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Improved performance of transparent p-type conductors $CuCrO_2$: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 $CuCr_{0.97}Mg_{0.03}O_2$ 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$^{-7}\Omega^{-1}$. 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 $CuCrO_2$: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 $CuFe_{0.98}Sn_{0.02}O_2$ 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 $CuCr_{0.97}Mg_{0.03}O_2$ 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 $CuCr_{0.97}Mg_{0.03}O_2$ 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 $mm.s^{-1}$ (15$mm.s^{-1}$ 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 $S.cm^{-1}$) 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

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

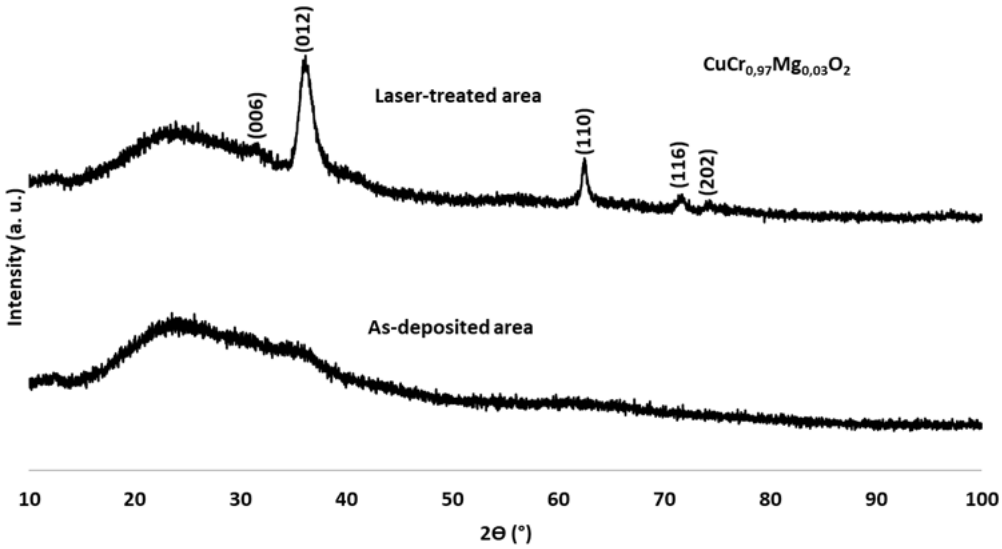

Figure 1: X-ray diffraction of the as-deposited regions and laser treated (P= 30mW, v= 15mm.s^{-1}; hatch spacing =2 µm, film thickness =100 nm).

Some laser conditions of insolation were then selected to treat surfaces of about 1cm^2. The hatch spacing used was 2µm 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 Ra roughness initially close to 2.5nm, becomes about 100 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 S.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 S.cm^{-1} measured on films of identical composition, treated at 600 °C [4]. The Haacke figure of merit (T^{10} / R_{square}) [22] therefore reaches the interesting value of 2.07x10$^{-7}\Omega^{-1}$.

