DEVELOPMENT OF A SETUP TO MEASURE PHOTOCONDUCTIVITY OF GeSn

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“si entre el món i els sentits hi ha posat la riquesa
de preguntes, matisos, raons, teories,
si d’això me n’ha fet llibertat i bellesa
i m’ha fet habitar plenituds i vertígens,

si m’ha estat un llenguatge per dir l’infinit,
si m’ha dit amb pocs mots unes lleis tan fructíferes,
si s’ha fet una part tan profunda de mi,
com puc dir-ne fredor, de la física?”

Mirall de vellut negre, 1981
David Jou
UNIVERSITAT POLITÈCNICA DE CATALUNYA

Abstract

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Physics Engineering

Development of a setup to measure photoconductivity of GeSn

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This thesis focuses on the design and development of a setup to measure photoconductivity and external quantum efficiency of GeSn. The setup consists of a tungsten-halogen lamp as a light source, a monochromator to select wavelength, and a path to direct the light beam until the sample of interest. This path is composed of a parabolic mirror to collimate the beam, two 45° mirrors to redirect the light, and a lens to correct the non-ideal behaviour of the beam. Before the sample, there is a beamsplitter with a power meter on its reflected side. A calibration of the setup has been done with a reference photodiode, obtaining successfully its responsivity curve. A solution to contact semiconductor samples is studied theoretically and experimentally, and the results are reported at the end. This work constitutes the base for the study of the spectral photoresponse of low bandgap semiconductors.
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Introduction

Recently, interest in driver-assistance systems and robotic cars has grown in the automotive industry. To make these technologies convenient, an inexpensive vision system has to be developed. Robotic cars need to be able to detect precisely, for example, a pedestrian crossing at 200 m away under any external condition like it would be darkness or fog. Light detection and ranging (LiDAR) sensors can cover this requirement with better performance than the conventional vision systems such as radars or the 2D cameras.

A Lidar is a device used for reconstructing 3D maps of the surrounding by measuring distances with pulsed laser light. Measuring the time of flight of the reflected photons with a detector allows to create a map with a resolution of the order of few cm, a considerably better performance compared to the radar [1]. Furthermore, lidars do not require external light illumination, which is an advantage with respect to 2D cameras.

Mapping of long distances requires a high-power emitting laser and an efficient photodetector. These characteristics are met by existent components on the visible range (VIS). However, the needed power in the VIS is covered by more than class I lasers, which can’t be used as a measure of safety. Thus, it is necessary to move to the infrared (IR) range, as class I IR lasers have ten times more power than the visible ones [2].

Infrared photodetectors are key devices in various fields apart from LiDARs, such as night vision, medical imaging or environmental sensing [3]. This has encouraged people to dig for improving their performance and lowering the fabrication cost, by simplifying the fabrication processes and increasing the production yield.

Nowadays, technology from III-V elements such as indium gallium arsenide (InGaAs), from II-VI like mercury cadmium telluride (MCT) are currently dominating the market of short-wave infrared (SWIR) (1.4 μm - 3 μm) imaging [3]. However, most of these materials require processes and elements that make them expensive, and inconvenient to use. Other possibilities are Silicon (Si) and Germanium (Ge) detectors, which provide good performance around the ranges 400-1100 nm and 1100 - 1500 nm respectively [4] [5]. Hence, there is still a gap to be taken up by a material which can fulfill the paired requirements of working in SWIR with good performance and inexpensive development.

A newly synthesized group IV alloy, GeSn, has shown promising properties for photodetection exploitation. Ge appeared first as an option to incorporate on Si optoelectronics. However, Ge light emission device performance was limited due to its indirect band gap. The addition of Tin (Sn) to form an alloy tunes the band gap as a function of composition, until the point that a direct band gap material can be obtained. Unfortunately, synthesizing this alloy is not straightforward, and ongoing research currently investigates deposition methods to obtain high-quality crystalline epitaxial GeSn on Si substrates.
The work presented in this thesis is part of a doctoral project about sputtering epitaxial deposition of GeSn on Ge and Si substrate for IR photodetection. In particular, it is focused on the development of a setup to measure photoconductivity and External Quantum Efficiency of GeSn.

The following pages will detail the procedure of the design and assembling, the specifications of the setup and its calibration. Particular attention will also be given to the contacting of the sample for photoconductivity measurements.

Through the reading of this thesis, the required theory behind the setup is covered with the aim to offer a self-explanatory report in optics and semiconductors.
Chapter 1

Theoretical background

1.1 Electrical resistivity

The electrical resistivity is an intrinsic property of a material quantifying its resistance against the flow of electric current. The lower the resistivity, the easier the electrons can move through the material. It is expressed in Ohms-meter (Ω m) and represented with the Greek letter $\rho$.

Generally, the resistivity is the connection between the electric field and the current density present in a material, given by the well-known proportionality relation named Ohm’s Law 1.1.

\[ \vec{E} = \rho \vec{J} \] (1.1)

However, most of the times it is not necessary to use directly this relation to obtain the resistivity. If the cross section and the physical properties of the examined sample are uniform, $\vec{E}$ and $\vec{J}$ are parallel and constant and the resistivity can be obtained with the geometric relation 1.2. The result comes considering the above conditions and a contacted sample with flowing current:

\[ \int_{a}^{b} E dx = \int_{a}^{b} \rho J dx = \rho \int_{a}^{b} \frac{I}{A} dx = \rho \frac{I}{A} (b - a) = V_a - V_b \]

\[ \rho = \frac{(V_a - V_b)A}{I(b - a)} = R \frac{A}{b - a} = R \frac{A}{l} \] (1.2)

Where,

- $\rho$ is the resistivity of the sample.
- $a$ and $b$ are the position of the contacts. $l$ is the distance between the contacts.
- $A$ is the cross section that the current is covering.
- $I$ is the total intensity flowing through the contacts.
- $V_a - V_b$ is the potential difference between the contacts due to the current.
- $R$ is the resistance of the sample, measured in $\Omega$.

The electrical resistivity gives automatically the electrical conductivity, that represents, on the other hand, the easiness with which a current flows through a material. It is represented with the letter $\sigma$ and is simply the reciprocal of the resistivity:

\[ \sigma = \frac{1}{\rho} \] (1.3)
Conductivity and resistivity can be expressed with the charge of the electron \( (e) \), the electron and hole mobility \( (\mu_n \text{ and } \mu_p) \) and the electron and hole concentration\(^1\) \((n \text{ and } p)\). The mobility is a quantity determining the ability of charged particles to move through a medium with an electric field. Thus, it is the proportional relation between the average velocity at which the charges are traveling under a certain electric field. It is expressed with \( \frac{cm^2}{V\cdot s} \).

\[
\sigma = e(\mu_n n + \mu_p p) \quad \left[ \frac{cm^2}{V\cdot s} \cdot \frac{1}{cm^3} \right] = \left[ \frac{1}{V\cdot cm} \right] = \left[ \frac{1}{\Omega\cdot cm} \right]
\]

As it will be explained in section 1.2.3, some semiconductors suffer variations in their conductivity, and so in their resistivity, by the absorption of light, making this parameter an interesting quantity to determine.

1.2 Semiconductor Basics

A semiconductor is a material whose electrical properties lie somewhere in between those of a conductor and an insulator. Quantitatively, one can distinguish a semiconductor when it’s electrical resistivity belongs to some value in the range of \( 10^{-2} - 10^9 \Omega\cdot cm \).

Likewise, another determinant characteristic from semiconductors is it’s bandgap energy, which is always found to be from 0 to 4 eV (0 eV would correspond to metals and above 4 eV would correspond to insulators) [6].

Nowadays, there is another well accepted definition which is a material that has a bandgap and that can be doped to conduct or to behave as a classical semiconductor. With this, the category of being a semiconductor has been enlarged, including materials such as diamond.

To understand the meaning of this last concepts, one should recall to the electronic band theory of solids. Although the development of this theory and its results is not the major objective of this report, it is interesting to provide a qualitative overview on its main ideas.

