Master Thesis

Laser Ablation of Graphene
Fundamental Processes and Applications

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Publication Date:
2013

Permanent Link:
https://doi.org/10.3929/ethz-a-010089121

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Front page illustration:

SEM image of graphene on silicon dioxide coated silicon wafer. The width of the page corresponds roughly to 30μm. The dark spots are caused by trapped water during wet transfer. The thin lines are folds that are a result of the growth process.
Abstract

The present report details the results of a fundamental study on laser processing of suspended and supported graphene and the demonstration of high accuracy patterning. For the first time the ablation threshold of graphene was measured. Furthermore, a first investigation on the ablation mechanism of graphene and the influence of substrate has been performed. The results show that graphene ablation is not a purely thermal process, but a complicated process involving many influencing factors. The presence of a substrate has a large influence on the ablation mechanism and will lead to a difference in the thresholds of supported and suspended samples. Laser patterning of graphene with a sub-micron accuracy has been demonstrated, which is an order of magnitude improvement over current attempts. The experimental methods and results will be highly useful in future application of laser patterning. Not only was the minimum energy for successful patterning measured, but also the influence of the substrate was investigated. The patterning experiment has demonstrated the capabilities of laser patterning and its feasibility for industrial applications.
Acknowledgment

First I would like to thank my supervisor Professor Grigoropoulos and the members of the Laser Thermal Lab at UC Berkeley for the warm welcome and the opportunity to join their group as a visiting scholar and for their assistance. It was a pleasure to work in this lab and I was able to gain a multitude of valuable experiences. The equipment and infrastructure that was provided was excellent and I am more than happy to have had the opportunity to work here. Furthermore, I want to emphasize my gratitude towards Jae-Hyuck Yoo. He introduced me to the lab and the equipment. Throughout the project his ideas and inputs have proven to be very useful. Many thanks also to Prof. Poulakakos for the support of the project and for giving me the chance to write my Master’s thesis in the USA. I also would like to thank Bastian Waag for the stimulating discussion we had and for his input to the project. Last but not least, I want to emphasize my gratitude to my parents, who always point me to the right direction.
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Chapter 1
Introduction

1.1 Background

Since the discovery of graphene in 2004 by Novoselov et al.\textsuperscript{1} there has been an ever growing interest in this material. Graphene consists of a single layer of carbon atoms, which are arranged in a honeycomb structure. It made it possible for the first time to work with single atomic layers in simple laboratory environments. Furthermore, the material has shown a variety of extraordinary properties. It has one of the highest thermal conductivities ever measured\textsuperscript{2}. Of special interest is the fact, that graphene is a zero bandgap semimetal\textsuperscript{3}. In addition it has an unexpectedly high optical absorption coefficient, which is 2.3\%\textsuperscript{4} and constant for the whole visible spectral range. This makes it possible to see graphene even with bare eyes.

Due to its extraordinary properties, attempts have been made for applications in many different areas. However, today the main bottleneck in the commercialisation of graphene is its synthesis and processing. Many different methods have been applied to pattern graphene. This is of great interest, since in theory a single layer of graphene can be turned into a whole electronic circuit by simply patterning it\textsuperscript{5}. The applied methods include amongst others electron beam lithography\textsuperscript{3,5}, ultraviolet lithography\textsuperscript{7}, scanning tunnelling microscope lithography\textsuperscript{8} and laser patterning\textsuperscript{9-13}. Although the latter does not achieve the accuracy offered by the lithographical methods, it has the advantage that it does not have any requirement on the substrate. Furthermore, it is a very fast process that can be performed in a single step and does not require any additional coating of the graphene samples, which might lead to residues.
Currently laser patterning of graphene is still in its infancy. Yoo et al. have performed studies on the ablation threshold of graphene on different substrate materials. Roberts et al. discussed the effect of multiple pulses on graphene regarding defect formation. Kalita et al. succeeded in selectively ablating graphene using a femtosecond laser. During the irradiation the sample was moved relative to the laser, which allowed the creation of graphene ribbons. The achieved resolution of the structures is about 5μm. In a similar manner Zhang et al. were also able to create graphene ribbons with a width of around 1μm.

1.2 Motivation for project

As described in the prior section many different aspects of graphene laser ablation have already been covered in previous studies. These have included investigations on the behaviour of graphene during ablation and also initial patterning attempts. However, there is room for the improvement of existing methods and further studies.

The existing study on the ablation threshold of graphene has been performed only for supported graphene. Since graphene consists of only one layer of carbon atoms, it is heavily influenced by its environment. This is for example the case in electrical and thermal conduction, where interaction with substrate material leads to a decrease of the conduction. In the study conducted by Yoo et al. it was noted that suspended graphene probably has a lower ablation threshold than supported graphene. However, the exact threshold and the mechanisms that could lead to this difference have not been explored in detail.

Laser patterning so far offers a resolution that is unsatisfactory for most semiconductor applications. As mentioned above, graphene is a zero bandgap material at large size. When cut into thin ribbons of a width around ~50nm a bandgap will form. Therefore, novel and fast patterning methods are highly desirable. Laser patterning offers several advantages over the other methods, but still needs improvement regarding the resolution.

1.3 Approach

The true ablation threshold of graphene can only be determined by ablating suspended graphene samples. Apart from that there are additional requirements. In order to reduce loss mechanisms such as thermal conduction of the laser pulse energy ultrashort pulses are required. Furthermore, it is necessary to apply single pulses, as multiple pulses might lead to the formation of defects and make it difficult to quantify the conductive losses, which occur between the pulses.

Due to these requirements the approach chosen in this project has been single pulse ablation of suspended graphene in order to determine the ablation threshold of graphene. In addition, ablation studies have also been performed on supported
graphene and under different environmental conditions in order to gain insight into the ablation mechanism and energy loss mechanism due to substrate interaction.

Attempts have also been made to pattern graphene. The goal was to improve the existing resolution, which is in the range of several microns. Similar to the existing studies, a laser with high pulse repetition rates was chosen. The motivation behind is that higher processing speeds can be applied. The most important aspects in these experiments are the precise control of the sample movement relative to the laser and a small focal point. These two requirements have been achieved using a high precision piezo-electric stage for the sample actuation and large magnification objective lenses.

1.4 Thesis outline

The second chapter of the thesis will provide a summary of the theoretical background. This includes Laser ablation in general and the technology behind femtosecond lasers. In addition it contains a section that will go into detail about the properties and characteristics of graphene, which are relevant to this work. It comprises the general properties of graphene, with a focus on its thermal and optical properties and its response to laser interaction.

The third chapter describes the study on the ablation threshold of graphene. It describes the sample preparation process, which has turned out to be one of the most crucial parts of the work. This chapter also contains experimental details about the identification of the ablation threshold. Another important part of the work has been the design and construction of a heater that was used during ablation. The results and their discussion will be provided in the last section of the chapter. This includes several theoretical frameworks, which can potentially give an explanation to the experimental results.

Laser patterning of graphene is discussed in the fourth chapter. It will mainly focus on the results of the experiments. The last two chapters contain a summary of the work and a discussion on possible next steps.
2.1 Introduction to lasers

The word laser is an acronym, which itself describes the function of the device. It stands for “light amplification by stimulated emission and radiation”. Lasers are devices that are able to emit light via stimulated emission. The main difference to conventional light sources is that the emitted light is both highly spatially and temporally coherent.

The basic principle of a laser is given in figure 1 below. It depicts a simplified model of a laser consisting of the gain medium and the resonator. The gain medium is the part of the laser that produces the actual radiation and can be modelled as a two level system. The idea behind lasers is that due to excitation of the gain medium, the constituent particles will reach an excited state. The state, in which more particles are in the excited state than in the relaxed state, is called population inversion. When photons with a certain wavelength collide with an excited particle, it will be stimulated to return to the ground state. During this process, which is called stimulated emission, it will emit a photon with the same phase, wavelength and direction as the incoming photon.

If the losses are not too large, stimulated emission will generate a constant current of photons with similar properties, since the emitted phonons will themselves lead to stimulated emissions again. In order to improve this amplification, the gain medium will be placed inside of an optical resonator. This resonator consists simply of two mirrors, one having a slightly lower reflectance than 100%. In such a configuration the photons will be reflected back and forth, creating amplification.
due to stimulated emission. By careful tuning it can be made sure that the amplification is balanced out with the transmission losses, since one of the mirrors is partially transparent. At the same time the resonator has another useful purpose. It only allows standing waves inside of it, which means that a limitation exists on the possible wavelength.

Figure 1 Simplified model of an ideal laser

The stimulated emission can be kept stable, as long as the gain medium can maintain its population inversion. It can be achieved by pumping, which describes the process of bringing the constituents of the gain medium back into the excited state. There are many different possibilities for pumping. The most common are excitation via electrical currents or electromagnetic radiation. A more detailed discussion on lasers is given by Svelto\textsuperscript{15}.

2.2 Laser beam characteristics

One of the most important parameters in laser processing is the beam shape of the given laser. It determines for example the size of the focal point, which sets the minimal size for laser processing. There are many different beam shapes, or so called laser modes, possible for each laser. The beam shape of each of the laser modes varies greatly. Figure 2 shows a cross section of the beam for different modes. However, the one that is of greatest importance in applications is the fundamental transverse mode or TEM\textsubscript{00}. It offers a single focal spot, which is crucial in most applications. Simply inserting an aperture into the resonator will lead to the selection of the fundamental mode, as all other modes cannot oscillate.
The exact beam shape of a laser, i.e. the electric field as a function of location, can be obtained analytically by solving the paraxial wave equation, which is the modified electromagnetic wave-equation with the simplification offered by the geometry and symmetry of laser devices. For a radial symmetry the paraxial wave-equation will offer the following solution for the fundamental laser modes\textsuperscript{15}.

The electric field of the fundamental mode is given as

$$E(r,z) = E_0 \frac{w_0}{w(z)} \exp \left\{ -\frac{r^2}{w(z)^2} - ikz - ikz \frac{r^2}{2R(z)} \right\}$$

(2.2.1)

where $E_0$ denotes the maximum electrical field. $w(z)$ is the beam width, which is the location at which the electrical field has been reduced by $1/e$ of $E_0$, and $w_0$ the minimum value of $w(z)$. An outline of the beam shape is shown in figure 3.
For a beam propagating in free space the width \( w(z) \) has the form

\[
w(z) = w_0 \sqrt{1 + \left( \frac{\lambda z}{\pi w_0^2} \right)^2}
\]  

(2.2.2)

the minimum focal area can be estimated using the relation

\[ A \approx \lambda^2 \]  

(2.2.3)

the value \( b \) in figure 3 is the depth of focus. It gives an approximate measure of the length of the focal point. It is defined as

\[ b = \frac{2\pi w_0^2}{\lambda} \]  

(2.2.4)

In order to achieve small focal points, large magnification objective lenses are usually used. Common lenses have magnifications of up to around 100x. These lenses can achieve focal points with a radius well below one micron. At the same time, as seen in equation (2.2.4), the depth of focus will also decrease. This makes it very challenging to work with large magnification objective lenses. The relative distance of the sample and the laser has only a very small error tolerance due to the small depth of focus.

