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### **► To cite this version:**

François Stock, Frederic Antoni, Dominique Aubel, Samar Hajjar-Garreau, Dominique Muller. Pure carbon conductive transparent electrodes synthesized by a full laser deposition and annealing process. Applied Surface Science, 2019, 505, pp.144505. <10.1016/j.apsusc.2019.144505>. <hal-03655768>

**HAL Id: hal-03655768**

**<https://hal.science/hal-03655768v1>**

Submitted on 29 Apr 2022

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Full Length Article

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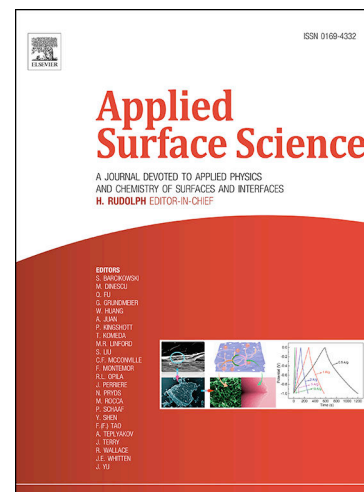
PII: S0169-4332(19)33321-5  
DOI: <https://doi.org/10.1016/j.apsusc.2019.144505>  
Reference: APSUSC 144505

To appear in: *Applied Surface Science*

Received Date: 9 September 2019  
Revised Date: 17 October 2019  
Accepted Date: 24 October 2019

Please cite this article as: F. Stock, F. Antoni, D. Aubel, S. Hajjar-Garreau, D. Muller, Pure carbon conductive transparent electrodes synthesized by a full laser deposition and annealing process, *Applied Surface Science* (2019), doi: <https://doi.org/10.1016/j.apsusc.2019.144505>

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# Pure carbon conductive transparent electrodes synthesized by a full laser deposition and annealing process.

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## Abstract

One of the biggest challenge that face optoelectronic and photovoltaic devices is the necessity to provide a reliable alternative to transparent conducting oxide (TCO) like Indium Thin Oxide (ITO). We recently published a study proposing a method to produce transparent conductive electrodes only based on carbon materials. In a first step, we use the Pulsed Laser Deposition (PLD) to produce high performance DLC. Those thin films own very interesting properties in kindship with diamond, like high transparency in the visible range, chemical inertness and biocompatibility. In addition, the DLC is a perfect electrical insulator and presents a relative high opacity in ultra-violet (UV). This particularity has a great interest to perform, in a second step, UV laser annealing over the DLC surface. The aim is to break the existing diamond bindings ( $sp^3$  hybridization) on the surface and allow atoms being reorganized in graphitic bindings ( $sp^2$  hybridization). We demonstrate that the increase of atomic graphitic bindings leads to a valuable surface conductivity. According to optimized annealing parameters, the surface conductivity reaches values comparable to ITO. We also show that the laser treatments only sparsely affects the DLC transparency. Moreover, this full laser-based process remains compatible with the standard microelectronic technological steps.

## Keywords

Pulsed Laser Deposition (PLD), Diamond-Like Carbon (DLC), Laser surface annealing, Transparent electrodes, graphitization.

## 1. Introduction

One of the nowadays commonly used transparent conductive material in optoelectronic and photovoltaic devices is Indium Tin Oxide (ITO). This oxide combines a very high transparency in the visible range (nearly 90 %) and an important electrical conductivity (around  $10^4 (\Omega\text{cm})^{-1}$ ) over wide areas [1-3]. ITO is mainly used as transparent conductive electrode deposited over photovoltaic cells or optoelectronic devices like capacitive touch panels or liquid crystal displays. However, the use of this material will face in important and increasing problem. Despite very interesting performances, the rarefaction of Indium combined to the impossibility of effectively recycle ITO will jeopardize the use of this technology. Therefore, a suitable alternative is needed to replace this metallic oxide in optoelectronic components. We propose an interesting and alternative solution using only pure carbon material elaborated by laser processes offering moreover a high compatibility level with standard opto and microelectronic technological steps.

An interesting carbon based material is the Diamond-Like Carbon (DLC). This material, already used as protective coating and as anti-reflexion layer in photovoltaic cells [4-6] offers a very good potential for optoelectrical applications. This amorphous form of carbon share many properties with diamond, like high optical transparency in the visible range [7,8]. DLC is an homogeneous mixture of carbon  $sp^2$  bindings (stable hybridization corresponding to graphitic carbon) and  $sp^3$  bindings (metastable hybridization corresponding to diamond) [9,10]. Due to its proximity to diamond and the presence of  $sp^3$  bindings, DLC is very high electrical insulator [7,11-12]. Nevertheless, this form of carbon remains an interesting transparent material valuable in photovoltaic and optoelectronic devices. DLC properties are highly depending on the elaboration process (and the associated parameters) used

to synthesize it [13-15]. In our approach, we use Pulsed Laser Deposition of graphite to obtain DLC thin films. This elaboration process while performed in high vacuum with a nuclear grade graphite target, PLD-DLC show a very high purity by offering hydrogen and oxygen-free layers. Very advantageous properties are obtained with this technique, allowing tuning the  $sp^3$  and  $sp^2$  bindings ratio by working at different wavelengths and energy densities [10, 16-17].

However, DLC being a strong insulator, other conductive forms of carbon have also our interest. Graphitic or graphenic forms of carbon show outstanding transport and conductivity properties. For example, graphene (a 2D material made of  $sp^2$  bounded carbon atoms organized in a honeycomb structure) present a record electron mobility reaching  $200\,000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  while keeping a very low optical absorption (typical 2.3 % per atomic layer) [18-20]. Well studied in the literature, graphene is obtained by various elaboration methods like chemical vapour deposition, aerosol or graphite exfoliation. However, it remains nowadays very hard to grow graphene over large surfaces or to transfer it on wide areas. Multilayer graphene or graphitic thin films also keep interesting conductivity and optical transmission properties. Combining those properties with DLC transparency is an interesting approach to obtain transparent conductive layers.