1.2.1 Band theory

A solid is formed by a large quantity of structured atoms, and so with an even more large quantity of electrons. When such a big amount of electrons are close, overlapping with neighbours’ wavefunctions and Pauli Exclusion Principle lead to a set of closely spaced energy levels, forming an energy band. In other words, the mixing of binding states leads to the formation of the filled lower valence band, while the mixing of the antibinding states leads to the empty upper conduction band. The energy difference between this two bands, if there is any, is the bandgap energy, and it is a characteristic of each material. Band theory derives such bands, providing the electronic band structure of the solid, in where one can predict the range of energies that an electron within the solid may have [7].

Energy band diagrams of semiconductors are rather complex. Fortunately, it is well accepted to simplify them using only the highest almost-filled band and the

---

\(^1\)The concept of hole will be explained in section 1.2.1
lowest almost-empty band, as these are the energy levels that play the most important role in the electronic activity of the material.

As pointed out previously, semiconductors differ from metals and insulators by the dimension of the bandgap. This value is small enough, without being zero, to let electrons from the valence band to get to the conduction band thanks to their thermal energy, which yields to an "almost-full" band below and an "almost-empty" band above. The fact of having charges and empty states at the same time in a band can let conduction occur. There is a common term to refer to a missing electron in the "almost-full" valence band, which is hole. This concept makes it easier to deal with conduction in the valence band, and it is treated as the flow of positive charges.

1.2.2 Metal-Semiconductor interface: Schottky contacts

To exploit semiconductor’s properties, it is often necessary to contact them with a metal to extract the charges. The interface suffers interesting changes that can be predicted by looking at the band alignment of the two materials put in contact.

A frequently used concept is the Fermi energy, which corresponds to the electrochemical potential of a solid. The Fermi energy is such that, at zero temperature and thermodynamic equilibrium, all states with lower energy are occupied and all states with higher energy are empty [8].

In a metal, the Fermi energy is given by the work function, which is the minimum energy required to bring an electron at rest to an infinite distance from the metal surface [7].

Generally, metals and semiconductors have different Fermi level. When they are put in contact, there is a tendency to reach equilibrium, which results in a constant electrochemical potential along the structure. It is achieved thanks to a flow of charges between the materials. This causes a band bending in the semiconductor due to the accumulation or depletion of charge at the interface, respectively for p- and n-type doped semiconductors. On the other hand, the position of the Fermi level in the metal does not vary considerably due to the high density of electrons in the metal. In this case a barrier equal to the difference between the metal’s Fermi level and the semiconductor’s conduction band is created at the interface, as shown in figure 1.1. This configuration predicts that the contact will have rectifying properties, that is, a diode behaviour [9]. In such case, they are called Schottky type contacts or Schottky diodes.
This diode behaviour is not desired when the metal-semiconductor contact is used to extract charges from the semiconductor, as the electrons and holes can’t flow through them easily due to the energy barriers that they need to overcome.

**Fermi level pinning**

In fact, it has been observed that the barrier height is not simply the difference between the metal’s Fermi level and the semiconductor’s conduction band, as there are more effects going on. A semiconductor may have dangling bonds in its surface, which means having singly occupied atomic orbitals. This gives to the surface extra states, that may lie in the forbidden energy gap and influence the band structure at the surface of the semiconductor [6]. If the gap is free of surface states, the position of the bulk bands with respect to the Fermi energy is constant along all the material, which was the case considered in the previous paragraph. However, the presence of high density surface states results in a band bending so as to equilibrate the Fermi level from the bulk to the surface of the semiconductor. This gives a depletion or accumulation layer (depending on the nature of the semiconductor) at the surface of the semiconductor even before the contact with a metal.

In the case then of the metal-semiconductor junction, the charge carriers moving from the semiconductor to the metal are trapped by the surface states of the semiconductor’s surface leading to almost insignificant changes in its Fermi level position. The barrier height at the interface will thus be independent from the work function of the metal. This behaviour is known as Fermi level pinning and is more or less evident depending on the material [10].

After this fast overview on physics of semiconductors, the reader is now prepared to move to the next section about the phenomena of photoconductivity, which is the main focus of this project.
1.2.3 Photoconductivity

Photoconductivity is the optoelectronic phenomenon that describes the increase of conductivity of a material due to the absorption of light radiation [11]. The absorption of photons of energy larger than the bandgap energy excite electrons from the valence band to the conduction band. Thus, an electron-hole pair is generated, so there are free charge carriers in the conduction and valence band that can contribute to conduction.

Apart from its technological applications, photoconductivity can be a tool to understand the internal processes of the material. It is defined from equation 1.4, considering the increase in conductivity due to photogenerated carriers.

\[
\sigma_{ph} = \Delta \sigma = e(\mu_n \Delta n + \mu_p \Delta p)
\]  

(1.5)

The simplest way to quantify this phenomenon is having incident monochromatic light on a material contacted with metallic electrodes through which a voltage is applied. The generated free carriers will contribute to the current flowing through the contacts due to the applied voltage. One can obtain this current with the help of a multimeter, and subtracting the dark current\(^2\) to it find the photogenerated current. From the latter, one can obtain then some important parameters such as the External Quantum Efficiency.

1.2.4 External Quantum Efficiency

The external quantum efficiency (EQE) is the ratio of the number of charge carriers collected at the contacts to the number of incident photons arriving on the surface of the material. It is a relevant parameter to characterize a semiconductor device as it summarizes its global response against light: the generation of free electrons and holes through the absorption of incident photons, their transport through the material, and their recombination. It is normally obtained as a function of the energy of the incident light, as absorption is strongly related to it. Thus, the EQE can be calculated from the photogenerated current divided by the incident power in function of the incident wavelength. More precisely, to obtain the previous defined ratio, one has to apply a factor to obtain the number of charges from the current and the number of photons from the optical power.

\[
EQE(\lambda) = \frac{hc}{\lambda e} \frac{I_{ph}}{P_{inc}}
\]

(1.6)

where \(I_{ph}\) is the photogenerated current, \(P_{inc}\) is the optical power incident on the sample, \(\lambda\) is the wavelength of the incident light and \(e\) is the elementary charge.

Strongly related to the EQE, there is the Internal Quantum Efficiency (IQE), which is as well interesting to determine and can be obtained in a similar way. The IQE is the ratio between the number of charge carriers collected at the contacts to the number of absorbed photons from the incident light. It represents how the semiconductor device treats the photogenerated charge carriers and it is obtained from the EQE and the absorption of the material.

\(^2\)The dark current is the current present in the material when there is no light reaching it. It is thus due to the applied voltage.
Chapter 2

The setup

In this chapter, a detailed explanation of the built setup to measure photoconductivity will be provided. Its objective is to give a clear understanding on the working principle of every present component.

Figure 2.1 presents an overview of the setup. It consists on a tungsten-halogen lamp as a light source, a monochromator to select wavelength, and a path to direct the light beam until the sample of interest. This path is composed of a parabolic mirror to collimate the beam, two 45° mirrors to redirect the light, and a lens to correct the non-ideal behaviour of the beam. Before the sample, there is a beamsplitter with a power meter on its reflected side. To isolate the measurements from background light, the output of the monochromator is coupled to a hole in a black box, containing the rest of the components, so that just the light of the beam illuminates the sample. Figure 2.2 shows the setup inside the black box.

![Diagram of the setup.](image)
Chapter 2. The setup

Figure 2.2: Part of the setup inside the black box.

The objective of the setup is to extract the variation of the conductivity as a function of incident wavelength, characterizing the optical properties of the samples. As GeSn absorbs in the IR range, a scan of wavelengths from 1200 nm to 2300 nm with a step size of 50 nm will be done, storing the data at each step.

In the following sections every component of the setup will be presented, going through the physics, their role in the setup, and quantitative specifications if there are any.

2.1 Light source

The first component of the setup is a light source. It is chosen to be a broadband light source so that wavelengths from a wide range can be selected.

A tungsten-halogen lamp is a type of incandescent lamp where the filament is composed of tungsten. It is located in a chamber (the bulb) filled with inert gas and a small amount of a halogen gas.

We used a tungsten-halogen lamp of 250 W, model TS428 from Princeton Instruments. Its emission spectrum is centered at 800 nm, and the output power decreases the further the wavelength goes into the IR. However, we will see that the employed components are very sensitive, so even with a small amount of light one can get the expected response.

