAL
open science

Improved performance of transparent p-type conductors CuCrO₂:Mg delafossite thin films through easy and low cost laser annealing

Frédéric Veron, Isabelle Pasquet, Yohann Thimont, Antoine Barnabé,
Philippe Tailhades

► To cite this version:

Frédéric Veron, Isabelle Pasquet, Yohann Thimont, Antoine Barnabé, Philippe Tailhades. Improved performance of transparent p-type conductors CuCrO₂:Mg delafossite thin films through easy and low cost laser annealing. *Materials Letters*, 2022, 313, pp.131795. 10.1016/j.matlet.2022.131795 . hal-03819782

HAL Id: hal-03819782

<https://hal.science/hal-03819782>

Submitted on 19 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Improved performance of transparent p-type conductors CuCrO₂:Mg delafossite thin films through easy and low cost laser annealing

F. Veron, I. Pasquet, Y. Thimont, A. Barnabé, Ph. Tailhades*

UMR CNRS 5085 Cirimat, Institut Carnot Chimie Balard Cirimat, Université Toulouse III Paul Sabatier, 118 Route de Narbonne, 31 062 Toulouse, France

*Corresponding author: philippe.tailhades@univ-tlse3.fr

Abstract: Films deposited on glass substrate by RF sputtering, were heat treated in air by a low power laser spot thanks to conventional photolithography machine, to obtain pure CuCr_{0.97}Mg_{0.03}O₂ delafossite with an optical transmittance of 0.58 and a conductivity of 5.8S.cm⁻¹. The Haacke's figure of merit is improved to reach 2.07x10⁻⁷Ω⁻¹. Laser annealing by a photolithography machine is thus very interesting for enhancing the p-type transparent conductor properties of such delafossite phases. A local annealing according to selected patterns could also be envisaged, opening up exciting prospects for fast and low cost making the most of these transparent p-type semiconductors.

Keywords: Delafossite, laser direct writing, p-type transparent conductors oxide (TCO)

1- Introduction

Different members of the copper delafossite family exhibit both good transparency and p-type electrical conductivity [1][2]. The latter are therefore of great interest in optoelectronics, in particular for developing transparent light-emitting diodes. However, delafossites often require heat treatments at high temperature (≥600°C for CuCrO₂:Mg) in order to achieve sufficient electronic and optical properties from the point of view of technological applications [3][4]. This constraint therefore excludes the use of many usual substrates of polymer type and even ordinary glass. However, the techniques of direct writing laser, which make it possible to strongly heat a layer absorbing the wavelength of the laser, while only slightly raising the temperature of a transparent substrate, could make it possible to circumvent this limitation. The control of the laser spot on a micron scale would also allow the production of specific patterns, sometimes required by transparent electronics.

The use of lasers to transform thin films, in particular on submicron surfaces, has been used for a long time, in the optical storage of information, which has experienced significant industrial exploitation via optical discs. Laser irradiation causes reversible or non-reversible phase or crystallization state changes on recording layers, when writing [5][6]. Although such layers have most often been alloys [7-9], some of them were formed by oxides [10-13]. Bits resulting from local transformations of oxides have thus been written by low power (few mW) focused lasers.

The laser direct writing processes have also been proposed to submit thin layers of oxides to laser insolation to form photonic, magneto-photonic or magnonic crystals [14][15]. Such processes have also been used to anneal thin films of transparent n-type semiconductors, such as doped zinc oxides [16][17] and indium tin oxides [18][19]. These treatments have made it possible to increase the conductivity of these materials.

Similar research has not yet been reported for transparent delafossite semiconductors devices, but only for thermoelectric $\text{CuFe}_{0.98}\text{Sn}_{0.02}\text{O}_2$ deposited from an aerosol on alumina substrate [20]. The electrical conductivity of the as-deposited film could be increased by one order of magnitude by 128 laser scans, approaching then the low conductivity of the bulk material.

In this work, laser anneals are therefore applied to demonstrate their potential in the use of films of a $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ delafossite, deposited on ordinary glass substrates. This oxide was chosen, taking into account its interesting electrical and optical properties [3][4] and its high thermal stability in air [21]. An ordinary photolithography machine was used for the annealing, in order to demonstrate that the proposed process does not require expensive equipment.

2- Experimental

100nm thick $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ films were deposited by radio-frequency cathodic sputtering from home-made ceramic target, according to a method already described in a previous work [21].

