

UV laser-induced reduction of spray coated graphene oxide layers for photovoltaic applications

Bachelor Thesis

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Abstract

In recent years, a great interest have been developed in the research of graphene and graphene oxide applications. In this thesis, we discuss about the laser-induced reduction of graphene oxide. The main goal is to find the proper parameters for the graphene oxide deposition on substrates as well as the uniform laser reduction of graphene oxide layers for large areas,

Firstly, we discuss about the basic principles of lasers and how they work. We briefly discuss about UV excimer lasers, in particular KrF excimer laser tecgnology. which is used in our expirements. Then, we continue discussing about graphene and graphene oxide synthesis and structure. Then, the laser-induced reduction of graphene oxide is explained. At last, we shortly refer to the basic theory behind UV-Vis spectroscopy and I-V measurements, which are used in the experimental procedure in order to characterize the laser-treated samples.

In the experimental procedure, we present materials and methods used. At first, there is a report in the production of the graphene oxide solution. Continuing, we make a statement at the GO deposition on the substrates prepared using the SimCoater spray coater. Then, we explain the experimental procedure for the laser reduction by illustrating, using different parameters for the reduction need. Lastly, different techniques have been used for the characterization of the laser-treated surface. Optical and electrical properties of the materials were studied by mean of UV-VIS spectroscopy and Two probe method, respectively.

The results are illustrated in the last section, where we discuss on the experimental results. During this thesis, as shown in this section, the spray-coated GO film uniformity is greatly improved. Then, we define the appropriate laser parameters for the successful laser-induced reduction of the GO film in a single spot area. Further, the best laser and scanning parameters are determined to achieve GO reduction over large areas. Absorbance and sheet resistance measurements provide a valuable feedback information for the success of the GO reduction process.

CHAPTER 1: Introduction

Graphene has attracted interest in the scientific field due to its extraordinary properties. Hence, many articles have been published about graphene and graphene based materials, its synthesis and applications. There are several applications such as biosensors, capacitors, solar cells transistors, etc. This thesis is focused on the photovoltaic applications, where a reduced graphene oxide film needed to be used in a graphene based tandem solar cell device.



Figure 1: Graphene based tandem solar cell device

The goal of this thesis is to produce a reduced graphene oxide film to be used in such a device. Why use graphene oxide since graphene has these extraordinary properties? The production of graphene oxide requires significantly less time for a larger larger scale of production. However, graphene oxide is not conductive, a problem which is easily solved by its reduction. Therefore, we need to deposit graphene oxide films with good sheet resistance and high transparency so that the light can transmit to the other tandem solar cell layers. We want a uniform deposition and a uniform reduction using a UV laser on the surface of the GO film. It has been a great effort by scientict to achieve that result



Figure 2: a) reduced graphene oxide film by Struchkov et al. [29] b) Sheet resistance of laser reduced graphene oxide by Sokolov et al. [30] c) Laser reduced graphene oxide film by Kymakis et al. [31]

Struchkov et al succeded in creating uniform GO films which had 22nm and 44nm thickness (Fig 2.a). Then they proceeded to the reduction of those films by using laser irradiation. In addition, as it is illustrated in Fig 2.b Sokolov et al. managed to reduce the sheet resistance of GO samples by using a KrF eximer laser and fluences ranging from 60mJ/cm² to 400mJ/cm². Last but not least, Kymakis et al. managed to provide transparent and highly conductive graphene layers, to be used as electrodes for organic electronic applications (Fig 2.c).

In this thesis, laser irradiation will be applied on graphene oxide films so that the sheet resistance will be significantly decreased. A brief introduction about lasers will follow, to outline their basic principles.

LASERS

LASER acronym stands for 'Light Amplification by Stimulated Emission of Radiation'. Someone can say that lasers are a special flashlight. However, there are some differences between lasers and flashlights. Due to their unique characteristics, lasers have several applications, such as in telecommunications, laboratory research and medicine, in graphics and grocery stores, as much as in the military. Characteristics that laser beams have over other ordinary light souces are:

- Monochromaticity: Light produced by lasers can almost be the same colour. On the other hand, common light sources produce light within a range of wavelengths
- Directionality: Lasers also have a high degree of directionality. Photons emitted by lasers travel nearly in the same direction. As a result, a laser beam can be focused on a small spot, greatly increasing its light intensity.
- Coherence: Two waves in a laser beam have nearly the same wavelength, same direction as well as the same phase.

A laser consist of three main components: a gain medium(solid, gas or liquid) that can amplify light by utilizing the basic process of stimulated emission, a pump source (electrical discharge, lamp), which creates a population inversion in the gain medium and two mirrors that form a resonator or optical cavity in order to trap light traveling back and forth between the two mirrors.

Depending on the gain medium, the laser can be operated either in a continuous wave (CW) or pulsed. Continuous wave lasers have a steady flow of coherent energy, with now change over time. In pulsed lasers, the beam is produced in a repetitive way with a pulse duration usually ranging from microseconds (long pulses), nanoseconds (short pulses, like the KrF laser used in our experiments) to femtoseconds-picoseconds(ultrashort pulses).

Three fundamental phenomena occur when an electromagnetic wave (EM) interacts with a material: spontaneous (a) and stimulated emission(b) and absorption (c) as it is shown in the figure below.