Other possible light sources have been considered in order to have more power in the IR range. In particular, we studied in depth the possibility of switching the tungsten-halogen lamp for a Pulsed Supercontinuum Laser Source, as it fits the requirement of being broadband and powerful at the same time. Specifically, the available model was the Power+ from NKT Photonics, with a 400-2400 nm spectrum with 1-6W of power up to 10mW/nm, and pulse width of 5 ps. For example at 1400 nm
and considering a bandwidth of 10 nm, the laser can give a power of around 35 mW, whereas the lamp gives 0.0234 mW.

However, we found that shining light with that high power on a pulse of 5 ps might produce spurious non-linear effects in the sample such as two-photon absorption [12]. This would lead to misunderstanding of the results as it would not be the phenomena of study.

To overcome this problem, temporal shaping of the ultrashort laser pulses can be employed to significantly reduce the associated pulse peak power [12]. There is more than one technique to achieve temporal pulse broadening, relying on different physical phenomena. The one proposed here would work by means of two principles: Considering that we have a transform-limited pulse (a pulse such that all the frequencies forming it are added in phase), the time-bandwidth product shows that a spectral reduction of the radiation would give pulse broadening in time. However, it is limited for the narrow FWHM of the pulse. So, in addition to the spectral reduction, one can introduce dispersive materials\(^1\) where different spectral components will acquire a change in their relative phases. It can be demonstrated that this dephasing leads to temporal broadening of the pulse.

This option has been discarded due to practical reasons related to the time required to build a pulse-broadening circuit, and to safety measures for the Supercontinuum Laser. It is a hazardous laser as it is class 4, and so a lot of protection is mandatory before turning it on. After a deep research to find every safety tool for it, I was noticed that I would receive the safety goggles after a month, an amount of time that I could not allow myself to wait at that point of the project.

### 2.2 Monochromator

A monochromator is an instrument capable of selecting light of a specific wavelength from a broad spectrum. Thus, it is commonly used in research for optical characterization to obtain spectral information. A monochromator can function based on two physical phenomena: optical dispersion, by means of a prism; or diffraction. The following section will focus on diffraction monochromators, as it is the type used in our setup.

#### 2.2.1 Reflective diffraction grating

The employed monochromator uses a reflective diffraction grating to achieve spatial separation of photons of different wavelength in the incident beam. A reflective diffraction grating is an optical component whose surface has equally spaced and parallel ridges with a specific shape. The reflected light undergoes interferences giving variations in the amplitude and phase, in such a way that the spatial separation of wavelengths takes place. This is because every wavelength has constructive interference at a different reflecting angle, following the well-known diffraction equation [13]:

\[
d(sin r + sin i) = n\lambda
\]

Where:

\[
d: \text{ is the distance between grooves}
\]

\(^1\)Dispersive media are characterized by a frequency dependent index of refraction \(n(w)\).
\( i \): is the angle of the incident light  
\( r \): is the angle of the reflected light  
\( n \): is an integer indicating the diffraction order.  
\( \lambda \): is the wavelength of the reflected light

Equation 2.1 can be obtained as follows: When light reaches a diffraction grating with a certain angle, specular reflection with respect to the groove’s angle occurs. This can be represented with respect to the normal of the substrate, which will give different angles between the incident and reflected light. Figure 2.3 below represents this description.

![Figure 2.3: Incident light ray in a diffraction grating](image)

In figure 2.4 we can see that every ray travels different paths. The outgoing beam will be the result of their interference: From the moment that the travelling path changes between these two rays, to the moment that they travel again together, a difference in phase appeared due to the difference in path. Constructive interference will occur when the path difference will introduce a difference in phase of a multiple of \( 2\pi \). In this case, the difference in phase in plane waves should be:

\[
kx_2 - kx_1 = n2\pi
\]

where \( k \) is the wave vector and \( x_1 \) and \( x_2 \) are the respective traveled paths of each ray. Further developing the expression,

\[
\frac{2\pi}{\lambda}(x_2 - x_1) = n2\pi
\]

\[
x_2 - x_1 = n\lambda
\]

\[
d \sin r - d \sin i = n\lambda
\]
Chapter 2. The setup

Taking into account that the angles should have the same coordinate’s origin, if we consider \( i \) positive, \( r \) should be negative, which leads to equation 2.1. As a consequence, light with a certain incident angle will give each wavelength at different angles of reflection. One can see that actually at each angle \( r \) we find the corresponding wavelength plus the results of giving integer values to \( n \).

The grating used in this work is a blazed diffraction grating. Blazed gratings are a form of gratings designed to give the maximum grating efficiency in a specific diffraction order. They can achieve this by playing with the angle of the grating and the substrate. Due to this design, this gratings are ideal for a particular wavelength, known as the blaze wavelength.

### 2.2.2 Diffraction grating monochromator

Diffraction grating monochromators, as their name states, are based on the use of a reflective diffraction grating. There are multiple options to decompose the spectral configuration of light with a diffraction grating. The monochromator used in this work uses a Czerny–Turner configuration, explained in the following paragraphs.

In Czerny-Turner configuration, focused light with a matching numerical aperture should enter the monochromator through a slit. All the light will thus reach a curved mirror which is placed at a distance from the slit equal to its focal length. The curved mirror collimates and redirects the light to the reflective diffraction grating. Collimation is essential for the proper functioning of the diffraction grating to guarantee spatial separation of the different wavelengths at the exit slit. The diffracted light from the grating reaches then another curved mirror, whose role is to focus the dispersed light to an exit slit. The rotation of the diffraction grating aligns the focused light from a selected wavelength with the exit slit.
The configuration shown brings the image of the entrance slit to the exit slit. Thus, an image of the size of the entrance slit is formed at each focusing point of each wavelength. This means that either the entrance and exit slits can be tuned to choose the intensity and the spectral resolution of the output.

The width of the entrance slit determines the amount of light entering to the monochromator whereas the with of the exit slit determines the spectral resolution of the output. Depending on how big is your image, you will need to close more or less the exit slit to achieve a certain spectral resolution. In other words, when your image is small enough, there is few overlapping between the diffracted light, which allows you open wide the exit slit. However, if your entrance slit is fully open to obtain high intensities, you will have at the output a lot of overlapping, which will force you to close the exit slit in order to get narrow bandwidth.

2.2.3 Filter Wheel

An essential accessory in the monochromator is a filter wheel. It is a wheel with some mounts for optical filters placed in a circular distribution, and it can be monitored manually or with Labview. A long-pass filter is placed in each mount, with the aim to block the higher than one orders of diffraction of the grating. A picture of an example of a filter wheel is shown in figure 2.6.
As seen in subsection 2.2.1, for each angle there are multiple wavelengths in constructive interference, corresponding to the result of giving integers to $n$. For $n > 1$, we obtain smaller and smaller wavelengths. Therefore, we need a long pass filter to block any possible wavelength under the desired one. Moreover, as we scan a wide range of wavelengths, we need a "tunable" filter, which is achieved by making the wheel rotate.

In our case, the filter wheel is coupled between the output of the lamp and the entrance slit of the monochromator.

### 2.2.4 Specifications of the monochromator

The filter wheel is equipped with the required filters so that while increasing the output wavelength of the monochromator you can block the second order of diffraction, as it is the most powerful one. The six available positions of the wheel are equipped with:

- F1: Empty
- F2: Longpass filter with 320 nm cut off wavelength
- F3: Longpass filter with 590 nm cut off wavelength
- F4: Longpass filter with 715 nm cut off wavelength
- F5: Longpass filter with 1300 nm cut off wavelength
- F6: All black

Regarding the monochromator, it is used with both slits fully open, as the maximum intensity is required. This gives a spectral resolution of 13 nm. It has been obtained at 900 nm with the spectrometer Ocean Optics USB2000+. Geometrical optics can probe that the spectral resolution remains constant with the wavelength in a diffraction grating monochromator. The grating inside is a 600 g/mm with 1.6 $\mu$m blaze, for a better performance at the IR range.
2.3 Optical path

After the monochromator, there is an optical path to redirect light to the sample. It is important to not lose light through it, and to quantify the amount of light reaching the sample to be able to improve the sensitivity of the setup.

