Photoinduced transport in magnetic layered structures

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Chapter 1

Introduction

After the discovery of the magnetism of lodestone by the ancient Greeks, magnetism was initially seen as a kind of “magic” phenomenon, which had no real use in daily life. The invention of the compass by the Chinese around 1000 A.D. can be regarded as the first real application of magnetism in a practical device. However, not until the great physicists in the 19th and 20th century a full explanation of the effect had been found. Nowadays, magnetic devices cannot be thought away from our daily lives. For example, the computer industry makes use of harddisk recording as the primary medium for large scale data storage. In the past, inductive sensors have been used to transform the magnetically stored data back into an electrical signal. Due to the arrival of new magnetoresistance materials, this readout process is nowadays carried out with improved speed and accuracy, leading to higher data densities.

Magnetoresistive elements are an example of the broader field of spintronics, which we will introduce in this chapter. One of the most promising structures for applications are so-called magnetic tunnel junctions, first discovered in 1995. Certain properties that are inherent to these devices, make them ideal candidates as new non-volatile memory elements, called MRAMs. As discussed in section 1.2, they are regarded as a possible replacement for conventional mainstream memory technologies. As an added advantage, they retain the information even without application of electrical power, e.g. making slow start-up times of a personal computer something of the past. In this thesis we will focus on several issues that are important for the applicability of these junctions in MRAM-like structures. For the first time we use a photoconductance technique, to study the electron transport in magnetic tunnel junction structures in more detail. After the technique is introduced, this chapter is rounded off by discussing the contents of the thesis.

1.1 Spintronics

Magnetism finds its origin in the angular momentum of an electron moving around the nucleus of an atom, as well as in its intrinsic angular momentum. The latter effect is called the spin of the electron. Uhlenbeck and Goudsmit in 1925 [1] suggested
Chapter 1. Introduction

Figure 1.1: Schematic drawings of a magnetic tunnel junction, illustrating the difference between parallel and antiparallel magnetizations of the two magnetic electrodes, illustrated by the vertical arrows. B represents the tunnel barrier. A parallel orientation (a) leads to a low resistive state, while an antiparallel orientation (b) induces a high resistance. The size of the horizontal arrows indicates the magnitude of the tunnel current $I$, when applying a bias voltage $V$ across the structure. This difference in conductance leads to the observed magnetoresistance effect, when switching from parallel ($P$) to antiparallel ($AP$) alignment.

that the spin of the electron can only have two distinct directions, either parallel or antiparallel to a quantization axis. These directions are designated with spin-up and spin-down, representing an angular momentum $\pm h/2$. The field which studies and exploits the spin-dependence of the electrical conductance in magnetic materials and devices is called magnetoelectronics or spintronics.

One of the first applications of spintronics has been in the form of so-called magnetoresistive devices [2]. The conductance of these structures depends critically on the applied magnetic field. Since the discovery of the giant magnetoresistance (GMR) effect in Fe/Cr multilayers in 1988 [3, 4], and later in many other types of magnetic multilayers, these structures have already found their way into commercial read-heads for harddisk recording.

Another magnetoresistance device, one we would like to focus on in this work, is the magnetic tunnel junction (MTJ). Although the functioning of the structure is similar to that of a GMR element, the underlying physics are completely different. In a magnetic tunnel junction, two magnetic electrodes, typically consisting of Co, Ni, Fe or their alloys, are separated by a 1-3 nm thin insulating layer. When applying a bias voltage across the insulator a small tunnel current will flow between the two electrodes (see Fig. 1.1). Already in the 1970s Tedrow and Meservey found, with the use of superconductor tunneling experiments, that the tunnel current in junctions containing one ferromagnetic electrode is spin-dependent [5]. They determined the spin-polarization of the ferromagnet by using the native oxide of a superconducting metal (in their case aluminum) as the tunnel barrier. To use this tunneling spin-polarization in a room-temperature operating magnetoresistive device, both electrodes need to be ferromagnetic. The tunnel probability will then depend on the relative magnetization of the two layers, resulting in a (high) low resistance when the two layers (assumed here to be identical) are magnetized (anti) parallel [see Fig.
1.1(a) and (b)].

However, the growth of a thin high quality insulator on top of another (ferromagnetic) material proved to be much more difficult. It took till the middle of the 1990s until a suitable method had been developed, to realize such structures. In 1995 Moodera et al. at MIT succeeded in realizing MTJs with a sizable magnetoresistance ratio ($\sim 20\%$) at room temperature, using Co and Ni$_{80}$Fe$_{20}$ as the electrodes and AlO$_x$ as the tunnel barrier [6]. To fabricate the tunnel barrier, he first deposited a thin Al metal layer, which was afterwards oxidized in a plasma environment. Up to now this method has proven to be the most suitable technique in forming thin high quality tunnel barriers.

Since then a lot of groups followed these initial experiments and worked towards optimizing the properties of MTJs, to make them suitable for device applications. In subsequent years, the observed MR effect at room-temperature in AlO$_x$ based MTJs has steadily increased to the current record of $\sim 70\%$ [7]. Since the MR effect is (in a wide thickness range) independent of the resistance, which is controlled by the barrier thickness (and height), developers are given an additional parameter of freedom. However, as we will see in the next section, the use of thinner barriers, to reduce the electronic noise and make downscaling possible, imposes high demands on the quality of the insulating barrier layer.

1.2 Magnetic RAM

As already discussed before, magnetoresistive structures have already found their way into read heads for the hard disk industry. However, besides as a magnetic field sensor, the structures can also be utilized as memory elements. Making use of its hysteresis, information can be stored in the magnetization direction of a thin layer. This implies that the information is retained, even when the electrical power is off, also known as nonvolatility. For a system containing two magnetic layers, two magnetization states can be realized: parallel or antiparallel. This means that a binary storage element or bit can be realized. The magnetoresistance effect can then be utilized to read out the information. Such memory devices are called magnetic random access memories or MRAMs [8]. Although in the past also GMR structures have been studied as storage elements, nowadays this field is completely governed by magnetic tunnel junctions (MTJs), ordered in a matrix like structure.

As illustrated in Fig. 1.2(a), each MTJ in a MRAM structure consists of a fixed reference layer and a magnetically switchable storage layer,\(^1\) positioned between two orthogonal metal lines: the bit line and the word write line. When applying currents through both lines, the induced magnetic fields $H_1$ and $H_2$ add up at the cross point, which is sufficient to change the magnetization of the storage layer. In this way a bit of information can be written. To read out a bit, a sense current is sent from the bit line, through the junction, to the word read line, after which the resulting voltage drop is measured. To overcome the problem of leakage currents through

\(^1\)Several schemes exist to accomplish this. The reader is referred to [2] for an overview of these techniques.
Chapter 1. Introduction

Figure 1.2: (a) Cross-section of the layer stack in a MRAM structure, and (b) a representation of MTJs arranged in a $2 \times 2$ matrix structure. By applying currents through the perpendicular bit and word-write lines, the induced magnetic fields $H_1$ and $H_2$ add up at the cross point, so that the field is high enough to switch the storage layer. The selection transistor is used for reading out a particular junction with the magnetoresistance effect, using a sense current from the bit line.

parallel junctions, a selection transistor is often positioned in series with the MTJ. This assures that upon readout, only current flows through the selected junction.

MRAM has the advantage that it combines several aspects of different memory types which are currently available [9]. It has the non-volatility of Flash, without the high voltage requirements, and without the limited endurance. It is expected to be scalable to higher bit densities. The read and write speeds are competitive to all but the fastest SRAMs, while the density is comparable to embedded DRAM, but without a destructive readout. Although also other emerging memory types are proposed, like phase-change or ferroelectric based memories, MRAM has good potential to become competitive in the near future. In view of the potential advantages, several companies are investing into the development of MRAM. Although Motorola has recently shown the industry’s first 4 Mbit demonstrator [10], others are competing strongly, most notably the IBM/Infineon partnership.

The first MRAM products are expected to become available at the end of 2004. However, the development of future MRAMs with even higher bit densities requires that several issues, relating to the fabrication, structure and functioning, still need to be addressed. For example, the scaling of MTJs to below lateral sizes of $\sim 100$ nm requires sufficient control over the oxidation process to create ultrathin and smooth barrier layers, without parasitic conductance paths that would lead to a reduced MR ratio. For extreme small thicknesses alternative barrier materials might be needed. As the lateral dimensions of the structures decrease, the current density required for switching will increase, while the thermal stability decreases. Several of the above issues will be discussed in this thesis, making use of a study of the photoconductance of MTJs.
1.3 Photoemission and photoconductance

Throughout this thesis we use photoconductance as a characterization tool for magnetic tunnel junctions. Photoconductance results from internal photoemission, an effect that arises when a junction is irradiated with light. Before discussing this effect in more detail, we first discuss the more well-known external photoemission effect. External photoemission is the process of electron ejection from a material into the vacuum, under the absorption of photons. Already at the end of the 19th century the latter effect was known. The most striking characteristic of this effect is that below a certain frequency, or above a certain wavelength, no electrons are emitted, independent of the intensity of incident light. From a classical viewpoint, this can not be explained.

In 1905 Einstein proposed a simple explanation of the effect [11]. He postulated that a beam of light can be viewed as a stream of particles, called photons, each having an energy equal to $h\nu$ (with $h$ representing Planck's constant, and $\nu$ the frequency of the light). With this he explained the observed photoelectric effect, because below a certain frequency the photons simply do not have enough energy to eject an electron from the material. Only when the energy of the photon exceeds a minimum energy, the workfunction, an electron can be freed from the material. Already since the experimental observation by Hertz in 1887 [12], photoemission has been used to study in detail the workfunction as well as the electronic structures of the valence band, and of core levels of materials. Among other things, this has greatly improved the knowledge on the bandstructures of various materials.

Besides at the outer surface, the interface with the vacuum, an energy barrier can also exist inside a layered material stack. For example, in a MTJ the bottom of the conduction band of the insulating barrier layer lies significantly above the Fermi-level in the adjacent magnetic layers. Since electrons are classically forbidden to travel through the insulator bandgap, an energy barrier is present. By illuminating such a structure with light with a photon energy which is below the workfunction of the metallic top electrode, no electrons will be ejected into the vacuum. However, when the photon energy is higher than the internal barrier height, electrons are able to cross the insulating layer. In devices in which the electrodes are short-circuited by external leads, this internal photoemission process can give rise to photoconductance, an effect that can be used to study the transport of “hot” photoexcited electrons, and with that the nature of the electronic barrier.

1.4 This thesis

Throughout this thesis, photoconductance in magnetic thin films plays a central role. The technique is primarily used to study issues that affect the applicability of magnetic tunnel junctions in devices such as MRAMs.

In chapter 2 a theoretical background is given on both spin-dependent tunneling as well as the photoconductance process. In later chapters, calculations based on the discussed models will be used to better understand the experimental results. A large amount of work was put into constructing an experimental setup with which
photoconductance experiments could be carried out on specific MTJs. In chapter 3 a detailed description of the setup, as well as of the techniques used to fabricate the junction structures is given. Chapter 4 provides basic insight in the possibilities of the technique to better understand the nature of the barrier, and the transport of hot electrons through the electrodes and the barrier. We focus in this chapter on standard junctions based on AlO$_x$ barriers, i.e. structures which are relevant to the development of MRAMs.

The following chapters describe the bulk of the experimental work, where photoconductance is used to better understand the transport properties in MTJ structures. In chapters 5, 6, and 7 the oxidation process, possibilities of using TaO$_x$ as an alternative barrier material, as well as an anneal treatment are studied respectively. In the last chapter the possibilities of exploiting the phenomenon of photoconductance are further explored, and a new spintronic device is proposed. It should show a photocurrent that depends critically on the relative magnetization of the internal magnetic structure. This shows that besides as a characterization tool, photoconductance can also be used to create novel structures with interesting properties.
A tunnel junction structure essentially consists of two electrodes separated by a thin insulating layer. The insulator serves as an energy barrier for the electrons in the electrodes. The conductance of such a structure is due to quantum-mechanical tunneling. During the 1960s and 1970s internal photoemission studies were recognized as an important tool for investigating energy barriers in thin-film sandwich structures, containing non-magnetic electrodes [13]. With the use of simple models, information on barrier height and shape could readily be extracted. Conceptually, the technique is quite simple (see Fig. 2.1): one shines monochromatic light onto a junction structure, and measures the resulting photocurrent. The incident photons will excite electrons in the electrodes, gaining an amount of energy equal to the photon energy. When the final state electron energy with respect to the Fermi level $E_F$ is higher than the internal barrier height $\phi$, some of the electrons will be able to enter the conduction band of the insulator. After leaving the barrier at the other side,

![Energy diagram illustrating the internal photoemission process. $E_F$ represents the Fermi energy, $h\nu$ the photon energy, and $\phi$ the barrier height.](image-url)
they will fall back to the Fermi level, due to various de-excitation processes. A net photocurrent results when the opposite contributions from the two electrodes do not cancel each other. From the onset of this current as a function of the photon energy $h\nu$, the barrier height can be accurately determined. In this thesis results of the first application of this technique to magnetic tunnel junctions (MTJs) are given.

In this chapter a more detailed picture of the photoconductance process will be presented. It will be shown that the interpretation of photocurrent curves is not always as trivial as it might seem. But first of all, a section describing the spin-polarized tunnel process, which gives rise to the “dark” conductance of magnetic tunnel junctions, will be presented.

### 2.1 Spin-polarized tunneling

The perpendicular conductance through thin metal/insulator/metal (MIM) junctions, is due to tunneling. This is a quantum-mechanical phenomenon, in which the electrons that impinge on the barrier have a finite probability to cross the insulating gap between the two conducting surfaces. The transmission probability $T(E)$ is a function of the energy $E$, and can be calculated by matching the wavefunctions and their derivatives at each interface, and deriving the ratio of the incoming and transmitted electron flux. However, without the application of a bias voltage, no net current will flow, due to equal and opposite electron fluxes.

When a bias voltage is applied across such a structure, the Fermi level in one of the electrodes is lowered by an amount $eV$ with respect to the other [see Fig. 2.2(a)]. This will lead to electrons flowing from filled states in one electrode to empty states in the other. With the use of Fermi’s golden rule, the corresponding tunnel current is then given by:

$$J \propto \int N_1(E) f(E) N_2(E + eV) \left[1 - f(E + eV)\right] T(E) \, dE. \quad (2.1)$$

The tunnel current is proportional to $N_1(E)$ and $N_2(E+eV)$, where $N_1(E)$ and $N_2(E)$ are the densities of states at an energy $E$ with respect to a local reference level (e.g. the Fermi-level) in the first and second electrode, respectively. The Fermi-Dirac distribution functions $f(E)$ and $[1 - f(E + eV)]$ are incorporated since only tunneling can take place between occupied states in the first electrode and unoccupied states in the second electrode. An analogous expression holds for electrons crossing the barrier in the opposite direction. The net tunnel current is then the difference of these two. In the case of a rectangular or trapezoidal barrier, the transmission probability is a complex function of Airy functions and their derivatives [14]. Although we will give a rigorous derivation in section 2.2.3, the exact expression is not very practical when analyzing experimental current-voltage measurements. In practice, the Wentzel-Kramers-Brillouin (WKB) approximation is often used to simplify the expression for the barrier transmission probability [15]. This approximation is valid for potentials varying slowly on a scale equal to the wavelength of the electron. Simons made use of the WKB approximation for the barrier transmission, and a simplified free-electron model for the electrodes, to give a mathematical expression for
2.1. Spin-polarized tunneling

Figure 2.2: Energy diagrams showing (a) the decay of the electron wavefunction through a potential barrier, and (b) the difference in density of states for majority and minority electrons. $E_F$ represents the Fermi energy, $\bar{\phi}$ the effective barrier height, $\Delta \phi$ the barrier asymmetry, $V$ the applied bias voltage, and $d$ the barrier thickness.

The tunnel current as a function of applied voltage [16]. The expression is valid for (nearly) square thick and high barriers, i.e. $\kappa d \gg 1$, with $\kappa$ the inverse decay length of the wavefunction in the barrier, for electrons at an energy $\bar{\phi}$ below the bottom of the conduction band, and $d$ the barrier thickness:

$$J(V) = \frac{J_0}{d^2} \left\{ \left( \bar{\phi} - \frac{eV}{2} \right) \exp \left[ -Ad \sqrt{\bar{\phi} - \frac{eV}{2}} \right] - \left( \bar{\phi} + \frac{eV}{2} \right) \exp \left[ -Ad \sqrt{\bar{\phi} + \frac{eV}{2}} \right] \right\},$$

(2.2)

where $A = 4\pi \sqrt{2m^*_e}/\hbar$, $J_0 = e/2\pi \hbar$, $m^*_e$ is the effective electron mass in the barrier conduction band, $e$ is the absolute value of the charge of the electron, and $\bar{\phi}$ is the average barrier height. This equation is often used to fit experimental current-voltage curves of M/I/M junctions, and to extract effective barrier parameters: height and thickness. However, since in his model the barrier is approximated by a rectangular shape, the extracted (average) barrier height can differ from the maximum (real) value for more realistic (complex) barriers. An implication of the assumption of a rectangular barrier is that the current-voltage characteristics are symmetric under voltage reversal.

To incorporate the possibility to analyze asymmetric conductance curves, Brinkman et al. [17] derived the following expression by explicitly including the barrier asymmetry $\Delta \phi$:

$$J(V) = G_0 \left[ V - \left( \frac{Ae}{48} \frac{d\Delta \phi}{\bar{\phi}^{3/2}} \right) V^2 + \left( \frac{A^2e^2}{96} \frac{d^2}{\bar{\phi}} \right) V^3 \right],$$

(2.3)
where $G_0$ is the conductance at zero bias voltage, which is given by $eJ_0A\sqrt{\phi}/(2d)$ \[\exp\left(-Ad\sqrt{\phi}\right)\]. $\Delta\phi$ is defined here as the difference between the barrier height at the right interface minus that at the left interface [see Fig. 2.2(a)]. In the literature the Simmons and Brinkman models are often used to determine (average) barrier heights.

Although the two models describe the current-voltage characteristics of tunnel junctions often reasonably well, they cannot account for the spin dependence of the tunnel current. This is due to the neglect of density of states (DOS) effects. Such DOS effects have been revealed by a number of fascinating experiments on MTJs. For example, one has observed a sign reversal of the magnetoresistance (MR) ratio with bias voltage [18], oscillations of the MR with interfacial seed-layer thickness [19], as well as an influence of the electrode crystallographic structure [20]. It goes too far to further delve into these aspects here, but the reader is referred to [21] for an overview of the more fundamental aspects of spin-polarized tunneling.

For the purpose of this work, the simple Julliere model [22] is sufficient to understand the basics of spin-dependent tunneling. The model is based on the following three assumptions:

- Due to the exchange splitting in a ferromagnetic material, the energy band structures for the two spins are different [see Fig. 2.2(b)], resulting in a difference in the densities of states at the Fermi-level for majority ($N_{maj}$) and minority ($N_{min}$) spin electrons.\(^1\) The spin polarization $P$, is now defined as

\[
P = \frac{N_{maj} - N_{min}}{N_{maj} + N_{min}}. \tag{2.4}
\]

- During the tunnel process the spin is conserved. This means that the current can essentially be separated in a majority and minority spin contribution.

- The tunnel current for each spin channel is proportional to the density of states at the Fermi-level for each electrode. Using equation (2.1), and neglecting finite temperature effects, this gives for the tunnel current $I_{\uparrow\uparrow}$ and $I_{\uparrow\downarrow}$ for parallel and anti parallel magnetizations, respectively:

\[
I_{\uparrow\uparrow} \propto N_{maj}N_{maj} + N_{min}N_{min} = N_{maj}^2 + N_{min}^2, \\
I_{\uparrow\downarrow} \propto N_{maj}N_{min} + N_{min}N_{maj} = 2N_{maj}N_{min}. \tag{2.5}
\]

The magnetoresistance ratio is now defined as:

\[
MR = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\uparrow}} = \frac{I_{\uparrow\downarrow} - I_{\uparrow\uparrow}}{I_{\uparrow\uparrow}} = \frac{2P_1P_2}{1 - P_1P_2}, \tag{2.6}
\]

with $P_1$ and $P_2$ the spin polarizations of the two electrodes.

\(^1\)This effect is also the reason why the material is magnetic. The magnetization, however, is determined by the difference of the energy-integral over the occupied density of states for both spins. It is therefore not equal to the polarization $P$!


Thus, changing the magnetizations of the two electrodes from parallel to antiparallel alignment gives rise to a magnetoresistance effect. A parallel alignment is easily accomplished by applying a large in-plane magnetic field. An antiparallel alignment can e.g. be accomplished by using two electrode materials with different coercivities (e.g. Co and Ni_{80}Fe_{20}), making use of the thickness and shape dependence of the coercivity, or by using an exchange bias layer. Such a layer consists of an antiferromagnet that artificially shifts the switching field of the adjacent magnetic layer to a higher value, creating a broad field interval of antiparallel alignment. Exchange biasing has the practical advantage that the same magnetic material can be used for both electrodes, e.g. a material with a high spin polarization. This last technique has been used in all the magnetic tunnel junction stacks, studied in this work (see section 3.1.3).

2.2 Photoconductance

In this section photoconductance will be discussed as a three-step process: the photoexcitation of the electrons, their transport towards the barrier, and the subsequent transmission over the barrier. The sum of the contribution due to these processes in both electrodes results in the eventual net photocurrent. The contribution to the photocurrent due to interband excitation in the barrier, which is only possible for photon energies \( h\nu > E_{\text{gap}} \), where \( E_{\text{gap}} \) is the bandgap of the barrier, will be treated in section 2.2.4. At the end a discussion on the overall efficiency of the photoconductance process is presented. Most of this section is based on the work by Kadlec [23]. Issues relating to our photoconductance experiments on MTJs will be emphasized.

2.2.1 Photoexcitation

Upon absorption of a photon an electron will be excited to a higher energy state. Therefore, to determine the amount of photoexcited electrons, one should first know the optical absorption in the junction structure.\(^2\) Starting from the Maxwell equations in conducting media, the wave equation for the electric field \( E \) is given by [24]:

\[
\nabla^2 E = \mu \epsilon \frac{\partial^2 E}{\partial t^2} + \mu \sigma \frac{\partial E}{\partial t},
\]

(2.7)

where \( \mu \) represents the magnetic permeability, \( \epsilon \) the electrical permittivity, and \( \sigma \) the conductivity of the material. The solutions to this equation are transverse plane waves of the form

\[
E(\rho, t) = E_0 \exp[i(\kappa \cdot \rho) - \omega t],
\]

(2.8)

where \( \kappa \) represents the wavevector, \( \rho \) the positional vector, and \( \omega \) the frequency of the light. The relation between the magnetic field \( H \) and the electric field \( E \) is given by

\[
H = \frac{1}{\mu \omega} (\kappa \times E).
\]

(2.9)

\(^2\)In the remainder of this thesis it is assumed that the excitation is directly proportional to the absorption.
Chapter 2. Theoretical background

Figure 2.3: Schematic representation of the propagation of electromagnetic waves through a multilayered medium. Each layer \( m \) is characterized by a refractive index \( \tilde{n}_m \) and a thickness \( d_m \). \( E_0^+ \) and \( E_0^- \) represent the amplitudes of an electromagnetic wave traveling in the positive and negative \( x \)-direction respectively.

As we have used a perpendicular incident light beam, the propagation of the electromagnetic waves in our structures can be described one-dimensionally. The junction is subdivided in \( n \) layers, each with their own (complex) refractive index \( \tilde{n} \) (see Fig. 2.3). At the interface between two adjacent layers, the electromagnetic field is partially reflected and transmitted. The relation between these two is governed by the Fresnel equations, which can be deduced from the boundary conditions as set by the Maxwell equations. The Fresnel equations for normal incidence are given by:

\[
\begin{align*}
    r_m &= \frac{\tilde{n}_{m-1} - \tilde{n}_m}{\tilde{n}_{m-1} + \tilde{n}_m}, \\
    t_m &= \frac{2\tilde{n}_{m-1}}{\tilde{n}_{m-1} + \tilde{n}_m}.
\end{align*}
\]

(2.10)

(2.11)

After propagation through the layer \( m \) the waves have undergone a phase shift \( \delta_m \), which is given by

\[
\delta_m = \frac{2\pi}{\lambda} d_m \tilde{n}_m.
\]

(2.12)

with \( \lambda \) the wavelength of the light and \( d_m \) the thickness of the layer \( m \). By combining the above relations, the propagation of electromagnetic radiation through a multilayered stack can now be described in a matrix formalism that relates the amplitude of the electromagnetic wave in one layer to that in the adjacent layer [25]:

\[
\begin{pmatrix}
    E_{m-1}^+ \\
    E_{m-1}^-
\end{pmatrix}
= \frac{1}{t_m} \begin{pmatrix}
    \exp(-i\delta_{m-1}) & r_m \exp(-i\delta_{m-1}) \\
    r_m \exp(i\delta_{m-1}) & \exp(i\delta_{m-1})
\end{pmatrix}
\begin{pmatrix}
    E_{m}^+ \\
    E_{m}^-
\end{pmatrix}.
\]

(2.13)

From the above matrix representation, the electric field in the complete stack can be recursively determined. The time-averaged rate of flow of electromagnetic energy (per m²) is given by the time-averaged Poynting vector

\[
\langle S \rangle_{\text{time}} = \frac{1}{2} \text{Re} \left( E^* \times H \right).
\]

(2.14)
2.2. Photoconductance

Figure 2.4: (a) Calculated Poynting vector and (b) absorptivity in the magnetic tunnel junction stack as described in section 3.1.3. The 354 nm (3.5 eV) light beam is incident from the left, and the glass substrate is to the right. The Poynting vector and absorptivity are normalized to the flux of incident photons.