Figure 3: Fundamendal phenomena [27]

When an atom is in an excited state (for example excited state 2), it can spontaneously decay into the ground state, emitting an EM wave with the frequency $f = \frac{E_2 - E_1}{h}$ where h is the Planck constant E₁, E₂ is the energy of the state 1 and 2 respectively (fig3.a).

Now, let's say that the atom is in its excited state 2. If it interacts with an EM wave with frequency $f = \frac{E_2 - E_1}{h}$, the atom may decay to the ground state with stimultaneous emission of EM radiation (stimulated emission). The emitting photon has the same frequency, direction, polarization and phase as the first photon (Fig. 3.b). This is the main distinction to the spontaneous emission, and is the reason why light emitted by the laser is coherent while other light sources like lamps or LEDs emit incoherent light which exploit spontaneous emission.

In the case of an atom in its ground state, if there are no perturbations (collisions with atoms or photons) the atom will remain in its groind state. However, if an EM wave with $f = \frac{E_2 - E_1}{h}$ incident onto the atom, the latter can be transited in its excited state 2 (Fig 3.c). This process is called absorption.

Ultraviolet Lasers: Excimers

Excimers today are based on precisely controlled electrical discharges and they rely on detailed knowledge of material chemistry. Originally, the term excimer referred to excited dimmers. However, nowadays it is used for all kinds of laser-active media that are characterized by bound excited states and dissociative ground states, more generally named exciplexes.

Excimer lasers have a variety of emission wavelengths in the whole UV region.



Figure 4: Wavelength/photon energy of various excimer transitions[27]

The shorter the wavelength, the higher the absorbance by most materials, resulting in sufficient quantum energy to induce photochemical reactions to cause molecules to dissociate. In addition to their high peak power in a pulse, the bond-breaking radiation allows ablative evaporation with main applications in micro-processing of different materials. Excimer lasers can emit laser pulses in a range of nanoseconds, which makes the procedures easy to happen frequently ("on the fly").[27] They also can have high pulse energies, on the scale of Joule, with repetition frequencies of a few kHz.

Excimer molecules are different from ordinary molecules. They can only exist as a form of a stable molecule only if they are in an excited state. If for a reason an excimer molecule loses its energy and falls to the ground state, the molecule breaks into individual atoms in a few picoseconds.

KrF excimer is an example excimer molecule. Kr is a noble gas, an inert element which doesn't normally form molecules because it has its outer shell of electrons full. Kr and F atoms push away

from each other when they come close. However, having electric discharge (electric field in a gase medium) of laser, Kr atoms absorb energy from electrons and become excited. Then, they approach F atoms, attracting them, and forming a stable KrF molecule in an excited state. The typical lifetime of that excited state of excimer molecules are in the nanosecond scale. They emit a photon and return to the ground state, and in a picosecond the molecule flies apart.

Excimer laser structure consists of a chamber containing the appropriate rare gases, in our case a small amount of Kr and F_2 plus a buffer gas such as He or Ne. The population inversion is created by an electrical current running from the high voltage electrode through the gas to the other electrode at ground voltage.

An electron collides with a Kr atom in the ground state, exciting it or even breaking an electron off the Kr. In addition, electrons colliding with an F_2 molecule can break the molecule and even ionize one of the F atoms. So the reactions are:

 $e+Kr \rightarrow Kr^{*}+e$ or $e+Kr \rightarrow Kr^{+}+2e$

$$e + F_2 \rightarrow F + F$$

 $Kr^{+}+F^{-}+(buffer gas such as He) \rightarrow KrF^{+}+(buffer gas such as He)$ or $2Kr^{+}+F_{2} \rightarrow 2KrF^{+}$

An excimer molecule corresponds to a condition of population inversion.

However, the excimer molecules can lose their energy without emitting photons, by giving off the energy in the form of heat. Possible reactions can be:

 $KrF^* + hf \rightarrow KrF + 2hf$ stimulated emission

 $KrF^* \rightarrow KrF + hf$ spontaneous emission

 $KrF^* + F_2 \rightarrow Kr + 3F + heat$, where F_2 dissosciates by the collision

hf is the photon. If the excimer molecule does not claim the energy by the first mechanism in the first few nanoseconds, the energy will be lost to the other mechanisms. In order to make sure the occurrence of stimulated emission before the energy is lost, we need high photon flux so that the photon gets to the excimer molecule between its creation and its spontaneous emission.

The buffer inert gas (He in our case) helps to remove heat inside the laser, because of its high thermal conductivity. In addition, it reacts as a catalyst, a chemical agent that makes easier the creation of KrF* molecules in the recombination process.[28]

Graphene

In the last years, a great amount of work has been done in investigating graphene, since its discovery by Konstantin Novoselov and Andre Geim in 2004 at the University of Manchester. There are over a hundred of thousands of publications about its properties, such as thermal and electrical conductivity, its electronic structure and many applications such as energy, storage, sensing, and others.