Their components, pictured in figure 2.1, are detailed in the following subsections.

2.3.1 Parabolic mirror

The most effective way not to lose light along the path is to have collimation of the beam. A beam is collimated when the rays are parallel. Thus, there is no divergence as light propagates. There are multiple ways to reach collimation. For this setup, it is achieved with a parabolic mirror.

A parabolic mirror is a mirror whose surface shape is designed by revolving a parabola around its axis of symmetry. The one used in our setup does not have this entire surface, but a piece of it, as shown in figure 2.7. Placing a point source at the focal point of the mirror gives a collimated beam, that is, it converts spherical wavefronts coming from the focal point into plane wavefronts. Of course, the reverse operation can also occur, so incident plane waves will focus on the focal point. The fact of using just a piece of the paraboloid gives an accessible position for the focal point. Otherwise, the incident and reflected beam would overlap, making it impossible to use for the desired application.

![Figure 2.7: Ray trace of the collimation of a light point source with a parabolic mirror.](image)

In our setup, we find right after the monochromator a parabolic mirror which collimates the beam and changes its direction by $90^\circ$, similar as pictured in figure 2.7.

2.3.2 $45^\circ$ Mirrors and lens

Once collimated, there are two mirrors and one lens before reaching the beamsplitter. The two $45^\circ$ mirrors change the beam direction. The lens is needed due to practical
issues. As the lamp is not an ideal point source, the parabolic mirror can’t collimate perfectly the beam, which is thus a bit divergent along the path. This problem can be solved easily by placing a lens with long focal distance to decrease the divergence of the beam. The one chosen here has 200 mm of focal distance and is made of Magnesium Fluoride, which gives a good performance from 0.2 \( \mu m \) to 6 \( \mu m \) (LA6007 from Thorlabs).

### 2.3.3 Plate Beamsplitter

Following, we find a beamsplitter. A beamsplitter is an optical device that splits incident light along two directions, as shown in figure 2.8.

![Figure 2.8: Ray tracing of the functioning of a plate beamsplitter. Figure from Edmund Optics.](image)

Plate beamsplitters are made of crown glass and most of the times a coating is added on their first surface to enhance reflection. Crown glass is a very used material for optical components as it has very low index of reflection and very low dispersion. The added coating is such that the absorption is low as well. Sometimes, beamsplitters can have an antireflection coating in the second surface to avoid second and more reflections \( R_2, T_2, R_3, T_3 \) (Figure 2.9).

The polarization, wavelength and angle of incidence of the light can tune the reflectance and transmittance coefficients leading to variations in the resulting beams. A scheme of this phenomenon is shown in figure 2.9.
The beamsplitter used in the setup is a 50:50 IR Fused Silica Plate Beamsplitter (BSW23) from Thorlabs, of 5 mm of thickness with a coating working for wavelengths of 0.9 - 2.6 µm.

It reflects 50 % of the incident light and transmit the other 50% although later on we will see that a calibration as a function of wavelength is required to obtain precisely the ratio.

Placing a power meter and the sample at its reflected and transmitted output respectively, allows to know the amount of light that is reaching the sample. It is thus possible to store the value for every wavelength, an information that will be useful later on.

At both sides of the beamsplitter there is a strong focusing lens to focus all the light in the power meter and in the sample. These lenses have a focal distance of 50 mm and are made of Magnesium Fluoride, which gives a good performance from 0.2 µm to 6 µm (LA6002 from Thorlabs).

### 2.4 Power Meter

In the setup there is the S148C Integrating sphere photodiode power sensor from Thorlabs. It is sensible to wavelengths from 1200 nm to 2500 nm, so it fits the requirements of the problem.

An integrating sphere is a spherical cavity whose inner surface presents a highly reflective and diffusive coating. It can have one or two small holes, called ports, for light to get in and out. Incident light undergoes multiple reflections, where it is scattered uniformly. Thus, light loses its directionality without losing power. Integrating spheres are commonly used as optical power meters by placing a sensor at the exit port.

As introduced in the above subsection 2.3.3, the power meter has the function to measure the light impinging on the sample, and it is placed at the reflected side of the beamsplitter, after a focusing lens.
Chapter 3

Calibration and measurements

In this chapter, the measurements performed with the setup are explained and developed. The first measurements had the aim of calibrating and testing its functioning. This part of the project has been crucial to gain a deep understanding of each optical component and their coupling into an optical path. The setup could be thus optimized to maximize the output and limit the optical power loss along the path.

Then, semiconductor samples were investigated. For this, a method for contacting the sample was studied. The reason why one should pay attention when contacting some semiconductors with metals is that Schottky barriers might appear, creating a high contact and non-linear resistance and thus blocking the generated charge carriers, as presented in section 1.2.2.

3.1 Calibration

The testing of the setup was performed on a reference photodiode from Thorlabs, trying to obtain its responsivity curve. The responsivity of a photodiode is the ratio of the electrical output per optical input, so the photogenerated Amperes per incident Watt of light. The values for the reference device are provided by the vendor.

The run of the setup consists in a scan of wavelengths in a desired range to illuminate the photodiode, which is located at the place of the sample and connected with the help of a breadbord to a load resistance and a multimeter. For each step, the photocurrent at the diode is recorded, together with the optical power measured at the power meter. This is controlled by a Labview code, who sets the monochromator and the filter wheel at every step, and communicates with the power meter and the multimeter to store the measured values.

3.1.1 Calibration in the VIS range

The design of the structure of the setup has first been conducted in the visible wavelength range, as this facilitates the alignment of the optical path. In addition, most of the optical components of the laboratory are optimized for this range, making the design easier.

Thus, the following measurements were done with the optical components detailed below:

- Filter wheel filled with:
  - F1: Empty
  - F2: Longpass filter with 320 nm cut off wavelength
  - F3: Longpass filter with 590 nm cut off wavelength
F4: Longpass filter with 660 nm cut off wavelength  
F5: Longpass filter with 715 nm cut off wavelength  
F6: All black

- Diffraction grating of 600 g/mm with 500 nm blaze  
- Lens of F=200 mm  
- Lens of F=50 mm x2  
- Beamsplitter  
- Power meter S120C from Thorlabs, covering 400 nm - 1100 nm

A new calibration of the beamsplitter was used in the results as the curve provided by Thorlabs was not giving the expected responsivity values of the photodiode. It was obtained by measuring the intensity of the focused light at the two sides of the beamsplitter with the power meter.

To improve the accuracy, an iris was placed at the output of the monochromator to cut the more divergent rays of the beam before collimation. This was necessary to decrease on the measurements the effect of the optical aberrations due to the non-ideal light source. A non-ideal light source does not allow to have collimation and thus the lenses can’t focus properly, leaving a halo surrounding the focused light. Therefore, the amount of light impinging the sample can’t be well predicted, giving a wrong calibration and wrong responsivity values.

Figure 3.1 shows the responsivity of the Si reference photodiode for wavelengths up to 1100 nm. The data is plotted next to the reference values extracted from the Thorlabs’ datasheet, in order to compare them.

![Figure 3.1: Responsivity of a Si photodiode measured with our setup (in blue) compared to the calibrated response from Thorlabs (in black).](image)

This data confirms that control in the impinged light on the sample can be achieved in order to get a good characterization. Even if the important range of work is the
infrared, this study was helpful to determine the necessary optical components and understand the behaviour of light along the setup. When switching to the infrared, this will guarantee that the optical path is efficient even though the beam is invisible to the eye.

3.1.2 Calibration in the IR range

To test the setup for higher wavelengths, a Ge reference photodiode from Thorlabs has been used, with the intention to reproduce its responsivity curve with our setup. All the optical components of the setup with the exception of the mirrors needed to be changed, as they don’t work properly for the IR range. Thus, another filters’ distribution for the filter wheel, diffraction grating, lenses, beamsplitter and power meter specially designed to treat higher wavelengths were required. This new configuration, reported in Chapter 2, is the final configuration used for the rest of the project.