The absorption at each position in the stack is then given by the derivative of the time-averaged Poynting vector

$$A = \frac{\delta \langle S \rangle}{\delta x}. \quad (2.15)$$

By normalizing the Poynting vector of the incident light beam by the energy of the used photons $h\nu$, the absorption gives directly the amount of photoexcited electrons per volume unit at each position in our multilayered stack. As an illustration, in Fig. 2.4 the normalized Poynting vector and absorptivity are shown, for an AlO$_x$ based MTJ structure as studied in this thesis. See section 3.1.3 for a more detailed description of the different layers and their functions. For the refractive index, either literature values for the bulk material [26], or experimentally determined values ($\tilde{n} = 2.4 + 2.82i$ for Ir$_{20}$Mn$_{80}$) have been used. The used energy (wavelength) of the incident light is 3.5 eV (354 nm), which is well above the expected barrier height. Since the bandgap of the AlO$_x$ insulator is higher than the used photon energy, the barrier itself is transparent for the incident light. With the above formalism the amount of photoexcited electrons at each position in the layer stack can thus be determined, separately for each photon energy.

If the bandgap of the insulator is low enough, or for that matter the used photon energy high enough, also absorption will take place in the barrier region. This means that upon absorption of a photon, an electron from the valence band will be excited to the conduction band. This process plays a crucial role in for example TaO$_x$ barriers, as described in chapter 6, and will be discussed further in section 2.2.4.
2.2.2 Transport of photoexcited electrons

Due to the polycrystalline or amorphous nature of the electrodes from which excitation occurs, the photoexcited electrons are assumed to have an isotropic momentum distribution. During movement through the multilayered stack, the momentum as well as the energy distribution of these hot-electrons is strongly modified, due to elastic and inelastic scatter processes. Upon arrival at the barrier interface, only those electrons which have a high enough kinetic energy and momentum component perpendicular to the barrier interface, are able to cross the barrier and can be collected at the other side. The transport of photoexcited carriers in the barrier itself will be treated in the next section. Here we will describe the diffusive motion through the electrodes, in terms of the following scatter processes, based on the work by Vlutters et al. [27]:

Inelastic scattering  Due to the Coulomb interaction hot electrons can lose part of their energy by exciting an electron from below the Fermi-level [28]. The average excitation will lower the energy of the electron by a factor 1.5 - 2. In our model treatment it is assumed that after such an inelastic scatter event the electron has not enough energy anymore to overcome the barrier and is thus essentially lost. This description is valid for photoexcited electrons with energies not much higher than the barrier height. The mean-free-path for this inelastic process will be called $\lambda_i$. By considering the volume density of empty states into which hot electrons can scatter, it may be seen that for a simple free-electron metal $\lambda_i$ depends on the energy of the electron as $(E - E_F)^{-2}$.

(Quasi-)elastic scattering  Besides a loss in energy, excited electrons can also change just their momentum in a scatter process. Such elastic processes can occur due to the presence of defects, lattice mismatches, or impurities. Also, quasi-elastic interactions with phonons, i.e. quantized vibrations of the lattice, can occur. Since phonon energies are only on the order of tens of meVs, these scatter events are regarded here as quasi-elastic. It is assumed that all scattering processes discussed above are isotropic, and can be described with an elastic mean-free-path $\lambda_e$.3

Interface scattering  At the interface between two layers, electrons can be partially reflected due to different band-structures of the materials. In addition, diffusive scattering, due to interface roughness, can occur. The latter diffusive interface scatter events are assumed to be elastic and isotropic.

To account for the above effects a simple model is developed that describes the flow of hot electrons through a multilayered stack. From literature, the determined elastic mean-free-paths are typically smaller than the inelastic mean-free-paths and than our electrode thicknesses [27, 29]. This implies that the momentum distribution at each position in our layer stack can be regarded as isotropic (both towards and away from the barrier). In this case the hot-electron transport can be described

---

3 Although $\lambda_e$ also depends on the electron energy [29], no treatment on the exact dependence is given in literature.
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$$Y^+(x) = Y^+(x) + \frac{1}{2} A(x) dx - \frac{1}{\lambda_i} Y^+(x) dx - \frac{1}{2\lambda_e} Y^+(x) dx + \frac{1}{2\lambda_e} Y^-(x+dx) dx,$$

$$(2.16)$$

$$Y^-(x) = Y^-(x) + \frac{1}{2} A(x) dx - \frac{1}{\lambda_i} Y^-(x+dx) dx - \frac{1}{2\lambda_e} Y^-(x+dx) dx + \frac{1}{2\lambda_e} Y^+(x) dx.$$

$$(2.17)$$

Figure 2.5: Representation of the different processes occurring during transport of photoexcited electrons through an infinitesimally thin slice of an electrode. $Y^+$ and $Y^-$ are the $x$-dependent hot-electron fluxes towards the substrate and air interfaces respectively. The one-dimensional mean-free-paths for elastic and inelastic scatter processes are $\tilde{\lambda}_i$ and $\tilde{\lambda}_e$ respectively, and the amount of electrons photoexcited in this slice $A(x) dx$ is given by equation (2.15).

one-dimensionally, with effective mean-free-paths $\tilde{\lambda}_i$ and $\tilde{\lambda}_e$ that are half their three-dimensional values.

As illustrated in Fig. 2.5, first we regard a thin slice of our (1D) layer stack, and distinguish two hot-electron fluxes: $Y^+$ for electrons moving toward the substrate and $Y^-$ for electrons moving toward the surface. The outflow of hot electrons from this layer can now be described as the sum of the inflow of electrons and the amount of electrons photoexcited in this thin layer $A(x) dx$ [see equation (2.15)], minus the amount lost due to elastic and inelastic scatter events. Due to the isotropy after excitation, newly generated photoelectrons are assumed to contribute equally to $Y^+$ and $Y^-$. Additionally, the elastic in-scattering of electrons which were first moving in the opposite direction, which is assumed to occur upon 50\% of the elastic scatter events, has to be included. The above processes are described with the following two coupled equations:
At each interface $i$, part of the incoming hot-electron flux will be transmitted and part will be reflected. Under the assumption of an isotropic momentum distribution at each position within our 1D approach (for both the positive and negative $x$-direction), making a strict distinction between diffusive scattering and specular reflection is not needed. The only parameter that is required is the reflection coefficient $r_i$, which is related to the transmission coefficient $t_i$ as

$$t_i = 1 - r_i. \tag{2.18}$$

At the outer interfaces with the substrate and the atmosphere total reflection is assumed, meaning $r_0 = r_n = 1$ and $t_0 = t_n = 0$. As we will see in section 2.2.3, the transmission at the barrier interfaces is typically less than a percent. This means that, for the purpose of calculating $Y^+$ and $Y^-$ in the electrodes, also the interfaces with the barrier layer can to a good approximation be regarded as fully reflective, i.e. $r_{\text{barrier}} = 1$. This implies that the electron transport in both electrodes is essentially independent of that in the other electrode (for a given absorption profile).

Using the above coefficients $t_i$ and $r_i$ as boundary conditions, the two coupled equations (2.16) and (2.17) can be numerically solved. First the hot electron current in the positive direction is calculated for the complete layer stack, while ignoring the in-scatter contribution. Then the current in the opposite direction is calculated, with the previous outcome as the in-scatter term. This is then continued until a self-consistent solution is reached. Only the hot-electron fluxes incident on the interfaces with the barrier, can (depending on the barrier transmission) eventually contribute to the photocurrent.

As an example, Fig. 2.6 shows the two hot-electron fluxes for our “standard” MTJ, as described in Fig. 3.1.3, where we made use of the calculated optical absorption profile as shown in Fig. 2.4. Experimentally obtained values for $\lambda_i$ are between roughly 1 and 20 nm, depending on the bandstructure of the material, as well as the structural quality, which depends crucially on the sample preparation [27, 30]. Values for $\lambda_e$ are more difficult to obtain, and are therefore just assumed to be half that of $\lambda_i$. Since the bandstructure and structural influences in our layer stack are not known, intermediate values of $\lambda_i = 10 \text{ nm}$ and $\lambda_e = 5 \text{ nm}$ have been used. The reflection coefficient $r_i$ also depends crucially on the structural quality of the interfaces. As an approximation all internal interfaces in both electrodes are regarded to reflect half of the incoming electrons, i.e. $r_i = 0.5$.

In Fig. 2.6 one can see that for those electrons traveling towards the barrier, $Y^+$ in the top electrode and $Y^-$ in the bottom electrode, each interface, close to the barrier, reduces the hot-electron flux. The use of the above input parameters leads to the conclusion that the electron flux reaching the barrier from the (directly illuminated) top electrode is higher than the electron flux from the (indirectly illuminated) bottom electrode. In section 4.3 the above analysis, together with a variation in electrode thickness, is used to make an estimation of the validity of the used mean-free-path parameters.
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2.2.3 Barrier transmission

The transmission of photoexcited electrons through the barrier is described in three different ways. First, the process is treated in a semi-classical way, making only use of the energy and momentum requirements for transmission, and neglecting tunneling and interference of the electron waves. After that, some aspects of the quantum mechanical nature of the transmission, and the consequences for the photocurrent yield are discussed. The section is rounded off, again in a semi-classical picture, by combining the contributions from the two electrodes, including elastic scattering in the barrier conduction band.

Semi-classical barrier transmission

We derive an approximate expression for the probability for an incoming electron to cross the barrier interface, by making use of several assumptions. First of all, the momentum distribution of electrons incident on the barrier is regarded as isotropic (see previous section). The densities of states in the electrodes are described within a free-electron model, neglecting the spin-splitting. Also, the distribution of excited electrons in $k$-space is regarded as uniform. This implies that matrix-element effects during excitation are neglected. As already discussed in section 2.2.2, since inelastically scattered electrons do not contribute anymore to the photocurrent (if the excitation energy above the barrier is sufficiently small), the energy (as well as the momentum) distribution of the electrons incident on the barrier is the same as

Figure 2.6: Calculated curves representing the hot-electron fluxes (electrons/s) in the electrodes of a MTJ, per unit incident photon flux (photons/s). The absorption profile from Fig. 2.4(b) was used in the calculations, and the layer stack is described in section 3.1.3. $Y^+$ (full curve) and $Y^-$ (dashed curve) are the fluxes towards the glass substrate and the air surface, respectively. The vertical dashed lines indicate the electrode/barrier as well as the outer interfaces. The following parameters were used: $\lambda_i = 10$ nm, $\lambda_e = 5$ nm, and $r_i = 0.5$ for the internal interfaces and $r_i = 1$ for the barrier and outer interfaces, respectively.
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Figure 2.7: Two-dimensional representation of a sphere in $k$-space. The area between the two solid circles represent the hot-electron states that are occupied after excitation with photons of energy $h\nu$. The gray area indicates the fraction that has a high enough perpendicular component of the $k$-vector to overcome the barrier. $E_F$ represents the Fermi energy, $\phi$ the barrier height, $h\nu$ the photon energy, and $m$ the electron mass.

that after excitation.

Within this (semi-)classical picture, the transmission can be calculated in a relatively simple way. The energy of a hot electron in the electrode can be written as

$$E = E_0 + E_x + \frac{\hbar^2 k^2}{2m},$$

(2.19)

where $k_\parallel$ is the component of the wavevector parallel to the electrode/barrier interface, and $E_0$ is the inner potential. By setting $E_0 = 0$, transmission will only occur for those electrons for which $(E_x - E_F) > \phi$, with $\phi$ representing the barrier height. The incident electrons occupy states in $k$-space that are present in the volume between two hemispheres, corresponding to the electron energies $E_F + h\nu$ and $E_F$ respectively. Due to the cylindrical symmetry of the problem this volume can be represented two-dimensionally, as in Fig. 2.7, with $k_x$ and $k_\parallel$ the components of the electron wavevector perpendicular and parallel to the electrode/barrier interface respectively. The fraction of the incident electrons that are able to cross the barrier is then proportional to the volume in $k$-space, represented by the gray area, for which the following equation holds

$$k_x > k_\phi \equiv \sqrt{\frac{2m(E_F + \phi)}{\hbar^2}}.$$

(2.20)

The transmission probability of hot electrons that arrive at the barrier is then given
2.2. Photoconductance

Figure 2.8: Calculated barrier transmission curves for both the exact treatment [equation (2.22)], as well as the Fowler approximation [equation (2.23)]. In (a) the barrier transmission function, and in (b) the square-root of that are plotted. The following parameters are used: $\phi = 3$ eV and $E_F = 10$ eV. The vertical dashed lines represent the top of the barrier. The inclined dashed lines in (b) represent linear extrapolations of the curves from 3-3.5 eV.

by

\[
T(h\nu) = \frac{k_{ho}}{2}\frac{\pi k_{\parallel}^3}{\pi k_{ho}^3 - \frac{4}{3}\pi k_F^3},
\]

(2.21)

where $k_F$, $k_{ho}$, and $k_\phi$ are defined in Fig. 2.7, and the factor 2 originates from the fact that only half of the excited electrons have a $k_x > 0$. By using expression (2.19), the integration can be carried out and equation (2.21) can be written in terms of energies:

\[
T(h\nu) = \frac{2}{3}(E_F + h\nu)^{3/2} - (E_F + h\nu)\sqrt{E_F + \phi + \frac{1}{3}(E_F + \phi)^{3/2}}.
\]

(2.22)

In Fig. 2.8(a) and (b) this transmission probability is plotted as a function of photon energy. For the case that $h\nu \ll E_F$, equation (2.22) can be approximated by

\[
T(h\nu) \approx \frac{(h\nu - \phi)^2}{4h\nu E_F},
\]

(2.23)

showing an almost quadratic dependence on the photon energy above the barrier, also known as the Fowler relation [31]. The quadratic dependence for photon energies close to the barrier height is often used to extract the barrier height from experimental photoconductance curves [13]. In Fig. 2.8(b) the square-root of both the exact transmission as well as the Fowler approximation are shown. In both cases a linear behavior is seen for energies up to roughly 0.5 eV above the barrier height.
Quantum-mechanical transmission

Due to the wave-like nature of the electron, the transmission should ideally be described quantum-mechanically. To determine the QM-transmission probability, the system is described one-dimensionally and subdivided in three regions, as shown in Fig. 2.9: the two electrodes and the barrier itself. The wavefunctions of the electrons in these regions are governed by the 1D time-independent Schrödinger equation:

\[
-\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} + U(x)\Psi(x) = E_x \Psi(x),
\]

with \( U(x) \) the potential that is given by:

\[
U(x) = \begin{cases} 
0 & \text{in region 1} \\
E_F + \phi - (qV + \Delta \phi) \frac{x}{s} & \text{in region 2} \\
-qV & \text{in region 3}
\end{cases}
\]

where \( V \) represents the applied bias voltage, \( \Delta \phi \) the barrier asymmetry, and \( s \) the barrier thickness. The solution of equation (2.24) in regions 1 and 3 are plane waves of the form

\[
\Psi_1(x) = A_1 \exp^{ik_1x} + B_1 \exp^{-ik_1x}
\]

\[
\Psi_3(x) = A_3 \exp^{ik_3x}
\]

(2.26)
with the wavevectors \( k_1 \) and \( k_3 \) given by:

\[
\begin{align*}
k_1 &= \sqrt{\frac{2m}{\hbar^2} E_x} \\
k_3 &= \sqrt{\frac{2m}{\hbar^2} (E_x + qV)}.
\end{align*}
\] (2.27)

In the barrier region itself, the solutions are given by a summation of Airy functions:

\[
\Psi_2(x) = A_2 Ai(z(x)) + B_2 Bi(z(x)),
\] (2.28)

with \( z(x) \) given by

\[
z(x) = \left\{ \frac{s \sqrt{2m}}{\hbar (qV + \Delta \phi)} \right\}^{2/3} \left[ E_F + \phi - (qV + \Delta \phi) \frac{x}{s} \right].
\] (2.29)

The constants \( B_1, A_2, B_2, \) and \( A_3 \) can be deduced by applying the boundary conditions of continuity of the wavefunctions and their derivatives at each interface. The transmission probability \( T_{1D}(E_x) \) is then given by the ratio of the transmitted over the incoming flux density:

\[
T_{1D}(E_x) = \frac{k_3 |A_3|^2}{k_1 |A_1|^2}.
\] (2.30)

The solution is a complex function of Airy functions and their derivatives, which gives no further insight. The reader is referred to [14] for an exact analytical expression.

We extend this approach to three dimensions, and calculate the average transmission probability for photoexcited electrons with energies between \( E_F \) and \( E_F + h\nu \). As before, when deriving the Fowler equation (2.23), we assume that these excited electrons are in states that are uniformly distributed in \( k \)-space. For this purpose, the fraction \( f(E_x) \) \( dE_x \) of incoming electrons, having a perpendicular component of the \( k \)-vector between

\[
\sqrt{\frac{2mE_x}{\hbar^2}} < k_x < \sqrt{\frac{2m(E_x + dE_x)}{\hbar^2}}.
\] (2.31)

has to be calculated. Consistent with equation (2.21) and (2.22), this fraction is given by

\[
f(E_x) \ dE_x = 2 \frac{\pi k_h^2 \ \frac{dk_x}{dk} \ dE_x}{3 \pi k_h^3} - \frac{\pi k_F^2 \ dE_x}{3 \pi k_F^3} = \frac{3}{4} \frac{E_F + h\nu - E_x}{(E_F + h\nu)^{3/2} - E_F^{3/2}} \frac{1}{\sqrt{E_x}} dE_x.
\] (2.32)

By integrating the above expression over the electron energies, the average three dimensional transmission probability can be determined:

\[
T_{3D}(h\nu) = \int_{E_F}^{E_F + h\nu} T_{1D}(E_x) f(E_x) dE_x.
\] (2.33)
Figure 2.10: Calculated curves for (a) the 1D quantum-mechanical transmission probability for a single electron as a function of $E_x$, and (b) the 3D-classical [equation (2.22)] and quantum-mechanical square-root of the transmission probability, averaged over an ensemble of electrons in states that are uniformly distributed in $k$-space in between the Fermi sphere and the sphere with radius $k_{\nu}$ (as defined in Fig. 2.7). The following parameters were used: $\phi = 3$ eV, $\Delta \phi = 0.3$ eV, $V = 0$ V, $s = 2.5$ nm, and $E_F = 10$ eV. The vertical dashed lines indicate the top of the barrier.

In Fig. 2.10(a) the 1D QM-transmission of a trapezoidal barrier is plotted as a function of the energy of the incoming electrons. Already slightly below the barrier the transmission is significantly different from zero, caused by the tunneling effect. The oscillatory behavior of $T_{1D}(E_x)$ is caused by the interference between reflected and transmitted electron waves. The implications of the quantum-mechanical treatment on the average 3D transmission probability of photoexcited electrons, as a function of the photon energy, are shown in Fig. 2.10(b). The oscillations in the transmission have almost completely been averaged out, but tunneling through the top of the barrier is still visible as an additional contribution to the photoyield just below the barrier height $\phi$. As we will see in section 4.1, this last effect is still visible in experimental curves. Linearly extrapolating the square-root of the barrier transmission to zero, leads quite accurately to $\phi$, indicating the validity of this approach for determining the barrier height. The slopes of the (square-root of the) classical and QM-transmission differ, due to the lower than unity 1D transmission probability in the latter case [Fig. 2.10(a)]. However, since we are only interested in the order of magnitude of the overall efficiency (section 2.2.5), this difference will not be further discussed.

As mentioned already, due to the integration over all electron states participating in the transmission, the oscillations in the 3D transmission probability are much reduced, but still present. These remaining oscillations will only be visible if the coherence between electron waves propagating in opposite directions is essentially not disturbed. At finite temperatures these hot electrons can easily scatter elastically
Figure 2.11: Sphere in $k$-space representing the occupied electron states at the barrier interface, after excitation with photons of energy $h\nu$. The gray area represents electrons with a kinetic energy between $E$ and $E + dE$, and a high enough $k_x$ to overcome the barrier. The parameters $k_F$, $k_{h\nu}$ and $k_F$ are defined in Fig. 2.7.

with phonons or imperfections in the amorphous barrier, destroying the coherence. The influence of this elastic scattering should ideally be included in the Schrödinger equation. However, this represents a very complex problem, which is beyond the scope of this thesis. Therefore, the scattering will be described classically in the same way as in section 2.2.2.

**Barrier transmission including elastic scattering in the barrier**

In this section we modify the expression (2.22) for the barrier transmission probability, by including in a semi-classical way the possibility for elastic scattering in the barrier conduction band. We assume an isotropic momentum distribution for the incident electrons, an energy dependent mean free path for elastic scattering, and neglect multiple scatter events. First of all, we calculate the contribution to the transmission probability for an incoming electron with a kinetic energy between $E$ and $E + dE$, without the influence of scattering. Consistent with equation (2.21), this contribution is given by the ratio of the volume corresponding to the gray area in Fig. 2.11 over the volume in between the spheres with radii $k_{h\nu}$ and $k_F$, and can be calculated by

$$
t(E)dE = 2 \frac{k_{dE}}{k_{eF}} \frac{\int \pi k_x^2 dk_x - \int \pi k_x^2 dk_x}{\pi k_F^3 - \pi k_{h\nu}^3},
$$

(2.34)
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Figure 2.12: (a) Energy diagram and (b) volume in $k$-space representing the isotropic scattering of electrons in the barrier conduction band. Four different regions can be discerned for the scattered electrons, indicated by the roman numerals, and explained in the text. The gray area in (b) represent electron states with a total energy between $E$ and $E + dE$, that have an insufficient perpendicular component of the $k$-vector to overcome the top of the barrier. $\Delta \phi$ represents the barrier asymmetry, $h\nu$ the photon energy, $V$ the applied bias voltage, $U(x)$ the potential as given by equation (2.25), $m^*$ the effective mass of the electron in the barrier conduction band, and $Y^+$ and $Y^-$ the electron flux incident on the barrier from the top and bottom electrode respectively.

in which $k_E$ and $k_{dE}$ are defined in Fig. 2.11. Rewriting the above expression in terms of energies gives for $E > E_F + \phi$:

$$t(E)dE = \frac{3}{2} \frac{\sqrt{E} - \sqrt{E_F + \phi}}{(E_F + h\nu)^{3/2} - E_F^{3/2}} dE.$$  \hspace{1cm} (2.35)

Due to the reduction of $k_x$ and the conservation of $k_\parallel$, the momentum distribution of electrons entering the barrier is highly anisotropic. However, by including elastic scattering in the barrier conduction band, the distribution inside the barrier will become more isotropic. In a one-dimensional picture this will simply lead to a reduction of the electrons reaching the opposite electrode. However, for an asymmetric barrier, and noting the three-dimensional movement of the electrons, some will have a reduced $k_x$ (and thus an enhanced $k_\parallel$) that is now insufficient to surmount the top of the barrier [see Fig. 2.12(a)]. Those electrons for which, in addition, $k_x < 0$ after elastic scattering, will reflect from the bottom of the conduction band, and thus all electrons for which $k_x$ is insufficiently large, will leave the barrier in the “downhill” direction. This implies that a flux of electrons crossing the barrier against the electric field will be more attenuated than a flux of electrons traveling in the opposite direction.