Figure 5: Graphene form[6]

Graphene is a 2-D material with carbon atoms in a hexagonal mesh. It is interesting for its:[7]

- high specific surface area (2630 m²g⁻¹)
- high intrinsic mobility (200,000cm²v⁻¹s⁻¹)
- thermal conductivity (approximately 5000Wm⁻¹K⁻¹)
- high optical transmittance (97.7%)
- good electrical conductivity

The electrical current is transferred either by negative charge carriers (electrons) or by positive charge carriers (holes) like semiconductors.





Figure 6: Zero band gap between valence and conductive band[7]

Figure 7: First Brillouin zone and band structure of graphene [9]

Graphene is a 2-D semiconductor with zero energy band gap between the conductive and valence band. The first Brillouin zone of graphene has two nonequivalent points (known as Dirac points) where the band crossing takes place. [8]

In Fig.7 [9] we see the first Brillouin zone and band structure of graphene. Vertical axis and horizonal axis represent the energy and the momentum space on the graphene lattice respectively. K and K' (Dirac points) are two nonequivalent corners of the zone. Γ is the center of the zone where the momentum is zero. Dirac points are points in the momentum space, on the edge of the Brillouin zone. There are two nonequivalent sets of three Dirac points. Those two sets give graphene valley degeneracy equal to two.

Comparing Graphene properties with other 2-D semiconductors makes graphene very interesting because:

- Graphene has zero bandgap (typical semiconductors have a finite bandgap). That makes the
 carrier charge to change at the Dirac points. In addition, the Fermi level in traditional
 semiconductors is in the bandgap, whereas in graphene it is always in the conduction or
 valence band.
- It has a linear dispersion relation (E~k) instead of quadratic dispersion (E~k²) which is the most common for 2-D semiconductors

- Graphene is a single layer of carbon atoms, much thinner than traditional 2-D electron gas (0.3nm compared to 5-50nm of the 2-D electron gas)
- It has a finite minimum conductivity as a result of the zero bandgap

Synthesis of Graphene

As mentioned before, Konstantin Novoselov and Andre Geim in 2004 first isolated graphene using the famous Scotch tape method.No other method can produce samples with high quality and high carrier mobility, even today. However, mechanical exfoliation requires a lot of time, for a small amount of production. The main concern for a larger scale of production is the quality, consistency and cost of the samples.

The most important synthesis methods are[9]:

- Mechanical exfoliation
- Thermal decomposition of SiC
- Chemical Vapor decomposition
- Reduction of graphene oxide

Mechanical exfoliation

As mentioned above, this method was developed by Novoselov and Geim. They used a highly oriented pyrolytic graphite (HOPG). 5Mm deep mesas were created by oxygen plasma etching. Then, a layer of photoresist was applied on the mesas. They baked the photoresist and then cleaved the HOPG of it. Then, they used Scotch tape to peel of graphite flakes from the mesas. Those graphite flakes were then placed in acetone on the surface of a Si/Si₂ wafer.

Using an optical microscope and SEM, these flakes were identified as few-layer graphene (FLG) with a length up to 1mm as it is shown in figure 8.



Figure 8: Graphene monolayer produced by mechanical exfoliation[9]

Thermal Decomposition of SiC

Silicon carbide is heated in an ultra-high vacuum chamber (UHV) at high temperatures (1000-1500°C). At these temperatures, silicon sublimates and carbon atoms are left behind on the surface.

In addition,, heating SiC in Ar at 900 mbar (by Emtsev et al), produced graphene layers with lower surface roughness, and continuous layers of lengths up to 50µm.

Chemical Vapor Deposition(CVD)

In order to grow a graphene layer, a metal is used as a catalyst and substrate (usually Nickel and Copper). The carbon is not present like in thermal decomposition, so it is supplied in gas form like methane.

The domain size of graphene by CVD is affected by the temperature, methane pressure and flow.



Figure 9: Dependance of graphene domain by temperature, methane pressure and flow[9]

Reduction of Graphene Oxide (GO)

The production of graphene can occur by the sonication and reduction of graphene oxide. This method is used in the experimental procedure, as it is discussed later.

During the oxidation process, polar O and OH groups are formed which make graphite oxide hydrophilic. So, it can be exfoliated in some solvents, like water, and then sonicated so that it will form GO nanoplatelets. Afterwards, the oxygen groups can be removed by several reducing agents.

Graphene can be produced by reducing GO either thermally or chemically.

However, the exact structure of GO is still not determined. Nevertheless, the type and proportion of oxygen bonds in the graphene lattice is considered in agreement.

Graphene oxide (GO)

<u>Structure</u>

A precise model structure for graphene oxide is debatable even today, as a result of its complexity [12].

There are many structure models for GO, like regular lattices composed of discrete repeated units.

Some of the older models are shown in the figure below:



Figure 10: Older models of GO structure[12]

However, the most recent models of graphene oxide structure, reject the lattice-based model, focusing on a nonstoichiometric, amorphous substitute. Anton Lerf and Jacek Klinowski proposed a structure model and published numerous papers on the structure of GO, which are widely cited in the up to date literature. They used solid-state nuclear magnetic resonance (NMR) spectroscopy to characterize the material.



Figure 11: Variations of GO model by Lerf and Klinowski[12]

<u>Synthesis</u>

Hummers Method [10]

Hummer's method is the most popular today for the production of graphene oxide. William S. Hummer and Richard E. Offeman developed a way to oxidate graphite by reacting it with a mixture of sulfuric acid (H₂SO₄), potassium permanganate (KMnO₄) and sodium nitrate (NaNo₃).