A photolithography machine Kloe Dilase250, equipped with a 405nm solid laser source with a maximal power of 300 mW, was used for the heat treatments under air atmosphere. The sample, maintained on the XY motorized sample holder, was moved with a scanning speed of 1 to 100 $\text{mm}\cdot\text{s}^{-1}$ (15 $\text{mm}\cdot\text{s}^{-1}$ was used for this work). The diameter of the focused laser spot was about 2 μm .

The films were characterized by a Bruker D8 X-ray diffractometer ($K\alpha_1$ and $K\alpha_2$ copper radiations), a D3000 Digital Instrument atomic force microscope (AFM), a Signatone four-points probes for electrical measurements and a Bentham PVE300 UV/visible/IR integrated spectrophotometer to determine the transmittance.

3- Results and discussion

No diffraction peak could be observed on the as-deposited samples due to the well-known nanocrystalline nature of the phases [3][4]. They are also poorly electrically conductor ($0.0045 \text{ S}\cdot\text{cm}^{-1}$) and dark brown in color. Treatments under the laser beam make it possible to greatly modify the characteristics of the samples. As soon as sufficient energy is supplied, the delafossite phase tends to crystallize and the optical absorption in the visible as well as the electrical resistivity, consequently decrease. Although it is difficult to specify the threshold beyond which the transformations become significant, lines heated by the laser show optical changes for provided energies per unit area E , greater than approximately

$1\text{J}\cdot\text{mm}^{-2}$. E is defined by $E=P/(v\cdot d)$ with P , d and v , power, diameter and travel speed of the laser spot respectively.

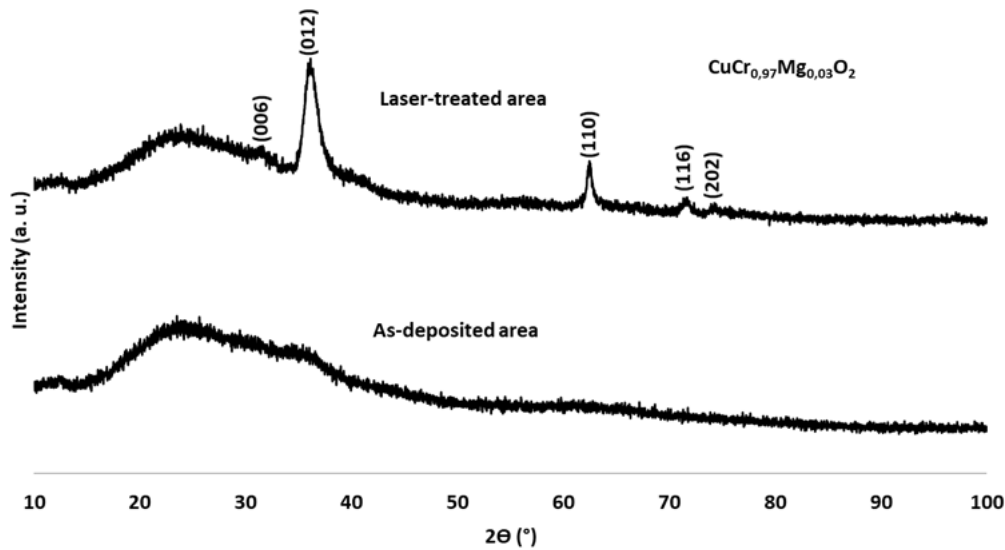


Figure 1: X-ray diffraction of the as-deposited regions and laser treated ($P= 30\text{mW}$, $v= 15\text{mm}\cdot\text{s}^{-1}$; hatch spacing = $2\ \mu\text{m}$, film thickness = $100\ \text{nm}$).

Some laser conditions of insolation were then selected to treat surfaces of about 1cm^2 . The hatch spacing used was $2\ \mu\text{m}$ to avoid leaving untreated spaces between two laser scans. The delafossite phase is then obtained as revealed by the X-ray diffraction pattern (Fig. 1), due to the absorption of the laser beam by the film and the resulting local increase in temperature that leads to crystallization. Depending on the processing conditions used, the samples exhibit different microstructures. Samples exposed at the highest energies per surface unit may be blistered, cracked and punctured in places. For more modest energies, the roughness and the size of the crystallites are admittedly significantly increased compared to the as-deposited sample, but the major defects reported previously can be virtually eliminated (Fig. 2). Due to treatment, the R_a roughness initially close to 2.5nm , becomes about $100\ \text{nm}$ after treatment. Micrometric holes can be found, evidence of strong mechanical stresses manifested during laser treatment due to the different thermal expansion of the oxide film and the substrate. Some iridescence is observed on the treated samples. It is due to laser insolation along parallel lines whose heights are of the order of magnitude of the wavelengths of visible light and whose effect is more or less similar to that of a diffraction grating. Such lines are noticeable on figure 2. The optical transmittance (Fig. 3) in the visible range increases from 0.41 to 0.58 thanks to the insolation process. The films free of crack become semiconductor with the highest conductivity of $5.8\ \text{S}\cdot\text{cm}^{-1}$ i.e. with an improvement of more than three orders of magnitude. This value is higher than the maximum conductivity of $1.4\ \text{S}\cdot\text{cm}^{-1}$ measured on films of identical composition, treated at $600\ ^\circ\text{C}$ [4]. The Haacke figure of merit ($T^{10} / R_{\text{square}}$) [22] therefore reaches the interesting value of $2.07\times 10^{-7}\ \Omega^{-1}$.