All the given relations up to this point apply to the electric field. However, in actual application it is much more likely to deal with the intensity of the laser. It is defined as

\[
I = \left| E_0 \right|^2 = I_0 \left( \frac{w_0}{w(z)} \right)^2 \exp \left( -\frac{2r^2}{w(z)^2} \right) 
\]  

(2.2.5)

The intensity distribution at the focal point therefore takes the form

\[
I = I_0 \exp \left( -\frac{2r^2}{w_0^2} \right) 
\]  

(2.2.6)

This shape resembles the Gaussian bell curve, after which the beam has been named. The beam width gives the location at which the intensity has decreased by the factor \( 1/e^2 \), which is about 13% of the maximum power.

### 2.3 Characteristics of graphene

Graphene is a single layer of carbon atoms that are arranged in a honeycomb structure. It is the basic constituent of many different kinds of carbon materials such as carbon nanotubes, fullerenes or graphite.
2.4.1 Electronic structure

The electronic structure of graphene has been discovered already before its existence was verified. It can be obtained by an analytical calculation using the tight binding model. This is only possible because of the special structure of graphene and the characteristics of its atomic bonds. The calculation was first performed by Wallace as a means to describe the band structure of graphite.

Each atom in graphene forms a sp$_{2}$-bond with each of the three surrounding atoms. The energy gap between the bonding and anti-bonding molecular orbitals for these electrons is very large. Therefore, these electrons will not play part in electrical conduction. In addition, due to symmetry reasons the last free valence electron, which is in the p$_{z}$ orbital, will not overlap with the other orbitals. This makes it possible to use the tight-binding model in order to calculate the electronic band structure of graphene.

The dispersion relation of graphene has the form

\[ E_{\pm}(k_x, k_z) = \pm \gamma_0 \sqrt{1 + 4 \cos \left( \frac{\sqrt{3} k_x a}{2} \right) \cos \left( \frac{k_x a}{2} \right) + 4 \cos \left( \frac{k_y a}{2} \right) - 4 \cos \left( \frac{\sqrt{3} k_y a}{2} \right) - 4 \cos \left( \frac{k_y a}{2} \right)} \]

(2.3.1)

where $a$ is a measure for the interatomic distances. It is given by the relation $a = \sqrt{3} a_{cc}$, where $a_{cc}$ is the distance to the next neighbour, which is 0.142nm. The parameter $\gamma_0$ is called the transfer integral between neighbouring $\pi$-orbitals and has a value of around 3eV. It appears as a parameter during the calculation.

Equation (2.3.1) shows that there are two energy bands. The occupation of the bands can be derived from the characteristics of the Brillouin zone of graphene. The primitive cell of graphene contains two atoms. This means that there are also two electrons in the Brillouin zone that can participate at conduction. Two electrons of opposing spin can fill each of the two bands. Therefore the valence band is completely filled, whereas the conduction band is completely empty.

The given structure resembles the electronic structure for semiconductors, but there is one major difference. In the case of graphene the valence band and the conduction bands touch at a special point called K-point, which has the wavevector $K$. Since the Fermi energy is defined as the maximum energy occupied at absolute zero temperature, it corresponds to the energy at the K-point. In condensed matter the electrons that are close to the Fermi level are the ones that are responsible for conduction. The reason is that these can be easily excited into the conduction band, where free states exist that are not blocked due to Pauli exclusion principle. Therefore, the characteristics of these electrons are also most important regarding the conductive properties of the solid. In the case of graphene, for electrons that are close to the K-point and thus close to the Fermi level, the dispersion relation can be simplified. It takes the form
\[
E_{\pm}(k) = \pm \hbar v_F |k - K|
\]

(2.3.2)

The parameter \(v_F\) is the electronic group velocity and is given by \(10^6\) m/s. This simple relation shows that the electrons behave as massless particles, since the effective mass is the derivative of energy with respect to the wavevector.

These results show some of the most interesting and important characteristics of graphene. It indicates that graphene has a potentially very high electrical conductivity. This has also been verified in experiments.18 Furthermore, the fact that graphene does not have a bandgap, but still distinct valence and conduction bands is of great importance for its optical properties. It is responsible for an effect called saturable absorption, which plays an important role in the interaction of lasers with graphene at large powers.

2.4.2 Thermal Properties

The thermal properties of graphene have been the subject of extensive studies2-19. It has been shown to have an extremely high thermal conductivity at room temperature20 of around 5000 Wm\(^{-1}\)K\(^{-1}\). For comparison under the same conditions copper has a thermal conductivity of 400 Wm\(^{-1}\)K\(^{-1}\) and Diamonds, which are usually considered the bulk material with the highest thermal conductivity, achieve values of around 2000 Wm\(^{-1}\)K\(^{-1}\).

The reason for this high value of thermal conductivity lies in the structure of graphene and carbon materials in general. Thermal conductivity is made up of two components, conduction via electrons or via phonons. Generally speaking the stronger the interatomic bonds in a material are, the larger the phonon component becomes in thermal conduction. Carbon allotropes, such as graphite of diamonds, have extremely strong bonds. Graphite has been a popular choice for thermal conduction, especially in the nuclear industry.

Despite many studies on the thermal conductivity of graphene, little has been done to determine its heat capacity19. Work has been performed to theoretically determine the behaviour of its heat capacity as a function of temperature. Detailed measurements have been made for graphite, which is expected to have a similar heat capacity, as it consists of graphene layers with only weak interlayer interaction.

Another very interesting property of graphene is its coefficient of thermal expansion. In general materials expand when the temperature increase. However, there are also some bulk materials that exhibit negative thermal expansion, often for a small, but sometimes also across a large range of temperature. The most common example for small temperature ranges is water, which gains its maximum density at 4°C. A material that contracts with increasing temperature on a large range is cubic Zirconium Tungstate21. Some materials do expand as a whole, when considering volumetric expansion, but will experience contraction along certain directions. This is the case for pyrolitic graphite, which expands in one direction, but at the same time contracts in the perpendicular direction22.
The direction, in which pyrolitic graphite contracts, is the in-plane direction of the single graphene layers, which are its basic building blocks. As expected it was shown that graphene has a negative thermal expansion coefficient. Yoon et al.\textsuperscript{23} were able to measure the value and also found out that the expansion coefficient depends on temperature, but stays negative in a range from 200K to 400K. At room temperature the expansion coefficient has a value of \(-8\times10^{-6}\).

Thermal properties play an important role in laser interaction. Conduction determines the spread of the laser energy into the material. Furthermore, the unusual thermal expansion coefficient of graphene will lead to tensile thermal stresses at elevated temperatures.

\subsection{2.4.3 Optical properties}

Probably the most surprising experience when performing experimental work with graphene is that it is visible to the bare eye. This is really surprising since it is only a single layer of atoms. Nonetheless, this layer of atoms is able to absorb enough light to be detected by the human eye. The absorption coefficient of graphene is 2.3\% and approximately constant across the whole visible spectral range\textsuperscript{6}. The absorption of a few layers is roughly the number of layers times the absorption of the individual layers.

The ability of graphene to absorb constantly over a large range of wavelengths is only limited to small powers. When it is subject to larger powers an effect called saturable absorption will set in. This effect is well-known in the field of lasers\textsuperscript{15}. When a body absorbs light, its electrons are excited from the ground state to the excited state. At low intensities these excited electrons will relax either via spontaneous or stimulated emission. However at large intensities not all photons can be absorbed, since there is only limited space in the conduction band. In principle Pauli blocking stops any further absorption of photons.

In lasers, saturable absorbers are used to achieve ultrashort laser pulses through a technique called mode-locking. Graphene also shows saturation of absorption at large laser powers. Due to its lack of a bandgap the saturable absorption is independent of the wavelength. The effect has been demonstrated experimentally and already been applied for ultrashort pulse lasers\textsuperscript{24-26}. As shown by Sun et al.\textsuperscript{24} the absorption coefficient of graphene reduces by about 8\% at an incident power of 266 MW/cm\textsuperscript{2}. At higher powers the reduction will be even larger.

The initial absorption of light though electrons is just the first step in the overall absorption process, several further steps occur afterwards. The detailed process has been the subject of extensive investigations\textsuperscript{27-30}. The next step, which happens on a timescale of some 10fs, is that the electrons reach a quasi-thermal distribution via electron-electron collisions with a characteristic electron temperature. After that the energy is transferred to graphene phonons during a timescale of a few ps. This process has been of special interest in the field of optoelectrical devices, since the energy transfer to phonons is highly undesired.
When graphene is supported by a substrate material, it has been observed that the currents obtained from the photo-excited electrons are an order of magnitude lower than in the suspended case. The reason is that after the initial excitation of the electrons, a large part of the energy is transferred into the substrate. This process has also been observed for other materials upon laser excitation. In the case of graphene it has been proposed that the transfer mechanism involves surface polar phonons (SSP) of the substrate material. SSP are phonons on the surface of a body. Given a substrate with a polar lattice structure, these phonons will give rise to an electrical field. The idea is that the energy loss into the substrate occurs through the interaction of the excited electrons and this electrical field. It was shown theoretically that the cooling rates of the excited electrons by both intrinsic phonons or SSP depend on the lattice and the electron temperature.

2.4.4 Production of graphene

The first production of graphene was realised by simply peeling off layers from graphite using scotch tape. Due to its simplicity this method has gained wide attention. However, peeling off layers from graphite is just the first step in the process of obtaining graphene. This method has been called micromechanical cleavage.

The main difficulties involved in micromechanical cleavage are finding single layer graphene and placing it on the desired position. After peeling off the tape, the cleaved material is transferred onto another substrate, usually SiO$_2$. After that the time consuming process of finding single layer graphene begins. There are several methods to distinguish single layer graphene from multilayer graphene, for example deposition of graphene on 100nm or 300nm SiO$_2$ will make it possible to find single layers with bare eyes. This method can be easily performed in a laboratory. In addition the obtained graphene is of high quality and consists of single crystals. However, this method has one main problem. It involves many time consuming steps and is not scalable. Many other methods have been proposed and are topics of research. These methods include liquid phase exfoliation, growth on SiC and also chemical vapour deposition (CVD). Especially the latter has been subject of intense research due to the several advantages it offers.

CVD is a common process in semiconductor industry. It is used on a regular basis for the production of for example polysilicon or silicon dioxide. The most common method is thermal CVD, which is based on a process that is detailed in the following. A gaseous precursor, which contains the coating material, is brought into contact with the substrate at elevated temperature. After exposure for a specified time span a layer of the material will form on the substrate. In graphene synthesis this method makes use of the special properties of certain metals for graphene growth.

Attempts to grow graphene have been made on several different metal substrates, including iridium, nickel and copper. The latter has been the most promising
substrate material. The first successful production of large areas of CVD graphene was performed in 2009\textsuperscript{37}. Copper has the special characteristic that graphene growth is a self-limited process. This means that after the deposition of the first layer of carbon, any further deposition stops. It has been shown that the area covered by single layer graphene is usually in the range of 95\% or above.

Although the method has been proven to be very promising, it has still certain drawbacks. Currently it is still not possible to produce single crystal graphene. In addition, due to thermal expansion mismatch and the elevated temperatures necessary during deposition, CVD graphene shows many ripples. As a result it has lower quality as exfoliated graphene. However, efforts are still on-going and large improvements have been made lately, such as the roll-to-roll production of graphene on 30 inch copper foil\textsuperscript{38}.

\subsection*{2.4 Laser ablation}

Laser processing has become a major processing technique since the introduction of lasers. It is being used in many areas such as spectroscopy, distance measurement, CD players, medicine and welding. The main advantage for lasers for all those applications is that it is spatially coherent, which allows extreme focusing and directional irradiation at very high intensities\textsuperscript{39}. Very popular methods such as laser patterning and laser welding rely on the concentrated energies that can be transferred by a laser to selectively ablate or melt material on the surface. A complete discussion of this topic is given by Baeuerle\textsuperscript{39}.