A redistribution of the longpass filters and the placing of the new grating in the monochromator required modifications in the Labview code, as the wheel needs to rotate in accordance with the new scanning of wavelengths.

Infrared beams can be tracked down with an IR detector card if they have a power density higher than the sensitivity of the card. This is not the case in the setup, so to align the photodiode and power meter at the respective focusing points of the light, 3D micropositioners have been installed. Small movements can be done while looking at the same time at the respective measuring instrument to find the maximum response which corresponds to the focused light. The micropositioners give to the setup a higher degree of accuracy, as well as a much more comfortable handling.

The responsivity curve for the Ge photodiode with this configuration is plotted in figure 3.2. The good agreement with the manufacturer curve confirms the correct performance of our setup in the near-infrared range.
3.2 Measurements of a semiconductor sample

In this section, semiconductor samples will be treated instead of photodiodes. Thus, another approach is required to make the measurements with the setup. This section will explain how this challenge has been faced.

3.2.1 Contacting GeSn

The goal of the setup is to characterize GeSn samples. This implies that a suitable method to contact them needs to be found, as well as how to drive the photogenerated charge carriers. These issues were not taken into account in the first measurements as the targets were commercial photodiodes. A photodiode is a pn junction, therefore it has an internal difference of potential which drives the generated charge carriers. In addition, it was bought from the manufacturer with the contact scheme.

As mentioned in section 1.2.2, by having a metal on GeSn a Schottky barrier appears, blocking thus the flow of charge carriers. Hence, the simple option of depositing two metals to create contacts and apply a bias voltage to collect the photogenerated carriers has been discarded.

One solution is based on modifying the surface states in order to reduce the Schottky barrier, as well as on finding the suitable metal to enhance this phenomenon. As an example, Chen et al. [14] proposed to treat samples with O₂ plasma, as it passivates dangling bonds and reduce interface states. This gives Fermi Level Depinning to the device and a reduction of the Schottky barrier, showing then an Ohmic-like behaviour. Also, Zheng et al. [15] found that an option can be to strongly dope the
semiconductor with Sb, as the Schottky barrier width is inversely proportional to the doping concentration. This facilitates the tunneling of electrons through the barrier.

However, the implementation of all these techniques is complex and long, and it involves modifications in the sample. As an alternative, a method to measure the resistivity of thin films even with the presence of Schottky barriers was found to be by making a 4-point probe measurement. In particular, we employed the Van der Pauw configuration. Obtaining the resistivity of the sample in the dark (ρ_{initial}) and the resistivity of the sample under illumination (ρ_{final}), gives the change in resistivity (and thus, in conductivity) due to photogenerated carriers, with relation 3.1.

\[ \sigma_{ph} = \Delta \sigma = \sigma_{final} - \sigma_{initial} = 1 - \frac{1}{\rho_{final}} \cdot \frac{\rho_{initial}}{\rho_{final}} \quad (3.1) \]

### 3.2.2 The Van der Pauw configuration

Van der Pauw proposed a special configuration of a 4-point probe measurement to measure the resistivity of a film.

A 4-point probe measurement consists on having four contacts on your sample, applying a current through the outer two, and measuring the voltage through the inner two. This has the advantage that the contact resistances do not have an influence on the measured voltage, so neither do the eventual Schottky barriers that may be present at the contacts.

The main reason is because as voltage measurements are made with high resistance instruments, few current is going through it, which makes that the contact resistance can’t influence much. The following figure represents a circuit for a 4-point measurement.

![Figure 3.3: Equivalent circuit diagram of a 4-point measurement. R_{cl} represent the contact resistance of each probe, R_s represents the resistance of the sample, thus what we want to measure, and R_M represents the resistance of the measuring instrument. Adapted figure from [16].](image-url)
The desired value is $V_S$ due to the current $I$. With it, a formula for the resistivity can be derived \[17\]. As $R_M$ is much higher than $R_s$, $I_1 \gg I_2$. Thus,

$$I = I_1 + I_2 \approx I_1$$
$$R_S I \approx R_S I_1$$
$$V_S = R_S I_1 = (R_{C2} + R_M + R_{C3}) I_2 \approx R_M I_2 = V_M$$

In most of the 4-point probes measurements, the probes are in a straight line on the sample. However, in the following subsection it will be shown a special distribution of the probes called the Van der Pauw configuration.

Van der Pauw’s resistivity theorem

Van der Pauw stated that the resistivity of a flat sample of arbitrary shape can be measured without knowing the current pattern if the following conditions are fulfilled \[17\]:

1. The contacts are at the circumference of the sample.
2. The contacts are sufficiently small \(^1\).
3. The sample is homogeneous in thickness.
4. The surface of the sample is singly connected, i.e., the sample does not have isolated holes.

The demonstration of this theorem was published by Van der Pauw and is developed in the appendix A.

The measurement works as follows: Considering we have a sample fulfilling the above mentioned conditions, with the four contacts consecutively named as A, B, C and D, we define $R_{AB,CD}$ as the potential difference $V_D - V_C$ between the contacts C and D per unit current between A and B (current entering the sample through contact A and leaving it through contact B). Similarly, we define $R_{BC,DA}$. It is shown in the appendix A that the following relation holds:

$$e^{-\pi d R_{AB,CD}/\rho} + e^{-\pi d R_{BC,DA}/\rho} = 1 \quad (3.2)$$

Where $\rho$ is the resistivity of the material and $d$ is the thickness of the material. As explained before, the expressions for the “resistances” are:

$$R_{AB,CD} = \frac{V_{CD}}{I_{AB}}$$
$$R_{BC,DA} = \frac{V_{DA}}{I_{BC}}$$

The most common form of expressing equation 3.2 is shown below. It can be obtained doing simple algebra (i.e. by doing a change of variables and expressing the exponentials by means of the hyperbolic cosine) \[18\].

$$\rho = \frac{\pi d}{\ln 2} \frac{(R_{AB,CD} + R_{BC,DA})}{2} \frac{1}{f \left( \frac{R_{AB,CD}}{R_{BC,DA}} \right)} \quad (3.3)$$

\(^1\)The last section of his paper provides an approach to estimate the relative error considering the dimensions of the contacts and the sample. It is explained below.
Where \( f \) is a function of the ratio \( R_{AB,CD} / R_{BC,DA} \) which satisfies:

\[
\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} = f \arccosh \left\{ \frac{\exp (\ln 2 / f)}{2} \right\} \tag{3.4}
\]

\[
\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} = f \arccosh \left\{ \frac{\exp (\ln 2 / f)}{2} \right\} .
\]

**Figure 3.4**: Function \( f \) plotted given the ratio \( \frac{R_{AB,CD}}{R_{BC,DA}} \). Figure extracted from [17].

Measurements can get a bit simpler if the sample has an axis of symmetry. In such case, if two contacts are placed on it, and the other two are placed symmetrically with respect to this line (figure 3.5 pictures this configuration), then:

\[
R_{AB,CD} = R_{BC,DA} \tag{3.5}
\]

Thus, one measurement is sufficient to obtain the resistivity [18]. This can be easily seen recalling the reciprocity theorem, where \( R_{BC,DA} = R_{DA,BC} \). On the other hand, thanks to the line of symmetry, \( R_{DA,BC} = R_{AB,CD} \). Thus the relation 3.5 is obtained.
This result assumes "sufficiently" small contacts located at the periphery of the sample. The unfulfillment of this conditions gives an error that can be estimated thanks to some expressions provided by Van der Pauw [17].

Considering a circular disc of diameter D and one of the four contacts to be non-ideal in dimension and location, the relative error that can be expected from the measurement is shown in figure 3.6. It is expressed as a function of the dimension of the contact in the direction of the periphery ($a$) and in the direction perpendicular to the periphery ($b$), as well as its misplacement from the border ($c$).
Having more than one non-ideal contact leads to the addition of the error for each of them. This result will be used as an approximation in the measurements of square samples although it is stated for a circular disc. By conformal mapping\(^2\), this relations can lead to obtain the error for a square sample. It has been demonstrated theoretically and experimentally that square samples achieve improvements over circular samples [19], that is, that the common expressions from figure 3.6 underestimates the relative error.