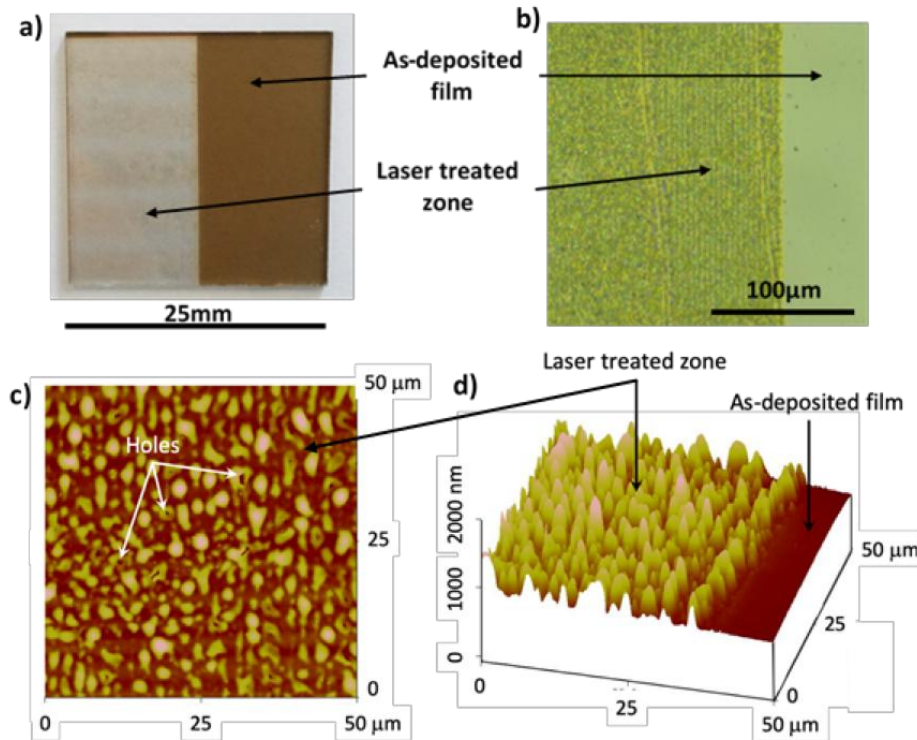


Figure 2: Global view and observation by optical microscopy of a film partially laser treated. Demonstration of changes in optical absorption and topography (Top images). AFM images of as-deposited and laser treated film (thickness=100 nm, $P=30\text{mW}$, $v=15\text{mm}\cdot\text{s}^{-1}$; hatch spacing= $2\mu\text{m}$)(Bottom images).