\subsubsection*{2.4.1 Principles of laser ablation}

The ablation process is one of the core aspects of this project. Both patterning and single pulse ablation are only possible due to the unique features of lasers. There are two basic processes for laser ablation, which are thermal and photochemical ablation. Often a third way of ablation is also named in literature, which is the photo-physical process. However, this is simply the case, where both thermal and photochemical aspects play a role during ablation.

Photochemical processes describe reactions that take place due to laser-induced excitation of a material. If the thermalization of the laser energy is very low, the material will achieve an excited state during laser interaction. Under such a condition chemical processes or direct bond breaking, i.e. excited atoms do not form molecule anymore, can take place. The special characteristic is that during photochemical processes the material itself does not change its temperature.

Thermal ablation is a more straightforward principle. The laser acts like a heat source. The energy absorbed by the substrate leads to melting, vaporization or even direct sublimation. According to Bauerle\textsuperscript{39}, a thermal process is given, when the thermal relaxation time $\tau_T$ of the material is smaller than the time of the initial processing step $\tau_R$, i.e. $\tau_T < \tau_R$. In simple words, this means that a thermal process is given, if the material reaches its melting or vaporization temperature, before
another mechanism of decomposition, such as a photochemical reaction, takes place.

Which one of the mechanisms takes place during ablation depends on the characteristics of the material and the laser. In the case of photochemical ablation it also depends strongly on the environment, i.e. the existence of other reactants. The characteristics of thermal ablation rely heavily on the duration of the laser interaction. It has a big influence on factors like the spread and loss of energy, quality of ablation site and plasma formation.

2.4.2 Ultrashort pulse ablation

One problem is frequently encountered when ablating materials with high thermal conductivities. Often the thermal energy brought into the substrate by a continuous or long pulse laser will be transported into the surrounding of the desired ablation site. This leads to the necessity for higher laser powers and also to inaccurate patterns. An example is shown in figure 4, which depicts the holes created using the same laser with different pulse durations. The improved localization of the energy also means that less energy is required to achieve the same volume decomposition. This makes it possible to ablate large bandgap materials.

![Figure 4 SEM pictures of holes in steel made with a 780nm laser with different pulse durations](image)

A simple figure can provide a first estimation for the localization of the laser energy, which is the heat penetration depth.

\[ l_T = 2\sqrt{D\tau} \]  

(2.4.1)

It is a characteristic figure obtained from the solution of the heat transfer equation for a point source in infinite space and determines the location at which the temperature of the point source has been decreased by a factor of 1/e. The parameter D is the thermal diffusivity of the material and \( \tau \) the characteristic time,
which is the pulse duration in this case. It clearly shows, that shorter pulses lead to a better localization of the energy.

Many other advantages arise from the short pulse duration. One of them concerns the interaction of the residues of ablation with the laser. During process the ablated material often vaporizes. A vapour plume will form above the ablation site, which is turned into plasma due to laser interaction. This plasma has a big influence on the ablation process. However, when ultrashort pulses are applied, these effects must not be considered. The reason is that the laser pulse is simply over before the plasma forms. Ultrashort pulses also limit the probability of chemical reactions, such as oxidization of the substrate at elevated temperatures. Similar as before the reason is related to the short time spans involved during process. The substrate will already have been ablated before any actual reaction can take place.
Chapter 3
Ablation Threshold of Graphene

3.1 Background

In a first study Yoo et al.\textsuperscript{9} were able to find the ablation threshold of supported graphene samples. Samples were ablated at different pulse energies and the resulting changes of the ablation areas were used to extrapolate the ablation threshold of graphene. In another step ablation of suspended samples were also attempted and achieved. However, no detailed study on the ablation threshold of suspended graphene was made. Also the ablation mechanism itself is still unknown.

Nevertheless, the study revealed two interesting effects. Figure 5 shows the SEM image of ablation site on a supported graphene sample. Apparently ablation leads to the formation of flower like structures. The authors suggest that the petals are actually double layers of graphene. During ablation some part of the graphene is vaporized, while some of the graphene folds back due to an unspecified mechanism. This effect has not been observed for suspended samples. Detailed investigations on the precise ablation threshold have not been performed. It has been shown that ablation can be achieved already with fluences, which are below the threshold fluence for supported graphene. Yet the exact mechanism has not been the subject of investigation. It has simply been stated that suspended graphene lacks the dissipation channel, which is provided in the supported case.
In general cases, for example for low fluences or long pulses, the difference in ablation threshold could be easily explained by the following. For supported graphene the energy that is brought into it partially dissipates into the substrate via diffusive thermal transport according to Fourier’s law. As this dissipation channel is missing in the supported case, the whole thermal energy remains in the graphene layer and thus smaller laser fluence is required. Unfortunately the given case is not that simple.

There are many possible causes for the differences in ablation threshold. It could arise from different ablation mechanisms or energy dissipation into the substrate. It has been suggested that the petal formation on supported graphene occurs in a process after the initial laser interaction. For suspended graphene such petals have not been observed. Therefore, the substrate must be the source of this effect. Although it is unclear what the exact mechanism is, it shows that different processes are involved in ablation.

In case the ablation mechanism does not account for the differences of the thresholds, a cooling process must exist that is responsible for the difference. In a previous chapter it was mentioned that the first step of absorption is due to electrons. In a process that lasts in the range of some 10fs the electrons reach equilibrium. These hot electrons pass on their energy to intrinsic phonons during a time scale of a few picoseconds. The energy dissipation must take place, before graphene reaches its final temperature, since otherwise the ablation will already occur before the energy transfer. This leaves two possibilities: either dissipation via direct coupling of hot electrons and extrinsic phonons or diffusive heat transfer during the energy exchange between the hot electrons and the intrinsic phonons. These options will be discussed in the following. The two ideas also serve as starting points for the experimental investigations.
3.1.1 Diffusive thermal transport as dissipation channel

In the case of very short pulses, especially in the femtosecond regime, thermal conduction can usually be neglected. But since graphene is very thin and has extraordinarily high thermal conductivity, a point could be made that here diffusive thermal conduction actually has an effect, even on such small time scales.

For the moment it is assumed that graphene ablation is a thermal process. This means that it is simply evaporated by the laser. The melting temperature of graphite is around 3000°C, which is assumed to be the same for graphene since the strongest interatomic bonds are similar for both materials. The energy transfer process between the hot electrons and the intrinsic phonons takes place in the course of a few picoseconds. For the sake of simplicity it is assumed that 5ps are required for the transfer. As an estimation, it will be assumed that instead of changing from 20°C to 3000°C, the graphene layer maintains a constant temperature of $T_g=1500°C$ during this period of time. Also since SiO$_2$ is highly transparent, it will be assumed that it does not absorb any energy. Since the horizontal dimensions of the problem, the beam diameter is around 1μm, are much larger than the vertical ones, graphene has a thickness of about 0.34nm, a one dimensional thermal transport model is used.

![Figure 6](image)

**Figure 6** On the left is a simplified model of the thermal transport problem. On the right is the equivalent thermal circuit

Figure 6 depicts the model problem. It is basically heat transfer in a semi-infinite slab with a thermal contact resistance. The solution of the temperature field for the semi infinite slab is well known\cite{41} and has the form
\[
\frac{T - T_0}{T_0 - T_i} = \text{erf}\left(\frac{x}{\sqrt{4 \beta t}}\right) \tag{3.1.1}
\]

\(T_0\) is the surface temperature of the slab, \(T_i\) the temperature at an infinite distance and \(\beta\) a parameter that contains the thermal properties of the material according to the relation \(\beta=D/(c_p\rho)\). The surface heat flux can be calculated from the temperature field

\[
q'(0,t) = -D \frac{\partial T}{\partial x}\bigg|_{x=0} = \frac{D(T_0 - T_i)}{\sqrt{\pi \beta t}} \tag{3.1.2}
\]

The substrate is commonly SiO\(_2\). The thermal energy loss during this time can be calculated by integration of the equation above and yield the following expression

\[
Q' = \int_0^\tau q''(0,t) \, dt = \frac{2D}{\sqrt{\pi \beta \tau}} (T_0 - T_i)\tau \tag{3.1.3}
\]

Here \(\tau\) is the time between the start of the energy transfer from the hot electrons to the intrinsic phonons and the ablation itself. This equation allows a definition of an equivalent thermal resistance for the slab, which is

\[
R_{\text{slab}} = \frac{\sqrt{\pi \beta \tau}}{2D} \tag{3.1.4}
\]

The contact resistance has been measured before\(^{42}\) and has a value of about \(R_{\text{cont}}=10^{-8}\) m\(^2\)K/W. The thermal characteristics of silicon dioxide are well known\(^{43}\). The values are \(D=1.4\) W/(mK), \(c_p=1000\) J/(kgK) and \(\rho=2200\) kg/m\(^3\). With an interaction time of \(\tau=5\) ps the total loss is approximately

\[
Q''_{\text{loss}} = \frac{T_g - T_{\text{room}}}{R_{\text{slab}} + R_{\text{cont}}} \tau = 0.07 \frac{mJ}{cm^2} \tag{3.1.5}
\]

Now the question arises: what is actually the significance of this value? One of the assumptions that have been made is that the ablation process is purely thermal. Furthermore, it was assumed that the thermal behaviour of graphene is similar to that of graphite. Theoretical studies have shown that the heat capacity of graphene is similar to that of graphite\(^{44}\). With that in mind, it is possible to calculate the thermal energy necessary to ablate graphene assuming a layer thickness of \(d=0.34\) nm, which corresponds to the interlayer distance in graphite

\[
I_{\text{mel}} = c_p d(T_{\text{mel}} - T_{\text{room}}) = 0.16 \frac{mJ}{cm^2} \tag{3.1.6}
\]

This results show that although usually diffusive thermal transport can be neglected in the femtosecond pulse regime, it could play a role here. The reason why usually
diffusive thermal transport is neglected is that the characteristic diffusion length is very small at these time scales. Here the system under discussion involves a layer of graphene, which is so small that thermal diffusion must be taken into account.

It should be kept in mind that many assumptions were made during the derivation of this result, the main one is that the behaviour of phonons is still governed by Fourier’s law. This is not necessarily true for ultrashort timescales or for the junction of graphene and substrate. Also an average temperature was taken for the graphene layer during the transfer process. A better method would be the use of the Two-Temperature model\textsuperscript{34,39}, but it requires specific material parameters such as the electron-phonon coupling factors, which are unavailable to this point. Nonetheless, this simple model is able to show that simple diffusive thermal transport could play a role in the energy dissipation.

### 3.1.2 Surface polar phonons as dissipation channel

The direct transfer of energy from hot electrons to extrinsic phonons is a possible dissipation pathway that also has to be taken into account. Surface phonons of polar materials, i.e. material with certain lattice structures, will generate a non-vanishing electrical field. The main idea is that the hot electrons interact with this electrical field and thus transfer the energy to the substrate.

Surface polar phonon (SPP) interaction was first observed as a source for scattering for inversion layers in semiconductor-dielectric junctions\textsuperscript{45,46}. Since the electrons in graphene show similar behaviour as the inversion layer electrons, this influence is to be expected. It was shown both theoretically and experimentally that SPP interaction can influence the electron transport in graphene\textsuperscript{47,48}. Furthermore, this interaction is shown to increase with temperature. The fact that SPP interaction also provides a cooling channel for hot electrons\textsuperscript{32} was shown theoretically by Freitag et al. In addition they were able to increase the photo-response in a device by suspending the graphene layer\textsuperscript{31}, which avoids SPP interaction.