100g of graphite flakes were mixed with 50g of sodium nitrate and 2.3L of 66° Be sulfuric acid in a jar which was ice-bathed at 0°C. The mixture was vigorously agitating and then 300g of potassium permanganate was added. However, the potassium permanganate flow was controlled, so that temperature increase was prevented (above 20°C).

Then, the ice-bath is removed, the suspension was brought to 35°C for 30 minutes and the mixture thickened in the process. Later, 4.5 L of water was slowly added to the mixture, causing violent effervescence and an increase in temperature to 98°C. The suspension had a brown colour and was maintained at that temperature for 15 minutes. Then, the suspension was further diluted to 14 L of warm water and treated with 3% hydrogen peroxide, turning into bright yellow colour. After that, it was filtered and washed with 14 L of warm water and dispersed in 32L of water to approximately 0.5% solids.

Then, graphite oxide was obtained in dry form by centrifugation and then dehydration at 40°C over phosphorous pentoxide in a vacuum.

Improved modified Hummer's method [13].

In this method, Sodium nitrate was removed from the reaction formula. 3g of graphite powder was added to the 70 mL of concentrated H_2SO_4 and stirred in an ice bath. Then, KMnO₄ was added slowly to sustain low temperatures. Afterwards, the suspension was transferred to an oil bath and stirred for half an hour. 150ML of water was added and stirred for 15 minutes at 95 °C. Then 500mL of water was added as well as 15mL of H_2O_2 (30%). The colour of the mixture turned from dark brown to yellow. After filtering and washing the mixture with 250mL aqueous HCl solution to remove metal ions, the resulting solid was dried in air and then diluted to 600mL, making graphite oxide aqueous dispersion. Then, to remove the remaining metal species, it was purified by dialysis for one week. Finally, it was diluted to 1.2 ,stirred overnight, and sonicated for 30 mins to exfoliate it to Graphene oxide. Then, the GO dispersion was centrifuged for 40 mins to remove unexfoliated GO. This improved Hummers method eliminates the production of toxic gases, simplifies the process of purifying waste liquid as well as reduces the cost of GO synthesis.

Laser-induced reduction of GO

Reduced graphene oxide can be produced with a variety of routes, such as thermal, chemical, electrical, laser or a combination of these methods. These years, laser-based routes are preferred, because they are environmentally friendly, they are fast (the process requires several minutes), they don't need hazardous gases and materials and they don't need high temperatures (resulting in that they are compatible with substrates that cant tolerate high temperatures such as polymers), they are energy-saving and they have high reproducibility in a controllable reduction.[23]

The GO lattice consists of oxygen functionalities, such as carboxyl and hydroxyl groups on the edges and epoxy and hydroxyl groups on the lattice. GO has disrupted sp² bonding networks which makes it an electrical insulator. However, the electrical conductivity can be restored by the removal of the oxygen groups by its reduction.

The laser reduction of graphene oxide can be achieved by either photothermal effect, photochemical effect or a combination of the two. There is a 3,2 eV energy threshold of GO photoreduction. As a result, to achieve GO reduction through the photochemical process, we need wavelengths shorter than 390nm (in the UV region). In addition, it was found that photochemical effects tend to happen using lasers with short wavelengths and ultrashort pulse widths. Using lasers with longer than 390nm wavelengths and long pulse width, the reduction is achieved by the photothermal effect. Localized temperatures higher than 2500°C are achieved, which leads to the break of the C-O, C=O and C-N bonds.

For the photochemical effect, the absorption of photons by the GO leads to the bond breaking, for minimum photon energy equal to 3.2 eV.

In the photothermal effect, the photon energies are absorbed by the electrons and they are excited, producing heat to the GO lattice. For high localized temperatures as discussed above, we have bond breaking and deoxidation of GO.[25]

However, the photochemical effect is always accompanied by thermal generation. Using a laser with 248nm wavelength (like the laser we use in the experimental procedure as discussed in the next sections), irradiating a GO solution can raise its temperature up to 60°C which is not adequate for the photothermal effect. However, the temperature of the GO flakes can reach up to 200°C which leads to thermal deoxygenation. .[24]

Characterization methods

UV-Vis Spectroscopy

UV-Vis spectroscopy is a technique which measures the absorbance or transmittance of light for wavelengths that range from 200nm to 1100nm depending of the light source used in the spectrometer (deuterium lamp for the UV region and tungsten lamp for the Vis region). It contains information for electronic and vibrational transitions [20].



As it is shown in Fig. 12, UV wavelengths range from 200nm to 400nm, Visible from 400nm to 800nm and NIR from 800nm to 1100nm.

UV-Vis spectroscopy is built on electronic transitions of organic molecules. When molecules absorb light, electrons are excited from the lower energy orbital which is the highest occupied molecular orbital (HOMO) to a higher unoccupied molecular orbital (LUMO) (Fig. 13).[17]



Figure 13: Excitation of electrons [16]

For molecules in general, vibrational and rotational motions can be excited by light absorption.

An electron is excited when the incident electromagnetic radiation frequency is the same as the energy difference between the two states.