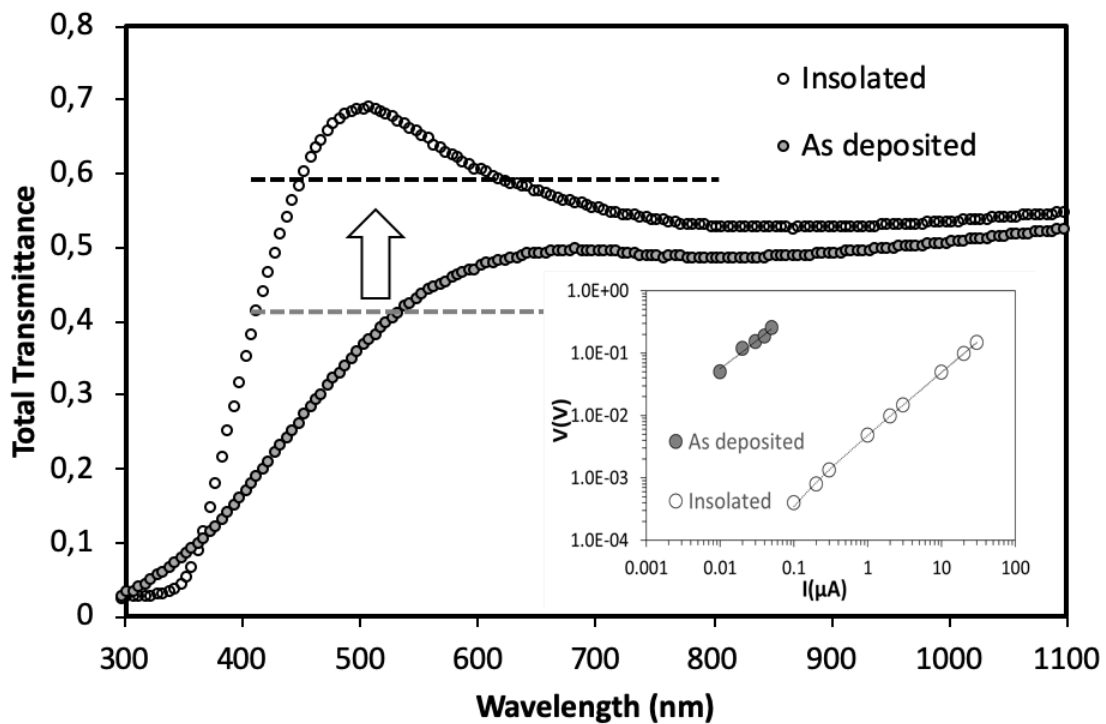


Figure 3: Optical total transmittance spectra (dot line corresponds to the average value in the visible range). In insert: $V(I)$ plot of the insolated film.

4- Conclusion

Films prepared by RF magnetron sputtering of a $\text{CuCr}_{0.97}\text{Mg}_{0.03}\text{O}_2$ target were heat treated by a low power laser spot of a conventional photolithography machine, to obtain pure delafossite. These materials have a higher electrical conductivity than after treatment in a conventional furnace. Their Haacke's figure of merit is also improved. Iridescence, generated by periodic laser insolation, is observed and microscopy also reveals a few micronic holes. These defects should be able to be corrected, by aperiodic exposure strategies and better control of the mechanical stresses resulting from a better choice of the expansion coefficients of the substrates and the sputtering conditions. Laser annealing by a photolithography machine is therefore a very interesting process for enhancing the transparent conducting oxide properties of the delafossite films. A local annealing according to selected patterns of a size less than ten micrometers, could also be envisaged, opening up exciting prospects for making the most of these transparent p-type TCO.

References

- [1] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, H. Hosono, P-type electrical conduction in transparent thin films of CuAlO_2 , *Nature*, 389 (1997) 939–942.
<https://doi.org/10.1038/40087>
- [2] T. Zhao, Q.-L. Liu, Z.-Y. Zhao, High-Throughput Screening Delafossite CuMO_2 (M = IIIA, 3d, 4d, 5d, and RE) Optoelectronic Functional Materials Based on First-Principles Calculations. *J. Phys. Chem. C* 123 (2019) 14292–14302.
<https://doi.org/10.1021/acs.jpcc.9b04481>
- [3] R. Nagarajan, A. Draeseke, A. Sleight and J. Tate, p-type conductivity in $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ films and powders, *J. Appl. Phys.* 89 (2001) 8022–8025
<https://doi.org/10.1063/1.1372636>
- [4] A. Barnabe, Y. Thimont, M. Lalanne, L. Presmanes, P. Tailhades, p-Type conducting transparent characteristics of delafossite Mg-doped CuCrO_2 thin films prepared by RF-sputtering, *J. Mater. Chem. C*, 3 (2015) 6012-6024
<https://doi.org/10.1039/c5tc01070e>
- [5] J. Feinleib, J. de Neufville, S. C. Moss, S. R. Ovshinsky, Rapid reversible light-induced crystallization of amorphous semiconductors, *Appl. Phys. Lett.* 18, (1971) 254
<https://doi.org/10.1063/1.1653653>
- [6] H. Palneedi, J. H. Park, D. Maurya, M. Peddigari, G-T. Hwang, V. Annapureddy, J-W. Kim, J-J. Choi, B-D. Hahn, S. Priya, K. J. Lee, J. Ryu, Laser Irradiation of Metal Oxide Films and Nanostructures: Applications and Advances, *Adv. Mat.* (2018) 1705148
<https://doi.org/10.1002/adma.201705148>
- [7] A. E. Bell, R. A. Bartolini, High-performance Te trilayer for optical recording, *Appl. Phys. Lett.* 34 (1979) 275
<https://doi.org/10.1063/1.90757>