Just after elastic scattering, at position $x$ in the barrier, the distribution of $k$-vectors of the scattered electrons is isotropic. The fraction of these scattered hot-electrons in the barrier conduction band with a total energy between $E$ and $E + dE$,
and an insufficient \( k_x \) to overcome the top of the barrier, is proportional to the volume in \( k \)-space that corresponds to the gray area in Fig. 2.12(b), and is given by

\[
f(E, x) = \frac{\bar{k}_{\Delta \phi}}{\frac{4}{3} \pi \bar{k}_{dE}^3 - \frac{4}{3} \pi k_E^3} \int_0^\pi (\bar{k}_{dE}^2 - k_x^2) \, dk_x - 2 \int_0^\pi (\bar{k}_{E}^2 - k_x^2) \, dk_x,
\]

\[
= \frac{1}{\bar{k}_{dE}^3 - k_E^3} \sqrt{\frac{\Delta \phi + qV}{E - U(x)}} \left( \int_0^\pi (\bar{k}_{dE}^2 - k_x^2) \, dk_x - 2 \int_0^\pi (\bar{k}_{E}^2 - k_x^2) \, dk_x \right),
\]

(2.36)
in which \( \bar{k}_{\Delta \phi}, \bar{k}_E, \) and \( \bar{k}_{dE} \) are now defined relative to the local bottom of the conduction band [see Fig. 2.12(b)], and \( U(x) \) is defined in equation (2.25). To describe the transport of hot-electrons in the barrier conduction band, we first regard a thin slice of the barrier between \( x \) and \( x + dx \). In this “layer” a fraction

\[
\frac{1}{\lambda_e} \exp \left( -\frac{x}{\lambda_e} \right) \, dx
\]

(2.37)
will be scattered elastically and isotropically, with \( \lambda_e \) the corresponding mean-free-path. This fraction can be subdivided in four subfractions, corresponding to four regions illustrated by roman numerals in Fig. 2.12. For electrons with a high enough perpendicular \( k \)-vector component to overcome the top of the barrier \( k_x > \bar{k}_{\Delta \phi} \), a fraction

\[
\frac{1}{2\lambda_e} \exp \left( -\frac{x}{\lambda_e} \right) \left[ 1 - f(E, x) \right] \, dx
\]

(2.38)
will continue to travel in the same direction and eventually leaves the barrier, contributing to the photocurrent (region IV). A same fraction will, however, leave the barrier in the opposite direction and thus does not contribute to the photocurrent (region I). For electrons with \( k_x < \bar{k}_{\Delta \phi} \), a fraction

\[
\frac{1}{2\lambda_e} \exp \left( -\frac{x}{\lambda_e} \right) f(E, x) \, dx
\]

(2.39)
will continue to travel in the “downhill” direction and eventually contributes to the photocurrent (region III). An equal amount starts off in the opposite direction, but reflects from the bottom of the conduction band, and also leaves the barrier in the “downhill” direction (region II). Summarizing the contributions from the four different regions, this leads to the following two equations for \( \Gamma^+(E) \) and \( \Gamma^-(E) \), the reduction of the transmission probability \( t(E) \) through the barrier layer with and against the electric field respectively, due to elastic scattering in the barrier:

\[
\Gamma^+(E) = 1 - \frac{1}{2} \int_0^s \frac{1}{\lambda_e} \exp \left( -\frac{x}{\lambda_e} \right) \left[ 1 - f(E, x) \right] \, dx,
\]

\[
\Gamma^- (E) = 1 - \frac{1}{2} \int_0^s \frac{1}{\lambda_e} \exp \left( -\frac{(s-x)}{\lambda_e} \right) \left[ 1 + f(E, x) \right] \, dx,
\]

(2.40)
where it has been assumed that the mean-free-path for elastic scattering $\lambda_{ee}$ is of the same order or higher than the barrier thickness $s$. Also, subsequent elastic scattering in the electrodes is neglected. This is a good approximation, because after elastic scattering, that randomizes $k$, the transmission probability over the barrier is strongly reduced. Since the mean-free-path for elastic scattering depends on the electron energy relative to the bottom of the conduction band, the ratio between $\Gamma^+(E)$ and $\Gamma^-(E)$ also depends on this precise energy relation. This implies that when $\Gamma^+(E)$ and $\Gamma^-(E)$ are nearly equal, the exact energy dependence of $\lambda_{ee}$ determines the overall shape of the photocurrent yield curves. Braunstein et al. [32], first suggested the following energy dependence of $\lambda_{ee}$:

$$\lambda_{ee}(E, x) = \frac{c}{[E - U(x)]}. \quad (2.41)$$

As we will see below, such an energy dependence is able to generate a sign-reversal of the net barrier transmission probability with photon energy.

The total average barrier transmission probability for an incident electron, after excitation by a photon of energy $h\nu$, is then given by integrating the product of the barrier transmission probability $t(E)$ [equation (2.35)] and the reduction factor $\Gamma^+\Gamma^-$ due to elastic scattering in the barrier [equation (2.40)] over the energy:

$$T^\pm(h\nu) = \int_{E_F + \phi}^{E_F + h\nu} t(E)\Gamma^\pm(E)dE, \quad (2.42)$$

with $+$ and $-$ for an electron flow with and against the electric field respectively.

In Fig. 2.13(a) and (b) calculated net barrier transmission probability curves for a trapezoidal barrier with different ratios of the incident hot-electron fluxes $Y_0^+ / Y_0^-$, as well as different applied bias voltages are shown, respectively. The barrier asymmetry $\Delta\phi$ is chosen such that electrons are accelerated to the bottom electrode. Together with the elastic scatter processes in the barrier conduction band, this makes the contribution from the bottom electrode decrease faster with photon energy than the contribution from the top electrode. For some $Y_0^- / Y_0^+$ ratios and for some applied voltages this can even lead to a sign reversal of the barrier transmission as a function of $h\nu$. In chapter 5 this effect is used to study the relative contribution from the two electrodes to the net photocurrent as a function of the barrier oxidation time.

In Fig. 2.13(b) the net negative barrier transmission already starts below $\phi$ for negative applied bias voltages. This is caused by the fact that for electrons traversing the barrier from the bottom electrode to the top one, the effective barrier height is lowered by an amount $qV$. This effect is used to explain the voltage dependence of experimental photocurrent yield curves of symmetric Al/AlO$_x$/Al junctions in section 4.1. This lowering of the onset of the negative photocurrent is limited to the barrier asymmetry $\Delta\phi$.\footnote{Due to the presence of the electric field, $E - U(x)$ depends on the position in the barrier. This means that also $\lambda_{ee}$ depends on $x$ and it should therefore be kept inside the integration mark.}

\footnote{The modification of the QM-transmission due to a changing electric field in the barrier will also induce a lowering of $\phi$. This effect is however neglected in Fig. 2.13.}
2.2. Photoconductance

Figure 2.13: Calculated net barrier transmission curves including elastic scattering in the barrier conduction band, for (a) different ratios of the incident forward and reverse hot-electron fluxes $Y^-/Y^+$, and (b) different applied bias voltages. The following parameters were used: $\phi = 3 \text{ eV}$, $\Delta \phi = 0.3 \text{ eV}$, $E_F = 10 \text{ eV}$, $s = 2.5 \text{ nm}$, and $c = 1.25 \text{ nm} \cdot \text{eV}$. In (a) no bias voltage was applied, and in (b) a ratio of $Y^-/Y^+ = 1.75$ was used. The vertical dashed lines indicate the barrier height $\phi$.

From the discussion in this section one can see that the experimental photoconductance curves will only correspond to the simple classical or quantum-mechanical transmission as described in the previous sections, when one of the two incident hot-electrons fluxes dominates. Otherwise the net photocurrent yield curve will be largely influenced by scattering processes and no quadratic dependence on the photon energy is expected. In these cases no effective $\phi$ can be determined. Furthermore, from a comparison of the barrier transmission, derived for a contribution from only one electrode [Fig. 2.8(a)], with the net barrier transmission from Fig. 2.13(a) and (b), one can see that electrons crossing the barrier in the opposite direction can strongly reduce the photocurrent yield. This can even, depending on $Y^-/Y^+$, give rise to a negative photocurrent yield.

2.2.4 Barrier excitation

If the energy of the incident photons is higher than the bandgap $E_{gap}$ of the insulator, also photoexcitation in the barrier can play a role [see Fig. 2.14(a)]. Upon absorption of a photon, an electron will then be excited from the valence to the conduction band, leaving behind a hole. Since we assume that the electrons and holes have, immediately after excitation, an isotropic momentum distribution, a potential gradient must be present in the barrier to obtain a net photocurrent. In this section, the effect of recombination of electron-hole pairs in the barrier is neglected. Due to the small barrier thickness in comparison to the optical absorption length, excitation occurs homogeneously throughout the barrier.
Chapter 2. Theoretical background

Figure 2.14: (a) Energy diagram and (b) volume in \( k \)-space illustrating the photoexcitation of electrons from the valence to the conduction band upon absorption of high energy photons. The origin of the sphere in (b) lies at the bottom of the conduction band at position \( x \), and the gray area represents those electron states that contribute to the photocurrent. \( E_F \) represents the Fermi energy, \( h\nu \) the photon energy, \( E_{gap} \) the bandgap of the insulator, \( \Delta \phi \) the barrier asymmetry, \( V \) the applied bias voltage, \( m^* \) the effective mass in the barrier conduction band, and \( \tilde{k}_{\Delta\phi} \) is defined in Fig. 2.12(b).

To calculate this contribution to the photocurrent, we make use of the same procedure as in the previous section. We consider electrons and assume a uniformly populated density of states in \( k \)-space.\(^6\) The occupied states in the barrier conduction band at a position \( x \), can then be represented by a sphere in \( k \)-space, illustrated in Fig. 2.14(b). This sphere can be subdivided in three different regions. Electrons in region I have a high enough \( |k_x| \) to overcome the top of the barrier and to reach the top electrode. An equal amount of electrons in region III, moves to the bottom electrode. This means that equal amounts of electrons in regions I and III will effectively cancel each others photocurrent contribution.\(^7\) The electrons in region II will all leave the barrier in the “downhill” direction (even if \( k_x < 0 \) they cannot overcome the barrier). This last fraction is given by the gray area in Fig. 2.14(b) and is given by

\[
f(h\nu, x) = \frac{\tilde{k}_{\Delta\phi}}{3\pi^2 \hbar^2 \nu^2} \int_0^\infty k_x^2 dk_x,
\]

\(^6\)Since just above the absorption edge excitation occurs from the top of the valence band to the bottom of the conduction band, the occupation of \( k \)-space is in such a case non-uniform. However, at elevated temperatures phonon assisted excitation plays a role, so that the electron and hole can have different \( k \)-vectors. This will lead to a more uniform distribution of hot electrons and hot holes in \( k \)-space.

\(^7\)Since the electrons already start with an isotropic momentum distribution, the influence of elastic scattering is neglected in this case.
\[ F = \frac{1}{s} \int_{0}^{s} f(h\nu, x) \, dx + \frac{1}{s} \int_{\frac{h\nu - E_{\text{gap}}}{\Delta\phi + qV}}^{s} f(h\nu, x) \, dx = \left( 1 - \frac{1}{5} \frac{h\nu - E_{\text{gap}}}{|\Delta\phi + qV|} \right). \] (2.45)

Since elastic scattering in the barrier conduction band is neglected, the fraction \( F \) is independent of \( s \). Similar expressions hold for the hole contribution. In Fig. 2.15(a) the above fraction is shown for an insulator with a 4 eV bandgap, for different electric fields inside the barrier. One can see that by increasing the electric field, more and more electrons contribute to the photocurrent, leading to an increase in magnitude and a reduction of the curvature. Multiplying the fraction \( F \) by the amount of absorbed photons in the barrier, gives now the resulting photocurrent. Since the excited electrons (holes) are now at the bottom (top) of the conductance (valence) band, the absorption rate depends strongly on the photon energy \( h\nu \). We assume that the absorption is proportional to the number of final states per unit volume available in the conduction band \([33]\):

\[ n(h\nu) = \frac{1}{3\pi^2} \left[ \frac{2m^*}{h^2} (h\nu - E_{\text{gap}}) \right]^{3/2}, \] (2.46)

in which \( m^* \) represents the effective mass of the electron in the conduction band.

By using the analysis of section 2.2.1, and using the refractive index of Ta\(_2\)O\(_5\) as an example \([34]\), an absorption (per nanometer) of \( \sim 10^{-3} \) electrons per incident photon is calculated for photons with an energy of 4.5 eV. Using this as a normalization, the photocurrent yield for interband excitation in a “Ta\(_2\)O\(_5\)” like insulator with a 4 eV bandgap is shown in Fig. 2.15(b) for a 1 nm thick barrier.

One can see that under the influence of an electric field, either due to the presence of a barrier asymmetry \( \Delta\phi \), or by applying a bias voltage \( V \), the photocurrent yield increases. However, for a high enough potential drop \( |\Delta\phi + qV| \), practically all of the photoexcited electrons (up to a certain energy) will contribute to the photocurrent, saturating the photocurrent yield. By applying a bias voltage opposite to the barrier.
asymmetry, the contribution to the photocurrent from these interband transitions can be reduced. Applying a voltage exactly equal to the barrier asymmetry, but of opposite sign, will cause this contribution to the photocurrent to vanish. This method is used in chapter 6 to determine the sign and magnitude of $\Delta \phi$ in a direct way.

### 2.2.5 Photoconductance efficiency

By combining the efficiencies of the different processes, as treated in the previous sections, the overall efficiency of the photoconductance process can be determined. The amount of electrons reaching the barrier interface, is in the order of $10^{-1}$ per incident photon, for a typical MTJ that we want to investigate (see Fig. 2.6). The efficiency of electrons crossing the barrier is roughly $10^{-2}$-$10^{-1}$ at each electrode. However, due to the fact that the two resulting currents have opposite signs, the net barrier transmission efficiency can be as low as $10^{-3}$ (see Fig. 2.13). This gives an overall photoconductance efficiency of $10^{-5}$-$10^{-4}$ electrons per incident photon. As we will see in section 4.1, this corresponds roughly to the experimentally observed values. This combined low efficiency for the photoconductance process implies that special attention has to be paid to the experimental setup. Only with a high enough signal to noise ratio can photoconductance be used to extract information on the barrier shape in tunnel junction structures (see section 3.2.2).

Although the thickness of the barrier layer is much smaller than the typical electrode thickness, the photoconductance efficiency due to electrons excited in the barrier, is much higher. Due to the fact that most electrons that are excited exit the bar-
2.3 Spin-dependent photoconductance

As described in section 2.1, the electron transport through the tunnel barrier is spin-dependent, which results in a tunnel magnetoresistance effect. In the photoconductance process, electrons also cross the barrier, but now at an energy significantly above the Fermi level. In principle, one may expect to see also a spin-dependence in the photocurrent. However, as already illustrated in Fig. 2.2, the spin-dependent tunneling effect is caused by a difference in the majority and minority density of states, at $E_F$ in the emitting electrode and at $E_F + qV$ in the collecting electrode. If one examines the density of states of the magnetic materials, as used in our junctions, in more detail, it is seen that for higher energies the density of states is not spin-polarized anymore.\(^8\) For Ni, Co, and Fe this occurs around 0.5, 1, and 2.5 eV above the Fermi level respectively [36]. For photon energies above these values, no spin-dependence of the photoyield is therefore expected. An obvious way around this would be to study MTJs with a low barrier height ($< 1$ eV). This was one of the original reasons of studying photoinduced transport in TaO$_x$ based junctions, as described in chapter 6. However, due to the small photocurrent yield just above the barrier, and the expected small effect, no spin-dependence in the photocurrent was observed in all our investigated samples. Moreover, one has to keep in mind that, in order to be able to measure this effect, the transport over the barrier should be ballistic, i.e. not disturbed by scatter effects. Recent experiments studying the ballistic transport over an AlO$_x$ barrier revealed strong spin-mixing, which leads to an absence of any spin-dependent transport effects [37].

A possible alternative to introduce a spin-dependence in the photocurrent, is by making use of the spin-dependent transport of hot-electrons through an all-metallic magnetic material. This effect is caused by a difference in scatter rates for majority and minority electrons, and is explicitly used in e.g. the spin-valve transistor [38] or the magnetic tunnel transistor [39]. However, this effect can not be exploited in our tunnel junction experiments, even in the case of ballistic barrier transmission, due to the inability to differentiate between hot and scattered electrons. A second barrier would be needed to separate the unscattered electrons from the thermalized ones. In chapter 8 a different system is proposed to explicitly make use of this difference in scatter rate to generate a spin-dependent photocurrent.

\(8\)This is partly the cause of the decay of the MR ratio with increasing applied voltage [35].
Chapter 3

Experimental procedures

From an experimental point of view photoconductance might seem a quite straightforward characterization technique for magnetic tunnel junctions. One only has to shine light with a certain wavelength on the junction structure and measure the resulting photocurrent. However, due to different issues relating to sample constraints, a lot of effort had to be invested in devising a setup which is able to determine the photoconductance properties reliably. In this chapter a detailed description of this measurement setup is preceded by a closer look at the sample preparation, with the emphasis on issues relating to photoconductance studies.

3.1 Sample preparation

For the relevance of the results of the photoconductance experiments to industrial applications, it is crucial that the studied samples are as close to “real” magnetic tunnel junctions (MTJs), as used in e.g. MRAMs, as possible. This means that the junctions are prepared with the same sputter-deposition procedure as used for large scale junction arrays, and that they are essentially optimized for their magneto-electronic properties. Some small deviations from the “standard recipe” are needed to be able to conduct our photoconductance experiments. However, it is always assured that the magneto-electronic properties are similar. In the following sections a closer look at the deposition, structuring and stack design of the MTJs, as used in this work, is presented.

3.1.1 Deposition setup

All the junction structures used for the photoconductance experiments, as described in the following chapters, are made in a Kurt J. Lesker ultrahigh vacuum deposition system, which is placed in a cleanroom environment, located at Philips Research Eindhoven. A picture of this system can be seen in Fig. 3.1. The system consists essentially of four separate chambers, individually pumped and connected via vacuum valves: a loadlock, and from left to right the deposition, transfer, and oxidation
chamber. After bake-out the system can reach a pressure of typically $1 \times 10^{-7}$ Pa. Six magnetron sputter-sources are mounted in the deposition chamber to grow different materials. With sputter powers around 20-50 W, and a partial pressure of 1 Pa, deposition rates of typically 0.2 nm/s are achieved. Thickness calibration is carried out with Rutherford backscattering spectrometry (RBS) on test samples, with roughly 10% accuracy. The system is equipped with an in-situ shadow-mask facility, which allows complex structures to be easily made without the need for lithography. Also an X-ray photoelectron spectrometer (XPS) is mounted on the transfer chamber to study the chemical composition of deposited samples.

### 3.1.2 Sample fabrication

The choice for the used substrate is based on the requirements, which are set by both good growth of the junction structure as well as compatibility with the photoconduction experiments. Crystalline silicon wafers (with or without thermal oxide) are often used as substrates for the growth of magnetic tunnel junctions, due to their extremely low roughness and widespread use in the semiconductor industry. How-
3.1. Sample preparation

However, due to the possibility of photoinduced interband transitions in the semiconductor, which leads to the generation of a significant photocurrent contribution, silicon wafers were rejected as substrates for the experiments described in this thesis. A suitable replacement has been found in Corning 1737 glass. Due to the Fusion process used in manufacturing these substrates [40], an extremely low roughness of 0.3 nm, comparable to that of mono-crystalline silicon, is achieved. The insulating properties of the substrate ensure that no undesirable photocurrent will be generated.

For our experiments 0.7 mm thick glass slides were used. After being cut in the proper dimensions (26 × 26 mm$^2$), the substrates were extensively cleaned in a boiling ammonia/ethanol solution to remove all organic material. They are then mounted on molybdenum plates and placed inside the load-lock. A maximum of five substrate plates and a mask can be loaded at once. After pumping down for typically 2 hours the pressure is good enough and the substrate-plate is transferred via the transfer chamber to the oxidation chamber. Here an oxygen-plasma is ignited to further clean the sample in-situ. Any residual hydrocarbons or water on the surface are then combusted and pumped away, resulting in a completely fresh surface.

Shadow mask deposition was chosen over lithography in order to define the junction structure, for several different reasons. First of all, deposition through shadow masks is a much simpler and less involved technique than lithography. This results in structures which are ready for performing measurements immediately after deposition, compared to days later for lithography. Different junction stacks can therefore be rapidly investigated. Also, the lithographic process used at Philips Research for junction definition on silicon substrates cannot be trivially translated to glass substrates. Since the focus of this work is to investigate tunnel junction structures with our photoconductance technique and not to make large junction arrays for certain applications, shadow mask deposition was chosen and proved to be the most suitable definition technique.

For the growth of the junction structure itself (as illustrated in Fig. 3.2), the sample is transported to the deposition chamber, where it is placed on a rotation-stage. Here a thin metal mask is brought into contact with the substrate. Through slits in the mask, the lateral electrode dimensions are defined. In this thesis several masks were used, with slit widths of 60, 110, and 200 µm. Two permanent magnets placed beneath the mask holder generate a magnetic field of approximately 16 kA/m at the sample, parallel to the slits. This applied field induces a preferential orientation of the magnetization in the magnetic layers, and a unidirectional anisotropy resulting from the exchange interaction with the antiferromagnetic exchange-bias layer. For growing the different materials, which compose the tunnel junction stack, recipes are written in the software of the sputter-machine. The substrate is then automatically rotated under the correct magnetron source, where an argon plasma is ignited. This leads to material being sputtered from the target, which is subsequently deposited through the slits in the mask onto the substrate. After deposition of the complete bottom electrode, the mask is removed and the chosen barrier material is then deposited homogeneously over the complete substrate. To form a high quality insulating barrier, the sample is transported to the oxidation chamber. Here an oxygen-plasma of 60 sccm is established and a plasma is ignited. The pressure during deposition is
Chapter 3. Experimental procedures

Figure 3.2: Schematic drawing (a) and several images (b) showing the different stages in fabricating junction structures using shadow mask technology to define the electrodes. The cross-section of two orthogonal stripe-shaped electrodes define the junction area. At their ends large contact-pads are present.

controlled at 9.3 Pa via a variable diaphragm valve above a turbo-molecular pump. The plasma power is kept constant at 35 W. Due to the high reactivity of the plasma an (amorphous) insulating barrier will form within seconds to minutes, depending on the barrier material and thickness. Subsequently the sample is transported back to the deposition chamber to deposit the top electrode. The mask is first rotated 90° before placing it into contact with the sample. In this way a cross-bar geometry is created, where the junction area is defined by the width of the slits in the mask. With a second recipe the complete top electrode is then grown. Per wafer 4 identical sets of 6 junctions are thus defined. After completion, the samples are taken out of the vacuum system. The complete deposition process takes roughly between 20 to 40 minutes per wafer, depending on the complexity and thickness of the layer stack. To improve the electrical contact to the sometimes very thin electrodes, the contact-pads are covered by an additional ± 50 nm thick gold layer, which is grown afterwards through an additional mask in a separate small sputter system.
3.2. Experimental setup

3.1.3 Stack design

The junction layer stacks used for our experiments were chosen such that several boundary conditions were simultaneously met. Besides needing a high magnetoresistance, so that our results can be compared to junctions developed for e.g. MRAM devices, certain limitations on the layer thicknesses are present due to the need of having optical access to the electrode layers. The typical stack used in our experiments is shown in Fig. 3.3(a). The function of the different layers will be briefly described below, starting from the substrate.

Both Ta and Ni$_{80}$Fe$_{20}$ are used as seed layers to induce the required (111) texture for the growth of the subsequent layers (Ni$_{80}$Fe$_{20}$ and Ir$_{20}$Mn$_{80}$, respectively). As the exchange biasing material to “pin” the magnetization of the bottom magnetic electrode, Ir$_{20}$Mn$_{80}$ is used. The fact that this layer is grown in a magnetic field induces a unidirectional crystalline anisotropy parallel to the long axis of the bottom electrode. On top of this layer the ferromagnetic electrode, consisting of Ni$_{80}$Fe$_{20}$ and Co$_{90}$Fe$_{10}$, is deposited. Co$_{90}$Fe$_{10}$ is used as the interface layer with the barrier, because of its high spin-polarization [41], which ultimately leads to a high magnetoresistance. To reduce the hysteresis of the magnetic electrode, the remainder of the layer consists of Ni$_{80}$Fe$_{20}$, which has a low coercivity. The barrier layer, which is deposited across the whole substrate, should be thin enough to enable quantum-mechanical tunneling, but at the same time be very smooth and without defects, which can otherwise severely reduce the reliability of the junction. Also a minimal resistance is needed to get around current-crowding effects, when the junction resistance is comparable to the square resistance of the leads [42]. In practice a thickness of 1-3 nm proves to be a suitable choice, resulting in resistance-area products of 1-10$^5$ M$\Omega$ $\mu$m$^2$. The top electrode consists again of the combined Co$_{90}$Fe$_{10}$ and Ni$_{80}$Fe$_{20}$ magnetic electrode, which is now capped by a thin Ta layer to prevent the electrode from oxidation when exposed to atmosphere. Fig. 3.3(b) shows a cross-sectional transmission electron microscope (TEM) image of such a stack.

By choosing the thickness of the complete stack to be in the same order of magnitude as the optical penetration depth in metals (a few tens of nanometers), the entire stack is accessible for photoexcitation and generation of hot electrons, which can eventually lead to a photocurrent.

3.2 Experimental setup

To be able to conduct photoconductance experiments on tunnel junction structures, a home-built experimental setup has been devised and realized. With this setup the electrical response of the junction on an incident light beam can be collected. Together with information from “regular” transport measurements (and possibly other techniques), a coherent picture of the shape of the potential barrier can be extracted. In this section a detailed description of the photoconductance setup, as used for the experiments described in the following chapters, is given. Starting from the requirements as imposed by the samples, the consequences for the experimental setup are given. After the capabilities and limitations of the used setup are shown, the de-
Figure 3.3: (a) Schematic representation of the layer stack for the magnetic tunnel junctions, as used in this thesis. All thicknesses are in nanometers. The function of each layer or combination of layers is indicated on the right. As an illustration, a cross-sectional TEM-image of a TaO$_x$ based junction stack is shown in (b).

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capping layer</td>
<td>3.5</td>
</tr>
<tr>
<td>Top magnetic electrode</td>
<td>10.0</td>
</tr>
<tr>
<td>Tunnel barrier</td>
<td>4.0</td>
</tr>
<tr>
<td>AlO$_x$ or TaO$_x$</td>
<td>1-3</td>
</tr>
<tr>
<td>Exchange bias layer</td>
<td>1.5</td>
</tr>
<tr>
<td>Bottom magnetic electrode</td>
<td>2.5</td>
</tr>
<tr>
<td>Seed layers</td>
<td>10.0</td>
</tr>
<tr>
<td>Seed layers</td>
<td>3.0</td>
</tr>
<tr>
<td>Substrate</td>
<td>3.5</td>
</tr>
<tr>
<td>Glass</td>
<td></td>
</tr>
</tbody>
</table>

3.2.1 Imposed requirements

As already stated in the previous section, the intention is to use photoconductance primarily as a characterization tool for MTJs. This means that the samples are in principle optimized for their magneto-electronic properties. This in turn imposes
3.2. Experimental setup

certain requirements on the setup.