The transfer process itself is a scattering process. Hot electrons, which are in an excited state, scatter with phonons, change their state and thus lose energy. In general, such transitions can be described with Fermi’s golden rule. In the simplest case the probability of transition, for the transition of an electron between states with the wavevectors \( k \) and \( k’ \) due to a phonon collision, has the form

\[
S(k,k') = \frac{2\pi}{\hbar} |M_{k,k’}|^2 \delta(E_k - E_{k’} \pm \hbar \omega_q)
\]  

The delta function describes the two different possible cases, when a phonon is produced, plus sign, or destroyed, minus sign. Both must adhere to the law of energy conservation. The parameter \( M_{k,k’} \) is the transition matrix element. It is defined as
\[ M_{i\ell} = \langle \Psi_{\ell,q} | H | \Psi_{\ell',q'} \rangle \] (3.1.8)

in which \( H' \) is the perturbation of the Hamiltonian, in this case it is the electric field generated by the surface polar phonon.

The equations above only describe the simplest case for a transition between two clearly defined states. The total transition possibility for the hot electrons must include all possible wavevectors and also the characteristics of the phonons. It is given as:

\[
S(k,k') = \frac{2\pi}{hA} \sum_q |M_{\ell\ell'}|^2 \left\{ \frac{N_{\omega_q} \delta_{\ell\ell'-q}}{(G)} \delta(E_{k'} - E_k - h\omega_q) \right\} \\
+ \left\{ \left( N_{\omega_q} + 1 \right) \delta_{\ell\ell'-q} \delta(E_{k'} - E_k + h\omega_q) \right\}
\] (3.1.9)

where \( A \) is the area of the unit cell. The transition matrix element contains the characteristics of the interaction between the phonons and the electrons. It has been calculated by Fratini et al.\(^{47}\). The function \( N_{\omega} \) is the phonon distribution. Since phonons are Bosons, it is the Bose-Einstein distribution,

\[ N_{\omega_q} = \frac{1}{\exp \left( \frac{\hbar \omega_q}{k_B T} \right) - 1} \] (3.1.10)

The summation over all \( q \) is necessary since all possible cases must be considered that fulfil the impulse conservation, which is given below.

\[ |q| = |k' - k| \] (3.1.11)

The transfer probability consists of two parts. Part I describes the probability of the absorption of a phonon, part II the emission of a phonon, i.e. energy loss of the electron. The distribution in the latter case is \( (N_{\omega}+1) \), since an additional phonon is produced, which explains the addition of one.

The total power transfer due to coupling is given as

\[ P = \frac{g_s g_v}{A} \sum_k \sum_{k'} S(k,k')(E_{k'} - E_k)f_k (1-f_{k'}) \] (3.1.12)

The factors \( g_s \) and \( g_v \) are the spin and valley degeneracies. \( f_k \) is the distribution of the electrons. Since the thermalisation of the photonic energy by the electrons is a very fast process it can be assumed that the electrons are in thermal equilibrium and thus follow the Fermi-Dirac distribution.
Finding the exact cooling powers involves large calculations. However the form of the cooling power makes it possible to draw certain conclusions. The transition probability is a function of the phonon distribution, which is a function of temperature, i.e. Bose-Einstein distribution. This distribution increases with temperature; therefore an increase in cooling power is to be expected at large temperatures.

Until now only the interaction of the electrons with the SPP have been considered. In order to understand the total cooling process it is also necessary to consider the interaction of the hot electrons with the substrate. Low et al.\(^3\)\(^2\) have performed this study, while considering all possible phonon interactions. As expected the cooling power increases with Temperature, but not only for the SPP but also for the intrinsic phonons. The ratio of the individual cooling powers are given in figure 7 below.

![Figure 7](image)

Figure 7 The graphs shows the individual contributions of each cooling channel to the total cooling of the hot electrons. \(T_L\) is the lattice temperature, \(T_e\) is the temperature of the electronic system. On the left is the case for \(T_e-T_L=10\)K, on the right the case for \(T_e-T_L=100\)K.

The figure shows that regardless of the difference of the temperatures of the electronic system and the lattice, at high lattice temperatures the cooling power of the intrinsic optical phonons will increase. This means that increasing the lattice temperature will lead to a nonlinear decrease of the relative SPP cooling power.

The equivalent thermal resistance of SPP coupling has been estimated to be on the order of \(R_{\text{SPP}}10^{-6}\text{m}^2\text{K/W}\), which is two orders of magnitude larger than the thermal resistance for phonon interaction between graphene and substrate. However, it should be kept in mind, that the temperature of the electronic systems is much higher than that of the lattice\(^3\)\(^3\),\(^4\)\(^9\). Therefore SPP coupling could also be a potential explanation for the ablation threshold difference.

### 3.2 Motivation and approach

In principle there are three main points to be addressed. The first is the ablation threshold of suspended graphene, which is also its real ablation threshold. The second is the ablation mechanism of graphene. The last one is the process that leads to the difference in ablation threshold for suspended and supported samples.
In the last section some ideas and theories have been presented. However, the first and most important study that needs to be performed is the verification of the fact that suspended graphene actually has a lower ablation threshold and its measurement.

The main challenge for the ablation of suspended graphene is the production of samples with sufficient quality. This is necessary since the ablation should be repeated many times to make a good analysis possible. Ablating the sample at different pulse energies and analysing the size variation of the ablation site can determine the threshold. Ultrashort pulses need to be used due to reasons given in chapter 2.

The current study focuses on the ablation characteristics of graphene. This does not require very high quality samples, as it is the case for device or electronic studies. Therefore CVD graphene is chosen to be the most viable option. It is easy to produce and via wet transfer it can be brought onto any substrate. Suspended samples can be made by simply transferring graphene onto substrates with trenches as shown in figure 8.

![Figure 8 Model of suspended graphene sample. Graphene transferred onto sample with trenches on the surface](image)

Finding the characteristics of the ablation and source for the difference in ablation threshold is a more challenging task. The most straightforward method would be to analyse the ablation process and the hot electron dynamics using optical measurements. However this approach requires a range of highly specialized equipment that is not currently available.

One possible approach is to change the environmental parameters in which the ablation takes place. Changes in the experimental results will reflect the influence of certain parameters and thus allow the characterization of the ablation process. For example in order to investigate the possible dissipation channels one could simply change the sample substrate, i.e. use polar and non-polar materials. Variations in the ablation threshold might reflect the influence of SPP interaction. However, the problem that arises in this experimental setup is that a change of substrate changes many other parameters as well. These include the adhesion strength of graphene, reflection of the incident laser pulse and ablation of the substrate itself. There might
be differences regarding the ablation threshold, but it will be difficult to relate them to a certain effect.

The approach that has been chosen originates from the presumption that ablation could be a thermal process. If that is the case, changing the temperature of the sample during ablation will impact the ablation threshold. This approach has the advantage that it does not require additional samples and that any changes in behaviour could be directly traced back to the influence of temperature.

For example, if ablation occurs simply by vaporization, temperature increase will lead to larger ablation areas at the same laser fluence for suspended graphene. The same experiments performed for supported graphene can reveal the characteristics of the energy dissipation. If diffusive thermal dissipation is the actual case, a temperature increase will lead to a linear decrease of dissipation, since it is proportional to the temperature difference of graphene and substrate. However, if SPP interaction is the dominant mechanism, a nonlinear relation is to be expected. If none of these effects are responsible for the difference in ablation threshold, it will also be revealed by this experiment.

Due to the reasons named above it has been decided to perform temperature-controlled ablation as a first experimental study. This leaves the question of how to change the sample temperature. The most straightforward way is to install a second laser into the beam path. But interaction between the lasers might lead to a change in the results. Furthermore, the resulting temperature due to laser heating needs to be measured in some way. This is not a problem when the sample is simply heated as a whole via thermal conduction by a heater.

Besides finding the ablation threshold of graphene, temperature-controlled ablation has been a main area of work in this project. It involves not just ablation of graphene, but also the design and production of a heater, which has to conform to several limitations, set by the sample and the laser ablation setup.

### 3.3 Experimental methods

The experiments involved several different steps. First and also most important was the sample preparation. It consists of the creation of samples with trenches and the wet transfer of graphene onto the samples. After that ablation was performed using an existing setup. As mentioned before a heater was designed, built and integrated into the existing setup. It was used in the temperature-controlled studies. The last step was the evaluation of the results with the electron microscope and the analysis of the images.

#### 3.3.1 Sample preparation

In order to create suspended graphene samples, it was necessary to obtain suitable substrates first. Polysilicon wafers (100) with a 100nm layer of SiO$_2$ were chosen. It has been shown before, that such a layer of SiO$_2$ helps in the visualization of
graphene\textsuperscript{35}. Furthermore, these wafers are a standard material in semiconductor industry, which makes them easy and cheap to obtain. In addition SiO\textsubscript{2} has a high ablation threshold. The Silicon makes it possible to create the trenches that are required for suspended graphene. It also improves the imaging of the samples under the SEM, which works best for conductive samples.

The trenches are made using controlled laser ablation. Direct ablation of SiO\textsubscript{2} requires very large laser pulse energies, since it has a very large bandgap. The ablation threshold has been reported for pulses of 100fs duration and 800nm wavelength\textsuperscript{50,51}, which is around a value of 2J/cm\textsuperscript{2}. It has been shown that the silicon layer beneath lowers the threshold due to a change of ablation mechanism\textsuperscript{52}. When subject to laser irradiation, the silicon will be vaporized at a much lower power. At a certain pulse energy, the pressure will be large enough to break the SiO\textsubscript{2} layer on top. The reported threshold is about 0.2-0.4J/cm\textsuperscript{2} for a laser with pulse duration of 9ps and wavelength of 355nm. This value should be a bit lower for shorter pulses, since it has been shown that ablation thresholds scale with the pulse duration.

This method has been used to create trenches. The exact procedure is sketched in figure 9. First a femtosecond laser with a wavelength of 400nm, a pulse repetition rate of 1kHz and pulse duration of 100fs was used (details about the laser and the setup are given in the next section). The laser is focused using a 50x objective lens in order to reach the desired spot size. Applying a pulse energy of about 1J/cm\textsuperscript{2} leads to the desired ablation of the sample. During laser irradiation the sample is moved using the stage at a speed of 1mm/s in order to create trenches. The exact width can be controlled by repeated ablation.

![Figure 9 Processing of substrate for suspended sample](image)

After initial ablation the trench has a depth of little more than 100nm, which is the thickness of the SiO\textsubscript{2} layer. It is made deeper by KOH etching. This etchant is highly selective and the etching speeds vary depending on the lattice direction. The
etching speed at 80°C is about 1μm/s. After 2 minute the trench will have a depth of around 2μm. Sometimes etching will lead to residual SiO$_2$ above the trench, which can be removed by sonification. Figure 10 is an SEM image of the actual trenches.

![SEM image of trenches](image)

**Figure 10** SEM image; top view of trenches. The area between the trenches is covered with graphene. The length L corresponds to 2.5μm.