3.2.3 Van der Pauw’s resistivity measurement

Before implementing the Van der Pauw’s measurements in the photoconductivity setup, resistivity measurements were performed on a crystalline Ge wafer of 525 \(\mu m\) of thickness. The proposed structure for contacting was tested on multiple samples cut in different shapes and sizes. The change in resistivity under illumination was also investigated. The reason why a crystalline Ge wafer is used in this section is that is a known material that will have a similar behaviour as GeSn. Thanks to its good quality, the study can be focused on the optimization of the measurement.

The instrument coupled to the setup to do the measurement is a Keithley SourceMeter, capable to provide either voltage or current, and measure at the same time. It has four connections, two for the source and two for sensing. For this reason, it is the ideal instrument for making four-point measurements.

To contact the sample, small silver paste droplets are deposited at the edge of it after doing a little scratch with a diamond tip to remove the native oxide, which otherwise would have insulated the sample. Then, four probes connected to the SourceMeter are contacted on the silver paste as shown in figure 3.7.

For this first approach, the values given by the SourceMeter are entered manually to a Matlab program to obtain the resistivity. This Matlab function provides a precise value of the resistivity, as it includes the calculation of the correction factor \(f\) from 3.4. The transcendental equation is solved by means of the Newton method.

As shown in a previous subsection 3.2.2, non ideal contacts for Van der Pauw measurements come with an error associated with the relative dimensions between the contacts and the sample. This will be kept in mind while presenting the next results.

\(^2\)The conformal mapping theorem is enunciated and used in appendix A
A study is required in order to understand the effect of the incident beam shape and of the magnitude of the current applied at the sample. The following subsections will show the development of this study.

In order to have a general overview on the behaviour of the samples, they have been subjected to full spectrum illumination instead of just sending single IR wavelengths. With this, more power is reaching the samples and we can obtain a more clearer response.

The choice of the current magnitude is in principle very broad. The only important things to take into account are that the dissipated power should not be too high to not heat the sample (less than 5 mW [20]), and the generated voltage has to be inside the resolution range of the measuring instrument. As this gives a large amount of possibilities, few different values for the current have been applied in every trial.

**Validation of Van der Pauw’s configuration**

First, it was important to know if the measurements obtained with this configuration gave in the practice a reliable result. For this, an accurate value for the resistivity of the sample in the dark can be obtained by the 4-point resistometer KLA TENCOR - OMNIMAP RS75, available in the Center of Microtechnology, EPFL. Forty measurements were done along the wafer, and a value of 52.1 $\Omega \text{cm}$ was obtained for a piece of crystalline Ge wafer, with a variation of $\pm 1.8\%$. As from the specifications of the instrument, the error is $\pm 1\%$, the Ge wafer showed to not be perfectly homogeneous.

After, the wafer was cleaved in a $1\text{cm}^2$ square and contacted to do a Van der Pauw resistivity measurement in the dark with our setup.

Three different currents were applied to obtain the resistivity. The results are shown in table 3.1.

<table>
<thead>
<tr>
<th>Current [mA]</th>
<th>Resistivity $[\Omega \text{cm}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \mu A$</td>
<td>47.1</td>
</tr>
<tr>
<td>$100 \mu A$</td>
<td>47.7</td>
</tr>
<tr>
<td>$10 \mu A$</td>
<td>50.9</td>
</tr>
</tbody>
</table>

**Table 3.1**: Resistivity values obtained with our setup with the Van der Pauw configuration.

Table 3.1 shows that different currents provide slightly different resistivity values. The average of this values gives $48.5\Omega \text{cm}$, with a relative error of 4.9%. This range does not enter inside the error bar of the presented resistivity measurement obtained with the resistometer. Hence, the sources of error need to be considered.

As seen in the previous section, the error due to non-ideal contacts can be estimated by 3.6. Table 3.2 shows the approximate dimensions of the four contacts present in the sample, defined as explained in figure 3.6. Taking the dimensions of the sample contacts, it can be obtained that the error due to the size and placement of the contacts can be of 2.5%.

<table>
<thead>
<tr>
<th>$l_a$ [mm]</th>
<th>$l_b$ [mm]</th>
<th>$l_c$ [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact 1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Contact 2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Contact 3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Contact 4</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Table 3.2**: Sizes of the non-ideal contacts of the $1\text{cm} \times 1\text{cm}$ Ge sample.
As the relative error between the measurements obtained is higher than 2.5%, it can be said that the non-ideality of the size and placement of the contacts is not the only present source of error. A part from the geometry, the physical contact might not be working perfectly due to imprecision with the scratch, the silver paste or the probes. In addition, most of the measurements were observed to have a settling time. It was determined manually, therefore probably introducing another source of error. Furthermore, even though the power was lower than 5mW, long measurements could have ended up heating either the sample or the metal contacts. Any type of variation in the configuration might have produced changes in the result. This shows that all the following measurements will have limited accuracy.

Shape of the incident light

An interesting thing to determine is if the sample needs to be illuminated uniformly or if the light can be focused in a point, which would be the easiest option.

Wide and uniform illumination is a difficult thing to put in practice, as if the beam is spread, there is a higher chance to lose light illuminating areas outside the sample surface.

The results of the effects of the incident beam are summarized in Table 3.3. The resistivity of the sample was first measured in dark conditions (Dark). The measurements were done on a 1cm² square crystalline Ge coming from a different wafer than in the previous section. This is the reason why the resistivity values in the dark differ a bit from the ones shown in Table 3.1.

Second, with the help of the micropositioners, the sample was placed such that the light was focused in its center (Focused, Centered). After, it was slightly moved in order to have the focused light near one of the sample’s edges (Focused, Decentered). Finally, back with the light in the center, the height of the sample was modified to have a wider illumination spot, still keeping all the light in (Wide, centered).

Point illumination induces in the sample an inhomogeneous distribution for the resistivity. In such cases, the Van der Pauw measurement is demonstrated to give the average, i.e. the result of the integral of the resistivity through the surface of the sample [21]. As the desired quantity to take into account is all the photogenerated charge carriers along the surface, it is concluded that the Van der Pauw measurement can still work with non-uniform resistivities and can be applied to 3.1 to obtain the photoconductivity.

To obtain higher accuracy, the two voltage measurements required to obtain the resistivity with equation 3.3 have been averaged with their respective symmetrical. That is, 4 measurements have been done for each shown resistivity value ($R_{AB,CD}$ should equal to $R_{CD,AB}$, and $R_{BC,DA}$ should equal to $R_{DA,BC}$).
Chapter 3. Calibration and measurements

Resistivity $[\Omega \text{cm}]$ for different illumination situations

<table>
<thead>
<tr>
<th>Current $[\mu \text{A}]$</th>
<th>Dark</th>
<th>Wide, Centered</th>
<th>Focused, Centered</th>
<th>Focused, Decentered</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mA</td>
<td>44.2</td>
<td>27.6</td>
<td>28.9</td>
<td>34.4</td>
</tr>
<tr>
<td>100 $\mu \text{mA}$</td>
<td>44.8</td>
<td>27.4</td>
<td>29.1</td>
<td>35.2</td>
</tr>
<tr>
<td>10 $\mu \text{mA}$</td>
<td>46.3</td>
<td>27.4</td>
<td>29.1</td>
<td>35.6</td>
</tr>
</tbody>
</table>

**Table 3.3:** Resistivity comparison between dark, wide illumination, centered point and decentered point.

<table>
<thead>
<tr>
<th></th>
<th>$l_a$ [mm]</th>
<th>$l_b$ [mm]</th>
<th>$l_c$ [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact 1</td>
<td>1.5</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>Contact 2</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Contact 3</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Contact 4</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Table 3.4:** Sizes of the non-ideal contacts of the 1cm x 1cm Ge sample.

The first thing that one should notice is that the decrease in resistivity between the dark and illumination conditions can be detected.