Since the combined efficiency of excitation, transport and collection can be quite low (see section 2.2.5), a large fluence (light power per junction surface area) is required. Also, a broad wavelength range is needed to access the variation in expected barrier heights \(0.5 < \phi < 3.5\) eV. The spectral resolution should be of the order of 0.1 eV. This relatively modest requirement is in practice sufficient, because of the absence of features with line widths corresponding to that energy scale, or smaller. These requirements led us to choose a gas-discharge lamp in combination with a monochromator, instead of a (tunable) laser system. In this way a simple, cheap and flexible system was obtained.

The maximum allowed lateral dimensions of the junctions depend on the barrier thickness, due to current-crowding effects, as described in section 3.1.3. A maximum junction area of \(200 \times 200\) µm\(^2\), as used in our experiments, imposes high requirements on the collection and focussing optics. Only with sufficient quality of the optical setup a small spot size can be realized. To be able to separate the small photocurrent from the background tunnel current, a phase-sensitive technique had to be used.

3.2.2 Photoconductance setup

In Fig. 3.4(a) an image of the setup is presented, which was realized by the author to conduct the photoconductance experiments as described in the following chapters. With the help of the schematic representation, shown in Fig. 3.4(b), a detailed description of the function of each part will be given.

As the light source a 75 W xenon gas-discharge lamp is used. Due to its small arc-size of \(0.4 \times 0.8\) mm\(^2\) and the high numerical aperture (N.A.) condenser lens, a collimated light-beam with high intensity is produced. To introduce the photon-energy variation in our experiments, this light beam is focused on the entrance slit of a 1/4 m Jobin-Yvon monochromator. The diffraction grating inside induces a wavelength-dependent position of the light at the exit slit. By rotating the grating, different wavelength components can be spatially filtered out by the exit slit. The width of this slit thus determines the resolution (and of course also the intensity) of the light beam. By using a slit width of 5 mm (and a 1200 lines/mm grating) a spectral resolution of roughly 20 nm is attained. This corresponds to a resolution of 0.02 and 0.25 eV for photon energies of 1 and 4 eV respectively. While this is sufficient for our experiments, the large slit width also provides a relatively large beam intensity. Since some experiments require high energy electrons to be produced, up to 5 eV above the Fermi level, care has to be taken to use only quartz-based optics, which is transparent in the ultraviolet (down to 250 nm).

To control the size of the light spot at the sample position (independent of the spectral resolution), the light beam is first focused onto a diaphragm which in turn is imaged on the junction. The position of the light spot relative to the junction is controlled by an XYZ stage beneath the sample. This is visually verified by imaging the reflected light with the use of a beam splitter and a CCD camera. A high N.A. of 0.55 at the last focusing lens ensures a high fluence at the sample position.
Figure 3.4: (a) Image and (b) schematic drawing of the experimental setup, with which all photoconductance experiments in this thesis have been carried out.
3.2. Experimental setup

![Graph showing light intensity vs. photon energy](image)

Figure 3.5: Incident light intensity on a 200×200 µm² junction, measured with the use of a calibrated photodetector at the sample position. The spectral dependence originates from the lamp spectrum, monochromator grating efficiency, as well as chromatic aberrations of the used lenses. The discontinuity at 2.8 eV is caused by the use of a high-pass filter, for \( h\nu < 2.8 \text{ eV} \), to block out the contribution of second order diffractions from the monochromator.

To measure the energy dependence of the induced photocurrent, the energy dependence of the light intensity at the sample due to the lamp spectrum, monochromator efficiency, and lens transmissions, has to be determined. In principle this calibration procedure can be carried out by measuring the spot intensity at the sample position with a calibrated photodetector. However, due to the natural dispersion of the refractive optics, as used in this setup, the eventual spot-size will change significantly with the wavelength (this is also known as chromatic aberration). This means that the spot intensity is no longer proportional to the incident photon flux at the junction (for a spot size larger than the junction area). To get around the need of a complicated compensation scheme, it was decided to keep the sample position fixed and to measure the integrated light intensity at the sample position, through a pinhole having the exact shape of the junction area. The complete wavelength variation can then be corrected for. A Si-based calibrated photodiode was used for this purpose. A typical calibration spectrum for a 200×200 µm² junction is shown in Fig. 3.5. Due to the incoherence of the light source and the broad spectral range, the spot size is not diffraction limited. This limits the fluence which can be obtained, and therefore special care has to be taken in measuring the resulting small electrical signals. An estimated efficiency of \( 10^{-5} \) electrons/incident photon (see section 2.2.5), together with a 30 µW light intensity, corresponds for example to an absolute photocurrent of only 300 pA!

To be able to separate the small photocurrent from the background tunnel cur-
Chapter 3. Experimental procedures

Figure 3.6: Simple electrical schematic of the measurement scheme, illustrating the two contributions to the measured current. $R_L$ represents the lead resistance, $R_J$ the junction resistance, and $C_J$ the junction capacitance.

rent, a phase-sensitive technique is used. By chopping the light beam with a mechanical chopper and registering only the in-phase electrical response (with the use of a lock-in detector), the dark current can effectively be filtered out. With the exception of the very high resistance junctions ($>10^4 \text{ M\Omega } \mu\text{m}^2$), the used modulation frequency of 330 Hz is sufficiently low, so that capacitance effects in the junction transport can be neglected.

The electrical response which is eventually induced in the junction structure, consists of both a photocurrent $I_{\text{photo}}$ as well as a photovoltage contribution. Due to the finite resistance of the measurement circuit (e.g. the lead resistances), a photoinduced charge will be built up at the junction electrodes. This induces a photovoltage which in turn results in a tunnel current $I_{\text{tunnel}}$, with a sign opposite to that of the photocurrent. As illustrated in Fig. 3.6, the current that one measures $I_{\text{meas}}$ is now a summation of these two:

$$I_{\text{meas}} = I_{\text{photo}} + I_{\text{tunnel}}.$$  \hspace{1cm} (3.1)

The relation between the current induced by the photovoltage $I_{\text{tunnel}}$ and the photocurrent $I_{\text{photo}}$ depends on the ratio of the lead resistance $R_L$ and junction resistance $R_J$. This results in the following expression for the photocurrent in terms of the measured current:

$$I_{\text{photo}} = I_{\text{meas}} \left(1 + \frac{R_L}{R_J}\right).$$  \hspace{1cm} (3.2)

The photocurrent is the physical quantity we would like to measure. Also, we would like to measure this current at a predefined constant voltage. As can be seen from equation (3.2), the measured current will only be equal to the photocurrent, i.e. the photovoltage can be neglected, when the lead resistance is negligible compared to the junction resistance. Since the resistances of the electrodes in our thin film samples can easily be of the same order as the junction resistance, this regime is almost never reached. Still, to be able to measure the photocurrent, an electrical compensation circuit is devised, where the potential across the junction is kept constant (even during the modulation of the current) at a predefined value. This is accomplished by feeding the difference between the measured and desired bias-voltage through an integration circuit [see Fig. 3.4(b)]. The integration time constant $\tau$ is chosen such
that the effective cut-off frequency of the system is higher than the modulation frequency \([43]\). Only then will the voltage across the junction effectively be constant. Since the effective time-constant of the system depends on the resistances, the former is only fulfilled for the used system and modulation frequency, if \(\frac{R_L}{R_J} < 1000\). This condition is less stringent than the requirement for absence of current-crowding effects \([42]\), and is therefore already fulfilled. The measured signals are eventually fed into an analog-digital converter and visualized on a personal computer with the use of a home-made Labview program.

The use of a lock-in amplifier also reduces the \(1/f\) noise, by artificially shifting the signal to a higher spectral region. Due to the mechanical limitations of the chopper and the limited spotsizes at the chopper position, the frequency could not be increased further. Since the cut-off frequency of the system is larger than the modulation frequency (otherwise the compensation scheme would not work), noise present in the dc tunnel current, that lies in the same frequency band as the photocurrent, is not filtered out by the lock-in amplifier. For low resistance junctions, the compensating voltage induces large tunnel current fluctuations. The noise associated with these fluctuations dominates the noise in the photocurrent, making large integration times necessary. Especially for curves measured at a few hundred mV bias voltage, spectra can take up to several hours to measure!

This same setup was also used to measure the (magneto) electronic transport properties. In that case the measurement circuit was replaced by a simple four-point \(I(V)\)-measurement setup. An electromagnet around the sample enables one to apply magnetic fields up to roughly 150 kA/m. More details on such an experimental setup can be found in reference \([21]\).

### 3.2.3 Limitations and possible improvements

Although the setup, as presented in the previous section, works quite well for determining photoconductance properties for relatively large-scale junctions (down to \(60 \times 60 \mu m^2\)), studying (sub)micron sized junctions is an entirely different ballgame. Also, to be able to study thinner (and thus lower resistance) barrier layers, the junction area should be reduced in order to circumvent current-crowding effects (see section 3.1.3). Since such small MTJs are most interesting for applications, some words of advice are in place.

The crucial limitation in the current setup is the limited light intensity per junction area. By decreasing the junction size, the electrical response thus drops proportionally, until it's below the detection limit. This in turn puts a lower limit on the barrier thickness which can be studied. An obvious way around this would be to use a more powerful (tunable) laser system as the light source. However, it would be difficult to find a laser system of which one can routinely vary the wavelength over the required broad energy range. Also, at a certain moment temperature induced effects will start to play a role. An alternative option could be to read out a large array of junctions, completely covered by the light spot, in a semi-parallel way. By adding up the electrical responses from each individual junction, an average photoconductance signal can be extracted, for junctions down to (sub)micron sizes. With a clever measurement scheme this could well be used to study the barrier shape in
complete MRAM like structures.
Chapter 4

Photoconductance in junction structures

Before showing how photoconductance can be used to study the shape of the barrier in magnetic tunnel junctions, we first present results of initial experiments on model junctions. We show the basic shape of photoconductance spectra, and discuss the various possibilities offered by the technique. We start off with experiments similar to those conducted in the 1970s on Al/AlO$_x$/Al junctions [13]. Different experimental conditions, such as applied bias voltage and incoming light direction will be discussed. By modifying the junction structure, also different aspects of the photoconductance process, such as workfunction and thickness dependence, will be treated. This chapter can thus be regarded as an introduction to the work on magnetic tunnel junctions as described in the following chapters.

4.1 Al/AlO$_x$/Al junctions

The Al/AlO$_x$/Al sandwich structures studied in this section have been grown in the same way as the magnetic tunnel junctions (see section 3.1), using 200 µm wide mask slits. Both aluminum electrodes have a thickness of 20 nm, and the barrier consists of 1.7 nm Al, plasma-oxidized for 200 s. In Fig. 4.1(a) the square-root of the measured photocurrent yield as a function of photon energy is shown. The light was incident on the top electrode, and no bias voltage was applied. The positive sign of the photocurrent implies an electron flow from top to bottom electrode. For photon energies between roughly 1.75 and 2.25 eV, a clear quadratic dependence on the photon energy $h\nu$ is visible. This is in correspondence with the classical barrier transmission as derived in section 2.2.3. By linear extrapolation a barrier height $\phi$ of 1.56±0.01 eV is determined. When $h\nu \gg \phi$ a deviation from the quadratic relation becomes visible, which is similar to that predicted by the Fowler relation [see equation (2.23) and Fig. 2.8(b)]. Although the noise-level increases significantly for low photon energies, a small photocurrent “tail” is visible [similar to Fig. 2.10(b)], indicative of tunnel transport through the top of the barrier.
Chapter 4. Photoconductance in junction structures

The determined barrier height has been compared to parameters extracted from a fit of the “regular” current-voltage characteristics of the same junction to the Brinkman model (see section 2.1). As can be seen in Fig. 4.1(b), the model describes the experimental characteristics quite well. The extracted barrier height \( \phi \) is somewhat larger than the one extracted from the photoconductance curve. However, one has to keep in mind that the Brinkman (as well as the Simmons) model suppose a simple trapezoidal (or rectangular) barrier shape with a free-electron like bandstructure. The extracted fit parameters are also influenced by the effective mass [see equation (2.2)], which is not known for these amorphous barriers (in our case just the free electron mass is used). Also, it should be noted that the barrier height and thickness cannot be determined independently within these models. For example, it has been shown that for non-uniform barrier thickness and height the determined parameters can differ significantly from the average values [44]. So, while the Simmons and Brinkman model can give some first indication of the barrier parameters, the barrier height determined from a Fowler plot yields the top of the tunnel barrier (averaged over the junction area) irrespective of the details of the barrier shape.

To study the influence of the barrier shape on the photoinduced transport in more detail, photoconductance curves have been measured for different applied bias voltages and illumination directions (see Fig. 4.2). The photocurrent yield is in the \( 10^{-5} \)-\( 10^{-4} \) range, consistent with that predicted from theoretical arguments (see section 2.2.5). As described in section 2.2.3, the photocurrent is a summation of two different contributions, originating from the two separate electrodes. The net photocur-
4.1. Al/AlO\textsubscript{x}/Al junctions

Figure 4.2: Photoconductance curves of an Al/AlO\textsubscript{x}/Al junction with different applied bias voltages, under illumination of (a) the top and (b) the bottom electrode. In both cases a positive photocurrent corresponds to an electron flux from top to bottom electrode.

The photocurrent depends now on the relative absorption, excitation, electrode transport, interface transmission, and transport in the barrier conduction band. These processes depend on details of the sample structure, but can also be influenced by experimental conditions. For example, by reversing the direction of incident light, only the relative absorption of the two electrodes changes, while all the other processes are kept constant. By comparing the two curves in Fig. 4.2(a) and (b) for zero applied voltage, it can be seen that the net photocurrent decreases, but remains positive. Since, for a symmetric junction, the absorbed energy is larger in the directly illuminated electrode than in the indirectly illuminated one, the other relevant processes (e.g. interface transmission) must be more efficient for hot electrons in the top electrode than electrons in the bottom electrode.

As can be seen in Fig. 4.2, applying a bias voltage across the barrier also changes the photocurrent yield. This is due to the fact that the barrier potential is modified in two different ways: the electric field inside the barrier conduction band, as well as the effective barrier heights at the two interfaces change [see Fig. 4.3(a)]. Both effects can in principle modify the ratio of the two electron fluxes reaching the opposite electrode. This then leads to a different net photocurrent yield curve. In all photoconductance curves throughout this thesis, the applied voltage is defined with respect to the top electrode. This means that under positive bias voltage, the electron flux (in the absence of incoming light) is directed from top to bottom electrode.

In Fig. 4.2 one can clearly see that applying a positive voltage enhances the photocurrent contribution from the top electrode, while a negative voltage enhances the

\footnote{Even for a “symmetric” Al/AlO\textsubscript{x}/Al junction, these processes may be different for the two electrodes. For example, due to the preparation method, the bulk electrode microstructure as well as the interfaces are different, which influences the hot-electron transport properties.}
Chapter 4. Photoconductance in junction structures

Figure 4.3: (a) Energy diagrams illustrating the change in the barrier potential for positive and negative applied bias voltage. The presence of a built-in field is neglected. $E_F$ represents the Fermi energy, $\phi$ the barrier height, $V$ the applied bias voltage, and $T$ and $B$ the top and bottom electrode respectively. In (b) schematic graphs illustrating the consequence for the separate (dashed curves), as well as the combined photocurrent yield (solid curve) are shown. $Y^+$ and $Y^-$ represent the contribution to the photoyield due to excitation in the top and bottom electrode respectively. It is assumed that more electrons from the top than the bottom electrode contribute to the photocurrent, e.g. the light is incident from the top.

reverse process. However, the striking feature in Fig. 4.2(a) is the occurrence of a sign reversal with photon energy for negative bias, which is absent for back illumination (b). As discussed in the last subsection of 2.2.3, classically this effect can have two different origins, which are related to the two different modifications of the barrier potential as discussed above. First of all, the onset of the photocurrent yield curves for the two electrodes differ now by an amount $eV$, with $V$ the applied bias voltage. Secondly, due to a directional preference induced by the electric field in the barrier conduction band for elastically and isotropically scattered electrons, one electron flux direction will decrease more than the other with increasing energy, leading to a sign-reversal for high enough $h\nu$. If we note that, for front illumination, the electron flux from top to bottom electrode is higher than that for the reverse process, the sign-reversal with negative voltage can already be explained by a lower effective barrier height for the bottom electrode as compared to the top electrode. This is illus-

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2This means that excitation, transport, and transmission are assumed to be independent of the other electrode. Quantum-mechanically the complete system should be described in a coherent way.
4.2. Different electrode materials

To investigate the influence of the electrode material on the photoconductance process, three junctions with different top electrodes, but which are otherwise identical, have been fabricated. The following layer stack is used: glass/3.5 nm Ta/15 nm Co_{90}Fe_{10}/1.7 nm Al + 240 s oxidation/20 nm M, where M is either Al, Ta, or Co_{90}Fe_{10}. The light is incident on the top electrode. In Fig. 4.4 photoconductance curves for these three junctions are shown. The results from a Fowler analysis of these curves are presented in Table 4.1, together with other parameters.

One can directly see that the determined barrier heights $\phi_{\text{photo}}$ are different for the different materials. A Co_{90}Fe_{10} top electrode induces a significantly higher barrier height than either Al or Ta. This can be understood by looking at the different

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One can deduce that for an asymmetric barrier potential, a similar relative shift of the effective barrier heights under an applied voltage is present.

Figure 4.4: Photoconductance curves for junctions consisting of a Co_{90}Fe_{10} bottom electrode, an AlO_x barrier, and a top electrode consisting of either Al, Ta, or Co_{90}Fe_{10}. The light was incident on the top electrode and no bias voltage was applied.

trated in Fig. 4.3(b) for a symmetric barrier potential. Since for back illumination the two hot-electron fluxes are already almost equal at zero bias, an equivalent relative shift of the onset energies will now not lead to a sign reversal within the observable photon energy range.

It can not be excluded that the second effect, namely scattering in the conduction band, also influences the ratio of the two electron fluxes. In chapter 5 we will see that for specific junctions such a sign-reversal can already be present without the application of a bias voltage. This implies that scattering in the barrier conduction band must play a role in the sign-reversal of the photocurrent.

4.2 Different electrode materials

To investigate the influence of the electrode material on the photoconductance process, three junctions with different top electrodes, but which are otherwise identical, have been fabricated. The following layer stack is used: glass/3.5 nm Ta/15 nm Co_{90}Fe_{10}/1.7 nm Al + 240 s oxidation/20 nm M, where M is either Al, Ta, or Co_{90}Fe_{10}. The light is incident on the top electrode. In Fig. 4.4 photoconductance curves for these three junctions are shown. The results from a Fowler analysis of these curves are presented in Table 4.1, together with other parameters.

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One can deduce that for an asymmetric barrier potential, a similar relative shift of the effective barrier heights under an applied voltage is present.
Chapter 4. Photoconductance in junction structures

Table 4.1: Several experimental as well as literature values of different junction parameters. The investigated stack consists of a Co$_{90}$Fe$_{10}$ bottom electrode, an AlO$_x$ barrier, and a top electrode of either Al, Ta, or Co$_{90}$Fe$_{10}$. Since the exact value of the workfunction depends on the structural orientation, and the layers are assumed to be amorphous or polycrystalline, an average over the different orientations is used [26]. For Co$_{90}$Fe$_{10}$ the indicated value is a weighed average of the two constituents.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Al</th>
<th>Ta</th>
<th>Co$<em>{90}$Fe$</em>{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_{\text{photo}}$ (eV)</td>
<td>2.05±0.05</td>
<td>1.93±0.05</td>
<td>2.66±0.03</td>
</tr>
<tr>
<td>$\phi_{\text{Brinkman}}$ (eV)</td>
<td>0.59</td>
<td>0.39</td>
<td>1.3</td>
</tr>
<tr>
<td>$\Delta \phi_{\text{Brinkman}}$ (eV)</td>
<td>0.04</td>
<td>-0.005</td>
<td>-0.5</td>
</tr>
<tr>
<td>$d_{\text{Brinkman}}$ (nm)</td>
<td>2.54</td>
<td>3.04</td>
<td>2.26</td>
</tr>
<tr>
<td>Workfunction (eV)</td>
<td>4.17</td>
<td>4.25</td>
<td>4.97</td>
</tr>
<tr>
<td>$R_{\text{junc}}$ (kΩ)</td>
<td>2.14</td>
<td>1.15</td>
<td>462</td>
</tr>
<tr>
<td>$c_M$</td>
<td>2.3</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

work functions for the different materials. Assuming that the vacuum level is continuous across the metal/oxide interface, the interfacial barrier heights are linearly related to the workfunctions. Indeed, by comparing $\phi_{\text{photo}}$ with the literature values for the workfunctions [26], a similar trend is visible, i.e. the value for Co$_{90}$Fe$_{10}$ is significantly higher than that for Al or Ta (see table 4.1). A similar trend is visible for the parameter $\phi_{\text{Brinkman}}$, extracted from a Brinkman fit to the current-voltage characteristics. Since the junction resistance is exponentially dependent both on barrier thickness as well as height (see section 2.1), also here a significant difference is expected. Indeed, as can be seen in Table 4.1, the junction resistance $R_{\text{junc}}$ for a Co$_{90}$Fe$_{10}$ top electrode is more than two orders of magnitude higher than that for the other two.

For photon energies not high above the barrier height, the photocurrent yield can be approximated by $c_M (h\nu - \phi_M)^2$ [see equation (2.23)], with $\phi_M$ representing the barrier height that depends on the material $M$ of the electrode. The normalized proportionality factors $c_M$, as extracted from Fig. 4.4, are shown in table 4.1. One can see that Al is more than twice as efficient in generating a photocurrent than either Ta or Co$_{90}$Fe$_{10}$. As discussed in the previous section, this means that either the absorption, excitation, transport, or barrier transmission is more efficient in Al than in Ta and Co$_{90}$Fe$_{10}$. The inner potentials of these three materials all lay between 8.5-10.5 eV [45], excluding a large influence of the Fermi energy on the difference in $c_M$. Since the imaginary component of the refractive index in Al is higher than that for Ta or Co$_{90}$Fe$_{10}$ [26], the absorption will be lower, and some other process must therefore be more efficient. Either a higher mean-free-path in Al, or a reduction in specular reflection or diffusive scattering at the Al/AlO$_x$ interface, due to respectively better band-matching or less interface roughness, might explain the difference in efficiency. Although the effect plays a crucial role in the next chapter, where the oxidation process of AlO$_x$ is studied in more detail, a conclusive explanation has not
4.3 Electrode thickness dependence

For the interpretation of photoconductance curves of sandwich structures, it is important to have knowledge on the position of excitation, for the electrons that contribute to the photocurrent. To investigate this distribution, several junctions with varying top electrode thickness have been studied under front illumination. The following layer stack has been used: glass/3.5 nm Ta/15 nm Co$_{90}$Fe$_{10}$/1.7 nm Al + 240 s oxidation/d Co$_{90}$Fe$_{10}$/3.5 nm Ta, where the thickness $d$ of the top Co$_{90}$Fe$_{10}$ layer was varied between 2.5 and 30 nm.

Before discussing the photoconductance results, the junctions have been characterized by current-voltage measurements. The obtained values for the junction resistance and the sheet conductance of the top electrode are presented in Fig. 4.5. One can see that below a thickness of roughly 10 nm the junction resistance drops sharply and the sheet conductance deviates from the linear curve. This implies that at smaller thicknesses the junction deviates from the “ideal” Co$_{90}$Fe$_{10}$/AlO$_x$/Co$_{90}$Fe$_{10}$ structure. It is known from literature that the growth of metal layers on top of an amorphous AlO$_x$ barrier can result in a non homogeneous surface coverage [46]. This suggests that at certain positions an AlO$_x$/Ta interface is present, which has a significantly lower barrier height, resulting in a lower junction resistance, as seen in the previous section.

Due to a mask induced shadowing effect during deposition, the electrode thickness will be lower at the edges. To circumvent possible issues due to such non-nominal electrode thickness, the photoconductance experiments have been carried yet been found.

![Figure 4.5: (a) Junction resistance and (b) sheet conductance of the top electrode for a Co$_{90}$Fe$_{10}$/AlO$_x$/Co$_{90}$Fe$_{10}$ junction structure with varying top electrode Co$_{90}$Fe$_{10}$ thickness.](image-url)
Chapter 4. Photoconductance in junction structures

Figure 4.6: (a) Photocurrent yield for Co$_{90}$Fe$_{10}$/AlO$_x$/Co$_{90}$Fe$_{10}$ junctions with varying top Co$_{90}$Fe$_{10}$ thickness. A photon energy of 3.5 eV was used, and the light was incident on the top electrode. From the last three measurement points, a decay length of 11.3±0.3 nm has been obtained. In (b) decay lengths as determined from calculations with different inelastic mean free paths are shown. The 1D model as discussed in section 2.2.2 is used with $\lambda_e = \frac{1}{2} \lambda_i$, and $r_i = 0.5$. The decay lengths are determined from the 10-30 nm thickness range, similar to (a). The horizontal dashed lines indicate the experimentally observed value.

out with a reduced spot size. This means that only the center 120 $\mu$m of the total 200×200 $\mu$m$^2$ junction area was illuminated. Due to the reduced spot size, the signal to noise ratio deteriorated, making it difficult to apply a Fowler analysis. Especially for the low resistance junctions, the expected reduction in barrier height, due to an increase of the AlO$_x$/Ta regions, could not be observed. However, for the junctions with a > 5 nm top Co$_{90}$Fe$_{10}$ thickness, a barrier height of 2.5±0.2 eV could still be extracted, which corresponds to the value obtained in the previous section.