After the creation of the trenches graphene is transferred onto it. The transfer follows roughly the same pattern as existing transfer processes$^{53,54}$, with some minor improvements. Single layer CVD graphene on copper foil was bought from ACS materials. The transfer process is shown in figure 11. In a first step PMMA is spin coated onto graphene. Thermal release tape is used to cover the opposite side to prevent unwanted coating, which would complicate the following process steps. After spin coating for 1 minute at 3000rpm the sample is dried on a hot plate at a temperature of about 90°C for 2min. After that the thermal release tape can be peeled off.

Copper removal is performed next. But first the graphene on the backside of the copper foil has to be removed. Polishing the foil or plasma etching, which is the most effective ways of graphene removal, are the usual methods. Here a simpler process is used. The sample is placed onto the copper etchant, a 30% solution of FeCl$_3$. It will be afloat since graphene is highly hydrophobic. The beaker is then placed into the sonicator for 1 min. This step will remove the backside graphene. Etching of copper takes usually around 30min at 80°C. After that only PMMA coated graphene remains, which appears as a thin floating film on the copper etchant.
The following step is the rinsing of the sample. Graphene is transferred using a glass slide and placed on DI water. This step is repeated 3 times in order to ensure that the copper etchant is removed. Now it can be transferred onto the prefabricated substrates. This step can be performed by simply scooping the graphene layer with the substrate. After that the sample needs to be dried. It is

**Figure 11** Graphene transfer process
placed onto a hotplate at a temperature of 90°C for about 5 min to evaporate most of the water, which still remains between the graphene layer and the substrate. Waiting another 1 day will ensure sufficient water vapour removal.

During the last process PMMA is removed from the sample. Before that it is annealed at a temperature of 150°C for 20 minutes, which has been shown to improve the adhesion between graphene and SiO₂. The removal can be performed using acetic acid or acetone, which is a more common method. The sample is simply put into the solution for around 30 min. During that time it is of prime importance not to stir the liquid, as fluid movement leads to fracture of suspended graphene. After that the sample is transferred into DI water for a last rinsing step. It is very important that during transfer the acetone does not dry out. The evaporation will also cause the suspended graphene to collapse. The best way to prevent this is to keep the sample parallel all the time. This way a large drop of acetone will form that will not evaporate during transfer.

A first indicator of the quality of the sample can be seen when the sample is removed from the DI water. If the PMMA removal was successful, no water will remain on the graphene. Therefore, the problem of evaporation is not an issue at this stage, as long as the PMMA has been removed appropriately. The quality of the final samples can only be checked under the SEM. Figure 12 shows the sample and a close up of suspended graphene. There is only partial coverage of the trenches, since some graphene collapses during the transfer. However, about 10-20% of the trenches are covered with graphene. The coverage ratio also depends highly on the width of the trenches. The covered area can reach lengths of up to a few 100μm, which is sufficient for ablation studies.

**Figure 12** Suspended graphene **Left**: optical image of the suspended graphene sample with 100x magnification. **Right**: Close up SEM image, the bright area is suspended graphene. The dark line is caused by the V-shape of the trench. The scale indicates a length of 2.5μm.
3.3.2 Laser ablation

The characteristics of the study and the materials involved set very high requirements on the laser. As mentioned before, the high thermal conductivity of graphene makes the use of ultrashort pulse lasers necessary. Furthermore, the suspended graphene samples require the diameter of the ablation sites to be in the range of a few micrometres. This means that large magnification objective lenses have to be used. The corresponding focal points will be very small, but also the focal length will be very short. The consequence is that the sample must be very well aligned. If samples are not perfectly perpendicular to the laser beam, movement will cause a change in the relative distance and the focal point will move out of the sample surface. For a laser with a wavelength of 400nm and a 100x objective lens, according to equations (2.2.3) and (2.2.4) the focal length is roughly

\[ b = 2\lambda = 800\text{nm} \]  

Therefore, any tilt will lead to a shift, which will change the incident laser intensity. The execution of the experiment is very challenging and requires very precise handling and equipment.

The setup that has been used in the studies is an existing system. The heart of the setup is a femtosecond laser, which generates pulses with duration of 100fs and a frequency of 1kHz at a wavelength of 800nm. The laser consists of a seed laser and an amplifier, which are both optically pumped individually. The components that are involved are all made by Spectra-Physics. A schematic representation of the setup is shown in figure 13. A photograph of the setup can be found in Appendix A.1.

![Figure 13: Schematic representation of the single pulse experimental setup. The arrow and crosshair indicate the possible direction of movement.](image)

The pulse itself is generated by Tsunami. It is a Ti:Sapphire laser that is capable of pulses with wavelengths of 700nm -1000nm and pulse durations of 60fs – 900fs. In
this setup it is used to generate a seed pulse of 800nm wavelength and 100fs duration. It is optically pumped by Millenia, which emits a continuous wave at 560nm wavelength.

In order to increase the lasing power, the initial seed pulse is amplified by Spitfire. It is a Ti:Sapphire regenerative amplifier, which is pumped using the pulsed Nd:YLF laser Empower. After that the pulse has a wavelength of 800nm. A second harmonic generator is used to tune the wavelength to 400nm. The power of the pulse can be controlled using a waveplate in its beam path, since the laser itself is polarized. Including the travel losses that occur between the laser itself and the sensor, the laser pulses reach an energy of up to 50μJ.

Multiple density filters with a total attenuation factor of $4.1 \times 10^{-4}$ are used in order to tune the pulse energies down to a range, where the substrate is not damaged. The attenuation between the sensor and the sample depends not only on the path but also on the objective lens that is used. During the studies 50x and 100x lenses were used, which lead to attenuations of 0.404 and 0.283.

As mentioned before the laser has a pulse duration of 100fs and a repetition rate of 1kHz. However, the experiments require single pulse ablation. This can be achieved by moving the sample. Therefore, the sample is placed on a stage that allows precise movement in the directions perpendicular to the beam. It is computer controlled and is able to perform pre-programmed movement patterns. Moving at a velocity of 3mm/s will lead to a distance of 3μm between individual pulses, thus allowing single pulse ablation. This way of generating single pulses is also the motivation for making suspended graphene over straight trenches.

The whole ablation process can be observed using the CCD camera. It has a very high resolution and allows the observation of supported graphene ablation sites with a diameter well below 1μm. However, this is not due to the fact that the graphene is visible, but more because laser radiation at even low fluences leads to a change the optical properties of the substrate material\textsuperscript{55,56}. In order to find the ablation threshold, the pulse energy is changed between individual runs. This has to be done manually by turning the waveplate until the pulse energy corresponds to the desired value.

For each pulse energy ablation is performed at multiple locations. The exact pattern is shown in figure 14. Several identical patches are created, which consist of rows of individual ablation spots. These rows are formed by moving the stage during ablation. In each of them a different pulse energy is used. This approach leads to a larger amount of results, which is necessary for the evaluation of the experiments, since there is some fluctuation between the size of individual ablation spots.
The experimental studies were performed using both 50x and 100x objective lenses on suspended and supported graphene samples. The ablation result for a supported sample is depicted in figure 15. Here a 100x objective lens was used and the stage was moved at a speed of 2mm/s. As in the previous study petal formation is observed.

The same procedure is done for suspended samples. Figure 16 is an image of the ablation. But instead of just processing the suspended graphene, the supported
parts next to it are also ablated. This makes it easier to compare the sizes and also minimizes differences arising due to different substrate quality. Suspended graphene does not form petals after ablation, which is an effect that has been observed before. The stage was moved at a speed of 3mm/s during ablation. The supported and suspended ablation for the top two rows was carried out at a fluence of 120mJ/cm², the bottom ones at a fluence of 80mJ/cm².

![Image](image.png)

**Figure 16** Ablation sites 100x lens, pulse energy is 282mJ/cm² top two rows and 225mJ/cm² bottom two rows. Scale corresponds to 5μm.

### 3.3.3 Heater design

A part of the experiment was also ablation at elevated temperatures. In order to perform this experiment, a heater was made, which fulfils certain requirements. It has to be thin in order to fit between the stage and the objective lens. An image of the heater during use is shown in the Appendix. At the same time it must be ensured that heat does not damage the stage and especially the objective lens. The heater should be able to achieve temperatures of up to 300°C and have an accuracy of ±1°C. This makes it necessary to monitor the temperature and to tune it accordingly.

A schematic representation of the control circuit is shown below in figure 17. The heart of the device is a thin resistive heater. Its power output is controlled using a basic temperature controller with auto-tune function. The input is the temperature, which is measured by a K-type thermocouple. It controls a solid-state relay, which is opened or shut depending on the measured temperature and thus controls the current flow though the resistive heater.
The form of the heater follows the requirements set by the environment and the given equipment, in this case the existing setup and the resistive heater. The device is basically a stack of layers of different materials with size of 2x2 inch, which is a consequence of the given size of the resistive heater. A model is shown in figure 18. The resistive heater is in the centre of the device. Above it is a layer of copper. It has been chosen due to its high thermal conductivity, which promotes thermal conduction in its direction and furthermore also leads to a very smooth temperature distribution. Groves are milled into this copper plate in order to clamp in the thermocouple and the sample using another thinner copper plate, which is the top of the device.

Below the resistive heater are two layers of ceramic paper, which work as the thermal insulation. The bottom layer is an aluminium plate, which is mainly used to clamp the thermal insulation. Screws hold this whole stack together. In order to provide the best possible thermal insulation, the heater is mounted on the stage via four legs. Initially these legs were made out of MACOR, which is a machinable ceramic that has extraordinary properties. Although it is a ceramic, it is possible to cut screw threads into it using carbide tools. It has a very low thermal conductivity and a very high melting temperature. Nevertheless, the legs and especially the threads are very sensitive. They often broke during mounting and had to be replaced multiple times. In the end they were replaced by aluminium legs, which resulted in a higher thermal flux. However, measurements showed that the temperature would not increase above the tolerated range.

The legs are simply mount to the aluminium back-plate on one side and on a Teflon plate on the other side, which can be mounted directly on the stage. The reason for this construction is that the screw holes on the stage are not through holes, meaning they can only be accessed from the top. Teflon is used because of its low thermal conductivity. The whole device was custom made in the student workshop.
Figure 18 Model of the heater

The shape of the device, especially the legs, and also the position of the thermocouple are the result of repeated numerical simulations using COMSOL. The motivation was not to provide the exact temperature values, but to give information about the properties of the system. For instance it has been shown that without legs, the stage will be heated up to high temperatures. It was also shown that copper would lead to a uniform temperature on the surface regardless of the thermal insulator or geometry, which makes the exact location of the thermocouple irrelevant. All this has been confirmed by temperature measurements on various locations of the heater during test runs.

The objective lens is a far more sensitive component than the stage. Therefore it is necessary to protect it from elevated temperature. Unfortunately the distance of the lens and the heater is very small. In the case of the 50x objective lens it is 2cm, in case of the 100x objective lens only 3.5mm. The thermal flux and surface temperatures of the lens as a function of the heater temperature is very difficult to obtain theoretically. The reason lies in the nature of the thermal transport, which involves a complicated flow of the heated air.

Experimental studies exist that have investigated the temperature over hot plates, which are subject to natural convection\textsuperscript{57}. The results suggest that the temperature of a body in a distance such as the given focal length might increase significantly. In order to evaluate the exact conditions, a test was conducted. A picture of the setup is shown in the Appendix. A broken objective lens was attached above the heater and a thermocouple was mounted onto the surface, which was facing the heater, in order to measure the temperature. The results are shown in figure 19. As expected high temperatures are reached. This means that in order to perform ablation at elevated temperatures it is necessary to somehow protect the lenses.
In order to limit the temperature of the lens, the heater has to be either thermally insulated or the lens has to be cooled. The first approach does not make sense here, since the beam path between the sample and the lens must not be blocked. Therefore, the lens has to be cooled. Whatever method is chosen, it must be guaranteed that it does not influence the ablation process, which means that there must not be any changes in the beam path.