The rotational (v) and vibrational (j) sublevels are shown in the figure below:



Figure 14: Vibrational and rotational sublevels of two electronic states of a molecule [19]

The energy change of a quantized system when light is absorbed or emitted for wavelength λ is

$$\Delta E = \frac{hc}{\lambda}$$
 where h is the Plank constant and c is the speed of light.

The light absorption on gases and solutions in the UV-Vis region is given by the Bouger-Lambert-Beer Law:

 $A = \log(I_0/I) = \varepsilon Cl$ where A is the absorbance, I, I_0 are the light intensities after and before the sample, ε is the extinction coefficient, C is the concentration and l is the path length.

The quantity I/I_0 is called Transmittance (T).

A typical UV-Vis spectrometer schematic is shown in the figure below.



Figure 15: UV-Vis spectrometer schematic

Sheet resistance

Electrical resistivity (ρ) is a quantity that describes how easily the electrical current flows in a material. The easier the electrical current flows, the lower the electrical resistivity is. Its unit of measurement is Ohm meters ($\Omega \times m$).



Figure 16: Simple model of electricity through a material.

As we can see in Fig.16, a simple model to understand resistivity is to consider the white circle as an electron, moving through the stationary atoms of the material (black circles). Collisions between the electrons and the atoms, slow down the electron, causing electrical resistivity.

Resistivity is an intrinsic electrical property of the material, not dependent on the size, shape or thickness of the material.

We know from the electromagnetic theory that, $E = \rho J$, where E is the electric field and J is the electrical current density.

However, E=V/l, where V is the voltage applied and l is the distance over the voltage is applied.

So
$$\frac{V}{l} = \rho J = \rho \frac{I}{A}$$
.

Rearranging the equation, we have $\frac{V}{I} = R = \rho \frac{l}{A}$, where R is the resistance and A is the cross section area.

Two probe technique

The resistivity of the sample in Fig. 17 is, $\rho = R \frac{A}{l}$, where A=wh.



Figure 17: 2 probe technique to measure the resistivity of a bar sample[22]

Sheet resistance $R_s = R x \frac{w}{l}$ is the resistance a square film would have (when w=l in Fig.17). The units for sheet resistance are Ohm per square (Ω /sq). Sheet resistance is not dependent on either the size of the square film or its thickness.

CHAPTER 2: Experimental procedure

Samples preparation

For the samples prepared, the following equipment and materials are used :

Graphene oxide (GO) aqueous solution, Distilled water, Sonicator bath, Microscope glass, glass coated with indium tin oxide (ITO), Silicon disc (substrates), Diamond cutter, Compressed air, Syringes, Isopropanol, Ethanol and SimCoater Spray Coater.

GO solution:

For the preparation of the GO solution, we mix 1 part of GO (5mL) aqueous solution and 3 parts (15 mL) of distilled water through syringes in 20ml bottles. The primary GO aqueous solution was purchased. Then, we submerge the final 20mL solution in the sonicator bath for three minutes at room temperature, in order to homogenize the GO solution.



Figure 18: GO aqueous solution





Figure 19: Sonicator bath

Figure 20: Final GO solution

Substrate preparation:

For the substrate preparation, the glass is carefully cut with the cutter into 1x1 cm² and 2x2 cm². Then the substrates are blown with compressed air and submerged in an ethanol solution in order to remove any glass leftovers. Continuing, 2-3 isopropanol droplets are deposited on the substrate surfaces, and then they are carefully wiped with optical lens tissues. Lastly, they are blown again with compressed air in order to have any remaining isopropanol evaporated.

GO deposition on substrates:

The deposition of GO solution on the substrates is done by the SimCoater Spray coater. The setup consists of: Spray coater, hot plate with XY axis movement, pump syringe, ultrasonic generator, compressed air supply and computer.



Figure 21: SimCoater Spray Coater



Figure 22: Syringe Pump



Figure 23: UltraSonic Generator

We open the program PathWrite on the computer to write the commands for the SimCoater in order to scan the proper path for the deposition. We choose to scan the area in a meander shape with a hatch of 8mm and an area of $6.5x5cm^2$ in order to have a uniform deposition. Then we transfer the program to the controller of the SimCoater, in order to be able to run it whenever is needed. When transferring the program to the controller, we choose a number of cycles the coater will run, resulting in different thicknesses of the GO layers deposited.

The samples are positioned and taped on the thermal base with thermal endurance tape. The thermal base is set to 100 degrees Celcius and we wait until it heats up. We fill the pump syringe with the GO solution and we set the pump ratio to 0.5 mL per minute.



Figure 24: Samples attached with thermal tape on the SimCoater

When the thermal base is heated, we run the program we want for the proper number of cycles, and we wait until the procedure is finished.

We store the samples in disk trays airtightly.

Laser reduction of Graphene-Oxide:

The laser used for the reduction of GO is KrF Excimer laser with λ =248nm wavelength, ns pulse duration and 1 Hz repetition rate.

The setup consists of the KrF excimer laser, 2 mirrors, 2 irises, an attenuator, XY stages and a digital oscilloscope.

At first, we turn on the hot and cold water pumps which are responsible to cool down the laser. Then we turn on the laser and we wait eight to ten minutes to heat up.