We already published a study [21] using an original and innovative two-step process, composed of a DLC elaboration by PLD followed by a laser surface annealing of DLC layers. The first step consists in the growth of DLC by PLD allowing the synthesis of hydrogen free layers that permits laser annealing. The relative high opacity of DLC in the UV range also allows a possible energy absorption in the first atomic layer of the DLC. Therefore, a second step of UV laser annealing has the effect to convert existing and dominating  $sp^3$  bounded atoms into a pure  $sp^2$  graphitic surface layer.  $Sp^3$  bindings are broken by the energy delivered by the successive laser shots permitting atomic reorganization in a stable graphitic form of carbon. This transformation affects the very first atomic layers and leads to the formation of a conductive film on the top of the deposited DLC film. The resulting structure is composed of a graphitic surface conductive layer (remaining highly transparent due to a very low thickness) set on the preliminary deposited DLC material. This approach allows obtaining interesting performances in term of transparency and conductivity.

## 2. Experimental details

### 2.1. Pulsed laser deposition of DLC

In this work, we use a standard PLD setup to perform DLC depositions. An excimer laser beam is focused with a  $45^\circ$  incidence angle on a high purity graphite target (99.999 %) placed into a high vacuum chamber (background pressure less than  $10^{-8}$  mbar, avoiding therefore any presence of oxygen inside the deposited films). As the laser hits the target, the matter is ablated perpendicularly to its surface, forming a plasma plume of the ablated species, which are collected on the substrate set in front of it. The target-substrate distance is set to 5 cm and kept constant in order to obtain a homogeneous sample coverage over  $1 \times 1\text{ cm}^2$ . To avoid crater formation by successive laser shots on its surface, the target is kept in rotation at 1 rpm for during the deposition time. The excimer laser (LAMBDA PHYSIK Compex 201) produces up to 600 mJ pulses (25 ns duration) at repetition rates from 1 to 10 Hz. By using a KrF gas mixture, the output ray is associated to a 248 nm wavelength and an ArF gas mixture leads to a 193 nm beam. With an optimal focus and considering all optical components energy losses, on-target fluences range is tuneable from 2 up to  $15\text{ J/cm}^2$  in KrF mode and 2 up to  $7\text{ J/cm}^2$  in ArF mode. All the deposition process is done at room temperature to obtain the highest adamant character as shown in previous studies [10, 21-23]. Previously cleaned (ethanol in ultrasonic bath) glass, quartz and  $\text{SiO}_2/\text{Si}$  are used as substrates. Glass and quartz permits transmittance measurements while  $\text{SiO}_2/\text{Si}$  substrates were used to measure conductivity as well as for X-ray Photoemission spectroscopy (XPS) analysis.

## 2.2. Laser surface annealing

Laser treatments of DLC surfaces are performed with the same excimer laser as for deposition. The 248 nm excimer laser beam passes through an optical homogenizer in order to obtain a 1 x 1 cm<sup>2</sup> top hat beam (better than 1% homogeneity). A home-designed chamber, equipped with a quartz window (for the UV laser input) was specially built in order to anneal samples under vacuum or neutral gas atmosphere. In this study, annealing is done under 0.5 mbar of static argon pressure. With this setup and induced mechanical constraints, the laser beam reaches a 5 x 5 mm<sup>2</sup> homogeneous size, allowing working with fluences in the range of 0.05 up to 0.36 J/cm<sup>2</sup> (far under the carbon ablation threshold). To obtain homogeneity for large area treatments, the chamber is fastened on a computer controlled XYZ table. A special designed software commands the successive table positions, ensuring homogenous sample coverage by setting a 90 % beam overlap between each position (in X and Y directions).

## 2.3. XPS measurement

All XPS measurement presented in this study are performed with a 1486.6 eV photons beam. The analysed surface is 4 mm<sup>2</sup>. Thanks to angle-resolved measurements, two different depths can be measured on each sample. Indeed, by using a 60° “grazing” incidence, a 4,8 nm ( $\pm$  0.3 nm) depth is measured, where a 20° “normal” incidence leads to the measuring of a 9,1 nm ( $\pm$  0.35 nm) in the layer depth. Combining both incidence measurements, an interesting set of data is obtained to investigate the structural modification in the DLC after laser annealing. To extract sp<sup>2</sup> and sp<sup>3</sup> binding percentages, we focus our analysis on the C1s peak representative of carbon atom bindings. This peak is deconvoluted in order to extract the sp<sup>2</sup> contribution (located around 284.5 eV) and the sp<sup>3</sup> contribution (located around 285.4 eV) [21, 24-26] as shown in Fig. 1. Measurements also reveal a very low oxygen surface contamination (less than 10 %). We highlighted that this oxygen presence comes from samples exposition to air during transfer (as depositions are performed under high vacuum PLD from an oxygen-free target). Therefore, we will not take it into account and consider DLC only made of pure carbon material. Moreover, in order to avoid an unexpected increase of sp<sup>2</sup> values in DLC, we strongly limited the desorption process at 100 °C for very short time. For the measurement set, we obtain less than 1 % peak shift for each of these contribution, guaranteeing a very fine precision of  $\pm$  0.5 % for each contribution.

## 2.4. Optical and electrical characterization setup

To evaluate the functional performances of our DLC layer after treatment, we mainly investigate transmittance and conductivity. For optical transmission measurements, we use an UV-visible spectrometer as type PERKIN-ELMER® Lambda 19. Typical glass-deposited DLC spectra are acquired from 300 to 850 nm (due to the glass UV cut-off wavelength located around 280 nm) while quartz substrates allows to measure down to 200 nm. A deuterium lamp generates UV light source while visible and infrared light is provided by a halogen lamp. A low scanning speed (30 nm.min<sup>-1</sup>) is chosen to ensure high accuracy measurements. Blank glass and quartz signals are also acquired allowing the determination of DLC single response by subtracting the substrate contribution.