The electrode thickness dependence of the photocurrent was measured with a photon energy $h\nu = 3.5$ eV, and the light incident on the top electrode. The results are shown in Fig. 4.6(a). From the three largest thicknesses, a decay length of 11.3±0.3 nm has been extracted. This decay length is determined by both the optical penetration depth as well as the elastic and inelastic mean free paths, $\lambda_e$ and $\lambda_i$ respectively. To extract information on $\lambda_i$, which determines largely the positional distribution of electrons that contribute to the photocurrent, we make use of the one-dimensional model as discussed in section 2.2.2. Again we chose an interface reflection of 0.5, and made use of the assumption that $\lambda_e = \frac{1}{2} \lambda_i$. For several values of $\lambda_i$, which were chosen the same for both Co$_{90}$Fe$_{10}$ and Ta, the decay length of a junction structure, with a 10-30 nm top Co$_{90}$Fe$_{10}$ layer, was determined. The results from these calculations are shown in Fig. 4.6(b), together with our experimentally obtained value. One can see that the inelastic mean free path that corresponds to

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4 Each measured spectra already took several hours to obtain.
the measured decay length is at least smaller than \( \sim 10 \) nm. Due to the fact that \( \lambda_i \) is smaller than the optical absorption depth for either Co or Fe at this energy: 10.9 and 10.3 nm respectively, \( \lambda_i \) cannot be determined more accurately within this scheme. However, the above does imply that most of the electrons that contribute to the photocurrent are generated within the first few nanometers adjacent to the barrier interface.
Chapter 4. Photoconductance in junction structures
Chapter 5

Barrier oxidation of AlO$_x$-based magnetic tunnel junctions

For the functioning of magnetic tunnel junction devices, the quality of the tunnel barrier is of utmost importance. The formation of a suboptimally oxidized barrier can lead to a loss of the tunneling spin polarization, and ultimately to a reduced magnetoresistance effect. In this chapter we use our photoconductance technique to study the effect of the barrier oxidation of Co$_{90}$Fe$_{10}$/AlO$_x$/Co$_{90}$Fe$_{10}$ structures on the MR ratio and the barrier shape in more detail. Together with "regular" current-voltage measurements, the viability of the technique as a characterization tool for complete magnetic tunnel junction devices is discussed.

5.1 Introduction

A magnetic tunnel junction (MTJ) consists essentially of two magnetic electrodes separated by a thin insulating tunnel barrier. The formation of the barrier layer is one of the most crucial steps in the fabrication of the MTJ. For example, the fact that only in the middle of the 1990s a significant tunnel magnetoresistance (MR) effect was realized at room temperature [6], nearly two decades after the first low temperature experiments by Julliere [22], can almost completely be attributed to the advancement in thin film growth.

Today, the barrier material which is most widely used, and most promising for applications, is aluminum oxide. The AlO$_x$ barrier is generally formed by plasma oxidation of a thin Al layer. For the magneto-electronic properties of the structure it is important that the barrier layer is as close to an ideal tunnel barrier as possible, i.e. it should have (magnetically) sharp interfaces and there should be no conductive paths through the barrier. Suboptimally oxidized junctions can show a severely reduced MR ratio, caused by a loss of spin polarization of the tunneling electrons [47, 48]. It is therefore important to control the oxidation process accurately.

Several techniques have previously been used to investigate the oxidation of thin
Chapter 5. Barrier oxidation of AlO$_x$-based magnetic tunnel junctions

However, most of these techniques use special samples or incomplete junctions, and the results could therefore not be directly related to other junction properties. In the following sections, we use our photoconductance technique to study the effect of the oxidation time on the barrier height and shape “afterwards” in complete MTJs. In this way a direct comparison with results from regular current-voltage measurements can be made.

5.2 Experimental

The studied junction structures have been prepared by UHV dc magnetron sputtering through metal contact masks onto glass substrates, resulting in 200×200 $\mu$m$^2$ junction areas. Details of the used preparation technique can be found in section 3.1. All MTJs have the same generic structure: glass/3.5 Ta/3.0 Ni$_{80}$Fe$_{20}$/10.0 Ir$_{20}$Mn$_{80}$/2.5 Ni$_{80}$Fe$_{20}$/1.5 Co$_{90}$Fe$_{10}$/1.7 Al + oxidation/4.0 Co$_{90}$Fe$_{10}$/10.0 Ni$_{80}$Fe$_{20}$/3.5 Ta, with all thicknesses in nanometers. The oxidation time of the Al layer was varied from 40 s up to 400 s. Even for the low oxidation times the junction resistance was always higher than four times the electrode sheet resistances, circumventing issues due to current-crowding effects [42]. No annealing steps were carried out afterwards.

For the conductance and magnetoconductance measurements, a four-point configuration has been used. The photoconductance studies have been carried out as outlined in section 3.2.2, with zero applied bias voltage across the junctions and with the light incident on the top electrode.

5.3 Results on barrier oxidation

To study the oxidation of the tunnel barrier in detail, the MTJs are initially characterized by their magneto-electronic properties. Further in-depth analysis is subsequently provided by results from photoconductance and current-voltage measurements respectively.

In Fig. 5.1(a) and (b) the MR ratio and the junction resistance are shown as a function of the oxidation time, respectively. The junction resistance shows a monotonic increase with oxidation time. We note that a strictly exponential increase would be expected if the oxide thickness would increase linearly with the oxidation time. It may be concluded from Fig. 5.1(b) that this is, in practice, not the case: the slope decreases with increasing oxidation time. From literature it is known that the oxidation of thin Al layers obeys quasilogarithmic kinetics, indicative of a Mott-Cabrera oxidation mechanism, effectively slowing down the oxidation for longer oxidation times [48, 49].

The MR ratio shows no such monotonic behavior. Instead, a maximum around an oxidation time of 120 s can be seen. This has also been observed by several other groups and is attributed to the complete oxidation of the Al layer [47, 50]. For short oxidation times some Al is still left, either at the ferromagnet/barrier interface or incorporated as metallic clusters inside the barrier. In the case of overoxidation,
5.3. Results on barrier oxidation

some of the Co or Fe in the bottom electrode will also start to oxidize, forming CoO$_x$ or FeO$_x$. Both effects are severely detrimental to the spin-polarization and thus the MR effect.

5.3.1 Photoconductance results

The same junctions from above have also been characterized by our photoconductance technique to study the oxidation process in more detail. In Fig. 5.2 various photocurrent yield curves, corresponding to the MTJs with different oxidation times, are presented. The different curves have been offset for clarity, with the horizontal lines corresponding to the zero current value. A positive photocurrent corresponds to an electron flux from top to bottom electrode and a negative photocurrent to the reverse process. A clear negative photocurrent is present for small photon energies and low oxidation times. Since these experiments are carried out with zero applied voltage across the junction, the effective barrier heights for excitation in the top and bottom electrode are the same. This result is different than that obtained for Al/AlO$_x$/Al junctions (see section 4.1), where a negative photocurrent contribution was only present in the case of a negative applied voltage. We attribute the observed sign-reversal to an imbalance in the incident positive and negative hot electron fluxes, combined with a directional preference in the barrier transport process. We will further discuss this below. The reader is referred to the last subsection of 2.2.3 for a more theoretical background.

To further investigate the origin of the negative part of the photocurrent, photoconductance experiments have been carried out on two model junctions, shown in Fig. 5.3, for either light incident on the top or the bottom electrode. For a junction with two Al electrodes [Fig. 5.3(a)], a positive photocurrent is observed, regardless
Figure 5.2: Photoconductance curves for AlO$_x$-based MTJs with different oxidation times. All curves are measured with zero applied voltage and with the light incident on the top electrode. The curves have been shifted for clarity. The horizontal lines correspond to the zero current value.

of the direction of the incident light. As already explained in section 4.1, for such a junction the absorption will be larger in the directly illuminated electrode, compared to the indirectly illuminated one. Since no negative photocurrent is observed for bottom illumination, this implies that electrons photoexcited in the top electrode have a higher chance of reaching the opposite electrode, compared to electrons excited in the bottom electrode. This must be related to a higher scatter rate at the bottom-electrode/barrier interface, and/or a modification of the barrier transport, due to scattering in the electric field in the barrier conduction band. The current due to electrons excited in the bottom electrode and traversing the barrier opposite to the electric field will then be attenuated. In contrast, electrons excited in the top electrode will reach the opposite electrode in spite of such processes.

For a junction consisting of an Al bottom electrode and a Co$_{90}$Fe$_{10}$ top electrode
5.3. Results on barrier oxidation

Figure 5.3: Photoconductance curves for two model junctions, for either light incident on the top (front) or the bottom (back) electrode. The junction structure in (a) and (b) consist of: glass/20 Al/1.7 Al + 140 s oxidation/15 Al, and glass/20 Al/1.7 Al + 90 s oxidation/6 Co90Fe10/3.5 Ta respectively. All thicknesses are in nanometers.

[Fig. 5.3(b)], a clear negative photocurrent is present for small photon energies. Since this effect is absent for a junction with identical electrodes, it is concluded that an Al electrode is more efficient than Co90Fe10 in generating hot electrons that eventually contribute to the photocurrent (as also observed in section 4.2). By reversing the direction of illumination, not only the amplitude [like Fig. 5.3(a)], but also the shape of the curve changes. This directly illustrates the two opposite contributions to the net photocurrent.

The photoconductance measurements for the MTJs for different oxidation times (Fig. 5.2) can now be interpreted as illustrated in Fig. 5.4. For small oxidation times, the barrier material is not yet completely oxidized, meaning that a small amount of metallic Al is left below the barrier. In agreement with the results shown in Fig. 5.3(b), this leads to a larger contribution from electrons excited in the bottom electrode, $Y^-$, as compared to that from electrons excited in the top electrode, $Y^+$. This will result in a net negative contribution to the photocurrent. However, due to an increase of the elastic scatter rate in the AlOx conduction band with energy, and due to the specific sign of the electric field in the barrier, the negative contribution decreases at higher photon energies. Such an explanation was first given in [32]. The suggested sign of the electric field corresponds to that inferred from a lower interfacial barrier height for Al, as compared to Co90Fe10 (see section 4.2). The positive photocurrent contribution is also subjected to these elastic scatter processes. However, since the sign of the electric field is now in the same direction as the initial electron flow, the positive contribution will hardly be attenuated (see also section 2.2.3). This will lead to a sign-reversal of the photoyield upon increasing $h\nu$.

The disappearance of a negative photocurrent around 120 s of oxidation, corre-
Chapter 5. Barrier oxidation of AlO$_x$-based magnetic tunnel junctions

Figure 5.4: (a) Energy diagram illustrating the photoexcitation and transport of electrons in an underoxidized AlO$_x$ based MTJ. The light is incident on the top electrode, and no bias voltage is applied. In (b) calculations of the separate contributions (dashed lines) of the top $Y^+$ and bottom electrode $Y^-$ to the net photocurrent (solid line) are shown. The dotted lines represent the contributions in absence of scattering in the conduction band. The classical model from section 2.2.3 is used, with the following parameters: $\phi = 3$ eV, $\Delta\phi = 0.3$ eV, $s = 2.5$ nm, $c = 1.25$ nm$\cdot$eV, and $Y^-/Y^+ = 1.75$.

Corresponds to the MTJ that showed the maximum MR [see Fig. 5.1(a)]. We conclude from this that the Al is then completely oxidized, reducing the negative contribution to the photocurrent $Y^-$, such that $Y^+ > Y^-$ for all observed photon energies. Since for overoxidized MTJs the photocurrent is dominated by electrons excited in the top electrode, the influence of scattering in the barrier conduction band will be hard to discern. This implies that from the above experiments no firm conclusion can be drawn on the sign of the built-in electric field $\Delta\phi$ for high (> 120 s) oxidation times.

The fact that even for the short oxidation times the MR ratio (and thus also the tunneling spin polarization) is still significantly above zero, indicates that only small regions of the interface at the bottom electrode consist of Al/AlO$_x$. It is maybe surprising that such (sub) monolayer amounts, present at only a small fraction of the interface area, can still have a profound influence on the photoconductance process. The apparent higher efficiency of Al compared to Co$_{90}$Fe$_{10}$ is therefore probably more an interface transmission than a bulk effect.$^1$

For the optimal and overoxidized junctions, the barrier height $\phi$ has been determined from a Fowler analysis of the photoconductance curves. As can be seen in Fig. 5.5(a), $\phi$ increases from roughly 2.5 to 2.8 eV with increasing oxidation time, indicative of an improvement of the insulating properties. In the next subsection, a comparison will be made with results from a Brinkman fit. For the underoxidized

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$^1$With bulk effect we mean processes that are related to more efficient hot-electron excitation and transport in the electrodes (see also section 4.2).
5.3. Results on barrier oxidation

Figure 5.5: (a) Barrier height, (b) barrier thickness, and (c) barrier asymmetry as extracted from a fit of the Brinkman model to the current-voltage characteristics of the $\text{AlO}_x$ MTJs with different oxidation times. In (a) the barrier height extracted from a Fowler analysis of the photocurrent curve is also shown. The insets in (c) represent energy diagrams illustrating the sign of the barrier asymmetry relative to the top T and bottom B electrode. The vertical dashed lines indicate the oxidation time where the MR is highest and the negative photocurrent contribution has disappeared.
Figure 5.6: Current-voltage characteristics of AlO$_x$ MTJs with varying oxidation times, for parallel magnetizations. The symbols indicate the measurements, and the solid lines are fits of the Brinkman model. The extracted fit parameters are visualized in Fig. 5.5.

junctions the photocurrent curve is more complex, resulting in the fact that no effective barrier height could be extracted. First, for incident photons with energy $h\nu$, the bottom to top electron current contribution can not be approximated by the simple Fowler relation $(h\nu - \phi)^2$, due to the energy dependence of the elastic scatter processes (see above). Second, for the underoxidized junctions the (negative) photocurrent starts already at a significantly lower photon energy compared to the optimal and overoxidized ones. This is either an indication of the effect of photon-assisted tunneling through the top of the barrier, a lower barrier height due to the incomplete formation of the barrier, or a combination of the two.

### 5.3.2 Current-voltage measurements

By studying the current-voltage characteristics of the different MTJs, additional information on the tunnel barrier can be extracted. In Fig. 5.6 the I(V) characteristics of the different junctions are shown for parallel magnetizations, together with fits from the Brinkman model (see section 2.1). What is immediately apparent is the change from an almost linear to a strongly non-linear I(V) curve with increasing oxidation time. This change is caused by the modification of the spacer layer due to an increase of the amount of incorporated oxygen. More detailed properties can be extracted from the parameters obtained from the Brinkman fit, as shown in Fig. 5.5.

The extracted barrier thickness increases monotonically with oxidation time, as already expected from the observed monotonic increase of the (logarithm of the)
5.3. Results on barrier oxidation

resistance area product [Fig. 5.1(b)]. Qualitatively a similar behavior was also measured by van de Veerdonk [51]. The extracted effective barrier height $\phi$ decreases rapidly above 120 s, which correspond to overoxidized junctions. However, the barrier height as determined from photoconductance curves shows a weak increase towards higher oxidation times. This discrepancy indicates that either the Brinkman model is not appropriate for these junctions, or that the effective barrier height for the tunneling electrons differs from that for photoexcited electrons. It should be noted that in the Brinkman (as well as the Simmons) model, the barrier is assumed to be trapezoidal, with $\phi$ as the average barrier height, whereas the value of $\phi$ as deduced from a (semi-classical) Fowler analysis is assumed to coincide with the maximum of the barrier. For overoxidized junctions it has been suggested that Co or Fe is being incorporated within (as impurities) or underneath (as CoO$_x$ or FeO$_x$) the barrier [51]. The resulting composite barrier can then support thermally and field-assisted electron transport via impurity states. A Brinkman fit then leads to an effective barrier height which is lower than the distance from the Fermi level to the top of the tunnel barrier.

Also, due to its exponential dependence on barrier thickness and height, the tunneling electrons will cross the barrier predominantly at those positions where the transmission is highest. For a non-homogenous barrier this leads to a strong non-homogeneous current distribution, i.e. localized in so-called hotspots. The resulting fit parameters are than also not representative anymore for the integral characteristics.$^2$ With our photoconductance method one measures essentially the barrier height averaged over the surface-area,$^3$ which gives a better indication of the overall barrier height.

In Fig. 5.5(c) also the barrier asymmetry parameter $\Delta \phi$, as extracted from the Brinkman fit, is shown. Here a clear sign change is visible between under and overoxidized MTJs, indicating a change in the barrier shape. For oxidation times $< 120$ s, the sign of the asymmetry corresponds to that inferred from the scattering argument [see Fig. 5.4(a)] and the difference in workfunctions between Al and Co$_{90}$Fe$_{10}$ (section 4.2). However, for high oxidation times, the sign of the asymmetry is opposite to that expected for a composite barrier with a low barrier height at the bottom interface. However, as discussed before, the parameters extracted from a Brinkman fit can easily deviate from the exact results. A more direct technique is needed to extract real quantitative values for the barrier asymmetry. In the next chapter we will use a special method to directly infer the barrier asymmetry from photoconductance measurements.

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$^2$Even for an ideal barrier shape, the tunnel current will be influenced by the density of states of the electrodes [see equation (2.1)], as well as the effective electron mass in the barrier. The former effect is neglected in the description by Brinkman. The effective mass in the barrier is assumed to be equal to the free electron mass.

$^3$Lateral barrier thickness variations have no strong influence on the lateral photocurrent distribution, since the photocurrent yield is (in first order) not dependent on the barrier thickness. Lateral barrier height variations, however, do influence the photocurrent, due to the quadratic dependence on the energy [see equation (2.23)]. This means that some non-linear influence of lateral variations in $\phi$ will be present, but these will be much smaller than the exponential variations in the tunnel current.
5.4 Conclusions

In this chapter we have shown the viability of photoconductance as a tool for studying the effect of the oxidation process on the barrier in AlO$_x$ based MTJs. The disappearance of a negative contribution to the photocurrent is argued to be caused by the complete oxidation of the Al barrier layer, and coincides with a maximum in the MR ratio. For overoxidized junctions, the determined barrier heights increase weakly with oxidation time, sharply contrasting to the barrier height extracted from a Brinkman fit to the current-voltage characteristics. Although parameters extracted from such fits can sometimes give an indication of the barrier height and shape, they will also reflect other effects on the I(V) curve, such as a non-homogeneous barrier thickness and height. In this respect, photoconductance is a much more direct method.
Chapter 6

Nature of the barrier in TaO$_x$ magnetic tunnel junctions

Although aluminum oxide is still the most studied barrier material in magnetic tunnel junctions, there are certain cases in which alternative barrier materials might be more useful. In this chapter, one of these different materials, namely TaO$_x$, is studied in more detail. It is shown that, due to its small bandgap, direct information regarding the barrier asymmetry can readily be obtained from photoconductance measurements. After that, results are shown from which structural changes in the barrier with increasing thickness have been inferred, leading to a reduction in the magnetoresistance ratio.

6.1 Introduction

The most crucial part in a magnetic tunnel junction (MTJ), both from a fundamental as well as a processing point of view is the tunnel barrier. To make the incorporation of these structures in magnetic memory devices such as MRAMs possible, certain requirements have to be satisfied. For example, the barrier layer must be thin enough to allow electrons to tunnel from one electrode to the other, while preserving their spin. But at the same time it should be of homogeneous thickness and void of defects, which could otherwise lead to a reduced lifetime of the structure. To supply the demand of ever increasing bit densities, downsizing of the junction area becomes an important issue [8]. To maintain or increase the readout speed, it is essential that the junction resistance does not increase, which would otherwise lead to an unacceptable electronic noise level. The resistance-area product (R×A) is therefore the parameter which has to be reduced. Since the tunneling probability depends exponentially both on the barrier thickness as well as on the (square root of the) barrier height, a reduction of the R×A product can therefore be accomplished by reducing either of the two.

The material which is most often used as the tunnel barrier is aluminum oxide.
By oxidizing a thin Al layer the highest magnetoresistance (MR) ratios at room temperature, up to \( \sim 70\% \), have been achieved [7]. However, experimentally it has been found that reducing the \( R \times A \) product by reducing the thickness of the deposited Al layer only works down to a certain limiting thickness, corresponding to a \( R \times A \) product of \( \sim 200 \, \Omega \mu m^2 \). Oxidizing even thinner Al layers results in a degradation of the junction properties, leading in particular to a reduced MR ratio [50]. A different method for reducing the \( R \times A \) product is by choosing a barrier material with a lower barrier height as compared to AlO\(_x\).

In the previous chapter we have determined the barrier heights of AlO\(_x\) based MTJs to be roughly between 2.5 and 3 eV. By using a barrier material with a much lower bandgap, a reduced barrier height might be expected. One possible candidate material is TaO\(_x\), which has a bandgap of \( \sim 4.2 \) eV (for bulk Ta\(_2\)O\(_5\)) [34], compared to \( \sim 8 \) eV for AlO\(_x\) [52]. Barrier heights obtained from fits of the Simmons or Brinkman models (section 2.1) to the current-voltage characteristics indeed showed significantly lower barrier heights [53, 54], viz. in between 0.3 and 1 eV. However, only small MR ratios (< 10\%) have been observed. At present, it is not known why the MR ratio observed in these studies, was limited to such low values.

As already discussed in section 2.3, the low barrier height in TaO\(_x\) MTJs may, in principle, also provide access to a spin-dependent photocurrent. Although this was one of the reasons to study TaO\(_x\) MTJs in the first place, no spin-dependence has been observed. This is caused either by spin-mixing of electrons in the barrier conduction band, or a significantly smaller spin polarization for electrons crossing the barrier above the Fermi level.

In the following sections we present results of photoconductance experiments, that we carried out to study TaO\(_x\) based MTJs in more detail. The relatively small bandgap of TaO\(_x\) makes it possible, within the limited spectral range of our setup, to make optical excitations in the barrier itself. From the experiments, important information regarding the barrier asymmetry could be obtained. Together with information from current-voltage measurements and structural studies, insight into the origin of the observed low MR ratio is obtained.

### 6.2 Experimental

The TaO\(_x\) based MTJs have been fabricated by sputter deposition through metallic shadow masks, in the same way as described in section 3.1. The following layer stack is used: glass/3.5 Ta/3.0 Ni\(_{80}\)Fe\(_{20}\)/10.0 Ir\(_{20}\)Mn\(_{80}\)/2.5 Ni\(_{80}\)Fe\(_{20}\)/1.5 Co\(_{90}\)Fe\(_{10}\)/TaO\(_x\) barrier/4.0 Co\(_{90}\)Fe\(_{10}\)/10.0 Ni\(_{80}\)Fe\(_{20}\)/3.5 Ta, with all thicknesses in nanometers. The junction area is defined by the width of the mask slits, which is varied between 60, 110, and 200 \( \mu m \). The TaO\(_x\) tunnel barrier is formed by first depositing a thin Ta layer over the complete substrate and subsequent oxidation in an oxygen plasma. The thickness of the Ta layer is varied between 0.8-1.4 nm, and the oxidation time between 5-240 s. No annealing steps were carried out afterwards. For the conductance, magnetoconductance, and photoconductance measurements, the setup as described in section 3.2.2 has been used.

To directly quantify the amount of oxygen incorporated in the barrier, Ruthera-
6.3 Direct observation of the barrier asymmetry

The shape of the barrier potential in a MTJ determines to a large extent the transport properties of the junction. The barrier is often simply described in terms of an ef-
Effective barrier height $\phi$. However, the actual shape of the barrier is more complex, and the parameter $\phi$ is not always sufficient in accurately describing the transport across the junction. For example, the presence of a built-in electric field, caused by different (effective) workfunctions of the two electrodes (see section 4.2), and/or a non-homogeneous barrier layer, can strongly modify the potential landscape. The barrier asymmetry parameter $\Delta \phi$ is then often used to extend the description of the barrier.

Several techniques exist to deduce $\Delta \phi$ from the current-voltage characteristics of the junction [17, 56]. However, these methods are indirect, as explained already in section 2.1. This means that the influence of the barrier shape itself can be masked by effects on the I(V) curve, such as a non-homogenous barrier thickness, as well as density of state effects. In this section we use a photoconductance method to directly probe the barrier asymmetry in MTJs independently and reliably.