Continuing, we align the laser setup as seen bellow:



Figure 25: Laser setup



Figure 26: Laser setup

When the setup is aligned correctly, we set the first iris to 1.8 cm in diameter. Then we place a power meter after the attenuator and connect it to the digital oscilloscope. By changing the direction of the attenuator, we change the total energy fluence of the laser beam transmitted. The full energy is measured when the attenuater is tilted by 90 degrees and no energy is measured at 45 degrees.

The laser energy is measured by measuring the voltage through a digital osxilloscope and converting it to energy by using a calibration equation of the power meter which is 0.4 Volt per mJ of energy.

Once we set the desired fluence, we place the sample prepared on the XY stages. Each sample is irradiated by choosing the proper parameters (as discussed in the next chapters) in order to achieve the desired number of laser pulses per spot. The parameters we are eligible to change are:

- XY stages velocity (each direction)
- Spot size (by altering the iris diameter)
- Repetition rate
- the hatch between each scanning line
- laser fluence

Characterization methods

After the laser reduction of the graphene oxide, we need some measurements to estimate the degree of reduction and decide whether it is useful in photovoltaic applications or not.

- For the optical measurements, PerkinElmer is used, a Lambda 950 UV-Vis spectrometer.
- For the electrical I-V measuremets, 2-probe method is used.

Ultra Violet- Visible optical measurements



Figure 27: UV-Vis spectrometer

UV-vis spectroscopy measures the light absorbance in the ultraviolet and visible spectrum.

The spectrometer setup consist of :

- an irradiation tungsten-halogen and deuterium light source which emits through different optics towards the monochromator slit.
- A monochromator with a diffraction barrier in order to have the incoming light beam transmitted to a small range of wavelengths
- a photomultiplier detector for high energy in the whole UV-Visible wavelength range

- An integrating sphere, which has high reflecting white walls for all wavelengths in all directions, arriving at the photomultiplier detector
- A computer connected to the detector, for the data analysing and processing
- The typical wavelength range is 175nm-3300nm.



Figure 28: UV-Vis transmittance lens and integrated sphere(right)

To start the measurement process, we have to turn on the spectrometer in order to heat it for 30 minutes. Then, we turn the computer on and open the Perkin elmer program (UV WinLab). For the transmittance measurements, we place the samples before the integrating sphere, while for the reflectance, we place the samples after the integrating sphere.





Figure 29: Graphene and Graphene Oxide UV-Vis absorption [2]

Figure 30: Graphene Oxide and reduced Graphene Oxide UV-Vis absorption [3]

The absorption peak of GO at 235nm corresponds to π - π ^{*} transitions of the remaining sp² C=C bonds which are shifted to 265 nm after the reduction of GO to graphene as it is illustrated in fig29,30. The π -conjugation network of graphene sheets is re-established after the reduction which is very important and contribute to the properties of rGO. As the π -conjugation increases, less energy for the π - π ^{*} transitions is required, which corresponds to the longer wavelength of the absorption peak observed.

Atomic Force Microscopy (A.F.M)

Atomic force microscopy is a technique that measures surface structure with extraordinary resolution and accuracy. The main difference between A.F.M and other ordinary microscopes like optical and electron microscope is that it doesn't require light or electron focusing onto the surface, but it feels the sample surface by a sharp probe, building a map of the sample's surface. This property of A.F.M differentiates it from an imaging microscope, which measures 2-D projection of the surface, having no information about its height. The A.F.M data must be treated to form an image we excpect from an imaging microscope. However, the data treatment is simple using simple analysis softwares. The main components of an A.F.M are the microscope stage, control electronics and a computer. The stage consist of the scanner which moves the AFM tip, a sample holder and a force sensor. A typical AFM stage is illustrated in Fig. 31.



Figure 31: AFM stage and its components[33]

I-V two-probe measurements

The setup consists of: a fixed base, 2 probes with 3-axis movement calibrator screws, computer



Figure 32: 2 probes for I-V measurments



Figure 33: Probe with calibrator screws for XYZ axis movement

At first, we apply to the samples a super high conductive silver paste. The paste is applied in two small droplets, with approximately 1cm distance between them. We let the samples dry.



Figure 34: Silver high conductive paint



Figure 35: Reduced graphene oxide samples with silver paint (higher number of laser pulses from top left to bottom right)

We turn on the computer and start the IV program. When the paste becomes dry, we place the sample on the base. Carefully, we move the probes via the proper screws toward the silver paste making sure neither the paste nor the graphene oxide (or reduced graphene oxide) layer gets scratched. In case of wrong probe placement or scratched samples, we end up with wrong results.



The measurements on the software are shown in the picture below:

Figure 36: PC user interface for IV measurements

The graph on the software is the electrical current as a function of the voltage applied through the needles. The slope of the equation given equals the resistance of the sample. Our goal is to measure the sheet resistance of each sample.

After the IV measurements, we measure for each sample the space between the two droplets of the super-conductive paste with a digital calliper.

CHAPTER 3: Results

SimCoater Uniformity

After the need to deposit GO solution on larger area substrates, it is visible with the naked eye that the coater is not spraying on the whole surface evenly, as it is illustrated below.



Figure 37: Large area of spray-coated graphene oxide layers. The different color within the same sample (see areas 3, 9 and 10) indicate a non-uniform GO thickness.