Conductivity measurements are performed with an ECOPIA HMS5000 apparatus. The setup is enhanced with 4 probes attached on printed circuit board in a Van der Pauw configuration. The 1 x 1 cm<sup>2</sup> sample is placed on the board and the probes are placed in the corners of the sample. A data set of at least 5 measures are made per sample and an average value is extracted.

In addition, a special designed testbench has been made to measure DLC surface resistance. The sample is embedded in a 3D printed plastic holder. Surface contact (on each side of the surface) is made with a single side copper epoxy board to obtain a 1 cm long contact on the sample. To optimize contact performances, a thin copper wire is soldered on the conductive face of the epoxy plate. The contacts are

pressed on the sample surface with 3 springs (for each contact) offering a homogeneous pressure all over the sample length. This setup able a direct measurement of the surface treated-DLC equivalent resistance and permits the use of the layer in an electrical circuit.

### 3. Results

#### 3.1. Evaluating best DLC properties to perform laser annealing

We compare the possibilities to perform laser annealing on ArF and KrF-made DLC. In order to obtain the best transparency performances, we first investigated laser annealing on ArF-deposited DLC. This DLC has a highest transparency as KrF-made DLC (as presented in Fig. 2). Therefore, starting from this material would have led to a better transparency on our layers. We use same treatment parameters for both DLC types. As conductivity is obtained on KrF-made DLC [21], we never able to obtain any conductivity on ArF-deposited DLC. We observe in that case an early DLC destruction even for low annealing fluences (nearby 0.2 J/cm<sup>2</sup>). By reducing this fluence to avoid DLC destruction, we never reach the energy threshold leading to conductivity apparition. XPS measurements show a slight graphitic binding increase after annealing. Nevertheless, the maximal sp<sup>2</sup> binding percentage never overpasses 20 %, which is not enough to obtain surface conductive layer. Therefore, KrF-produced DLC (due to initial higher amount of sp<sup>2</sup> bindings) is the best candidate to perform laser surface annealing. Moreover, as demonstrated in [10], we select KrF-DLC deposited at 5 J/cm<sup>2</sup> due to the highest adamant character of the obtained DLC at this fluence, leading to a highest initial optical transparency. For all the following study, we only consider DLC deposition performed at 5 J/cm<sup>2</sup> in KrF mode.

#### 3.2. XPS analysis, structural changes modelling and graphitized depth estimation

In this paragraph, we investigate the structural changes induced by laser surface annealing on KrF-DLC. As reference, XPS measurements have been made on untreated KrF-DLC. The reference reveals a 60.9 % of sp<sup>3</sup> bindings and 39.1 % sp<sup>2</sup> bounded atoms homogenously distributed in the entire layer. Angle resolved measurements confirm the homogenous character of the DLC film after deposition. DLC were annealed with various sets of parameters (fluence and number of shots). To keep in the efficiency range as demonstrated in a previous study [21], the fluence is tuned from 0.1 up to 0.2 J/cm<sup>2</sup> for a maximum of 10000 shots. A clear increase of sp<sup>2</sup> bindings percentage is observed as soon as the annealing fluence is raised. The same behaviour is detected as the number of shots also increase [21]. A significant difference between normal and grazing incidence analyses is obtained, showing highest amount of sp<sup>2</sup> in the surface measurement.

We propose here a simple model in which we consider that the annealed DLC is composed of a fully-graphitized layer (pure sp<sup>2</sup> bindings) located at the surface of the film. As the relative opacity of the DLC at 248 nm has been demonstrated, we also believe that the in-depth DLC is not affected by laser annealing and keep the same structure (same amount of atomic bindings) than before annealing. We have then a structure composed of two layers, in which we will extract the thickness of the surface graphitized part. The XPS beam permits to estimate the DLC volume analysed. We approximate the analysed volume as a cylinder considering the dimension ratio between the analysis depth (a few nanometers) and the beam section (S) on the surface (in the mm<sup>2</sup> range). As the initial contained sp<sup>2</sup> in the depth ( $\alpha_I$ ) is known such as the sp<sup>2</sup> bindings measured after annealing ( $\alpha_T$ ), we can express the relative thickness (x) of the full graphitic layer as following:

$$S\alpha_T = S(x + (1 - x)\alpha_I)$$

As this equation is solved, we can calculated the absolute thickness of the full sp<sup>2</sup> part of the DLC film ( $d_{\text{GRAPH}}$ ) regarding the XPS beam penetration depth ( $d_{\text{XPS}}$ ), as given by the next formula :



$$d_{GRAPH} = x d_{XPS}$$

This modelisation also able to estimate the total amount of the full-graphitized layer in term of number of graphitic monolayers. Knowing the approached pure sp<sup>2</sup> depth and considering the thickness of one graphite 2D plan ( $Z = 3.4 \text{ \AA}$ ), we can calculate the number of equivalent graphitic monolayers ( $n_{GML}$ ) that composes the film.

$$n_{GML} = 1 + \frac{d_{GRAPH}}{Z}$$

We use this model to extract graphitic layer thicknesses from the XPS measurements. For each annealing parameters sets, we perform the calculation for grazing and normal analyses and calculate an average thickness between both results.

Firstly, we observe (Tab. 1) that both measures lead to coherent and correlated results. For 0.1 J/cm<sup>2</sup>, a typical graphitic thickness around 1.3 nm is calculated for 1000 and 10000 shots. As the fluence is raised to 0.2 J/cm<sup>2</sup>, the graphitic layer thickness increased up to 1.74 nm for 1000 shots and reaches a 2.69 nm for 10000 shots. For this last one, we must add that the sample is sparsely affected by very small graphitic defects (which start to appear by annealing at the very high limit of the defined parameters range), which slightly boost the XPS measured sp<sup>2</sup> binding percentage.

It is also interesting to underline that no significant difference between 1000 and 10000 shots is observed for a 0.1 J/cm<sup>2</sup> fluence, meaning hereby that at low fluences, the DLC is not affected by an increase of the shots amount. It is then mainly the fluence, which controls the graphitized depth. This is confirmed by the increase of the graphitized layer depth for the 0.2 J/cm<sup>2</sup> annealing.