The approach that finally has been chosen is to make use of convective thermal transport. It is possible to estimate cooling rates, but it is very difficult to calculate the temperature of the air. For laminar flow it is possible to use boundary layer theory to calculate the temperature distribution above the heater. But this approach depends highly on the geometry and the results are not very accurate. Thus tests were conducted. Convection is generated using a standard 120mm computer-cooling fan, and a compressor with a 5mm nozzle attached to it. The nozzle could be directed right at the objective lens, while the fan can simply generate an air flow over the hot surface. The temperature of the lens was measured with an additional thermocouple. While it is unclear what the exact operation temperatures for the lenses are, it has been decided to set 50°C as the maximum temperature.

The results show that the fan itself would be sufficient for the 50x lens for the whole temperature range. At a heater temperature of 300°C a lens surface temperature of 42°C is achieved. For the 100x lens using the fan and the compressor in unison, would also allow experiments up to 300°C, at which point the lens has a measured temperature of 48°C. Unfortunately no flow meter was available. Therefore, no exact data on the airflow during convective is available. But since the primary target is the cooling of the setup, this empirical result satisfies the needs.
During the ablation study the heater is mounted onto the movable stage, with the sample clamped into it. It is very important to fix the sample and the heater tightly. Otherwise, for reasons that are unclear yet, during operation at elevated temperatures, fluctuation of the size of the focal point is visible with the CCD camera. Since the temperature controller is able to maintain the set temperature within an error of ±0.1°C, vertical thermal expansion of the stage cannot be the reason. Also convective cooling is not the reason, since the effect is also visible when the fan is turned off. The most likely explanation is that during the rise of hot air the sample or the stage is slightly tilted back and forth. If not fastened tightly this movement could occur, which would then again impact the focal point.

3.3.4 Evaluation of ablation results

The ablation of the samples is not the last experimental step. In order to characterise the ablation sites it is necessary to measure their size. The sizes of the ablation spots are well below 1μm. Some structures, such as the petals that form during supported ablation, require even a resolution of less than 100nm. It is impossible to achieve this resolution even with the best optical microscopes. Instead another technique is necessary.

The most common methods in nanotechnology are atomic force microscopy and electron microscopy. The first is very accurate, but very slow and difficult to use. The second offers a lower resolution, but is sufficient for the given needs. Also availability was a prime concern. Thus the device of choice is the LEO scanning electron microscope (SEM).

The working principle of scanning electron microscopes is based on the use of rays of electrons instead of light. The electrons are emitted by an electron gun, either by heating or applying very strong electrical fields. Similar to optical microscopes, lenses have to be used to focus the beam. However, here the lenses are magnetic coils that focus the beam by the Lorentz force acting on the electrons. When the electrons hit the surface, two possible effects might occur. They can be simply backscattered elastically. Those electrons have a high energy and originate from an average depth of around 100nm below the surface. The other effect is the generation of secondary electrons, which is the result of inelastic scattering. Due to the physical processes involved in this effect, the secondary electrons originate roughly from within 2nm below the surface. These electrons are ideal for the analysis of the surface.

A requirement for samples used in SEMs is that they need to be conductive. The constant bombardment with electrons will lead to a charging of the sample, which decreases the image quality dramatically. However if the sample is conductive, the surplus charges are simply drained by the ground. Usually insulating samples are coated with a thin layer of gold, e.g. 10nm, before taking the image. Graphene is just a single layer of atoms. If the substrate is not damaged, the heights difference between the ablated spot and its surrounding equals the thickness of one layer of carbon atoms. Sputtering a layer of gold, though it increases the quality of the
image, would make it impossible to see the ablation sites. This has also been confirmed in experiments.

Fortunately graphene is a very conductive material. It is very well visible when placed on a Si wafer with a 100nm SiO$_2$ layer on top. Attempts have also been made using pure quartz substrates. In that case charging effects occur and the best possible resolution is very low.

The analysis of the SEM images is performed using the programme ImageJ. It is a free to use programme, which is usually applied by Biologists. It can be used to measure the size of specific features in an image as long as a scale is given as reference. The most practical feature is that the program is able to distinguish features by their colour. As seen in figures 15 and 16 the ablation site differs from the surrounding by colour. Therefore this program can be used to easily measure the size of multiple ablation spots. The results can be used to find the ablation threshold.

### 3.4 Results and discussion

Two sets of results were obtained during the experimental studies. The first is the ablation threshold of suspended graphene at constant temperature. It was confirmed that the threshold is indeed lower than for supported graphene. Furthermore, the other and more important result is the behaviour of the ablation at elevated temperatures. It has been shown that while suspended graphene is highly sensitive to the temperature, supported graphene ablation is nearly independent of any temperature fields. Both results reveal many interesting aspects about the laser graphene interaction, cooling pathways and ablation mechanisms. The details will be discussed in this chapter.

#### 3.4.1 Graphene ablation at ambient temperature

In order to find the ablation threshold the graphene samples were ablated within a specified range of pulse energies. As shown in the chapter before, many patches consisting of lines of ablation spots at constant pulse energies were made. The patches usually have a length of around 0.5mm. The range of pulse energies that is to be used has been specified in first studies by ablation at very high and low energies.

The most straightforward way to find the ablation threshold would be to simply decrease the pulse energies until no visible ablation occurs. However, the problem of this method is that at low fluences, due to the small focal depth, already minor shifts of the sample relative to the laser will result in a lack of ablation. A better approach is to analyse the change of the ablation site with different pulse energy.

When an ideal Gaussian beam is given, the size of the ablation site and the fluence can be derived from the shape of the beam$^{58,59}$
\[ \Phi_{\text{th}} = \Phi_0 \ln \left( -2 \frac{r_{\text{hole}}^2}{w_0^2} \right) \]

\[ D^2 = 2w_0^2 \ln \left( \frac{\Phi_0}{\Phi_{\text{th}}} \right) = 2w_0^2 \ln \left( \frac{\Phi_{\text{av}}}{\Phi_{\text{th}}} \right) \]

in which, \( \Phi_0 \) is the maximum fluence in the middle of the beam and \( D \) is the diameter of the ablation site. The average fluence is defined as \( \Phi_{\text{av}} = E/(\pi w_0^2) \). This relation is based on the assumption the edge of the ablation site is the location, where the fluence sinks below the threshold fluence. This means that horizontal thermal transport is neglected. It should be noted that although not absolutely correct, usually in literature the average fluence is used instead of the maximum fluence. However, it does not change the result dramatically since it does not have any influence on the slope of the function, but it simplifies the analysis of experimental data.

Another advantage of this relation is that it is not necessary to measure the spotsize. The spot radius can be found by simply plotting the diameter of the ablation versus the logarithm of the pulse energy. The slope of this graph can be used to find the spotsize. This value can then be used to plot the data according to equation (3.4.1). The crossing point of the graph with the axis can be used to determine the ablation threshold. The result is presented in figure 24 below. In the supported case the area is defined as the total ablated area, without subtracting the petals, as Yoo et al.\(^9\) had done. The reason is that the ablation mechanism itself is unclear, especially how the folds are formed and how the middle part is ablated. Therefore, the definition of the threshold should be kept as simple as possible. In this case it means that the ablated area is defined simply as the area where graphene is removed from the surface.
The graph shows that the ablation threshold is independent of the objective lens. As a general procedure, during evaluation only ablation sites with an area between the 25th and 75th percentile were taken into account. Each point is the average of a large number of individual ablation spots. The slopes of the graphs are different, which is a consequence of the different sizes of the focal points. Using equation (3.4.1) it is possible to calculate the beam radii. For the 50x objective lens the radius is 635nm and for the 100x objective lens 361nm. This is in good agreement with the beam radius of 640nm, which was achieved in the prior study for the 100x lens with a laser wavelength of 800nm instead of the 400nm that were used here. During the study it has been assumed that horizontal heat dissipation can be neglected. If it played a major role, the ablation threshold should be different for 50x and 100x objective lenses, since the boundary to surface ratio is different for both focal points. This means that more energy should dissipate for the 100x lens. However, this is not the case, which shows that it was a good assumption.

For supported graphene the threshold is 63mJ/cm². It is lower than the previous result, which was 98mJ/cm² due to the different definition of ablation area. However, if the petals are considered the results are very close. The only difference of the two studies is the applied wavelength. Since graphene does not have a bandgap, ablation should also be independent of the wavelength.

As indicated by prior investigations, there is a clear difference for the ablation threshold between supported and suspended graphene. The threshold for suspended graphene is 46mJ/cm². The size of the ablated areas is well reproducible, especially for ablation of supported samples using the 50x objective lens. The reason is that this is the experiment that requires the least accuracy during alignment, because of the relatively large focal length of the lens.
The value of the ablation threshold of suspended graphene is a good first indicator for the actual ablation mechanism of graphene. Many studies have shown that the laser energy is transformed into thermal energy after a short time. Assuming that graphene has thermal properties that are similar to those of graphite, the energy to simply vaporize it should be roughly \( I_{\text{vap}} = 0.16 \text{mJ/cm}^2 \) as given by equation (3.1.6). This value can be viewed as an upper boundary for the necessary energy, since if other mechanisms lead to ablation the actual value should even be smaller. However, the ablation threshold measured in the experiments is 46\( \text{mJ/cm}^2 \). When taking into account the linear absorption coefficient of \( \alpha = 0.02 \), the energy required per area for ablation is still 0.92\( \text{mJ/cm}^2 \), which is much higher than what has been expected.

Most probably the reason for this high ablation threshold is that the energy, which is really absorbed by the graphene layer, is much smaller. This is due to saturable absorption, an effect that has been observed and even utilized in graphene before. Quantifying the magnitude of the saturable absorption is very difficult, especially since this is a ultrafast, dynamic process, which also takes place far from equilibrium. However, saturation effects are already visible at very low fluences. It has been reported that at a fluence of 226\( \text{MW/cm}^2 \), as opposed to an fluence of 500\( \text{GW/cm}^2 \) given in ablation, there has been already a decrease of absorption of 8\%.

### 3.4.2 Graphene ablation at elevated temperatures

The first study of temperature-controlled ablation was performed on supported samples, since these samples are easier to make. The experiments were only performed using the 50x objective lens. The reason is that it has a greater depth of focus, which simplifies the experiment. Furthermore, due to the greater distance of the focus point to the lens, it is less likely to be damaged by the heater.

A major point of difficulty during the experiments was the fact, that increasing the temperature of the setup made it necessary to realign the stage. The focal depth of the 50x objective lens is only 5\( \mu \text{m} \), which means that a shift of 2.5\( \mu \text{m} \) will lead to the loss of focus. Thermal expansion of the setup, especially of the copper parts, will shift the sample out of focus. Furthermore, since the thickness of the stage is not perfectly uniform, expansion also causes tilting. This made it necessary to align the stage during the experiment.