By illuminating the junction structure with photons, with energies above the bandgap of the tunnel barrier, electrons in the insulator will be excited from the valence to the conduction band. Those electrons which have upon generation a kinetic energy that is smaller than that which is required to reach the top of the barrier, will...
6.3. Direct observation of the barrier asymmetry

Figure 6.3: Examples of (the square-root of the absolute) photoconductance curves of TaO$_x$-based MTJs, illustrating the presence or absence of a quadratic dependence on the photon energy. In (a) 1.2 nm, and (b) 1.4 nm Ta barrier layers, subjected to different oxidation times are shown respectively. For clarity, the curves corresponding to a negative photocurrent $I_{\text{photo}}$ are shown below the zero current line. Only for certain oxidation times it has been possible to linearly extrapolate the 2-2.5 eV photon energy region to zero current (indicated by the dotted lines), in order to determine the barrier height $\phi$.

all leave the barrier in the “downhill” direction (see section 2.2.4). This induces a directional preference for the excited electrons and will thus result in a net photocurrent. The sign and magnitude of $\Delta \phi$ can then easily be derived by determining the applied bias voltage at which the photocurrent changes sign.

In Fig. 6.2(a) typical photoconductance curves are shown for a TaO$_x$ MTJ under the application of different bias voltages. The light was incident on the top electrode, and a positive photocurrent corresponds to an electron flux from top to bottom electrode. Two different regimes can be distinguished. For low photon energies, up to approximately 4.2 eV (dashed vertical line in Fig. 6.2), electrons will be excited only in the electrodes. The resulting net photocurrent yield depends then critically on the relative absorption, excitation, electrode transport, interface transmission, and barrier transport of the two electrodes (see section 2.2.3). In contrast to the AlO$_x$-based MTJs discussed in chapter 5, the net photocurrent yield is mostly not dominated by an electron flux from only one of the two electrodes. This implies that no clear quadratic behavior with photon energy is observed. As illustrated in Fig. 6.3, only for certain oxidation times, e.g. for (drastic) under or overoxidation, the photocurrent yield is reasonably described by the Fowler relation [equation (2.23)]. For such junctions, barrier heights of roughly 1-1.5 eV are determined. Also, it is difficult to infer the sign, let alone the magnitude of $\Delta \phi$ from this energy range of the photoconductance curves. For that, we look at a different region of the spectrum.

For photon energies above the bandgap of the insulator, also electron-hole pairs will be generated in the insulator (see section 2.2.4). Since these excitations are con-
Chapter 6. Nature of the barrier in TaO$_x$ magnetic tunnel junctions

Figure 6.4: Photoconductance curves of a TaO$_x$ MTJ (1.2 nm Ta and 50 s oxidation) for (a) illumination of the top electrode and (b) illumination of the bottom electrode. Although the low energy (< 4.2 eV) photocurrent does depend on the illumination direction, the voltage dependent additional photocurrent due to interband excitations at high energies (> 4.2 eV) changes sign at essentially the same voltage, 75±10 meV.

defined to a single layer, the sign of this photocurrent contribution corresponds now directly to the sign of the electric field in the barrier. Also, the net photocurrent yield is, in contrast to excitation from the electrodes, not reduced by a second opposite electron flux, or by reflections from the barrier interfaces. Due to this larger efficiency, the contribution from interband transitions will dominate at higher energies (see also section 2.2.5). To directly demonstrate the onset of excitations in the insulator, an optical transmission spectrum of a single TaO$_x$ layer on a quartz substrate is shown in Fig. 6.2(b). From this a bandgap of roughly 4.2 eV is determined, which is in good correspondence with values found for stoichiometric Ta$_2$O$_5$ [34].

From the high-energy part (> 4.2 eV) of the photoconductance curves in Fig. 6.2(a) it can be seen that, for this junction, the photocurrent due to interband excitations changes sign around an applied bias voltage of ~150 mV, with an uncertainty of ~15 mV due to the background photocurrent from electrode excitations. As illustrated in Fig. 6.2(c) this implies that the average electric field in the insulator becomes zero at ~150 mV, and this voltage therefore directly corresponds to the barrier asymmetry $\Delta \phi$. In this way $\Delta \phi$ can be determined quite accurately in complete junction devices.

To exclude an influence of the absorption profile on the determination of $\Delta \phi$, photoconductance curves have been measured for a representative TaO$_x$ MTJ, under different directions of illumination. From Fig. 6.4 we can see that by reversing the incident light direction from front to back illumination, the voltage dependent additional high-energy (> 4.2 eV) photocurrent changes sign at essentially the same voltage, 75±10 meV for this junction. Since the optical penetration depth in TaO$_x$ above 4.2 eV is much larger than the thickness of the barrier [34], the excitation oc-
6.3. Direct observation of the barrier asymmetry

curs homogeneously throughout the barrier layer. The electrons and holes, which are formed upon the excitation, have in a first approximation an isotropic momentum distribution. Combined with the independence on the direction of incident light, this directly shows that the asymmetry of the potential landscape determines the sign of the photocurrent.

Fig. 6.4 shows that the contribution from excitations in the electrodes \((h\nu < 4.2 \text{ eV})\) depends strongly on the direction of illumination. A clear transition from positive to negative photocurrents is visible when switching from front to back illumination. The photocurrent for small photon energies is due to carriers excited in the top electrode going towards the bottom electrode, and due to carriers excited in the bottom electrode traversing the barrier in the opposite direction. Since the bandgap of \(\text{TaO}_x\) is only 4.2 eV, and since the barrier for electron transport is roughly 1-1.5 eV (see above), the photon energy is, in principle, high enough to create a hole photocurrent for \(h\nu > 2.7 \text{ eV}\). However, when switching between front and back illumination, the amount of absorbed photons will decrease in the top electrode, and increase in the bottom one. Since in Fig. 6.4 the positive contribution decreases and the negative contribution increases, this directly shows that a negative photocurrent originates from electrons excited in the bottom electrode and not from holes excited in the top electrode. Similar reasoning holds for a positive photocurrent. Apparently holes play no significant part in the photocurrent generation.

In previous work asymmetric tunnel conductance curves were found for suboptimally oxidized MTJs with the same top and bottom electrode materials, suggesting a non-symmetric barrier profile [57, 58, 59]. To directly investigate the relation between the barrier oxidation state and the asymmetry of the tunnel barrier, a series of MTJs with different Ta thicknesses and oxidation times are studied. In Fig. 6.5(a) the MR ratio for each of the junctions is shown. For the MTJs with a 1.0 and 1.2 nm Ta layer thickness, a clear maximum in the MR is present. For \(\text{AlO}_x\) this behavior is well known, and is attributed to the complete oxidation of the barrier layer, without oxidizing the underlying magnetic electrode [58, 59]. For the above \(\text{TaO}_x\) junctions, also the barrier asymmetry was determined from photoconductance experiments, and is plotted in Fig. 6.5(b). For the oxidation time where the barrier is symmetric, the corresponding junction shows a maximum in the MR. This supports the simple picture, where a completely oxidized barrier, sandwiched between two identical electrodes, has a symmetric potential profile. This in contrast to results from a Brinkman fit, for which optimally oxidized junctions were found to have effective barrier asymmetries significantly different from zero: -50 and -100 mV for a 1.0 and 1.2 nm oxidized Ta layer respectively. Also, no sign-reversal with oxidation time has been observed from Brinkman fits. As stated before, these barrier parameters can reflect a possibly heterogeneous tunnel current distribution and can be influenced by density of state effects. This in contrast to photoconductance which yields directly the laterally average barrier asymmetry.

Apparently under or overoxidation of the barrier material causes an asymmetry in the barrier potential with differing signs. Within a simple picture, in which the interface dipole is essentially the same as that for the metal/vacuum interface, such an asymmetry could be explained by a difference in workfunctions for the two electrodes (Ta has a lower workfunction than Co or Fe, as shown in section 4.2). Al-
Chapter 6. Nature of the barrier in TaO$_x$ magnetic tunnel junctions

Figure 6.5: For MTJs with TaO$_x$ based tunnel barriers, (a) the MR ratio, (b) the barrier asymmetry $\Delta \phi$ as determined by photoconductance, and (c) the $R \times A$ product are shown. In (a) the thicknesses of the deposited Ta layers are shown. The vertical dashed lines correspond to the oxidation times where the barrier is symmetric and the MR ratio has a maximum. The insets in (b) represent energy diagrams, defining the sign of the barrier asymmetry relative to the top T and bottom B electrode.

Alternatively, the effect could result from an inhomogeneous oxygen distribution in the barrier (resulting in a varying bandgap), or from a combination of these two causes. From photoconductance experiments on junctions where the complete bottom electrode is replaced by a 35 nm Ta layer, on top of which a TaO$_x$/Co$_{90}$Fe$_{10}$ structure is present, indeed a large negative barrier asymmetry of $\sim$-500 mV is found.

Due to the limited photon energy range of our experimental setup, only relatively
6.4 Barrier thickness dependent magnetoresistance

low bandgap barriers can be studied in this way. This implies that we have not been able to measure $\Delta \phi$ directly in AlO$_x$ based MTJs (which has a bandgap of roughly 8 eV [52]). However, judging from the above discussion, one would expect a similar sign-reversal with oxidation time for AlO$_x$ barriers. Although this is in agreement with the results from the Brinkman fits of Fig. 5.5(c), similar fits for the TaO$_x$ MTJs did not show the expected sign-reversal. Only with the use of a vacuum UV setup, so that higher photon energies are available, a definite answer can be given.

6.4 Barrier thickness dependent magnetoresistance

As seen in Fig. 6.5(a), the MR ratio of TaO$_x$ based MTJs does not only depend on the oxidation time, for a fixed thickness of the Ta layer before oxidation, but also on that Ta layer thickness itself. The MR drops sharply with increasing thickness, and completely vanishes for a thickness of 1.4 nm or more. In contrast, for junctions based on AlO$_x$ barriers, the MR ratio is mostly independent of the Al thickness.\(^1\) Also the magnitude of the MR ratio is significantly lower than that for AlO$_x$ based MTJs, where as-deposited junctions can already show MR ratios of over 20% [see Fig. 5.1(a)]. This difference might be of an intrinsic origin, i.e. a lower effective spin polarization at the TaO$_x$/Co$_{90}$Fe$_{10}$ interface compared to AlO$_x$/Co$_{90}$Fe$_{10}$, caused by different decay lengths of s and d-type electron states (with different polarizations) in the tunnel barrier, or a lower barrier height. Or it might be of extrinsic origin, related to structural changes in the TaO$_x$ barrier with increasing thickness. Since it is quite difficult to extract experimental information on the intrinsic properties, we focus in this section on the structural characteristics.

In Fig. 6.5(c) the R×A product is plotted for all deposited TaO$_x$ junctions. For a certain Ta thickness, a monotonic increase with oxidation time is observed, similar to that for AlO$_x$ [see Fig. 5.1(b)]. This is related to the fact that for longer oxidation times, more and more oxygen is incorporated in the barrier, improving the insulating properties of the junction. However, the interesting feature that can be seen is that, for the same oxidation time, the R×A product decreases with increasing Ta thickness. To clarify this behavior, RBS analysis was carried out on similar planar layer stacks. A representative spectrum, and the exact layer stack can be seen in Fig. 6.1. In Fig. 6.6(a) and (b) the determined oxygen content is plotted as a function of oxidation time (for constant Ta thickness), as well as Ta thickness (for constant oxidation time) respectively. As shown in Fig. 6.6(a), the incorporation of oxygen follows a simple log(t) behavior, similar to what is found for AlO$_x$ [48]. However, with increasing Ta thickness, a significant reduction in the oxygen content, after a fixed oxidation time (60 s), is observed [Fig. 6.6(b)], consistent with the observed decrease of the R×A product. This directly contradicts the naive picture of a simple oxidation process where the time-dependent oxidation rate is independent of the layer structure. For AlO$_x$ it has been argued that the oxidation proceeds predominantly along grain boundaries [48, 61]. If the grain sizes increase with increasing Ta layer thickness [62],

\(^1\)Only for extremely thin barriers, below roughly 0.6 nm, a reduction of the MR ratio is observed, due to the presence of pinholes [60].
the oxidation rate after a given oxidation time is expected to decrease with increasing Ta layer thickness. Furthermore, since Ta expands almost 250% after oxidation, compared to only 25% for Al [54], this will lead to a less uniform barrier layer. These two effects would indeed lead to a decrease of the $R \times A$ product with increasing Ta layer thickness, after a fixed oxidation time. Also, the increase of the barrier inhomogeneity with increasing Ta barrier thickness might explain the observed lower value of the MR ratio. It is then assumed that the effective spin-polarization is negatively affected by an increasing probability of adverse conductance processes via non-magnetic barrier or interface states.

To further investigate the proposed structural changes with thickness, results from photoconductance experiments of junctions with different Ta layer thicknesses have been compared. In Fig. 6.7 photocurrent yield curves for a 1.2 and 1.4 nm Ta layer, oxidized for different oxidation times are presented. As a function of oxidation time the low energy ($< 4.2$ eV) photocurrent is seen to decrease and become negative. This is partially caused by the fact that the built-in electric field $\Delta \phi$ changes sign (as can be seen from the high energy part): scatter processes in the barrier change the electron transport (as described in the last subsection of 2.2.3). However, this cannot be the complete story. For a 1.4 nm Ta barrier layer, the low energy photocurrent is already negative when the asymmetry $\Delta \phi$ is still positive [see Fig. 6.7(b)]. This is in contrast to a 1.2 nm (and thinner) Ta layer [Fig. 6.7(a)]. This indicates that the photo-excitation, the hot-electron transport, and/or the interface transmission in the top electrode decreases relative to the bottom electrode with increasing Ta thickness. Structural changes in the barrier with increasing Ta thickness can of course have a profound influence on the previous processes that determine the photocurrent. However, to determine the exact magnitude of these effects, a more quantitative
6.5 Conclusions

In this chapter TaO$_x$ has been investigated as a possible alternative barrier material in MTJs. The significantly lower barrier height makes it, in principle, an attractive option for low R×A junctions. Due to its low bandgap (∼4.2 eV), direct information on the barrier asymmetry has been extracted from photoconductance measurements. The optimal oxidation time, corresponding to a maximum in the MR ratio, shows a symmetric barrier profile. Together with current-voltage measurements and structural characterizations, evidence for a decrease in tunnel barrier quality with increasing Ta thickness has been found. This possibly explains the observed strong reduction in MR with increasing Ta layer thickness, and maybe even the relatively low MR ratio (∼7%) for the thinnest barriers studied. This ultimately limits the incorporation of TaO$_x$ in application relevant devices.

Figure 6.7: Zero bias photoconductance curves for (a) 1.2 nm Ta and (b) 1.4 nm Ta oxidized for various oxidation times. The low energy (< 4.2 eV) photocurrent tends towards negative values with increasing oxidation time. Due to the fact that in (b) this contribution is already negative when the high energy photocurrent (> 4.2 eV) is still in the opposite direction, the former effect cannot be solely explained by a negative built-in voltage $\Delta\phi$.

analysis would be needed.

6.5 Conclusions

In this chapter TaO$_x$ has been investigated as a possible alternative barrier material in MTJs. The significantly lower barrier height makes it, in principle, an attractive option for low R×A junctions. Due to its low bandgap (∼4.2 eV), direct information on the barrier asymmetry has been extracted from photoconductance measurements. The optimal oxidation time, corresponding to a maximum in the MR ratio, shows a symmetric barrier profile. Together with current-voltage measurements and structural characterizations, evidence for a decrease in tunnel barrier quality with increasing Ta thickness has been found. This possibly explains the observed strong reduction in MR with increasing Ta layer thickness, and maybe even the relatively low MR ratio (∼7%) for the thinnest barriers studied. This ultimately limits the incorporation of TaO$_x$ in application relevant devices.
Chapter 6. Nature of the barrier in TaO$_x$ magnetic tunnel junctions
Chapter 7

Barrier modification due to anneal treatment

A very useful process step in fabricating magnetic tunnel junctions is a modest anneal treatment in the presence of a high magnetic field. Roughly a doubling of the magnetoresistance ratio is commonly observed. In this chapter we will investigate the processes that take place upon this anneal treatment. For both AlO$_x$ as well as TaO$_x$ based junctions, the increase of the magnetoresistance ratio is, from photocurrent experiments, found to be correlated to the barrier oxidation state. The observed changes in the potential landscape of the barrier layer, are argued to be caused by a redistribution of the oxygen content or a change of the interface structure.

7.1 Introduction

Ever since the discovery of large magnetoresistance (MR) effects in magnetic tunnel junctions (MTJs) [6], improvement of the MR ratio has been one of the aims of the research of these structures. Higher MR ratios translate into increased signal to noise ratios in applications such as MRAMs [8]. Several groups have found that subjecting MTJs to a modest temperature treatment, up to roughly 200-300 °C for several tens of minutes, in the presence of a magnetic field, significantly enhances the MR ratio [63, 64]. This effect has been attributed to a redistribution of the oxygen in the barrier layer [63], and/or a change of the barrier interface structure [66]. However, obtaining direct evidence of changes in the barrier layer is difficult. Due to the interfacial sensitivity of the spin polarized tunneling process [67], small changes can already have a profound influence on the MR effect. Also, due to the extremely small barrier thickness, the use of techniques with only modest depth resolution, such as

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Annealing at even higher temperatures is accompanied by a sharp drop in the MR. This is most probably related to the diffusion of Mn from the exchange bias layer towards the barrier [65]. This is, however, an entirely different subject and will not be treated in this chapter.
Rutherford backscattering spectrometry (RBS) or X-ray photoelectron spectroscopy (XPS), to observe changes in the depth profile is difficult, to say the least.

With the use of a photoconductance method, we have shown that structural changes in the barrier as a function of oxidation time have a profound influence on the barrier height and asymmetry (see chapters 5 and 6). From these earlier studies, photoconductance seems therefore a suitable technique to study the influence of an anneal treatment in more detail.

In this chapter, the influence of an anneal treatment on AlO$_x$ barrier material that is used in MTJs that are presently being developed for MRAM applications, as well as TaO$_x$ MTJs is investigated. A study of TaO$_x$ based MTJs is included, since they offer the possibility to gather direct information on the barrier asymmetry from photoconductance experiments (see section 6.3). Both types show upon annealing a significant increase in MR ratio, as well as a shift of the “ optimum” oxidation time towards higher values. The results of our photoconductance experiments support the point of view that the increase of the MR ratio is caused by a modification of the oxygen distribution, or a change in the bottom electrode/barrier interface structure.

### 7.2 Experimental

The investigated samples are made by sputter deposition through metal contact masks, resulting in 60 x 60 and 200 x 200 µm$^2$ junction areas, for TaO$_x$ and AlO$_x$ based MTJs, respectively (see section 3.1). The following layer stack is used: glass/3.5 Ta/3.0 Ni$_{80}$Fe$_{20}$/10.0 Ir$_{20}$Mn$_{80}$/2.5 Ni$_{80}$Fe$_{20}$/1.5 Co$_{90}$Fe$_{10}$/TaO$_x$ or AlO$_x$ barrier/4.0 Co$_{90}$Fe$_{10}$/10.0 Ni$_{80}$Fe$_{20}$/3.5 Ta, with all thicknesses in nanometers. The TaO$_x$ or AlO$_x$ barrier layers are made by first depositing 1.0 nm Ta or 1.7 nm Al over the complete substrate, followed by plasma-oxidation for 8-16 s and 50-400 s respectively.

After fabrication the samples are annealed in an oven, under an argon gas flow. This prevents the electrodes from oxidation at the elevated temperatures. During annealing, a high in-plane magnetic field of approximately 1000 kA/m is applied, to keep the Ir$_{20}$Mn$_{80}$ exchange bias layer aligned. Each anneal step takes roughly 25 minutes. After each anneal step the (magneto)conductance is measured and a photoconductance study is carried out. Subsequently, the sample is subjected to a next anneal step, at a temperature that is 25 °C higher than during the previous anneal.

### 7.3 Temperature induced barrier changes

To demonstrate the effects of an anneal treatment, the MR ratio as well as the resistance is shown in Fig. 7.1 for a typical AlO$_x$ and TaO$_x$ MTJ, respectively. The barriers consist of 1.7 nm Al and 1.0 nm Ta, oxidized for 200 s and 12 s respectively. For both the AlO$_x$ and the TaO$_x$ based structures, a significant increase in the MR ratio is observed, consistent with the findings of other groups [63, 66]. In both cases the MR ratio roughly doubles with respect to the as-deposited values. Above a certain op-
7.3. Temperature induced barrier changes

Figure 7.1: (a), (b) Magnetoresistance and (c), (d) resistance of a typical AlO$_x$ and TaO$_x$ MTJ after various anneal steps. The AlO$_x$ and TaO$_x$ barrier layers consist of 1.7 nm Al and 1.0 nm Ta, oxidized for 200 s and 12 s respectively.

To better understand the drop in R × A product for the AlO$_x$ MTJs, shown in Fig. 7.1(c), the same junction has also been studied by photoconductance measurements. In Fig. 7.2(a) photocurrent yield curves as a function of photon energy are shown for the 200 s oxidized AlO$_x$ barrier, for different anneal temperatures. From a Fowler analysis (see section 2.2.3) the barrier heights have been determined and are plotted in Fig. 7.2(b). A slight decrease of ≈0.1 eV in the barrier height φ with anneal temperature is visible. Although not shown here, a similar trend is also present for the

timum anneal temperature, degradation sets in. This happens much earlier in the case of TaO$_x$ (above 150 °C) as compared to AlO$_x$ (above 225 °C). This difference is not understood, but might be related to a higher inhomogeneity of the barrier oxide, caused by the larger expansion of the TaO$_x$ barrier during oxidation (see section 6.4). Both the AlO$_x$ as well as the TaO$_x$ based MTJs show changes in the resistance (R × A product) with increasing anneal temperature. Although these changes differ in sign, as discussed in more detail below, both results are indicative of an anneal treatment induced modification of the barrier layer.
Chapter 7. Barrier modification due to anneal treatment

Figure 7.2: (a) Photoconductance curves and (b) the determined barrier heights for an AlO$_x$ based MTJ, annealed at different temperatures. The barrier was formed by oxidizing a 1.7 nm Al layer for 200 s. The light is incident on the top electrode, and no bias voltage is applied.

AlO$_x$ MTJs with different oxidation times. Due to the exponential dependence of the tunnel probability on the (square-root of the) barrier height, such a small decrease in $\phi$, can already significantly influence the $R \times A$ product. However, the reduction of a factor $\sim 6$ as observed in Fig. 7.1(c), requires an additional small reduction in the (nominal) barrier thickness of 2.2 nm by $\sim 0.1$ nm, and/or in the effective mass of $\sim 0.05$ m$_e$ (from 1). The above shows that the change of the magneto-electronic properties after annealing, is accompanied by a change in the potential landscape of the tunnel barrier. For the underoxidized MTJs that exhibited a negative contribution to the photocurrent (see Fig. 5.2), no significant change in this contribution after an anneal treatment was observed. This indicates that some unoxidized Al is still left below the barrier, even after the barrier modification.

Due to a significant photocurrent contribution from both electrodes in the case of TaO$_x$, no simple quadratic $h\nu$-dependence of the photocurrent yield is observed (see section 6.3). Therefore, we could not accurately determine $\phi$, let alone small changes in $\phi$. The observed increase in $R \times A$ product with anneal temperature as observed in Fig. 7.1(d), might be due to an improvement of the initially low structural quality of the barrier (see section 6.4). A redistribution of the oxygen might then improve the insulating properties, e.g. it might indicate that metallic pinholes are eliminated. To investigate the possible role of the oxygen distribution in the improvement of the magneto electronic properties of the MTJs, the junctions are characterized, not only as a function of anneal temperature, but also as a function of the oxidation time. We will first focus on the results for AlO$_x$ barriers, after which a comparison is made with results from the TaO$_x$ MTJs.

In Fig. 7.3(a) the MR curves of the previously studied AlO$_x$ MTJ are shown, as a function of applied magnetic field, for different anneal temperatures. Besides the increase in the maximum MR ratio, also the shape of the curves change. The applied
7.3. Temperature induced barrier changes

Figure 7.3: Magnetoresistance of AlO$_x$ based MTJs, as a function of (a) applied magnetic field, and (b) oxidation time for different anneal temperatures. In (a) the MTJ was oxidized for 200 s.

Field at which the pinned layer switches, shifts to higher negative fields, and the high resistance “plateau” becomes more flat. This is caused by the improvement of the exchange-biasing during heating in a magnetic field [68]. However, this cannot be the sole reason for the improvement of the MR. Comparing the curves for 175 °C and 225 °C, hardly any improvement in the anti-parallel alignment is visible. Still, a ∼20 % increase in MR is present.

To investigate this additional increase in MR, junctions with different oxidation times were studied in more detail [see Fig. 7.3(b)]. Similar as the results shown in Fig. 5.1, a clear maximum as a function of oxidation time is visible. After an anneal treatment to 225 °C, a modification of the curve is visible. The increase in MR is much larger for overoxidized MTJs (e.g. 400 s) than for underoxidized ones (e.g. 50 s). Also a small shift of the maximum is just visible from ∼120 s to ∼200 s. This already clearly demonstrates an influence of the oxygen content on the improvement of the MR.

In Fig. 7.4(a) results from similar magnetoconductance measurements on TaO$_x$-based MTJs are shown. Again a maximum for a certain oxidation time is seen, related to the “optimal” oxidation of the Ta layer. Although difficult to see, this maximum shifts to slightly higher oxidation times after an anneal treatment (from 10 s in the as-deposited state to 12 s after annealing at 150 °C), similar to the AlO$_x$ MTJs [see Fig. 7.3(b)]. The degradation of the MR ratio with high anneal temperatures [see Fig. 7.1(b)] sets in sooner for overoxidized TaO$_x$ MTJs, than for underoxidized ones. This might be related to the large expansion of Ta during oxidation (see section 6.4).