This approximation seems to be very simple in a first approach, but it is important to notice that it shows very interesting and reliable results as correlated by other measurements (transmittance...) performed in this study.

### 3.3. Transmittance measurements

In this part, we focus on the optical properties of the DLC regarding the annealing parameters. It is also important to remember (Fig. 3) that for as deposited DLC, the optical transmittance is highly dependent of the film thickness, in the way that, when the layer thickness is raised, the optical transmittance is reduced (linear behaviour).

We perform DLC (KrF - 5 J/cm<sup>2</sup> - 20 nm) deposition on glass substrates, and we anneal those layers at various fluences for 1000 shots. For each measurement (Fig. 4), we observe the same transmittance behaviour. Indeed, for untreated DLC, the transmittance obey to a quasi-linear evolution over the visible range and the near UV. After annealing, this behaviour changes leading to a more constant value over the visible range and a harder sink down in the deep UV. This modification is also confirmed by optical visual observation showing a DLC appearing brown before annealing and presenting a greyer metallic colour after surface treatment. Furthermore, we clearly observe that despite various annealing fluences, we obtain equivalent transmittances after treatments, suggesting that the annealing fluence has a negligible impact on the transparency of the films. Moreover, it is also interesting to notice that in each case, a transmittance comparable to standard ITO [1] is obtained.

We also observe that, after annealing, the transmittance is higher for all the samples deposited on glass. This behaviour was not reported on quartz [21]. In this previous study, we measured the same change of transmittance shape before and after annealing, but globally keeping the same mean value. In fact, as we are being able to estimate a 6 pure sp<sup>2</sup> atomic layers on a 0.2 J/cm<sup>2</sup> (1000 shots) treated sample, we can justify the transmittance behaviour on quartz. At the infrared limit (800 nm), after annealing the transmittance is narrowing for about 14 %. Knowing, that one graphene layer has an optical absorption of 2.3 %, it means that the 6 graphitic layers top structure has an absorption of about

13.8 %, corresponding perfectly with the transparency loss in the near infrared domain. This point able us to validate the estimation of the graphitized thickness.

To shortly conclude on transmittance measurements and obtained performances, we show that laser annealing parameters have a reduced impact on the transmittance. Obtained results clearly demonstrate comparable performances to ITO, which are very promising for this technology.

### 3.4. Conductivity measurements

In a first approach, conductivity measurements are performed considering the total DLC thickness. Previously published results [21] present interesting conductivity especially for annealing made at 0.2 J/cm<sup>2</sup>. Nevertheless, we here demonstrate that the DLC structure after laser annealing is converted in a conductive graphitic layer set on the unaffected DLC layer, remaining insulated. The measured conductivity is therefore mainly underestimated due to the conductive layer thickness overestimation.

As we have precise XPS measurements performed on samples processed in the same conditions (SiO<sub>2</sub> substrate and 20 nm of KrF-DLC at 5 J/cm<sup>2</sup>), we are able to reevaluate (proportionally) the real conductivity of the surface graphitic layer. As expected, results (Tab. 2) show very interesting values in term of conductivity. If annealing performed at 0.1 J/cm<sup>2</sup> for 10000 shots still remains very low ( $3.17 \times 10^{-2} (\Omega\text{cm})^{-1}$ ) and is unusable for the expected applications, samples annealed at 0.2 J/cm<sup>2</sup> show high conductivity values ( $3.35 \times 10^4 (\Omega\text{cm})^{-1}$  for 1000 shots and  $3.72 \times 10^5 (\Omega\text{cm})^{-1}$  for 10000 shots). We conclude that annealing at 0.2 J/cm<sup>2</sup> for 1000 shots offers the best results (at 10000 shots, the surface presents some appearing defects).

We also investigated conductivity measurements on DLC deposited on glass substrate at various fluences for 1000 shots. It is important to notice, that results (Fig. 5) do not present the same values obtained on other substrates. Indeed, annealing at 0.2 J/cm<sup>2</sup> leads to high conductivity on SiO<sub>2</sub>, but shows lower value on quartz and on glass. We report that tuning the annealing fluence (for each substrate) permits to increase the conductivity. For example on glass, the best conductivity ( $1.08 \times 10^3 (\Omega\text{cm})^{-1}$ ) is reach for a fluence of 0.15 J/cm<sup>2</sup>. Values remains slightly under the performances obtained on SiO<sub>2</sub>.

These measurements show that the nature of the substrate is also affecting the conductivity. However, it is possible to refine annealing parameters to approach ITO conductivity. We also remember here that, the conductivity comparison between different substrates is made regarding a full DLC thickness (due to substrate effects on quartz and glass, we cannot guarantee that the same thickness of DLC is graphitized by laser annealing, so we keep the same thickness to obtain comparative measurements). Therefore, presented conductivity shows the worst case and are clearly underestimate compared to data presented previously (Tab. 2).

### 3.5. Integration as transparent resistor

We previously demonstrated that a very good transmittance and conductivity is obtained using a 0.2 J/cm<sup>2</sup> fluence with 1000 shots annealing parameter. This quartz deposited sample (Fig. 6) is placed in the resistor measurement testbench (described in 2.3). An approximate resistance of 4.17 k $\Omega$  is measured thanks to a high precision ohmmeter. As sample is rotated in an other orientation, we obtain significantly the same value confirming the homogeneity of the surface conductive layer.

The testbench is integrated in an electrical circuit composed of a stabilized DC power supply and a red light emitting diode (LED). The DLC film will then play the role of LED current limiting resistor. Different supply voltages are set (10, 20 and 30 V) and corresponding currents are measured (respectively 1.99, 4.39 and 6.83 mA). In each case, the LED is on and current is stable in the circuit.



From this data, we calculated the power dissipated in the DLC layer. This power dissipation reaches 194 mW when a 30 V supply voltage is applied without DLC destruction.