Figure 38: PathWrite user interface, 3 overlapping meanders as the coating pattern

Our goal is to find the proper pattern in order to have a uniform coating on the whole surface

As we can see in Fig. 37, the initial scanning pattern parameters of the Spray Coater, create uniformities on the coated area. The scanning pattern on PathWrite program is shown in Fig. 38. There are three overlapping meanders of 50mm length each, and the hatch between two consecutive verical lines is equal to 8 mm.

It is visible that in the areas where meanders overlap one another, the thickness of the GO layers on the glass substrate is significantly higher. The darker colour of some areas of the film, indicates its higher thickness. UV-Vis absorbance spectra of the film in Fig. 37 confirm that the sample does not have a uniform surface. The figure below (Fig. 39) shows that different areas of the sample in figure 37 have different absorbances. Areas with darker colours are expected to have higher absorbance.



Figure 39: UV-Vis absorbance as a function the of wavelength for the samples in Fig. 37

Samples in areas 3,4,9,10 (see Fig. 37) have higher absorbance than the samples in the rest areas. So, it is clear that a new coating pattern must be created, in order for the GO films uniformity to be improved.

The new pattern created is a continuous meander with hatch between two vertical lines equal to 8mm. The total length of the meander is 129mm The scanning pattern on PathWrite is shown in figure 40.

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Figure 40: PathWrite user interface, one meander



Figure 41: Large area of spray-coated graphene oxide layers using the pattern of Fig. 40

In Fig. 41, we illustrate see a GO film coated on a glass substrate which seems uniform in the whole surface. However, that needs to be confirmed optically with UV-Vis measurements.



Figure 42: UV-Vis absorbance as a function of the wavelength for the samples in figure 41

As it is shown in figure 42, the samples in areas 1-6 have approximately equal absorbance. Samples in areas 7-9 have lower absorbance because they were placed in the lower edge of the scanning area of the Spray Coater, which leads to the lower thickness of the film. We can conclude that we have a uniform GO deposition on the whole area, excluding the spraying edges of the SimCoater spray coater.

SimCoater Calibration

Now that we have improved the uniformity of the spray-coated GO layers, there is the need of the spray-coater device callibration. We should be able to control the correlation of the number of cycles (number of times where the pattern in Fig. 40 is repeated) with the GO film thickness

We prepare glass substrates as it was discussed in a previous section and we run the program with different numbers of cycles for each sample (40,60,67 90,130,167). Then, the thickness of each sample is measured with A.F.M (Atomic Force Microscopy).

A typical AFM images are shown in figures 43,44.



Figure 43: AFM of 60 cycles of GO



Figure 44: AFM processing for the sample of Fig. 43

For each sample, we have approximately 15-20 AFM measurements. We calculate the average thickness and error for each sample. Then we make a graph with the thickness of each sample as a function of the number of cycles.

The result is shown in the Figure below :



Figure 45: Thickness of GO layers as a function of the number of cycles

The average thickness for each number of cycles is $thickness = \frac{1}{n} \sum_{i=1}^{n} n_i$ and the standard deviation is $SD_{thickness} = \sqrt{\left(\frac{1}{(n-1)} \sum_{i=1}^{n} (n_i - thickness)^2\right)}$

The equation of the linear relationship between the thickness and the number of cycles is :

 $thickness = (0.504 nm \pm 0.011 nm) \times cycles$ with an error in thickness equal to $D(thickness) = 0,011 \times cycles(nm)$

In addition, we want to correlate the thickness of the graphene oxide layers coated on glass with their UV-Vis light transmittance in certain wavelengths for an easy and quick estimation of the film's thickness.

Transmittance for GO on glass samples with different thicknesses (2 samples tested for each thickness) is shown in the figure below.



Figure 46: UV-Vis transmittance as a function of the wavelength

As it is illustrated in fig 46, the film transmits more light for lower thicknesses, as expected. The similar curvature of each curve and the equal transmittance of each pair of samples, guarantees the uniformity of the spray-coated GO film.

Then for wavelengths λ =400nm, λ =500nm, and λ =600nm we plot the graph of transmittance as a function of the thickness of the graphene oxide film coated on the glass as shown in the figures below.



Figure 47: UV-Vis transmittance for λ =400nm



Figure 48: UV-Vis transmittance for λ =500nm



Figure 49: UV-Vis transmittance for λ *=600nm*

The equations for the relation between Transmittance and thickness for each wavelength are:

- $\lambda = 400$ nm Tranmittance = $(82.2 \pm 1.2) (0.360 \pm 0.024)t$
- $\lambda = 500$ nm Tranmittance = $(24.3 \pm 2.2)e^{-t/(36 \pm 15)} + (67.6 \pm 2.9)$
- $\lambda = 600$ nm Tranmittance = $(21, 6 \pm 1, 7)e^{-t/(20, 8 \pm 2, 5)} + (76, 00 \pm 0, 40)$

where t=thickness.

Those equations are useful, in order to estimate the thickness of an unknown graphene oxide film on a glass substrate by simply measuring its UV-Vis transmittance, at a specific wavelength. Wavelength λ =600nm is preferable, because of an increased uncertainty of the spectrometer in the measured values in the near-UV regime.