Focused light *centered* and *decentered* show different values of resistivity between each other although the amount of light reaching the sample was the same. The generation of charge carriers out of the center of the sample implies that some of them have to travel more to reach the contacts. Recombination is more likely to happen, leading to not read all the photogenerated carriers at the voltage probes and thus obtaining higher resistivity. In addition, as in the *decentered* case the charges are generated close to the edge of the sample, surface effects might influence them more than when the generation is in the center of the sample. In the surface, there is a deviation of the perfect periodicity of the lattice. Therefore, energy states in the bandgap become added recombination centers, reducing the lifetime of free charge carriers.

Looking now at the results for *wide* and *focused centered* illumination, one can conclude that the size of the illumination surface, as long as the same amount of light is reaching the sample, does not significantly affect on the measured resistivity. This could be understood thinking that the shape of the illumination doesn’t matter if the photogenerated carriers can be collected through the contacts.

**Shape of the sample**

Van der Pauw’s resistivity theorem is demonstrated to work for any shape of the target. As this might not be intuitive, some measurements to a lamella of random shape as shown in Figure 3.8 have been done and summarized in table 3.5. The sample’s shape reminds of a triangle (of around 5.28 $cm^2$), which then has been cut in a triangle as well, but smaller (of around 0.65 $cm^2$).
**Figure 3.8:** Van der Pauw measurement on a lamella of random shape

<table>
<thead>
<tr>
<th>Current applied</th>
<th>Big &quot;triangle&quot;</th>
<th>Small &quot;triangle&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dark</td>
<td>Light</td>
</tr>
<tr>
<td>1mA</td>
<td>44.2</td>
<td>41.9</td>
</tr>
<tr>
<td>100 μmA</td>
<td>48.0</td>
<td>42.9</td>
</tr>
<tr>
<td>10 μmA</td>
<td>45.7</td>
<td>41.6</td>
</tr>
</tbody>
</table>

**Table 3.5:** Resistivity comparison between different shapes of the sample.

The resistivity values in the dark (Big "triangle", Dark and Small "triangle", dark) are around the ones found in table 3.3. This result was expected as the material was the same, proving that the sample shape does not have an influence on the measurement.

Regarding the change under light (Big "triangle", Light and Small "triangle", Light), there are some variations. The resistivity shows a very small change between light and dark in the larger sample, probably because the carriers recombine before reaching the contacts due to its large size. The small sample shows that the light can be similarly collected as it was with symmetric samples.

It can be noticed that the resistivity under light for the Small "triangle" Light is around 23Ωcm whereas the resistivity under light of the square sample is around 27.5Ωcm. This might be because the square sample undergoes more recombination as it is larger than the small triangle (recall that the square has a surface of 1cm² and the small triangle has 0.65cm²).

**Size of the sample to enhance carrier collection**

The aim is to obtain the change in resistivity as a function of the incident wavelength and optical power. Monochromatic light has been shone in order to see if it could result in a measurable change in resistivity even with low power.

A 1cm² square sample has been measured under light of 1400nm, as it is known to have high absorption in Ge [22]. The results are shown in table 3.6. As it was
found to not be able to measure a clear change in resistivity, the previous experiments suggested that smaller samples could give a better performance. The same wafer was diced in 3mm squares, which were subjected to 1400nm light. The resistivities obtained are shown in table 3.6.

<table>
<thead>
<tr>
<th>Current applied</th>
<th>Resistivity [Ω cm]</th>
<th>1 cm square</th>
<th>0.3 cm square</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dark</td>
<td>Light</td>
<td>Dark</td>
</tr>
<tr>
<td>1mA</td>
<td>45.5</td>
<td>45.2</td>
<td>39.1</td>
</tr>
<tr>
<td>100 µm</td>
<td>46.7</td>
<td>46.3</td>
<td>43.4</td>
</tr>
<tr>
<td>10 µm</td>
<td>48.2</td>
<td>47.6</td>
<td>45.3</td>
</tr>
</tbody>
</table>

**Table 3.6**: Resistivity comparison between different sizes of the sample under monochromatic light of 1400 nm.

The change in resistivity due to incident light is rather small. However, this reduction of the response is expected as the incident power is much lower with respect to the broadband illumination. As long as a change in the resistivity is measured, the characterization can be performed, as it will take into account the incident power to make a fair comparison between the response under different incident wavelengths.

For the case of 0.3 cm square, the difference is slightly clearer. This may show that to enhance charge carriers collection, smaller samples can be used. We conclude that for the present incident power, smaller samples than the ones tested here should be measured in order to see if there can be more collection. Still, one should consider that the smaller the sample, the higher the errors due to non-ideal contacts. This can be seen in the disagreement between different applied currents of this last measurements, and suggests that another method to contact the sample might be required. Some options can be by means of microprocessing techniques such as lithography and deposition in the Center of MicroNanotechnology.

An interesting thing to pay attention on when analyzing all the results so far, is that the increase in applied current, i.e. in voltage through the contacts, does not intensify significantly charge carrier’s collection even after probing that not all the photogenerated carriers are being collected. This behaviour is not very well explained as the intuition would say that the higher the voltage difference, the more the carriers can travel.
Chapter 4

Overview and outlook

A setup to measure photoconductivity for the IR range has been built and characterized, with a careful study on the impact of every component in order to optimize its performance. With the help of a reference photodiode, the optical part of the setup has been proved to work successfully after the use of an iris to decrease the effect of having a non-ideal point light source.

As future measurements need to be done to semiconductor samples, a method to contact them and extract their response under illumination has been investigated and probed. Van der Pauw’s 4-point probes resistivity measurements have been done with and without light to quantify the change in resistivity of crystalline Ge wafers.

The study has shown that the resistivity in dark conditions can be obtained if the contacts on the sample are sufficiently small in relation with the sample size. As predicted, the shape of the sample does not affect the measurement. However, a comparison with a known value of the resistivity in the dark shows that for the moment, the configuration has various sources of error. On one hand, the size, shape and placement of the contacts give an error that can be predicted with Van der Pauw’s theorem. On the other hand, practical limitations such as physical bad contact or imperfect electrical connections may increase the error bar, as well as the heating of the sample.

The change in resistivity can be measured successfully if the incident optical power is sufficiently high. The smaller the sample, the easier it is to collect the photogenerated carriers as less recombination takes place. Thus, for lower incident power, smaller samples seem the only solution to characterize the change in resistivity.

With the measurements done so far, the optimal configuration to collect all the photogenerated charge carriers has not been found. Nevertheless, it is suspected that the collection of charge carriers is strongly related to the size of the sample. Thus, the near future work will consist on fabricate smaller samples with proper contacts and try to measure their change in resistivity under monochromatic light. On the same time, the incident power should be recorded, and research should be done to find a reliable photoconductivity curve of Ge and match both results.

From the results obtained, it can be thought that a spectral response will be difficult to obtain, as the low power induces a small change in resistivity that might be lost inside the total error bar of the measurement. A solution that has started to be studied is the implementation of a lock-in amplifier in the electrical circuit. This instrument is capable to extract a signal of known frequency from an extremely noisy environment.
After the study of the measurements and optimization of the configuration, a Labview code to make a scan of wavelengths and store the data at each step will be necessary to obtain the spectral response of the sample. In concrete, the code used at the beginning of the project needs to be adapted to the 4-point probe resistivity measurement.
Appendix A

Demonstration of Van der Pauw’s resistivity theorem

This appendix will explain a demonstration published by Van der Pauw in [17] and [18] for the formula 3.2. Finding this measurement technique very elegant and the original paper lacking some details, I decided to understand it better by developing the demonstration by myself. The demonstration starts showing that it holds for a particular shape of a conducting lamella, and it follows demonstrating that this implies that it will hold for any shape of the sample.

Consider an infinite lamella, with thickness $d$ and resistivity $\rho$. At a point M we apply a current $2i$, that spreads radially. Thus, through the lamella there is a current density of

$$J = \frac{2i}{2\pi rd} \quad (A.1)$$

which at the same time, thanks to Ohm’s Law, there is an electric field with the same direction.

$$E = \rho J = \frac{\rho i}{\pi rd} \quad (A.2)$$

If we consider two points O and P aligned with M, as in figure A.1, we can easily obtain their potential difference due to the current at M:

$$V_P - V_O = \int_P^O Edr = \int_P^O Edr = \frac{\rho i}{\pi d} \int_P^O \frac{dr}{r} =$$

$$V_P - V_O = \frac{\rho i}{\pi d} \ln \frac{a+b+c}{a+b} \quad (A.3)$$
Appendix A. Demonstration of Van der Pauw’s resistivity theorem

Figure A.1: Graphical support for the derivation of formula 3.3. Figure extracted from [18].