This simple test confirms that treated DLC layers are able to drive current and dissipate power. The layers are then finely usable as transparent resistor and show a promising potential for integration as transparent conductive electrodes.

#### 4. Discussion

To evaluate the structural modification induced by the laser annealing, we consider a simple approach based on a structure made of two superposed layers, composed of a fully graphitized surface conductive layer set on an unaffected DLC insulated transparent material. Looking back on all the obtained results (conductivity, transmittance, XPS...), the validity of the model is demonstrated being in high accordance and correlation with structural and functional analyses.

Another point concerns the transmittance evolution. It is demonstrated that annealing parameters have no influence on the transmittance after treatment. It is the same for the change of the transmittance behaviour before and after annealing (which is in accordance with the colour change linked to the surface graphitization). The theoretical transparency after annealing has to be slightly reduced in correlation with the graphitization happening on the DLC surface (as it is observed on quartz substrates). Nevertheless, the increase of the transparency after annealing on glass substrates needs to be discussed. No clear explanation can be given yet for this effect. We can assume in the case of glass substrates (which are not transparent at 248 nm) that a part of the annealing laser beam is absorbed in the glass leading to more structural changes than expected. These changes could be responsible of reducing some DLC structural defects in the layer depth, driving then to the transparency increase. Nonetheless, this point is positive inducing a transparency increase which leads to better optical performances.

A similar substrate effect is highlighted by conductivity measurements, showing a lower conductivity on glass and quartz substrates than on SiO<sub>2</sub>(63nm)/Si. As known, quartz and glass do not have the same optical behaviour at 248 nm. As quartz keeps a high transparency in the UV range, glass is fully opaque under 280 nm. It means that for a laser treatment performed on glass, the remaining part of the laser energy reaching the DLC-substrate interface is fully absorbed in the glass, leading therefore to a local thermal effect. This point leads to undesirable changes on DLC at the interface and in the layer depth, slightly modifying the DLC structure and leading to a conductivity variation. We also show that those effects could be countered with the tuning of the annealing fluence.

#### 5. Conclusion

In this study, we demonstrate the possibility to elaborate pure carbon transparent conductive electrodes by a full laser process. We proved that KrF deposited DLC (despite lower transparency compared to ArF-deposited DLC) is the best material to perform laser annealing to graphitize the DLC surface (over less than 2 nm). A homogeneous surface graphitization happens on DLC when the film is annealed with a fluence set between 0.1 and 0.25 J/cm<sup>2</sup> as it has been demonstrated by XPS measurements. Combining XPS grazing and normal incidence measurements with a simple structure model, permits to estimate the thickness of the full-graphitized layer, typically around 1.74 nm for the best obtained sample (in term of conductivity and transparency).

In term of performances, 0.2 J/cm<sup>2</sup> and 1000 shots show the best results on SiO<sub>2</sub> and quartz substrates, reaching a  $3.35 \times 10^4$  (Ωcm)<sup>-1</sup> conductivity with consideration of the 1.74 nm full graphitized thickness. Higher conductivity is obtained for 10000 shots, but samples present in that case some surface defects affecting the transmittance. In term of transparency, DLC on glass shows

systematically values in the same range than ITO. We demonstrate therefore that our process able us to produce pure carbon transparent conductive electrodes reaching ITO performances.

Finally, the integration of samples as transparent resistors proved the possibility to use treated DLC as functional electrical components and represent interesting perspectives for future applications. Following studies will investigate the substrate effects observed when annealing DLC on glass substrate and refine annealing parameters to obtain better performances in terms of transparency and conductivity.

### **Acknowledgement**

We specially acknowledge Mr ROQUES Stephane, Mr DIETRICH Florent and Mr MUGLER Florian for the technical and material support to carry on this study.

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## Figures

Fig. 1. XPS C1s deconvoluted peak for a DLC deposited at  $5 \text{ J/cm}^2$  (KrF) and annealed at  $0.2 \text{ J/cm}^2$  for 1000 shots. This sample presents very good performances in term of conductivity and transparency.

Fig. 2. Transmittance of DLC (20 nm) deposited at  $5 \text{ J/cm}^2$  for two different laser wavelengths.

Fig. 3. Transmittance of DLC (KrF) deposited at  $5 \text{ J/cm}^2$  for different film thicknesses.

Fig. 4. Transmittance of DLC (KrF - 20 nm -  $5 \text{ J/cm}^2$ ) annealed at 1000 shots at various fluences.

Fig. 5. Measured conductivity for DLC (KrF -  $5 \text{ J/cm}^2$  - 20 nm) deposited on different substrates regarding laser annealing fluences.

Fig. 6. Picture of a 20 nm of DLC deposited on quartz and annealed with  $0.2 \text{ J/cm}^2$  for 1000 shots.

## Tables

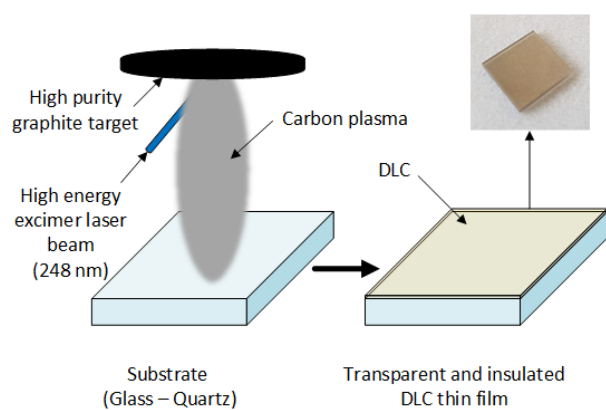
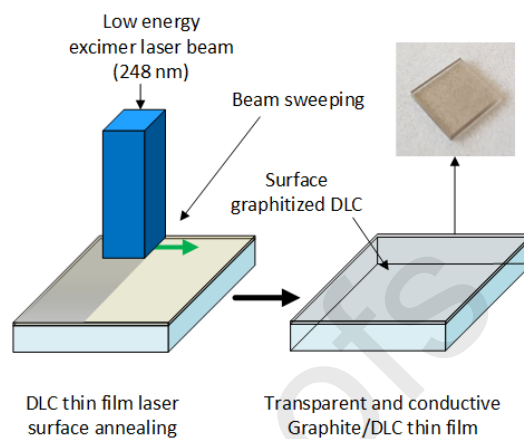
Tab. 1. Graphitic thicknesses and equivalent atomic layer estimations for both angle XPS analyses and for various annealing parameters on DLC (KrF -  $5 \text{ J/cm}^2$  - 20 nm).