For these same junctions, the barrier asymmetry has been determined from photoconductance experiments. The results are shown in Fig. 7.4(b). A clear shift in the

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2Since for TaO$_x$ based MTJs the shapes of the MR curves are similar to that of the AlO$_x$ MTJs [Fig. 7.3(a)], they are not shown separately.
Chapter 7. Barrier modification due to anneal treatment

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Figure 7.4: (a) Magnetoresistance ratio, and (b) barrier asymmetry as a function of oxidation time for TaO$_x$ based MTJs annealed at different temperatures. The barrier asymmetry in (b) was determined from photoconductance measurements (see chapter 6). The insets in (b) represent energy diagrams defining the sign of the asymmetry relative to the top T and bottom B electrode.

barrier asymmetry towards negative values is observed. The oxidation time where the barrier profile is symmetric lies now at a higher value, roughly corresponding to the new maximum in the MR. Extending the discussion in section 6.3, we conclude that for the highest MR, and thus a (laterally averaged) symmetric barrier profile, one should anneal junctions that, before annealing, would be characterized as “slightly overoxidized”.

From a Brinkman fit (section 2.1) to the current-voltage characteristics of both TaO$_x$ and AlO$_x$ based MTJs, the observed trend in the barrier asymmetry, could not be corroborated. Also the extracted barrier thickness and height did not show a clear trend as a function of anneal temperature. As already discussed before (section 4.1), Brinkman fit parameters should only be seen as a first approximation of the barrier parameters. Only a more direct technique, such as photoconductance, can be used to quantitatively measure the barrier height and asymmetry.

7.4 Conclusions

For both AlO$_x$ as well as TaO$_x$ based MTJs, the observed increase of the MR ratio after an anneal treatment is accompanied by a modification of the barrier shape. Related to the different bandgaps of the two materials, our photoconductance setup provides access to either the barrier height $\phi$, viz. for AlO$_x$, or the barrier asymmetry $\Delta\phi$, viz. for TaO$_x$ based MTJs. Upon annealing of AlO$_x$ junctions a small reduction of $\phi$ is observed. For TaO$_x$ junctions, $\Delta\phi$ becomes more negative and the optimum oxidation time, that is found to coincide with a symmetric barrier profile, shifts to higher values. Although both effects are indicative of either a redistribution of the
7.4. Conclusions

Figure 7.5: Schematic crosssections of an AlO$_x$ or TaO$_x$ MTJ layer stack, for (a) an underoxidized and (b) an overoxidized barrier layer. The oxidation is assumed to be predominantly along grain boundaries (dashed lines). The arrows indicate the redistribution of the oxygen content during annealing.

oxygen content in the barrier, or an improvement of the interface morphology, the processes that take place are not the same. This follows from the different dependence of the R×A product on anneal temperature [Fig. 7.1(c) and (d)].

Still, the fact that initially overoxidized junctions exhibit a higher increase in MR than the initially underoxidized ones, can be explained within a simple representation of the barrier morphology, as shown in Fig. 7.5. As already shown by others [48, 61], the oxidation of thin barrier layers occurs predominantly along grain boundaries, implying that immediately after oxidation a non-homogeneous oxygen distribution is present in the barrier layer. Since for both AlO$_x$ and TaO$_x$ MTJs, the barrier shape changes with annealing, either the oxygen redistributes itself, and/or the interface morphology improves. From direct measurements of the spin-polarization in AlO$_x$-based superconducting junctions [69], one can conclude that the top interface does not significantly change during an anneal treatment. So the improvement of the MR ratio, apart from the “trivial” exchange bias improvement, must originate from changes at the bottom interface, or from within the barrier layer itself. For underoxidized junctions, not enough oxygen is present to completely oxidize the barrier layer. So even when the oxygen redistributes itself, some regions of unoxidized barrier material are still left behind. The oxygen homogenization apparently leads to a modification of the barrier shape, resulting in a modification of the R×A product. The increase in the MR ratio is in this case mostly due to an improvement of the exchange biasing effect. For slightly overoxidized MTJs, the (small) pockets of unoxidized barrier material that are still left, are filled up during annealing by the oxygen that originally resided in small oxidized parts of the bottom electrode, leading to a change in $\Delta\phi$ and $\phi$. This oxidation/reduction process is driven by the large negative free enthalpy of AlO$_x$ or TaO$_x$ as compared to that of (Co-Fe)O$_x$. Now an additional increase in the MR ratio due to the improvement of the effective spin-polarization of the bottom electrode is present, leading to a shift of the maximum MR ratio to higher oxidation times. We therefore conclude that for obtaining the highest MR, one should anneal junctions that are characterized as slightly overoxidized in the as-deposited state.
Chapter 7. Barrier modification due to anneal treatment
Chapter 8
Towards an optical spin valve structure

In this chapter we propose a novel spintronic device, combining certain aspects of the photoexcitation process as outlined in chapter 2, with magnetic sensitivity. The basic idea is to illuminate a spin-valve structure on top of a semiconductor substrate with sub-bandgap photons. Photoexcited electrons that traverse the spin-valve structure and are able to enter the semiconductor conduction band, constitute a photocurrent, whose amplitude depends critically on the alignment of the two ferromagnetic layers in the spin valve. After a basic description of the functioning of the structure, the expected device performance is discussed, using simulations for realistic sets of parameters. Thereafter, results from structural, magnetic, as well as electrical characterizations on initial samples are shown, illustrating the viability of the device. These initial structures did not yet show any magnetic sensitivity. At the end, recommendations are given for improvements that should finally lead to a fully functioning spintronic device.

8.1 Introduction

In the previous chapters we have used our photoconductance method to study the potential landscape in magnetic tunnel junctions in more detail. However, besides as a characterization tool, photoexcitation can also be exploited to add new functionality to traditional structures. For example, as already mentioned in section 2.3, the transport of hot electrons through a magnetic layer depends on the spin of the electron. This effect has already been exploited in for example the spin-valve transistor (SVT) [38], or the magnetic tunnel transistor (MTT) [70], to obtain huge magnetoconductance effects (> 100%) at room temperature. The basic structure of these devices is shown in Fig. 8.1. Both systems contain a n-doped semiconductor collector that is separated from a magnetic metal base layer by a Schottky barrier, which filters the hot electrons from inelastically scattered ones. The base is formed by a magnetic tri-layer to spin filter the injected electrons. In the case of the SVT, the hot electrons...
are injected from a n-type semiconductor emitter into the base layer by thermionic injection over a second Schottky barrier, while the MTT makes use of a tunnel barrier. Both devices have their pros and cons, depending on the particular application one has in mind.

In this chapter we propose a new hot-electron based spintronic device, which utilizes photoexcitation to inject the electrons in the structure. The basic functioning is illustrated with the schematic energy diagram shown in Fig. 8.2. The structure consists of a magnetic trilayer, capped by a thick absorption layer, on top of a n-doped semiconductor substrate. Due to charge redistribution at the metal-semiconductor interface, the conduction band of the n-type semiconductor bends upwards, forming a Schottky barrier [71]. This potential barrier serves as a high-pass filter for the collection of the hot-electrons.

Due to different elastic and inelastic scatter rates for spin up and spin down electrons in a magnetic material [72], the hot-electron flux will be partially spin-polarized after the first magnetic layer. The second magnetic layer then serves as a kind of spin-analyzer. By switching the magnetization of the two magnetic layers independently, the structure behaves as a spin-valve. In the parallel orientation, scattering reduces predominantly only one of the spin currents, resulting in a large photocurrent. For an anti-parallel orientation, electrons with both spins are scattered, sharply reducing the collected photocurrent. Switching between these two cases will result in a large magnetophotocurrent effect.

By illuminating the sample with photons with an energy $h\nu$, below the bandgap
8.2 Simulations

To better understand the parameters that are important for the functioning of our proposed optical spin-valve structure, various calculations are made, using the one-dimensional model for transport through a multilayered stack, as described in section 2.2.2. First, we have to extend this description by specifically including spin-valve structure. SC indicates an n-type semiconductor, and all other layers are metallic. The two layers containing arrows represent magnetic materials. An ohmic contact is present at the backside of the semiconductor. \[ E_F \] represents the Fermi energy, \[ h\nu \] the photon energy, \[ \phi \] the height of the Schottky barrier at the metal-semiconductor interface, and \[ E_{gap} \] the bandgap of the semiconductor.

\[ E_{gap} \] of the semiconductor, the substrate is essentially transparent, and photoexcitation occurs only in the metal layers. However, since absorption will take place throughout all metal layers (including the spin-valve), the layer stack has to be optimized, such that most collected electrons pass through both the magnetic layers. Only then can one expect a huge magnetic field induced modulation of the collected current, comparable to that observed in SVTs and MTTs. The optical excitation makes the flux of the injected electrons (controlled by the light intensity), and their energy (controlled by the wavelength of the light) independent of each other. However, due to interband absorption in the semiconductor, the spectral range for conducting experiments is limited to energies below the bandgap.

For studying hot-electron transport in magnetic multilayers, the optical spin-valve has some advantages over the SVT and MTT. Firstly, essentially no structuring is necessary, since only two electrical contacts are needed, instead of three in the case of a transistor. Also, with the use of so-called wedge-shaped samples and the localization offered by the light spot, a whole range of thicknesses can be studied in a single sample, making it quite suitable for fundamental studies of the important length scales.
Chapter 8. Towards an optical spin valve structure

Table 8.1: Optical constants at $h\nu = 0.95$ eV, as used in the calculations for the absorptivity of our proposed optical spin-valve structure [73]. The refractive index is defined as $\tilde{n} = n + ik$, and $\lambda_{abs} = \frac{1}{\pi \tilde{n}}$ represents the optical penetration depth.

<table>
<thead>
<tr>
<th></th>
<th>Au</th>
<th>Fe</th>
<th>GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>0.411</td>
<td>3.475</td>
<td>3.409</td>
</tr>
<tr>
<td>$k$</td>
<td>8.335</td>
<td>4.975</td>
<td></td>
</tr>
<tr>
<td>$\lambda_{abs}$ (nm)</td>
<td>12.5</td>
<td>21</td>
<td>-</td>
</tr>
</tbody>
</table>

dependent scattering.

We assume that upon excitation in non-magnetic, as well as magnetic layers, electrons of both spin directions are excited with equal probabilities.\(^2\) However, the spin-degeneracy is lifted due to different elastic and inelastic scatter rates during transport of the hot electrons through the magnetic layers, and due to possible spin-dependent scattering and specular reflection at the nonmagnetic/magnetic interfaces [72]. In our model we assume that a spin-up electron, whose spin is aligned parallel with the magnetic moment of the layer will scatter relatively little, implying a high elastic and inelastic scatter length $\lambda_{e\uparrow}$ and $\lambda_{i\uparrow}$. A spin-down electron will however scatter relatively strongly as described by lower scatter lengths $\lambda_{e\downarrow}$ and $\lambda_{i\downarrow}$. By calculating the photocurrent yield $Y$ separately for both spin-channels,\(^3\) and for parallel and antiparallel alignment respectively, the magnetophotocurrent (MPC) ratio can be calculated by

$$MPC = \frac{Y_P - Y_{AP}}{Y_{AP}} = \frac{Y_{\uparrow\uparrow} + Y_{\downarrow\downarrow} - Y_{\uparrow\downarrow} - Y_{\downarrow\uparrow}}{Y_{\uparrow\uparrow} + Y_{\downarrow\downarrow}},$$

where the two arrows indicate the contribution from electrons that are spin-up ($\uparrow$) or spin-down ($\downarrow$) in the first or second magnetic layer respectively. The photocurrent yields are studied at the collector position.

In the following subsections we will first give a description of our proposed optical spin-valve structure. After that all parameters that play a role in the transport process and the resulting MPC ratio and photocurrent yield will be discussed separately. We will discuss those parameters that are most crucial for the functioning of the device most extensively.

8.2.1 Proposed optical spin-valve

In Fig. 8.3(a) and (b) the calculated absorption profile and hot-electron fluxes in a proposed optical spin-valve structure are shown, respectively. The layer stack consists of GaAs(100)/5 nm Fe/5 nm Au/5 nm Fe/25 nm Au. Why we chose this particular set of materials will become clear later on. We made use of the optical constants

\(^2\)The description can however easily be adapted to include spin-polarized photo-excitation, if the optical matrix elements would be known.

\(^3\)In correspondence with Vlutters et al. [27], we neglect spin-mixing in the metallic layers.
8.2. Simulations

Figure 8.3: Calculations of (a) the absorptivity per incident photon, and (b) the positive hot-electron flux (electrons traveling towards the GaAs substrate) for an optical spin-valve structure. The calculations are based on the one-dimensional model as discussed in section 2.2.1 and 2.2.2. The optical constants, that are given in table 8.1 for 0.95 eV photons, are used in the calculations. In (b) the following parameters were used: \( \lambda_e = \frac{1}{2} \lambda_i \), for Au: \( \lambda_i = 37.5 \) nm, for Fe: \( \lambda_{i\uparrow} = 10 \) nm and \( \lambda_{i\downarrow} = 5 \) nm, \( r_i = 0.5 \) and \( r_i = 1 \) for the internal and external interfaces respectively. The curves, indicated with the different arrows, represent the electron fluxes for majority and minority spin-electrons in parallel and antiparallel alignment.

Given in table 8.1 for a photon energy of 0.95 eV, which is in between the bandgap of GaAs (1.42 eV) [71] and the Schottky barrier height at the Fe-GaAs interface (0.6 eV) [74]. As in section 2.2.2, the mean-free-path for elastic scattering is assumed to be half of that for inelastic scattering. In this case, the transport can be fully described one-dimensionally, with effective scatter lengths \( \lambda_e \) and \( \lambda_i \), which are half their 3D values. As already discussed in section 2.2.2, it is difficult to determine \( \lambda_e \) and \( \lambda_i \) separately, let alone their spin-dependence. Experimentally one often observes a single decay length for spin-up electrons and one for spin-down electrons. The experimentally determined mean-free-paths for spin-up electrons around 1 eV above \( E_F \) vary roughly between 2 - 10 nm [72, 75, 76], depending on the magnetic material, substrate choice, and deposition method used. The spin-down mean-free-path is typically less than half of that. Since the mean-free-paths for our structure are not known, we chose intermediate values of \( \lambda_{i\uparrow} = 10 \) nm and \( \lambda_{i\downarrow} = 5 \) nm for our Fe layers. Values for Au also vary quite significantly, but are generally much higher, viz. in between 10 - 40 nm [30, 77, 78]. Later, we will study the influence of \( \lambda_i \), but as an example we used a value of 37.5 nm, which is three times the absorption length \( \lambda_{abs} \), in Fig. 8.3(b). For the internal interfaces a spin-independent reflection coefficient of 0.5 was used, while the surface and collector interface are regarded as fully reflective. For the latter this is a good approximation, since the barrier transmission is \( \sim 10^{-2} \) at the used energy and assumed barrier height (see section 2.2.3). Since the barrier transmission only changes the yield, but not the spin-dependence, this additional reduction is not accounted for in the remainder of this chapter.
Figure 8.4: Calculations of the fraction of the collected photocurrent of an optical spin-valve structure, that originates from electrons photoexcited in the top Au absorption layer, as a function of its thickness, for parallel magnetizations. The different curves represent different ratios of the inelastic mean-free-path and the absorption length in the top Au layer: $\frac{\lambda_i}{\lambda_{abs}}$, where $\lambda_{abs} = 12.5 \text{ nm}$. The remainder of the parameters are the same as those used in Fig. 8.3.

Together with equation (8.1) the different curves in Fig. 8.3(b) can be used to calculate the magnetophotocurrent ratio of the collected photocurrent. Due to the fact that not all collected electrons traversed both magnetic layers, a relatively low MPC ratio of 3.8% is obtained. If we neglect the excitation in the spin-valve layers, i.e. if all collected electrons have traveled across both magnetic layers, a MPC of 74.4% is calculated. This shows directly the need to optimize the layer stack.

8.2.2 Influence of transport parameters

To directly study the influence of the inelastic mean-free-path $\lambda_i$ of the top Au absorption layer, various calculations are made of the fraction of the photocurrent that originates from excitation in the top Au layer, as a function of the thickness of this layer (for parallel magnetizations).\footnote{This is done by neglecting photoexcitation in the Fe/Au/Fe multilayer, but still using the same procedure as outlined in section 2.2.2. This means that electrons, excited in the multilayer, that are backscattered into the top Au layer, and then are still able to contribute to the photocurrent, are neglected.} In Fig. 8.4 curves are presented for various values of $\lambda_i$, relative to the optical absorption length $\lambda_{abs}$ in Au. One can see that only for the case that $\frac{\lambda_i}{\lambda_{abs}} \approx 1.5$, the ratio of electrons excited in the top Au-layer will approach unity for large Au thicknesses. The ratio approaches unity faster for larger values of $\lambda_i$. Only then most of the collected electrons will have traversed both magnetic layers, so that a high MPC ratio can be expected. The observed mean-free-paths of nearly free-electron metals are much higher than for metals with more complex band structures. Since Au is one of the few materials for which mean-free-
8.2. Simulations

Figure 8.5: Calculations of the influence of the inelastic mean-free-path on (a) the magnetophotocurrent ratio and (b) the photocurrent yield, as a function of the Au absorption layer thickness. The different curves indicate different $\lambda_i/\lambda_{abs}$ ratios, with $\lambda_{abs} = 12.5$ nm. The curves in (b) are calculated for parallel magnetizations. The other parameters are the same as those used in Fig. 8.3.

paths have been determined that are higher than the optical absorption depth [77], this was the primary reason to chose Au as the material for the absorption layer.

The final effect of the Au thickness and $\lambda_i/\lambda_{abs}$ ratio on the MPC ratio and the photocurrent yield is shown in Fig. 8.5(a) and (b) respectively. The Au layer and $\lambda_i/\lambda_{abs}$ dependence of the magnetophotocurrent is similar as that of the fraction of the photocurrent due to electrons excited in the top Au layer, shown in Fig. 8.4, except for the small thickness regime. Here also excitation in the topmost Fe layer contributes somewhat to the magnetophotocurrent ratio. This last effect also implies that, even when almost no electrons from the absorption layer reach the semiconductor collector, a small MPC ratio of roughly 1% remains. Recently such a small effect was observed in a so-called spin-valve photodiode [79]. The structure essentially consists of a magnetic tunnel transistor, with optical access to the spin-valve layers. Since no effort was employed to effectively increase the ratio of collected hot-electrons travelling through the complete spin-valve stack, their measured effect is limited to such low values.

We conclude that, from a point of view of obtaining a sizable MPC ratio, both a high $\lambda_i$ and a large absorption layer thickness are a prerequisite. However, as can be seen in Fig. 8.5(b), increasing the top Au layer also dramatically decreases the resulting photocurrent yield. Practical signal-to-noise ratios determine whether this would limit the application of large absorption layer thicknesses.

In the previous calculations we made use of an interface reflection coefficient of $r_i = 0.5$ for each (internal) interface, which corresponds roughly to the high diffusivity parameter used in [27]. The influence of this parameter on both the MPC and the photocurrent yield are shown in Fig. 8.6(a) and (b) respectively. When going from full transmission at each interface ($r_i = 0$) to full reflection ($r_i = 1$), the
Chapter 8. Towards an optical spin valve structure

Figure 8.6: Calculations of (a) the magnetophotocurrent ratio, and (b) the photocurrent yield as a function of the 1D interface reflectivity parameter $r_i$. Different curves correspond to different values of $\lambda_i/\lambda_{abs}$, with $\lambda_{abs} = 12.5$ nm. A thickness for the Au absorption layer of 25 nm is used. The curves in (b) are calculated for parallel magnetizations. All other parameters are the same as in Fig. 8.3.

MPC ratio decreases dramatically, while the photocurrent yield changes only little. As already discussed in section 2.2.2, interface scattering and reflection can occur extrinsically, e.g. caused by defects or imperfections, or intrinsically, due to different energy-bands of the two materials. Due to the small lattice mismatch between GaAs, Fe and Au (see section 8.4.1), the complete layer stack can be grown fully epitaxially [80]. It is expected that this will reduce the extrinsic interface scatter probabilities, leading to an improved MPC ratio. Since the top absorption layer will then also be monocrystalline, some improvement of $\lambda_i$ can also be expected.

8.2.3 Obtainable magnetophotocurrent ratios

After discussing the different parameters that are important for the functioning of our device, the question arises what typical MPC ratios we can obtain by optimizing all layer thicknesses. Since the spin-polarization of hot electrons will increase when traveling through a magnetic layer, increasing its thickness will initially lead to an increased MPC. However, since the fraction of the photocurrent due to electrons photoexcited in the top layer also depends on the thickness of the magnetic layers in the spin-valve, the actual MPC ratio is not always a monotonic function of this thickness.

In Fig. 8.7 we plotted the MPC ratio (a) and (b), as well as the photocurrent yield (c) and (d) as a function of the Fe layer thicknesses.\(^5\) The curves correspond either to various $\lambda_i/\lambda_{abs}$ ratios [(a) and (c)], or to various top Au layer thicknesses [(b) and (d)]. Also curves for only excitation in the Au top layer are shown for comparison.

\(^5\)Both Fe layer thicknesses are varied simultaneously, and the Fe thickness indicated in Fig. 8.7 indicates the thickness of a single Fe layer.
8.2. Simulations

Figure 8.7: Calculations of (a) and (b) the magnetophotocurrent ratio, and (c) and (d) the photocurrent yield of a GaAs/Fe/Au/Fe/Au optical spin-valve structure, as a function of the Fe thickness. The various curves in (a) and (c) give the results for various ratios of $\lambda_i/\lambda_{abs}$ in the 150 nm thick top Au layer, with $\lambda_{abs} = 12.5$ nm. In (b) and (d) calculated curves are presented for different thicknesses $t_{Au,t}$ of the top Au layer, with $\lambda_i/\lambda_{abs} = 3$. All other parameters are the same as those used in Fig. 8.3. The curves indicated by “Full MPC” represent the result of calculations in which photoexcitation in the Fe/Au/Fe spin-valve is neglected.

One can see that for a finite $\lambda_i$ or top Au layer thickness, it is expected that the MPC ratio is optimal at a certain finite Fe layer thickness. Increasing the Fe thickness further will decrease the fraction of the photocurrent due to electrons excited in the top electrode, effectively reducing the MPC ratio. The photocurrent yield just decreases with increasing Fe layer thickness, except for small values of $\lambda_i$ in the absorption layer and small Fe thicknesses. In that case, most collected electrons originate from excitations in the spin-valve layers. A small increase in thickness will then result in a higher absorption and therefore in more collected electrons. For larger thicknesses, the fact that in the Fe layer $\lambda_i < \lambda_{abs}$ leads to a decrease in the photocurrent.

In a practical device the maximum obtainable MPC ratio is therefore limited, as already seen in the previous section, by the realistic value of $\lambda_i/\lambda_{abs}$ for the top ab-
sorption layer. Experimentally observed values for this parameter in Au are roughly between 1-3 [77, 78, 81].

8.3 Sample preparation

A major reason for proposing the optical spin-valve layer stack that has been discussed above, consisting of GaAs/Fe/Au/Fe/Au, is that the lattice constants of the different materials are very similar [33]. As mentioned already, this is expected to lead to relatively small (in)elastic scattering probabilities in the metal layers, and low interface reflectivities, conditions which are beneficial for obtaining a high MPC ratio. However, in order to be able to grow the layers epitaxially, the atoms have to be deposited with a low kinetic energy, otherwise intermixing will occur. Therefore, we could not use sputter deposition, as discussed in section 3.1, for the sample preparation. Instead we used evaporation deposition in an ultrahigh vacuum (UHV) molecular beam epitaxy (MBE) deposition system.

The GaAs substrate consists of a n⁺ doped GaAs(100) wafer, with a 540 nm GaAs epilayer on top ($n = 10^{16} \text{ cm}^{-3}$ Si-doping level), capped by As. The low doped epilayer provides a relatively thick depletion region of the Schottky diode, ensuring low leakage currents [71], while at the same time provides an epitaxial surface for the growth of the metal layers. On the backside an AuGe/Ni/Au layer stack is deposited to create an ohmic contact to the highly doped semiconductor. The wafer is cut into $12 \times 3 \text{ mm}^2$ pieces, which are placed on a substrate holder. Prior to the deposition of our spin-valve stack, the As is removed by in-situ sputter-annealing. The Au and Fe layers are grown by evaporation from a Knudsen cell, and from an e-beam evaporation source respectively. During growth the background pressure always stayed below $10^{-10} \text{ mbar}$, and the substrate temperature around 50 °C. The growth rate was monitored with a calibrated quartz crystal microbalance, and was typically around 0.5 nm/min.