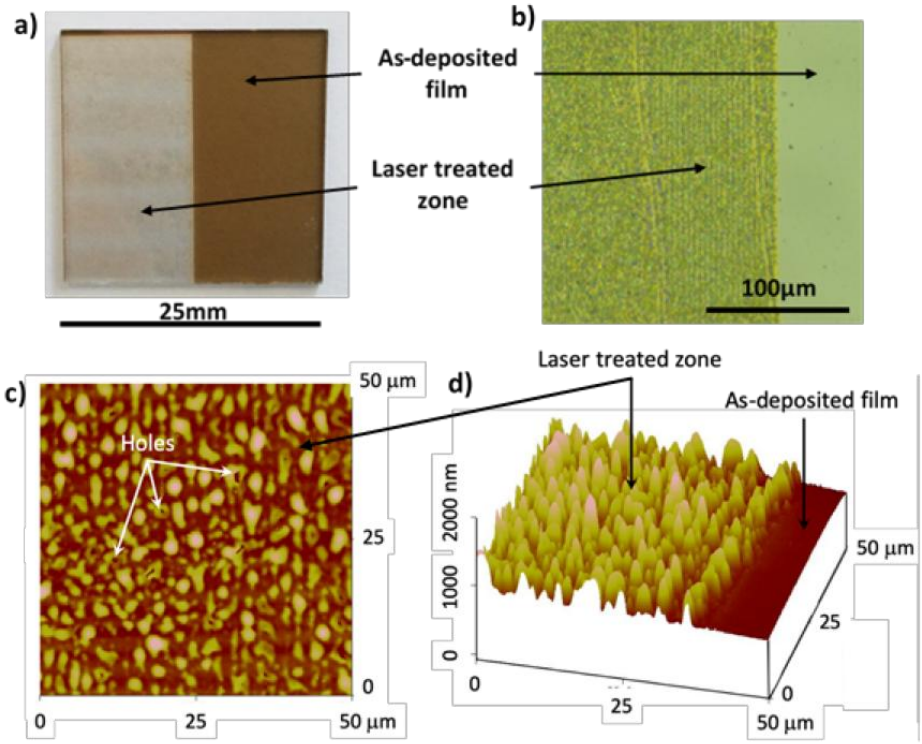

Figure 2: Global view and observation by optical microscopy of a film partially laser treated. Demonstration of changes in optical absorption and topography (Top images). AFM images of as-deposited and laser treated film (thickness=100 nm, P=30mW, v=15mm.s^{-1}; hatch spacing=2µm)(Bottom images).

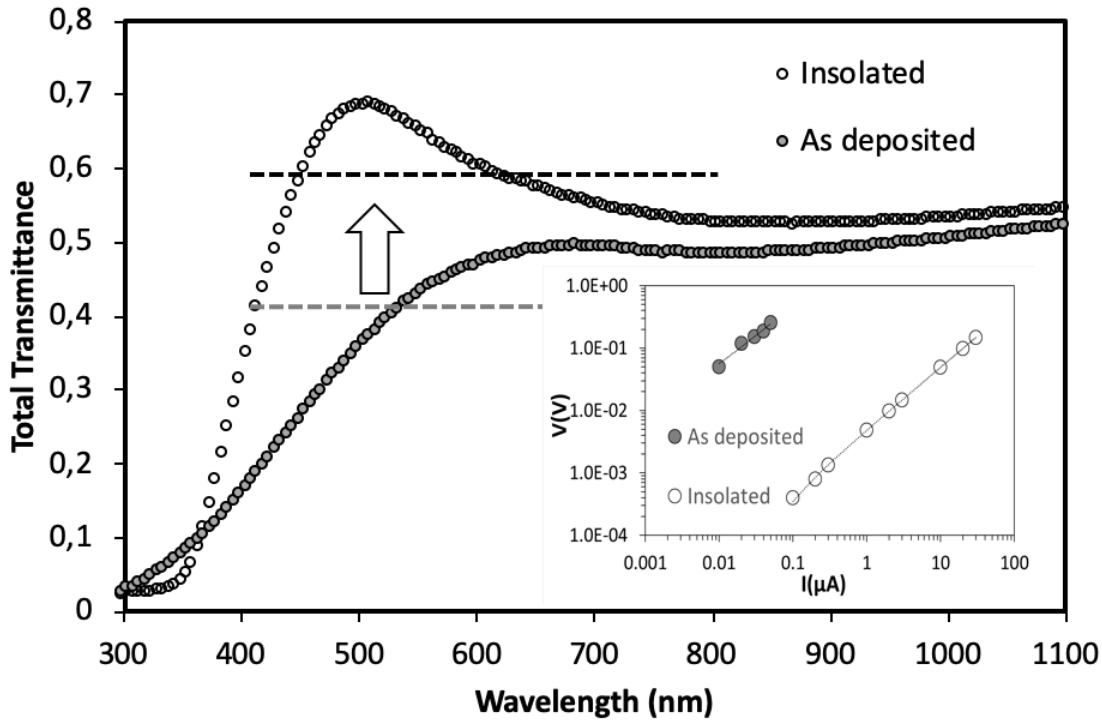

Figure 3: Optical total transmittance spectra (dot line corresponds to the average value in the visible range). In insert: V(I) plot of the insolated film.

4- Conclusion

Films prepared by RF magnetron sputtering of a $CuCr_{0.97}Mg_{0.03}O_2$ 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.

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