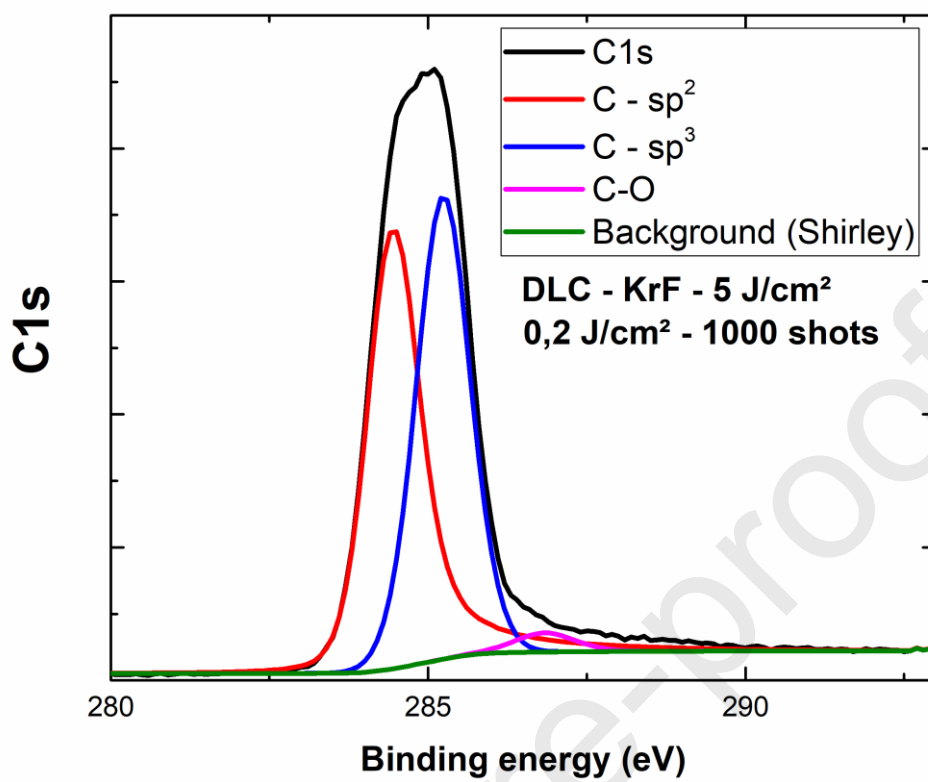
Tab. 2. Conductivity revaluation of  $\text{SiO}_2$  deposited DLC (KrF -  $5 \text{ J/cm}^2$  - 20 nm) considering the real graphitized thickness as deduced from XPS analyses.