- [8] K. Watanabe, T. Oyama, Y. Aoki, N. Sato, S. Miyaoka, New optical recording material for DRAW discs, SPIE Proceedings 0382 (1983) 191
<https://doi.org/10.1117/12.970199>
- [9] Y. Nakane, N. Sato, H. Makino, S. Miyaoka, Principles of laser recording mechanism by forming an alloy in the multilayer of thin metallic films, SPIE Proceedings 0529 (1985) 76
<https://doi.org/10.1117/12.946435>
- [10] T. Ohta, K. Notera, K. Kimura, N. Akahira, M. Takenaga, New write-once media based on Te-TeO for optical disks, SPIE Proceedings 0695 (1987) Optical Mass Data Storage II
<https://doi.org/10.1117/12.936809>
- [11] L. Bouet, Ph. Tailhades, I. Pasquet, S. Lebrun, C. Bonningue, A. Rousset, Cation-deficient spinel ferrites: application for high-density write once optical recording, Jap. J. Appl. Phys. 38 (1999) 1826-1828
<https://doi.org/10.1143/JJAP.38.1826>
- [12] Ph. Tailhades, L. Presmanes, I. Pasquet, C. Bonningue, F. Laporte, Spinel oxides thin films for write-once optical recording with blue laser sources, Trans. Magn. Soc. Japan 2, (2002) 198-201
<https://doi.org/10.3379/tmjpn2001.2.198>
- [13] Z. Jiang, Y. Geng, D.H. Gu, Write-once medium with BiOx thin films for blue laser recording, Chin. Opt. Lett. 6, 4 (2008) 294-296
- [14] I. Pasquet, L. Presmanes, C. Bonningue, Ph. Tailhades, Patterned ferrimagnetic thin films of spinel ferrites obtained directly by laser irradiation, Appl. Surf. Sci. 283 (2013) 283-289.
<https://doi.org/10.1016/j.apsusc.2013.05.160>
- [15] A. Rodenas, G. Zhou, D. Jaque, M. Gu, Direct laser writing of three-dimensional photonic structures in Nd:yttrium aluminum garnet laser ceramics, Appl. Phys. Lett. 93, (2008) 151104
<https://doi.org/10.1063/1.2998258>
- [16] GH Jo, J. Kang, M. Kamiko, J-G Ha, S-M Koo, J-H Koh, Enhanced electrical mobilities of laser annealed Ga doped ZnO thin films, J. Nanosci. Nanotechnol. 20, 1 (2020) 520-523.
<https://doi.org/10.1166/jnn.2020.17266>
- [17] H-C Lin, F. Stehlin, O. Soppera, H-W Zan, C-H Li, F. Wieder, A. Ponche, D. Berling, B-H. Yeh, K-H Wang, Deep ultraviolet laser direct write for patterning sol-gel InGaZnO semiconducting micro/nanowires and improving field-effect mobility, Sci. Rep. 5 (2015) 10490
<https://doi.org/10.1038/srep10490>

- [18] A. Solieman, A.H. Moharram, M.A. Aegerter, Patterning of nanoparticulate transparent conductive ITO films using UV light irradiation and UV laser beam writing, *Appl. Surf. Sci.* 256, 6 (2010) 1925-1929
<https://doi.org/10.1016/j.apsusc.2009.10.039>
- [19] C-W. Cheng, J-S. Chen, H-H. Chen, Patterning of crystalline ITO using infrared nanosecond fiber laser pulses, *Mater. Manuf. Processes* 25, 7 (2010) 684-688
<https://doi.org/10.1080/10426914.2010.489592>
- [20] T. Nazareus, J. Kita, R. Moos, J. Exner, Laser-Annealing of Thermoelectric $\text{CuFe}_{0.98}\text{Sn}_{0.02}\text{O}_2$ Films Produced by Powder Aerosol Deposition Method, *Adv. Mater. Interfaces* 7,22 (2020) 2001114
<https://doi.org/10.1002/admi.202001114>
- [21] M. Lalanne, A. Barnabé, F. Mathieu, Ph. Tailhades, Synthesis and Thermostructural Studies of a $\text{CuFe}_{1-x}\text{Cr}_x\text{O}_2$ Delafossite Solid Solution with $0 < x < 1$. *Inorganic Chemistry* 48 (2009) 6065–6071.
<https://doi.org/10.1021/ic900437x>
- [22] G. Haacke, New figure of merit for transparent conductors. *J. Appl. Phys.* 47, 9 (1976) 4086-89.
<https://doi.org/10.1063/1.323240>