The approach that was chosen during the first attempts was derived from the earlier studies. In principle the procedure that was applied during room temperature ablation was repeated for different temperatures. The experiment was performed starting at room temperature increasing with intervals of 50\(^\circ\text{C}\). An upper limit of 300\(^\circ\text{C}\) was chosen to protect the lens from any damage and to prevent oxidation of graphene.\(^{60-62}\) Since ablation was carried out over a range of 7 temperatures, very large areas of graphene had to be ablated in order to create sufficient ablation sites for analysis. But at the same time the alignment was not very accurate due to temperature influence. Given a small tilt, movement of the stage over a large
distance will result in a major vertical shift, which impacts the relative distance of the sample and lens. As a result there the data did not show any meaningful trends.

For suspended samples an even larger area would be required, since there is only partial coverage of the trenches. Furthermore, another effect was observed. While the ablation sites of supported graphene did not show any difference, heating of the sample to 300°C would lead to the fracture of suspended graphene layers with ablation holes, while pristine graphene remained intact. Figure 26 shows the sample after heating. The suspended graphene had been subject to ablation with a 100x objective lens prior to heating.

The reason for the fracture can be found in the thermal expansion or better thermal contraction of graphene. The thermal stresses that are generated are not large enough to cause fracture of pristine graphene. However, after ablation there will be a hole inside the layer. Holes cause an increase of stress, especially if there are corners with very small radii.

![Figure 21](image)

**Figure 21 Left:** 100x ablation sites created at room temperature after heating to 300°C. Note that supported ablation sites did not change. **Right:** Pristine graphene after heating to 300°C. The scale bar indicates 2μm

Because of the reasons mentioned above, it was necessary to choose another approach. Instead of ablating at a range of pulse energies for each temperature, it was decided to perform ablation at all temperatures for just one pulse energy, which leads to improved and repeatable results. Furthermore, ablation of suspended graphene was only performed up to a temperature of 150°C, which has been shown to be the temperature, where significant fracture of graphene ablation sites can still be avoided.

First the results of suspended graphene will be shown and discussed. The reason is that it can be treated as an isolated system, which simplifies the analysis. Also it is more suitable to provide information on the ablation mechanism. Figure 27 shows the ablation area depending on the temperature for suspended graphene. Ablation was performed for all temperatures on one sample. After each run the temperature would be increased and ablation was performed again. As to be expected temperature increase leads to an increase of ablation area. As before only ablation sites with an area between the 25th and 75th percentile were considered.
Figure 22 Ablation area for suspended graphene in relation to temperature. 50x objective lens was used at a fluence of 104mJ/cm².

The analysis of these results requires a model to understand the effect of an increase in temperature on ablation. The most straightforward approach is to simply assume that the thermal energy adds to the total energy that is brought into the sample. This is equivalent to ablation with a different fluence as shown in figure 29. The lower curve is the original intensity distribution. Temperature increase simply shifts the curve to a higher fluence value, which leads to a larger ablation area.

Figure 23 Effect of temperature increase on fluence
Application of this model requires a modification of the prior used relation between the ablation area and fluence. Now the thermal energy has to be included. The new relation is

\[
D^2 = 2w_0^2 \ln \left( \frac{\Phi_{av}}{\Phi_{ih} - \Phi_{add}(\Delta T)} \right)
\]  

(3.4.2)

The additional term is simply the thermal energy that has been added by heating, which is

\[
\Phi_{add}(\Delta T) = \frac{1}{\alpha} c_p d \Delta T
\]

The reason is that the equation does not take into account that a part of the incident laser energy is not absorbed. All fluences are simply the total values. However, the thermal energy does not experience any absorption losses. Therefore, in order to account the effect of the temperature correctly, it must be multiplied by the factor \(1/\alpha\). The equation can be rearranged to show the effect of temperature more clearly

\[
- \frac{\Phi_{av}}{\exp \left( \frac{D^2}{2w_0^2} \right) \Phi_{ih}} = \frac{1}{\alpha} c_p d \Delta T
\]

(3.4.3)

The results are plotted according to equation (3.4.3) for suspended graphene with a linear fit.

**Figure 24** Plot of experimental results according to equation (3.4.3)

Comparing the linear fit and equation (3.4.3) it is possible to find several important values. The most straightforward one is the threshold fluence for suspended graphene, which has been determined before. The fit of the data is given by
\[ y = 0.2385 \Delta T - 42 \], which means that the threshold fluence has a value of 42mJ/cm\(^2\), which compares well to the value of 46mJ/cm\(^2\) obtained before. Unfortunately since the absorption coefficient is not known, the heat capacity cannot be calculated.

The model itself was based on the fact that temperature leads to a shift of the fluence to higher values as shown in figure 29. The experimental data makes it possible to calculate how much the pulse is actually shifted by a given temperature difference.

\[
\Phi_{\text{add}} = \frac{1}{\alpha} c_p d \Delta T = 0.24 \frac{mJ}{cm^2 K} \times \Delta T \quad (3.4.4)
\]

This allows the calculation of the temperature at which the whole pulse would be shifted above the threshold, which would be the vaporization temperature of graphene according to the model. In this case, considering a threshold value of about 42mJ/cm\(^2\)-46mJ/cm\(^2\), it means that a temperature of around 210°C would result in the vaporization of graphene. This is obviously incorrect as shown by previous experimental results, which means that there must be an inherent flaw to the model. Therefore, ablation of suspended graphene must be based on another mechanism than pure vaporization.

The possibility that thermal stress itself causes the fracture of graphene and thus leads to this large increase of ablation area can be ruled out due to the procedure of the experiment. The data is always obtained in one run, which means that an area that has been ablated at 50°C is subject to the final temperature of 150°C at a later point in time without cooling in between. If thermal stress were the only reason, all ablation sites should have the same size.

An explanation is that ablation of suspended graphene is a combined process of vaporization and fracture. The figure 25 shows the details of this theory. When the laser hits the suspended sample, a small area is evaporated due to the high intensity. At the same time the surrounding area is damaged and thus weakened. Since the creation of damaged areas requires a much lower temperature than the vaporization, it is more sensitive to temperature changes. The large thermal gradient induced in the graphene layer (about 3000°C in the centre and ambient temperature in a distance of a few microns) leads to subsequent fracture.

The slope of the thermal gradient is a function of the intensity. This is a consequence of the Gaussian shape of the beam. Therefore, at very small fluences, the gradient will be relatively small. Furthermore, the vaporized area is very small in these cases, which leads to less stress concentration. This could result in ablation sites, where the centre is vaporized without fracture of the outlying parts. Indeed an effect has been observed that could support this theory. The image on the right side of figure 31 shows the result of ablation at a very low pulse energy. As can be seen the area around the ablation site has been modified. This effect is only visible for very small fluences. However, it is unknown what the exact effect for this modification is. Possible explanations are chemical reactions, such as oxidation, or destruction of individual carbon bonds.
Until now only suspended graphene has been discussed. The results for supported graphene are also very interesting, since if could provide information on the dissipation channel. In this case it was possible to carry out the experiment to temperatures of up to 300°C, since the problem of thermal stress induced fracture did not occur. The results are given in the figure below. Unlike in the suspended case there was very little or no dependence of the ablation on temperature, even on a larger temperature range. As in the previous case the results are very reproducible. Again ablation sites with an area between the 25th and 75th percentile were considered.

**Figure 25** Left: Ablation of suspended graphene with 50x objective lens at 100mJ/cm². Right: Model for ablation

**Figure 26** Ablation area for supported graphene in relation to temperature. 50x objective lens was used at a fluence of 104mJ/cm².

During the analysis of the results for suspended graphene the theory has been put forward that the temperature dependency is actually a consequence of the
characteristics of the ablation mechanism. These results here provide additional evidence. If ablation was just vaporization of graphene, a cooling channel would have to exist for supported graphene, which by coincidence exactly balances out the effect of added thermal energy. Apart from this first unlikely property, the cooling power would also have to increase with increasing temperature. Neither SPP interaction nor thermal dissipation has this characteristic. As a consequence it becomes obvious that just as with suspended graphene other effects than vaporization also play a role during ablation.

Contrary to suspended graphene, the ablation mechanism of supported graphene is independent of temperature. An explanation could be that the damaged area, which has been the reason for the large temperature dependency for suspended graphene, does not fracture since it is held back by the substrate.
Chapter 4
Patterning of Graphene

4.1 Background

Transferring graphene onto different kinds of substrates is a well-known process by now. However, in order to realize device applications it is important to be able to control the geometry of the graphene layer. This is especially important in wafer scale processes. Ideally a large area of graphene would be transferred on the wafer and processed using standard processes.

Many methods have been used already to pattern graphene. These include electron beam lithography\textsuperscript{3,6}, ultraviolet lithography\textsuperscript{7}, scanning tunnelling microscope lithography\textsuperscript{8} and laser patterning\textsuperscript{9-13}. At this point laser patterning still provides insufficient resolution. Kalita\textsuperscript{11} et al. were able to create ribbons of 5\,μm width. Improvements were made by Zhang\textsuperscript{13} et al., who were able to achieve a ribbon width of 1\,μm. However, laser patterning could provide many advantages over the current methods. It is a faster process than e-beam lithography and can be performed for all kinds of substrates. Furthermore laser processing can be performed under ambient conditions.

4.2 Motivation and Approach

From the theoretical point of view there is certainly room for improvement. As pointed out before, the minimum focal area of a laser is roughly the square of the wavelength. This means, that the minimum width of ablation is roughly the wavelength of the laser. Furthermore in the case of ribbons, the width is only limited
by the accuracy of the movement of the stage. For example given a laser beam with a focal width of 500nm, ablating two lines, which are 510nm apart relative to their mid-line, would result in a graphene ribbon of 10nm width. Of course this thought experiment ignores many important aspects such as edge quality and the impact of thermal transport in such a thin line. Nevertheless, it shows the potential that laser patterning has.

Ideally patterning would be carried out on suspended graphene, due to its superior electrical and thermal properties. However, at this point it is still impossible to make very large areas of suspended graphene. Furthermore, most structures need to be supported, since graphene is not stiff enough due to its thinness. Therefore, the focus will be on supported samples.

In the prior chapter single pulse ablation has been discussed. When carried out on supported samples, petals made of double layers of graphene will form. This is an undesirable feature, but as it turns out it can be avoided. This was first noticed when line markings were made on the sample during single pulse ablation studies, which served the purpose to simplify finding the processed area under the SEM. Instead of moving the stage at a speed, where the ablation spots would be apart from each other, low speeds were chosen. Figure 24 shows such a line. It was created by moving the stage at a speed of 0.1mm/s, which means that at a pulse repetition rate of 1kHz the ablation spots are only 100nm apart from each other.

![Figure 27: Linear ablation using Spitfire setup at low stage movement speed (0.1mm/s). Ablation with 50x and fluence of 316mJ/cm². Scale bar indicates 10μm](image)

The reason for the lack of petals is unclear, just as the mechanism that leads to their formation in first place. It should be noted that ablation was performed above the single pulse ablation threshold. This shows that the reason for the lack of petals is not that graphene is evaporated in several steps or that gradual heating decreases the impact of thermal shock. One possible explanation is that the area that is ablated each time, since it is only a small fraction of the total beam spot area, is simply too small to lead to petal formation. Another possibility is that the petals are linked to the geometry of the ablation spot. It means that if an area is ablated that is very thin and long, such as in this case, no petals will form.

Applying this approach makes it possible to make smooth edges without petals. At the same time it puts an upper limit to the processing speed of the laser. The reason is that two temporally adjacent pulses must overlap locally for this method
to work. Therefore the most straightforward approach is chosen for the experiments. A laser with a higher pulse repetition rate, which allows a higher processing speed, will be used for patterning studies.