In fact, the infinite lamella can be cut by this straight line and one side of it can be omitted, keeping a half infinite plane: as no current flows across this line, the result of \( V_P - V_O \) remains the same, but with the total intensity divided by two.

Consider now a point N with a current \( i \) flowing out, located as in figure A.1 c). The difference of potential between O and P due to this current can be obtained with the same procedure, leading to

\[
V_P - V_O = +\frac{\rho i}{\pi d} \ln \frac{b + c}{b} \tag{A.4}
\]

Having current entering at M and flowing out at N generates a potential difference between O and P that can be obtained, by the superposition principle, adding the two previous results:

\[
V_P - V_O = +\frac{\rho i}{\pi d} \ln \frac{(a + b)(b + c)}{(a + b + c)b} \\
R_{MN,OP} = \frac{\rho}{\pi d} \ln \frac{(a + b)(b + c)}{(a + b + c)b} \\
\frac{(a + b + c)b}{(a + b)(b + c)} = \exp \left(-\frac{\pi d}{\rho} R_{MN,OP} \right) \tag{A.5}
\]

Easily you can obtain the expression for the case where current flows in at N and out at O:

\[
\frac{ac}{(a + b)(b + c)} = \exp \left(-\frac{\pi d}{\rho} R_{NO,PM} \right) \tag{A.6}
\]

Adding A.5 and A.6 one directly obtain 3.2, as

\[
\frac{(a + b + c)b}{(a + b)(b + c)} + \frac{ac}{(a + b)(b + c)} = ab + b^2 + bc + ac \\
\frac{ab + ac + b^2 + bc}{ab + ac + b^2 + bc} = 1
\]
Appendix A. Demonstration of Van der Pauw’s resistivity theorem

Recall that this expression will give us the resistivity of a semi infinite sample, which is not, of course, of our interest. However, it is proved by the theory of conformal mapping that this relation holds for a general shape.

The Riemann mapping theorem states that if \( D \) is a simply connected\(^1\) non-empty open domain of the complex plane, and \( D \) is not the entire complex plane, then there exists an holomorphic\(^2\) and bijective function, known as the conformal map, mapping \( D \) onto an open unit disc. This two domains are called to be conformally equivalent [23]. The use of this theorem is what justifies why the sample has to fulfill the conditions imposed in the formulation of the theorem, seen in section 3.2.2.

Assume that our semi infinite sample coincides with the upper half complex \( z \)-plane, where \( z = x + iy \), and so the edge with points M, N, O and P is the real axis. We introduce there an holomorphic function \( f(z) = u(x,y) + iv(x,y) \), which consequently satisfies the Cauchy-Reimann equations\(^3\). \( u \) and \( v \) are real functions of \( x \) and \( y \) and \( f \) is chosen such that \( u \) is the potential field along the plane created by the current entering the sample.

Taking two random points of this semi infinite plane, the net current that traverses their path is given by the integral along the path of the scalar product between the current density and the surface vector of the cross section that the current is facing (due to the thickness of the considered sample). Thus, it is obtained that:

\[
I_{1,2} = \int_{1}^{2} \vec{J}_{1,2} \cdot \vec{S}_{1,2} = \int_{1}^{2} \frac{\vec{E}}{\rho} \cdot d\vec{s} = \frac{d}{\rho} \int_{1}^{2} \vec{E} \, d\vec{s} \tag{A.7}
\]

\[\text{FIGURE A.2: Graphical representation of integral A.7.} \quad \vec{J} \text{ is the current density due to the entering current. } \vec{S} \text{ is the surface vector that the current is traversing, i.e perpendicular to the path uniting 1 and 2.}
\]

\(^1\)Intuitively, a domain is simply connected if it has no holes. Disks are simply connected whereas annuli are not.

\(^2\)An holomorphic function is a complex function of complex variables differentiable at every point of its domain.

\(^3\)\[ \frac{\partial u}{\partial x} = \frac{\partial v}{\partial y}, \quad \frac{\partial u}{\partial y} = -\frac{\partial v}{\partial x} \]
Appendix A. Demonstration of Van der Pauw’s resistivity theorem

The electric field can be expressed using the divergence of the potential function \( \vec{E} = -\vec{\nabla} V \), thus \( \vec{E} = -\vec{\nabla} u \) and the Cauchy-Reimann equations for \( f(z) \). The surface unitary vector can be expressed as \((-dy, dx)\) thanks to its orthogonality with the curve. Hence:

\[
\vec{E} \cdot d\vec{s} = \left(-\frac{\partial V}{\partial x}, -\frac{\partial V}{\partial y}\right) (-dy, dx) = \frac{\partial u}{\partial x} dy - \frac{\partial u}{\partial y} dx = \frac{\partial v}{\partial x} dx + \frac{\partial v}{\partial y} dy
\]

Therefore,

\[
I_{1,2} = \frac{d}{\rho} \int_{1}^{2} \left(\frac{\partial v}{\partial x} dx + \frac{\partial v}{\partial y} dy\right) = \frac{d}{\rho} (v_2 - v_1) \quad (A.8)
\]

This equation shows that, for example, if one travels from two points lying on the real axis at the left side of M, the function \( v(x, y) \) will remain constant as no net current is traversing this path \( \vec{E} \cdot d\vec{r} = 0 \) as they will be parallel, so \( I_{1,2} = 0 \) and \( v \) at 1 equals \( v \) at 2. But when passing through M, the function \( v \) will increase by \( 1 \rho / d \), and when passing through N will increase by \(-1 \rho / d\), as around this points all the current flowing traverses the path. A graphic description is showed at figure A.3.

![Graphical description of integral A.8. Current entering at M and creating a radial electric field at the sample.](image)

Keeping this result in our minds, we consider now a sample of arbitrary shape lying in another complex plane \( t - \text{plane} \), where \( t = r + is \). By the conformal mapping theorem, it is possible to find an analytic function \( t(z) \) such that the previous upper half plane is mapped onto the sample just introduced. We can obtain then A, B, C and D, images of the points M, N, O and P. Furthermore, we can also obtain a function \( k(t) = l + im = k(t(z)) = f(z) \) equivalent to the previous one. Thus, when evaluated at the same respective points they give the same result.
Therefore, when traveling along the boundary of the sample in the \( t - \text{plane} \), \( m \) remains constant until it reaches \( A \), where it will increase by \( I \rho / d \), and so on (figure A.4). Consequently, if we choose a current \( I' \) to enter at \( A \) and leave at \( B \), and a thickness and resistivity of the sample \( d' \) and \( \rho' \) such that \( I \rho / d = I' \rho' / d' \), we have

\[
v_2 - v_1 = m_2 - m_1 = \frac{I \rho}{d} = \frac{I' \rho'}{d'}
\]

Thus,

\[
l' = \frac{d'}{\rho'} (m_2 - m_1) = \frac{d'}{\rho'} \int_1^2 \left( \frac{\partial m}{\partial r} dr + \frac{\partial m}{\partial s} ds \right) = \frac{d'}{\rho'} \int_1^2 \left( - \frac{\partial l}{\partial s} dr + \frac{\partial l}{\partial r} ds \right)
\]

As \( l \) represents the potential in the sample of arbitrary shape due to the current \( I' \) entering at \( A \), and \( l \) is equivalent to \( v \), \( V_D - V_C = V_P - V_O \). Hence, it can be obtained that \( (R_{AB,CD} d'/\rho') \) remains invariant under conformal transformation:

\[
\rho d \left( R_{AB,CD} + R_{BC,DA} \right) = \frac{\rho}{d} R_{AB,CD} + \frac{\rho}{d} R_{BC,DA} = \frac{\pi f}{2 \ln 2} = \frac{\rho'}{d'} R_{MN,OP} + \frac{\rho'}{d'} R_{NO,PM}
\]
Bibliography