UV Laser-induced reduction of Graphene Oxide layers

We need reduced graphene oxide films for photovoltaic applications, with $3x3cm^2$ total area. However, the KrF excimer laser can emit a laser beam with a spot of maximum 2cm in diameter. So, it is necessary to use XY stages, in order to scan the samples with the laser and treat the whole surface. The scanning process is achieved by moving the sample. The sample is placed on top of an XY translational stage. The scanning speed is therefore achieved by choosing the appropriate scanning velocity of the XY stage.

We radiate 80nm GO films with 100 laser pulses per spot (PPS), and try to have the same degree of reduction of the films in a spot as in a straight line using the XY stages.

 $PPS = \frac{f \times d}{u}$, where PPS are pulses per spot, d is the diameter of the iris in Fig. 26, f is the laser repetition rate and u is the speed of the stages. We use f=5Hz and d=5mm. That means the stages speed must be u=0.25mm/s in order to achieve 100PPS. We also irradiate a GO sample with 100 laser pulses in a single spot to use as control-measurement. The fluence measured is 20mJ/cm².

After the laser reduction, we measure the UV-Vis absorbance of each sample and compare it with the absorbance of the sample with the single spot.



Figure 50: UV-Vis absorbance as a function of the wavelength for different scanning velocitiy

As we can see in Fig. 50, the single spot and the line treated with speed u=0.25 mm/s have the exact same absorbance, meaning that we have the same reduction degree.

For speeds higher than u=0.25mm/s, we have fewer PPS therefore less reduction which results in lower UV-Vis absorbance. For speeds lower than u=0.25mm/s, we have more PPS therefore more reduction which leads to higher UV-Vis absorbance. The higher the degree of reduction is, the darker the colour of the film is, resulting in higher absorbance.

Then, we examine the hatch between two consecutive scanning lines, in order to have a uniform reduction of the whole area of the sample. The hatch values we tested were chosen to be close to the laser spot diameter.

For the reduction, we use f=5Hz, d=5mm and u=0.25mm/s $F=20mJ/cm^2$.



Figure 51: UV-Vis absorbance as a function of the wavelength for different hatch

In Fig. 51, we see the UV-Vis absorbance of the reduced graphene oxide films prepared.

The UV-vis absorbance measured between the two scanning lines is equal to the absorbance of the control reduced GO line, when the hatch between two laser reduced GO lines is 4.25mm.

The sample with h=4.50mm has lower absorbance, which means less reduction between the two lines. On the other hand, the samples with smaller hatch have higher absorbance, therefore they have higher reduction.



Figure 52: rGO samples (hatch from top to bottom) a)1 line, 4.5mm b)4mm, 5mm c)4.25mm, 4.1mm d) 3mm, 3.5mm

As it is illustrated in the figure above (Fig. 52), for hatch h=4.5mm and h=5mm there is spacing in between the two reduced lines (bottom lines of Fig.52 a,b). What is shown in the UV-Vis absorbance in Fig. 51 is confirmed even with the naked eye with the sample with h=4.25mm having the most uniform reduction. Samples with lower hatch have higher degree of reduction, even ablation occurs when hatch is too small (for h=3mm, h=3.5mm).

Resistivity of reduced graphene oxide

The reduction of graphene oxide provides significantly lower sheet resistance. The prepared GO films are irradiated with different number of pulses per spot and different fluences. In addition, the reduction of a large area is compared with the reduction in a single spot area. The thickness of the GO films used is 80nm in all cases.

As it is shown in the figures below (Fig. 53, 54), the untreated graphene oxide have approximately $10^7 \text{K}\Omega/\text{sq}$ sheet resistance, while the laser treated GO films with 100 laser pulses have 5 orders of magnitude lower sheet resistance.

It is also shown that samples with rGO over a large area have similar sheet resistance with rGO spot samples with the same number of laser pulses per spot. In addition, rGO samples reduced with the higher fluence of energy $F=25mJ/cm^2$ have lower sheet resistance than samples reduced with $F=20mJ/cm^2$.



Figure 53: Sheet Resistance of rGO samples as a function of the number of laser pulses



Figure 54: Sheet Resistance of rGO samples as a function of the number of laser pulses

Conclusion

In this work, we discussed about the laser-induced reduction of graphene oxide layers. At first, a good coating was needed in order to have a uniform graphene oxide film deposition on the surface of the substrates. So, the SimCoater spray coater was efficiently modified, by creating a new pattern for the graphene oxide deposition. The result was confirmed both optically (UV-Vis measurements) and with the naked eye.

In addition, the need to have rGO layers on larger areas with a uniform reduction on the whole surface. The proper reduction parameters were found so that we have the same degree of reduction in a single laser spot area and in scanning lines.

The result was confirmed both optically and electrically. Films irradiated with the same number of pulses in a single spot and in a scanning line have the same UV-Vis absorbance. They also have equal sheet resistance. Moreover, we can see a drastic reduction in sheet resistance of graphene oxide layers with a small number of laser pulses irradiated (50-100 laser pulses).

As a conclusion, films prepared can be used in photovoltaic applications and more specifically the tandem solar cell device, since they have good sheet resistance and high optical transparency. Next goal is to achieve thinner films which have good film uniformity, low sheet resistance and higher transparency.

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