The main goal is to achieve a higher resolution than the previous studies. To do so it is necessary to minimize the size of the focal point and to increase the accuracy of the sample movement relative to the laser beam. Minimal focal points are achieved using a 100x objective lens. This leads to a focal point with a radius of about 600nm at a wavelength of 780nm. The sample will be moved using high accuracy stage. Another issue is that vibration could have a negative impact on the pattern quality. Thus a vibration-isolated optical table will be used during patterning.

### 4.3 Experimental Methods

The sample preparation process is identical to the one that has been introduced in the previous chapter. CVD graphene is transferred onto a silicon wafer with a 100nm layer of silicon dioxide on top. In this case sample preparation is actually simpler than before, since suspended graphene is not necessary.

A simplified model of the setup is shown below in figure 28. Usually it is used for two-photon polymerization. The heart of the setup is the FemtoFiber pro laser. It is based on an Ytterbium and Erbium doped fibre. The generated laser has a wavelength of 780nm, a pulse duration of about 100fs and a repetition rate of 80MHz. The laser power is tuned using a computer-controlled waveplate that can be automatically set to certain angles with high accuracy. This makes power measurements during the experiment redundant. A computer-controlled shutter can be used to block the beam when necessary. The laser is focused using a 100x objective lens.

A special feature of the setup is the optical table that the setup is mounted on. The legs of the table are four air cushions, which are controlled to balance out any vibration. This isolates the table and the experimental setup from any outside vibrations. Another special feature of the setup is that it has two stages that are connected to each other. Directly attached to the optical table is a linear motor stage. It is actuated by common linear motors. On top of it is a high precision piezoelectric stage. Both stages allow movement in all three dimensions.

The reason for combining two stages lies in their individual characteristics. As the name suggests, the piezo-stage is based on a piezoelectric material. These materials deform when a voltage is applied to them and can thus be used as actuators. It is very precise, meaning that it has an accuracy of down to 1nm. However, the range of movement is very limited. It can only move 100μm in all three dimensions. Because of this limit of range a linear stage was added. It can be used for experiments that require less accuracy, but larger ranges of movement. Furthermore, it proves to be very useful during the initial alignment of the laser and the sample. It is of great importance that the sample is well aligned relative to the beam. Especially any tilt of the sample must be avoided. Alignment is usually performed each time before starting an experiment.
The stages are both controlled by a computer. The entire movement sequence of the stages is written as a code. After initial alignment it is just necessary to run this code and the patterning will be performed automatically, including the adjustment of laser power when necessary. All patterns were created using the piezo-stage only due to its high accuracy.

### 4.4 Results and discussion

The main goal of the study was to demonstrate the creation of different patterns. Furthermore, an attempt was made to achieve higher resolutions than prior ablation experiments. The goal was not to study the fundamental patterning processes and to find out the ideal ablation parameters. In depth studies could not be performed, since the laser broke down, had to be shipped in for maintenance and is currently still being repaired. This section will focus on the results that have been made, which serve as a demonstration of the capabilities of laser processing.

The power of the laser was measured with a sensor in the beam path before the objective lens. As in the prior setup the objective lens and the additional mirrors in the beam path lead to considerable attenuation of the laser power. During the studies the power directly measured by the sensor was considered as the main parameter in order to facilitate the experiment. However, before any measurement of the attenuation could be made, the laser broke down. Thus the actual power can only be estimated. In prior studies, where a 50x objective lens was used, an attenuation rate of 0.375 was measured. During the single pulse ablation experiment with the other setup the attenuation for the 100x and 50x lenses were determined to be 0.283 and 0.404. Assuming that the power attenuation is constant...
for the objective lens, this results in a ratio of 0.263 for the 100x objective lens in the current setup.

The key to a successful ablation was the optimal control of the piezo-stage. However, it is not possible to control its speed. The control-software allows the delay of different lines of command and the execution of dwell-commands, which simply stops any output of commands for a given time. Indirectly it was possible to have an influence on the movement speed of the stage. The movement was broken down into many small steps, with short breaks in between. It was shown in initial parametrical studies that this approach is highly beneficial. When the stage is made to move large distances without intermediate steps, it will often overshoot the distance and oscillate, before the control system manages to move it into to the desired location. This has the side effect that the laser will leave undesirable patterns.

Some of the patterning results are shown below. Figure 29 shows a structure that was created with the goal of conductivity measurements of laser-patterned graphene in mind. This structure would make it possible to measure the conductivity of the thin ribbon in the middle with simple methods due to the relatively large areas on either side. The width of the ribbon is about 500nm, which is roughly an order of magnitude less than what has been done in previous studies.

![Graphene pattern for possible conductivity measurements. Ablation was carried out with 100x objective lens at a power of 138mW (measured before objective lens). The scale bar indicates 10μm](image)

The method of moving the stage in many consecutive small steps made it possible to cut lines that are not perpendicular to the actual direction of the axes of the stage. This is demonstrated in figure 30. Here triangular patterns were cut into graphene. This could be used as an approach to achieve very thin structures. The tip of the triangle has a width of less than 100nm.
An attempt was also made to create thin ribbons. The most straightforward way is to simply adjust the distance between the two ablated lines. Moreover, it is also possible to tune the laser power, since the width of the ablated area is related to the laser power. Figure 31 shows the result of patterning, while adjusting the ablation line distance. The thinnest ribbon has a width of about 100nm.

It was possible to achieve even smaller feature sizes, however an important problem came up. As can be seen in the prior figures, besides ablation, laser interaction leads to the modification of graphene. This is revealed as a change in
colour, which can be observed close to the edges of the ablated areas. Furthermore, the edges are of very poor quality. Most are very rough, with dents and nicks of a size of about ten nanometres. This should not be an issue for ribbons with large width of several hundreds of nanometres. At the range of a few ten nanometres, where graphene starts to exhibit a bandgap, the quality of the edge will be a major issue.
The main topic of the project has been the single pulse ablation of graphene. The controlled ablation of suspended graphene was performed. This involved the production of large areas of suspended graphene. Furthermore, appropriate methods were found to achieve single pulse ablation. Suspended samples were created by wet transfer of CVD graphene on a pre-processed substrate with trenches. These were made by a combination of laser processing and consecutive etching.

The experiments have confirmed that the ablation threshold of suspended graphene is lower than that of supported graphene, which has been indicated by prior studies. Upon ablation supported graphene forms petals, which is not observed for suspended graphene. In addition it was shown that the ablation threshold is independent from the magnification of the objective lens.

After the measurement of the threshold a first attempt was made to determine the ablation mechanism. This was done by ablation at elevated temperatures. The experiments revealed that suspended samples are very sensitive. An increase in temperature would lead to a significant increase in ablation area. Using a model that relates the thermal energy and the size of the ablation area it was possible to conclude that ablation is not a purely thermal process. Instead it is more likely that modification of the graphene or stresses due to the large thermal gradients during laser interaction play an important role during ablation. Precise analysis of suspended graphene at low fluences reveals a change of the regions adjacent to the ablated area, which could be a first indicator in support of this theory.
Ablation was also carried out for supported samples at elevated temperatures. It was shown that contrary to suspended graphene, there was no dependency on temperature. This provides further evidence that pure evaporation is not the sole mechanism for ablation. An explanation for the difference in ablation threshold was also found. Supported samples do not require more energy for ablation due the existence of a substrate related cooling channel. The more likely reason is that there is a fundamental difference of the ablation mechanisms.

In the course of the study a heating device was built in order to enable the temperature dependent ablation study. It is based on a resistive heater that is connected to a controller, which regulates the temperature using the input from a thermocouple. In initial tests it was found that cooling is necessary in order to protect the objective lens. This was done using convective cooling, by simply adding a fan and a compressor to the setup.

An additional part of the project has been the patterning of graphene. It was shown that there is essentially no limit to the geometry of the sample. Many different patterns were created using laser ablation. Furthermore, ribbons down to a size of less than 100nm were created. However the width is limited by the roughness of the edges.

Due to the sensitivity of graphene to its environment, this has been the first study on the true ablation threshold of graphene. Furthermore, the first investigation on the ablation mechanism of graphene and the influence of substrate has been performed. It was shown that the substrate has a big influence on the ablation mechanism itself. This data will be highly useful in future application of laser patterning. Not only is the minimum energy for successful patterning known at this point, but also the influence of the substrate. Furthermore, the patterning experiments have improved the current resolution by an order of magnitude. This demonstrates the capabilities of laser patterning and the feasibility of graphene as a conductor for industrial applications.
This study has provided data on the true ablation threshold of graphene, insight into the fundamental mechanisms of laser ablation and a demonstration of the capabilities of laser patterning. However, there are still many open questions that need to be solved in following investigations.

The first major issue concerns the ablation mechanism. Although the present study has shown that pure vaporization is not the decisive mechanism, the actual processes are still unknown. A first indication could be the observed modification of graphene close to the ablation area. A detailed analysis of this region could give information about the type of modification. The most straightforward method would be a measurement using a tunnel electron microscope. Based on the structure of the graphene an explanation can be found on the ablation mechanism.

The processes leading to the formation of petals is still unknown. It has been shown that it occurs for supported graphene independent of the substrate and the temperature up to 300°C. At very low fluences petals become very irregular and small. Since suspended graphene does not show any signs of petal formation, the substrate must be the cause for its formation. Thermal mismatch stress can be ruled out as a reason, since the induced thermal stresses are too small. However, vaporization of the substrate could lead to the formation of a vapour plume. The increase of pressure would lead to the partial fracture of graphene. This hypothesis could be verified by performing ablation studies in a gas chromatograph with atomic emission detector. The detected total mass and characteristic of the atoms would give information about any possible substrate ablation.
The method of production of the suspended samples could be a simple process to produce and also contact suspended graphene. A layer of conductive material could be first brought onto the substrate surface by evaporation, such as gold. In the next step the trenches can be created and wet-transfer performed just as in during the prior process. After that one will obtain suspended graphene that can be easily contacted through the conductive layer beneath it. This could be very interesting for device applications of suspended graphene, such as high response photodetectors.

It has been demonstrated that patterning can be done in sub-micron regime. The SEM images show that the laser induces modifications of the graphene, which are not clearly characterized. High resolution Raman spectroscopy or TEM will be able to provide details about this effect. The latter approach is especially interesting, since it could provide details about the edge and the quality.

Before laser patterning of graphene can be introduced to actual applications, detailed parametrical studies are necessary. These involve for example finding the optimal processing speed and laser power. Furthermore measurements on the characteristics need to be made. A pattern for conductivity measurements has been presented in this report. A similar geometry could be used to measure the thermal conductivity. These measurements will be very important, since it has been shown that graphene is greatly influenced by its processing methods.

First applications of patterning would be the creation of simple circuit devices. Since there is basically to limit to the possible shapes of the patterns, it is possible to create whole circuits using the laser alone. This method is very promising, because it can be carried out at high speeds on various substrates. A potential first application could be the creation of a transparent conductor including contacts for flexible electronics.
Appendix

Appendix 1 Single-pulse ablation setup. The image shows the laser and the amplifier
Appendix 2 Single-pulse ablation setup. The image shows the stage and the objective lens holder at the end of the beam path. On the right is the controller circuit for the heater.
Appendix 3 Single-pulse ablation setup. The image shows the stage with the heater mounted on top and the objective lens.
Appendix 4 Suspended graphene sample. The graphene layer and the area with trenches are well visible.
Appendix 5 Patterning setup in current state. Laser and parts of the components are missing due to maintenance. Piezo-stage is highlighted
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