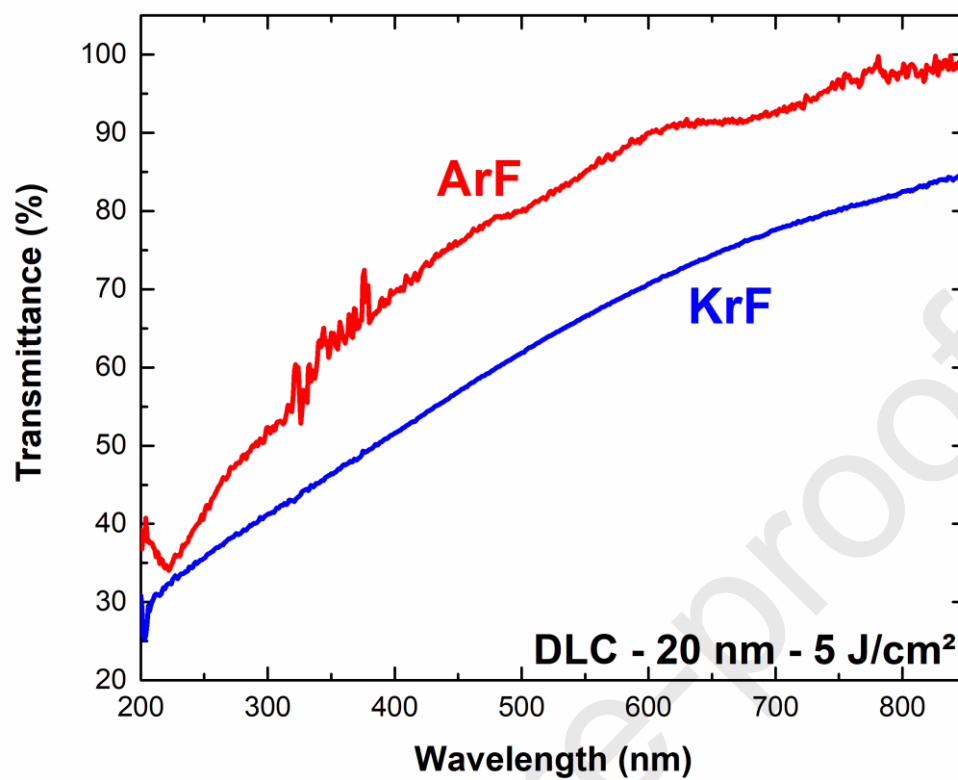
## **Highlights:**

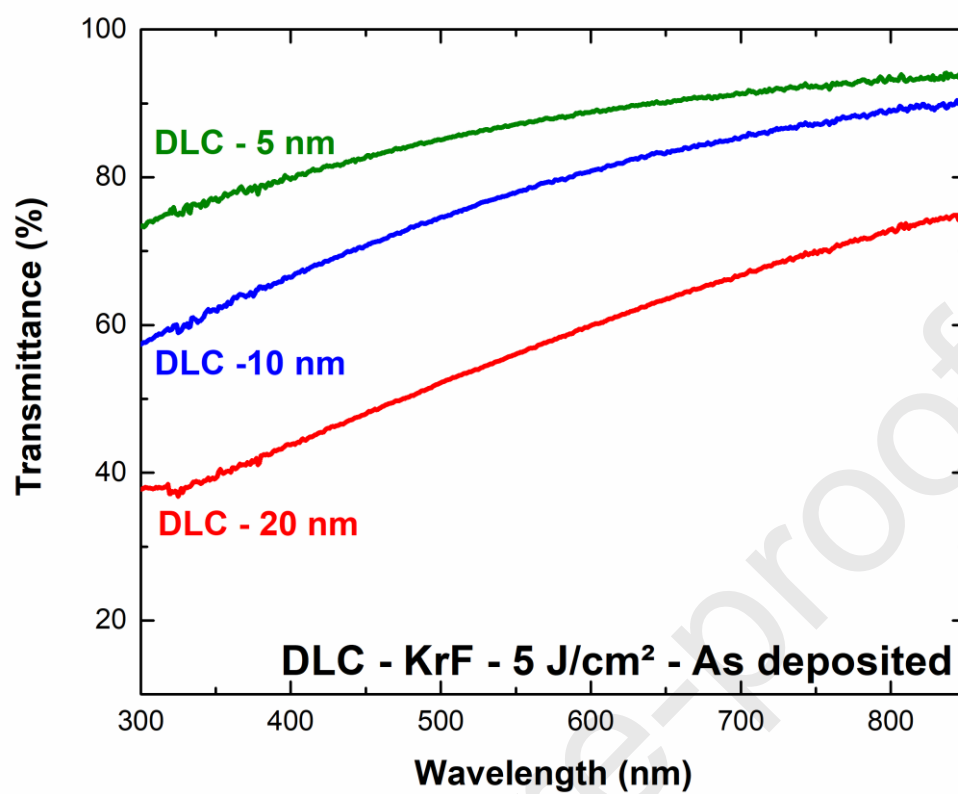
- Producing a pure carbon and laser based alternative to Indium Tin Oxide (ITO).
- KrF-deposited Diamond-Like Carbon (DLC) best candidate to UV laser surface annealing.
- UV laser surface annealing to fully graphitize DLC top layer over few nanometers.
- Conductivity and transparency performances tuneable by annealing parameters.

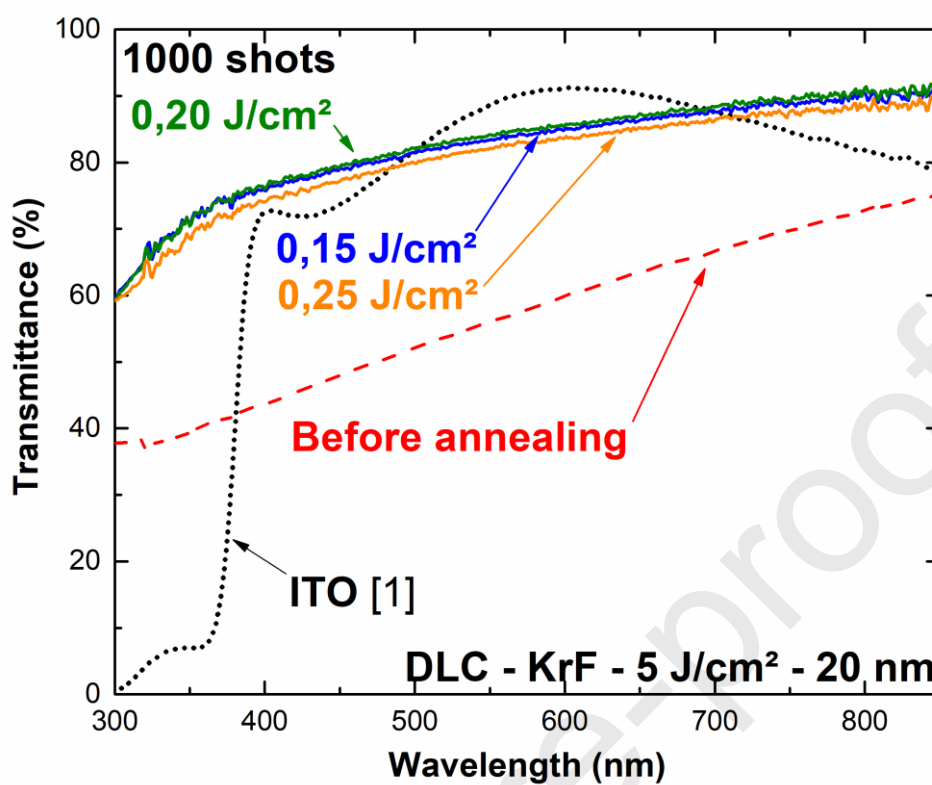


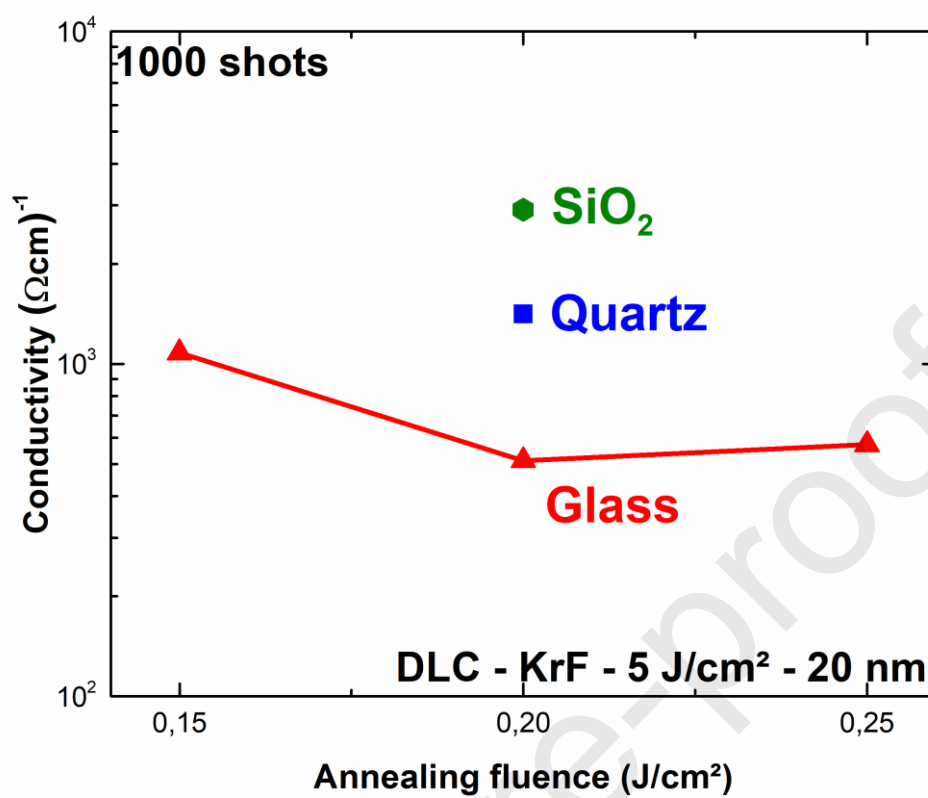
**1 First Step : Diamond-Like Carbon (DLC) growth by Pulsed Laser Deposition (PLD)****2 Second Step : DLC graphitization by laser surface annealing**



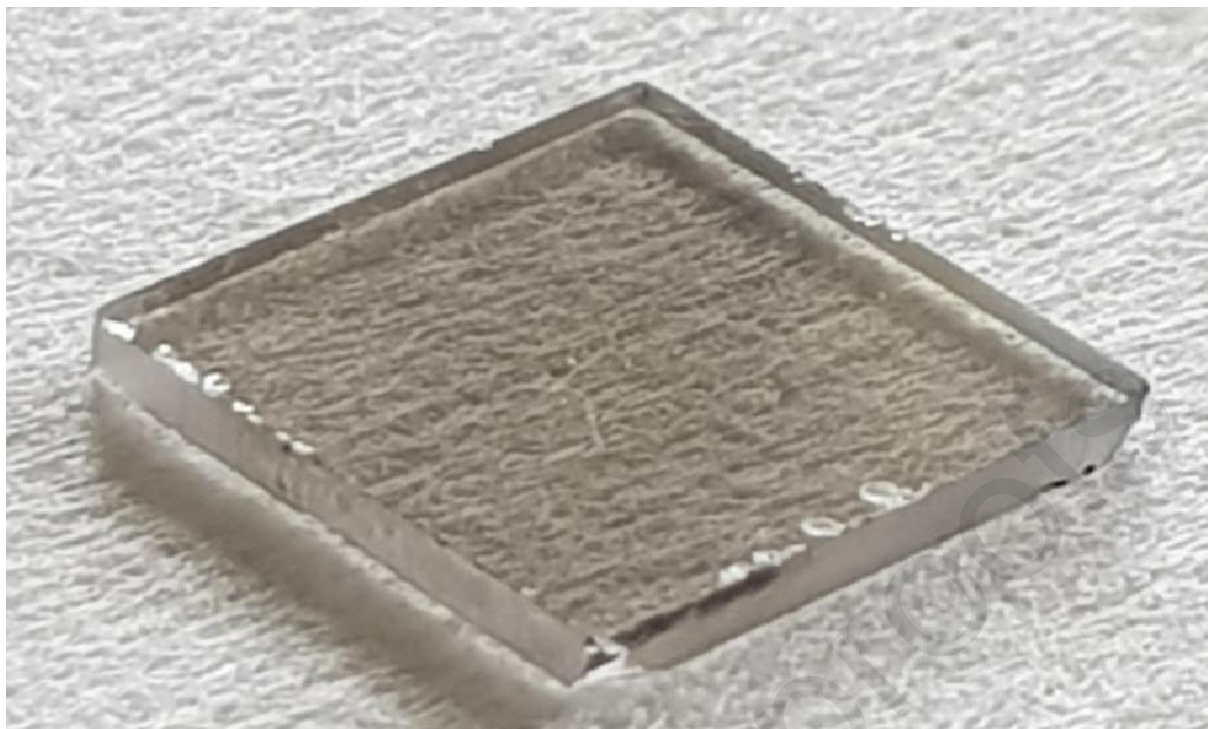












Annealing fluence J/cm <sup>2</sup>	Number of shots	Grazing incidence			Normal incidence			Average estimation	
		sp <sup>2</sup> %	Graphitic thickness nm	Number of layers	sp <sup>2</sup> %	Graphitic thickness nm	Number of layers	Graphitic thickness nm	Number of layers
0.1	1000	51.8	1.00	4	49.9	1.61	6	1.31	5
	10000	53.3	1.12	5	49.5	1.56	6	1.34	5
0.2	1000	59.7	1.62	6	51.5	1.86	7	1.74	6
	10000	68	2.28	8	59.8	3.09	11	2.69	9

Annealing fluence J/cm <sup>2</sup>	Number of shots	Measured conductivity (DLC - 20 nm) ( $\Omega\text{cm}$ ) <sup>-1</sup>	Graphitic thickness nm	Estimated graphitic layer conductivity ( $\Omega\text{cm}$ ) <sup>-1</sup>
0.1	10000	$2,13 \times 10^{-3}$	1,34	$3,17 \times 10^{-2}$
0.2	1000	$2,91 \times 10^3$	1,74	$3,35 \times 10^4$
	10000	$5 \times 10^4$	2,69	$3,72 \times 10^5$