To prevent the formation of possible leakage paths, due to deposition at the edges of the sample, a special mask system is used. In Fig. 8.8(a) a schematic drawing of the substrate holder and mask system is shown. The mask consists of a round molybdenum plate, containing three different slits. The mask can be rotated so that one of the three different openings can be placed on top of the substrate, which is fastened beneath the mask by clamps. One of the slits is large enough to completely expose the sample. This one is used to clean the sample in-situ by sputter-annealing. The second slit measures roughly $10 \times 1 \text{ mm}^2$ and is used to mask the edges of the substrate. A third slit, measuring roughly $8 \times 0.5 \text{ mm}^2$, is used so that material sputtered through this opening can be completely covered by the second slit. In the remainder of this chapter, the Au layers have been deposited through the larger slit, and Fe through the smaller slit. In this way, the Fe layers are protected from oxidation after taking the sample out of the vacuum system. Due to the fact that the mask is quite close to the substrate, and fastened in the center, a shutter can be placed close to the surface.

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6The Ge diffuses into the semiconductor causing the high doping, while the Ni prevents diffusion in the opposite direction. Au serves as the contact material.
8.4 Sample characterization

Before we can begin to conduct photoconductance studies on the proposed optical spin-valve structure, the deposited samples are first characterized, in order to investigate the validity of the claims made in the previous sections. We begin by studying the sample structure, in order to investigate the epitaxy of the deposited layer stack. After that a model structure is characterized magnetically, to see whether it can be switched between perfectly parallel and antiparallel states. At the end, we study the current-voltage characteristics, so that we can say something about the quality of the Schottky barrier.

8.4.1 Structural characterization

In order to investigate the structure of the surface during growth and of the “bulk” of the layers, two different techniques are used: low energy electron diffraction (LEED) and transmission electron microscopy (TEM), respectively. With LEED, electrons with kinetic energies between roughly 20 and 500 eV are emitted onto the surface of the sample. By moving the shutter at a constant speed, parallel to the sample surface, wedge shaped samples can easily be grown. In Fig. 8.8(b) a schematic drawing of a cross-section of a typical stack is shown. Due to the fact that the material source is of finite size, some shadowing is present at the edges.\footnote{Since the pressure during deposition is now much lower than in the case of sputtering, the distribution of incoming atoms, and therefore in principle also the shadowing effect, is much smaller. However, since the mask or shutter is now not in contact with the substrate, but roughly 1 mm above it, some shadowing will still be present.}

Figure 8.8: Schematic drawings of (a) the substrate/mask system, and (b) an example of the resulting layer stack. In (a) three different mask slits are visible, which can be rotated on top of the sample. Due to the close proximity of the mask and the sample, a shutter can be placed close to the sample surface, for the possibility of wedge growth. In (b) non-sharp edges of the layers are visible, caused by shadowing of the masks during deposition.
Figure 8.9: Low energy electron diffraction (LEED) patterns, measured at each interface of our optical spin-valve stack. The spectra are recorded at different electron energies between 40 and 140 eV, and under different sample orientations. Clear interference spots are visible at each interface.

which one wants to study. The diffraction pattern of these electrons is then investigated. Due to the small penetration depth at these energies, LEED is only sensitive to the top few monolayers. In Fig. 8.9 diffraction patterns are shown for each interface of our layer stack. Since these spectra have been measured at different electron energies, and under different sample orientations, they will not be discussed quantitatively. However, qualitatively one can immediately see that clear interference spots are present at each interface. This directly indicates that long-range order exists for the surface lattice reconstructions, caused by the very similar lattice constants of the three materials [33]. The increased size of the spots, relative to that of the clean GaAs(100) surface, indicates that some surface roughness is present.

To investigate the epitaxy in the perpendicular direction, cross-sectional TEM images have been made. The technique images the transmission of an electron beam through a thin layer of material. The sample to be investigated is first mechanically polished to a thickness of roughly 10 µm. Before being placed in the microscope, the sample is further thinned down by low-angle ion-milling. The resulting image of our optical spin-valve stack was recorded in a TECNAI F30ST TEM microscope at 300 kV, and is shown in Fig. 8.10. Due to the epitaxy of the layers (and the perpendicular orientation in the incoming electron beam), the atomic structure can be visualized. The topmost Au layer is fully monocrystalline even up to 20 nm, while in the Fe layers a lot of strain-contrast is visible. The latter effect is caused by the

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8For a polycrystalline or amorphous surface, the electron diffraction would be randomized, resulting in an image without contrast.

9The Au(100)-plane is rotated 45° with respect to that of Fe and GaAs.
8.4. Sample characterization

Figure 8.10: Cross-sectional transmission electron microscopy (TEM) image of our proposed optical spin-valve stack. Some strain-induced contrast variations are visible in the Fe/Au/Fe spin-valve layers.

∼2% mismatch between the (100) lattice parameters of Fe and GaAs [33].

So, although some deformation is present in the optical spin-valve stack, the epitaxial quality of the layers as well as the interfaces is quite high. This is expected to positively affect the magnetophotoconductance of the layer stack.

8.4.2 Magnetic switching behavior

To be able to study the spin-dependence of the hot-electron transport, the two magnetic layers of the spin-valve should be switchable between a parallel and an antiparallel alignment. In our experiments with magnetic tunnel junctions, we made use of exchange biasing to artificially shift the hysteresis loop of the adjacent magnetic layer along the field axis (see section 3.1.3). However, in this case an additional exchange bias layer was rejected as the source for antiparallel alignment, since $\lambda_e$ and $\lambda_i$ are very small in these complex materials. Instead we made use of the different coercivities of the two Fe layers, probably caused by the different domain wall nucleation and pinning that arises from the growth on different underlayers (GaAs vs. Au). The Au interlayer serves only to decouple the two magnetic layers. Unfortunately it decreases the magnetophotocurrent ratio, due to additional optical absorption and due to inelastic scattering. Therefore we strived to make this interlayer as thin as possible.

To investigate the magnetic switching behavior of our spin-valve structure, a
Figure 8.11: Characterization of the magnetic switching behavior of a wedge shaped optical spin-valve stack. In (a) a schematic cross-section of the studied sample is shown. In (b) and (c) the results from an in-plane GMR and resistance measurement are presented. The measurements have been performed using a four-point probe scheme. For specific Au interlayer thicknesses, the magnetoresistance curves as a function of applied magnetic field are shown in Fig. 8.12.

A wedge-shaped sample is grown on an undoped GaAs substrate. The layer stack consists of: GaAs(100)/2 nm Fe/0-5 nm Au/2 nm Fe/3 nm Au. The magnetic switching behavior is studied using an in-plane current-voltage measurement, while making use of the giant magnetoresistance (GMR) effect. In Fig. 8.11 the measured resistance and GMR ratio are plotted as a function of interlayer thickness. As expected, the resistance decreases monotonically with increasing Au interlayer thickness. However, the GMR ratio shows an oscillating behavior. From literature it is known that in an epitaxial Fe/Au/Fe multilayer, an interlayer-coupling, oscillating between ferro- and antiferromagnetic, is present for small interlayer thicknesses [80]. To study this in more detail, we look at the resistance curves as a function of applied magnetic...
8.4. Sample characterization

Field, shown in Fig. 8.12. We indeed see that below roughly 3 nm, the two layers switch at different signs of the applied field, indicative of antiferromagnetic interlayer coupling.

For our purpose it is sufficient to have a well-defined field-interval of antiparallel alignment. From Fig. 8.12 we can see that above an interlayer thickness of \( \sim 4.25 \text{ nm} \) no or only small magnetic coupling is present, and a broad plateau of antiparallel alignment can be obtained. So this value will be regarded as a lower limit for the interlayer thickness in our optical spin-valve structures.

8.4.3 Current-voltage characteristics

To investigate the quality of the deposited Schottky barrier, the current-voltage characteristics of two different diode structures have been measured. In Fig. 8.13 the I(V) characteristics of a GaAs(100)/Au diode, as well as that of a GaAs(100)/Fe/Au diode are shown, on both a linear (a) as well as a logarithmic scale (b). The GaAs-Au sample is included because of the photoconductance experiments discussed in the next section. Both diodes have an interface area of \( 1 \times 10 \text{ mm}^2 \), but for the second sample a \( 0.5 \times 8 \text{ mm}^2 \) sized part of the interface consists of Fe-GaAs instead of Au-GaAs.

Although the literature values for the Schottky barrier heights at the Au-GaAs and Fe-GaAs interface differ significantly, viz. 0.9 [71] and 0.6 eV [74] respectively,

\[ 10 \] A parallel alignment can easily be accomplished by applying a large in-plane magnetic field.
the measured current-voltage characteristics are quite similar. Both samples show a clear rectifying behavior on a linear scale, but when plotted logarithmically, a sizable leakage current becomes apparent (visible for reverse bias). Because of the higher barrier height at the Au-GaAs interface, it was assumed that for the GaAs(100)/Fe/Au diode, most of the current flows through the Fe-GaAs interface. However, it is known that interface diffusion can severely deteriorate the electrical properties of the Au-GaAs interface [82], leading to a heterogeneous current distribution. Also, when studied under an optical microscope, defects are visible on the GaAs(100) surface, probably caused by damage that occurred during preparation of the ohmic contact on the back-side. Together with a relatively large diode-area, this leads to the result that no clear barrier height could be extracted from a fit to the thermionic emission theory [71]. The fact that the interfaces are thus clearly not perfect, can negatively affect the measured (magneto)photoconductance. For example, defects at the metal-semiconductor interface can act as scatter centers for the incoming hot-electron flux, reducing the photocurrent yield. At the same time, photoexcitations from interface states reduce the MPC ratio, due to an additional (non-polarized) contribution to the photocurrent yield. This shows the importance of a clean well-defined interface for the functioning of the optical spin-valve.

8.5 Photoconductance experiments

Unfortunately, photoconductance experiments on a full optical spin-valve stack, did not show any magnetophotoconductance effect. In this section we will show results from experiments on model structures to support the idea that this is due to
8.5. Photoconductance experiments

substantial interface scattering and photoemission from interface states at the metal-semiconductor Schottky barrier.

After initial sample characterization, as discussed in the previous sections, the photoconductance of various Schottky diode systems is studied. In contrast to the experiments carried out on magnetic tunnel junctions, a diode laser is used instead of a lamp and monochromator, in order to enhance the flux of incoming photons, as well as to provide a relatively small spot size of $\sim 50 \mu m$. A 5 mW diode laser was used, emitting infrared light at 1310 nm, i.e. $h\nu = 0.95$ eV, which is in between the 1.42 eV bandgap of GaAs [71], and the expected barrier heights ($\leq 0.9$ eV). A mechanical chopper, in combination with a lock-in amplifier, shifts the photoinduced signal, as measured with a simple current-amplifier, to a region of the spectrum with a reduced $1/f$-noise. A frequency of 330 Hz is used, and all measurements are carried out without the application of a bias voltage.

First, we carried out a number of experiments on model samples, with the purpose to determine the magnitude of the inelastic mean-free-path $\lambda_i$ in Au. Knowledge of $\lambda_i$ is crucial for the understanding of the functioning of the proposed optical spin-valve (see section 8.2.2). Photoconductance experiments are carried out on two wedge-shaped model samples: GaAs(100)/0-30 nm Au and GaAs(100)/2 nm Fe/2-30 nm Au (the same samples as discussed in section 8.4.3). By moving the sample under the light spot, parallel to the wedge direction, the photocurrent as a function of thickness can easily be determined. The GaAs/Au diode structure is included in order to be able to deduce $\lambda_i$ in the Au layer, without complicating optical absorption and scatter events in the Fe/Au/Fe spin-valve. Because of possible different structural properties between Au grown on GaAs vs. Au grown on Fe, results are compared to those measured on a structure with a 2 nm Fe layer at the interface with GaAs. In this way a possible microstructure induced difference in transport properties would become visible.

In Fig. 8.14(a) and (b) schematic top-views of the two samples are shown, as obtained from deposition through the two mask slits. In (c) and (d) photocurrent scans, perpendicular to the wedge direction, are shown. For the Au thickness range studied, a clear decrease of the photocurrent with thickness is observed. For the GaAs/Fe/Au sample (d), a clear distinction can be seen between the GaAs-Au regions (the outer edges) and the GaAs-Fe-Au regions (in the middle). This difference will be further discussed below. For both samples peaks are present at the edges of the diode structure. This is caused by an enhancement of the photocurrent yield, due to a decreasing thickness towards the edges, caused by the shadowing effect during deposition [see Fig. 8.8(b)].

To study the thickness dependence of the photocurrent in more detail, results from scans, parallel to the wedge direction, are presented in Fig. 8.15 (c) and (d) for the two different structures, respectively. For the GaAs/Fe/Au sample (d), two curves [(1) and (2)] are presented, corresponding to scans across the GaAs-Au and GaAs-Fe-Au regions respectively [see Fig. 8.14(b) and (d)]. With increasing Au thickness, all three curves show a sharp initial increase in the photocurrent, followed by an exponential decrease. For the GaAs/Au and the GaAs/Fe/Au diodes, a decay length $\lambda_{decay}$ of 10.9$\pm$0.1 nm, 11.5$\pm$0.1 nm (GaAs-Au interface), and 10.6$\pm$0.1 nm (GaAs-Fe interface) are determined for the 15-30 nm thickness range, respectively.
Figure 8.14: Schematic topviews (a) and (b), and photocurrent scans (c) and (d) for wedge-shaped GaAs/Au and GaAs/Fe/Au Schottky diodes respectively. The photocurrent scans are measured perpendicular to the wedge direction at different positions, corresponding to different Au thicknesses (indicated on the right). In (b) and (d) two scan directions parallel to the Au-wedge are indicated, and represent scans at (1) the GaAs-Au and (2) the GaAs-Fe interface-regions, respectively [see Fig. 8.15(d)].

The uncertainty in these decay lengths is relatively small. However, due to the non-flat Y-position dependencies, visible in the cross-sections, and due to a non-perfect parallel scan direction, the real uncertainty will be larger. The three determined values are then not significantly different anymore, and $\lambda_{\text{decay}} = 11.0 \pm 0.5$ nm.

For both structures, calculations of the photocurrent yield, based on the assumptions discussed in section 8.2.1, are plotted as a function of Au thickness in Fig. 8.15(e) and (f), for various ratios of the inelastic mean-free-path $\lambda_i$ and the absorption length $\lambda_{\text{abs}}$ in Au. In contrast to the experimental curves for the GaAs/Au and GaAs/Fe/Au samples, the shapes of the calculated curves for these two different structures differ significantly. Due to additional absorption and scattering in the Fe layer, a clear maximum in the photocurrent yield is absent. From a comparison between the maximum in the measured curve (c) and in the calculations (e) for the GaAs/Au sample, one could conclude that $\lambda_i$ is roughly 8 times larger than $\lambda_{\text{abs}}$. However, since a maximum at approximately the same (5 nm) Au layer thickness is also observed for the GaAs/Fe/Au sample, in contrast to the calculations (for $\lambda_i/\lambda_{\text{abs}} \sim 8$), some other process must also play a role.

In Fig. 8.16 we plotted the ratio $\lambda_{\text{decay}}/\lambda_{\text{abs}}$, as determined from the 15-30 nm...
Figure 8.15: Results of photoconductance studies on two Schottky diode structures. In (a) and (b) schematic drawings of the sample cross-sections are shown. In (c) and (d) results from a scan along the wedge, while in (e) and (f) results from calculations for GaAs/Au and GaAs/2 nm Fe/Au wedges are shown, respectively. The calculations are made for different $\lambda_i/\lambda_{abs}$ ratios, while the assumptions given in section 8.2.1 are used. In (d) two curves are shown, for scans (1) and (2) along the GaAs-Au and the GaAs-Fe-Au parts of the structure, respectively [see Fig. 8.14(b) and (d)].
Chapter 8. Towards an optical spin valve structure

Figure 8.16: Normalized decay lengths, as a function of $\lambda_i/\lambda_{abs}$, as calculated for the two model structures shown in Fig. 8.15, for a Au thickness range of 15-30 nm. $\lambda_i$ represents the inelastic mean-free-path, $\lambda_{abs}$ the absorption length, and $\lambda_{decay}$ the photocurrent decay length in Au. The region in between the dotted lines indicates the range of measured decay lengths.

thickness ranges of the calculations from Fig. 8.15(e) and (f), as a function of the ratio $\lambda_i/\lambda_{abs}$. One can clearly see that when $\lambda_i > \lambda_{abs}$, which is a requirement for obtaining a magnetophotoconductance ratio that is higher than only 1-2% (see section 8.2.2), the measured decay length $\lambda_{decay}$ should be larger than the absorption length $\lambda_{abs}$. This is clearly not the case, judging from the previous results. This indicates that the $\lambda_i/\lambda_{abs}$ ratio of $\sim 8$, determined above, cannot be correct. The fact that the shape of the measured photocurrent curves for the two model structures is very similar, leads us to believe that we are maybe not measuring electrons excited in the “bulk” of the layers, but at the metal-semiconductor interface, e.g. from interface states formed due to defects. Since these electrons only have to travel a very small distance before being collected, they contribute relatively much to the photocurrent. This contribution will also be independent from the metal layers on top. In that case, $\lambda_{decay}$ is expected to be equal to the decay of the optical absorptivity at the metal-semiconductor interface with increasing Au thickness (11.2 and 11.4 nm for the GaAs/Au and GaAs/Fe/Au samples respectively), which is consistent with the experimental results.

Further evidence for the above hypothesis is given by an estimation of the absolute photocurrent from the above calculations. Using an incoming light intensity of $\sim 5$ mW, a barrier transmission of roughly $10^{-2}$, and the calculated incoming electron flux, a photocurrent is calculated, that is roughly 2 orders of magnitude larger than the measured current. This indicates that most of the electrons reaching the interface are not able to enter the semiconductor, probably due to extensive scattering at the interface. The relatively small effect of additional interface excitations can then
easily dominate the complete photocurrent.

Also a full optical spin-valve stack, consisting of GaAs(100)/2 nm Fe/5 nm Au/2 nm Fe/2-30 nm Au was investigated. Photoconductance scans along the Au wedge showed a similar behavior as that for the previous two samples, i.e. a decay length that is somewhat smaller than the optical absorption length. Also no magnetocurrent effect, larger than 0.1\%, is observed. As already discussed in section 8.2.3, even for the case that $\lambda_i < \lambda_{abs}$, a small $\sim1\%$ effect should be present. The fact that even this small effect is not present, further supports the point of view that we are actually not measuring electrons that are photoexcited in the “bulk” of the layer stack, but instead electrons that are excited from interface or defect states at the metal-semiconductor interface.

8.6 Conclusions and recommendations

No magnetophotocurrent effect was observed for GaAs/Fe/Au/Fe/Au structures. Measurements on GaAs/Au and GaAs/Fe/Au model structures strongly indicated that the measured photocurrent actually does not originate from within the “bulk” of the metal layer stack. Instead defect or impurity states in the semiconductor or at the metal-semiconductor interface dominate the collected current. An improvement of the photoconductance characteristics is therefore expected for an improved metal-semiconductor interface, containing less defects and impurities. Spectral measurements of the photoconductance or optical absorption would give more insight into the nature of these parasitic effects.

As a first test, it might be easier to investigate more simple Au-Si Schottky diodes, to determine the mean-free-path in Au. Already in the 1960s, decay lengths of the photocurrent, larger than the optical penetration depth, have been observed for these systems [77]. Increasing the Au thickness to a few hundred, instead of a few tens of nanometers, will also increase the potential for a large MPC ratio, as shown in section 8.2.2.

Although the choice of Fe as the magnetic material was motivated by the beneficial effect on the MPC ratio of its epitaxial growth on GaAs, it also has a relatively low complex component of the refractive index $k$. This leads to a high absorption in the Fe layers, as seen in Fig. 8.3, deteriorating the potential for high MPC ratios. From this point of view Co and Ni seem a more appropriate choice [73]. Due to a lower interface scattering, Cu instead of Au will then be a more suitable choice as the interlayer material [83]. Since magnetophotoconductance effects have very recently been observed in non-epitaxial Si-based spin-valve photodiode structures [79], this might be a better route to success.
Bibliography


Summary

In the relatively new field of magneto-electronics or spintronics, magnetic tunnel junction (MTJ) devices are of particular interest, due to their applicability as magnetic solid state memory elements (MRAMs). Since the information in such structures is stored in the magnetization of the layers, it is retained even in the absence of electrical power. This so-called non-volatility, together with high magnetoresistance (MR) ratios upon readout, make them ideal candidates as replacements for mainstream memory technologies. However, several issues, among others, relating to the scalability to below $\sim 100$ nm, still need to be solved. In this thesis we have used a novel photoconductance technique to study some of these issues in MTJs that are important for the incorporation in MRAM structures.

In chapter 2 we first give a theoretical background on the spin-polarized tunneling process, which ultimately determines the magnitude of the MR effect. After that, the photoconductance process is described within a simple three-step model. The photoexcitation, hot-electron transport, and the barrier transmission are each treated subsequently. It is shown that important information on the barrier shape in tunnel junctions can be extracted from photoconductance experiments. The overall efficiency of the internal photoemission process, is expected to be as low as $10^{-5}$ electrons per incident photon. Therefore, special attention had to be paid to an experimental setup with which such experiments can be carried out.

A description of the experimental setup in chapter 3, as used for the photoconductance experiments on MTJs, is preceded by a discussion on the sample preparation. By making use of a phase-sensitive technique, together with a novel voltage-stabilization scheme, photocurrent yield curves could be extracted from relatively large scale ($200 \times 200$ $\mu$m$^2$) junctions. Since these large-scale junctions show similar magneto-electronic properties as (sub)micron sized MTJs, the conclusions are considered to be the same for these more application relevant structures.

Before applying photoconductance to study MTJs, some basic characteristics of the technique are demonstrated in chapter 4. By applying a bias voltage across the structure, and using different directions of the incident light, information on the separate contributions from the two electrodes can be extracted. Also, it is shown that the barrier shape is not only determined by the barrier material, but also by that of the electrodes. By varying the thickness of one of these, it has been concluded that most of the electrons that contribute to the photocurrent are generated within the first few nanometers adjacent to the barrier interface.
In the following three chapters, the bulk of the experimental results on MTJs, obtained within this work, are presented. First, the modification of the bottom electrode/barrier interface in a Co$_{90}$Fe$_{10}$/AlO$_x$/Co$_{90}$Fe$_{10}$ MTJ during oxidation is studied in chapter 5. Due to the extreme interface sensitivity of the spin-polarized tunneling effect, the oxidation of the 1-3 nm thin barrier layer needs to be controlled very accurately. From a photoconductance study of the barrier oxidation, the observed additional contribution from the underoxidized bottom electrode in the photocurrent yield can be used to verify this process accurately.

To realistically downscale MTJs to below submicron sizes, the resistance-area product of the structure should also decrease, to not lead to unacceptable electronic noise levels. One of the options to realize this, is by using a barrier material with a lower barrier height than the mostly used AlO$_x$. In chapter 6 we study the possible role of TaO$_x$ as an alternative barrier material in MTJs. Its low bandgap ($\sim$ 4.2 eV) made it possible to obtain direct information on the barrier asymmetry from photoconductance experiments. With increasing oxidation time, the barrier asymmetry has been found to increase monotonically, leading to a sign-reversal for initial negative asymmetry. The optimal oxidation time, corresponding to a maximum in the MR, has been found to coincide with the oxidation time at which the barrier potential is symmetric. Due to a decrease in structural quality with increasing Ta thickness, the maximum MR ratio decreases rapidly from 7% for the thinnest barriers studied, to 0% for less than twice that thickness. This ultimately limits the incorporation of TaO$_x$ in application relevant devices.

One of the most useful process steps in the fabrication of application relevant MTJs, is a modest anneal treatment in the presence of a high magnetic field. In chapter 7 we show that the accompanying increase in MR ratio, for both AlO$_x$ and TaO$_x$ MTJs, corresponds to a modification of the barrier potential profile. This change is argued to be caused by a redistribution of the oxygen at the bottom electrode/barrier interface. For obtaining the highest MR one should anneal junctions that are characterized as “slightly overoxidized” in the as-deposited state.

Chapter 8 shows that photoconductance cannot only be used as a characterization tool, but that it can also be used to create novel spintronic structures with interesting properties. An optical spin-valve structure is proposed, where the collected photocurrent yield depends strongly on the relative orientation of the internal magnetic structure. Results of various calculations are presented, showing the presence of a significant magnetophotocurrent effect for realistic material stacks. The most critical parameter is the ratio between the inelastic mean-free-path and the optical absorption depth in the top most layer. With suitable optimization of the material layer stack, relative effects of over 100 % are expected to be realizable. Although initial samples did not show any dependence of the photocurrent on the applied magnetic field, recommendations for improvements are given that should finally lead to a fully functioning optical spin-valve.
Samenvatting

In het relatief nieuwe vakgebied van magneto-elektronica of spintronica zijn magnetische tunnel juncties (MTJs) van specifiek belang, vanwege hun mogelijke toepassing als magnetische vaste stof geheugens (MRAMs). Aangezien de informatie in dit soort structuren opgeslagen ligt in de magnetisatie van de lagen, blijft deze behouden zelfs zonder de aanwezigheid van elektrische spanning. Deze zogenaamde niet-vluchtigheid, gecombineerd met de hoge magnetoweerstandswaarden bij het uitlezen, maakt dat deze structuren ideale kandidaten zijn voor de vervanging van huidige standaard geheugen technieken. Echter, verschillende aspecten, die gerelateerd zijn aan het schalen van deze structuren tot onder de $\sim 100$ nm, moeten nog opgelost worden. In dit proefschrift beschrijf ik hoe ik gebruik heb gemaakt van een nieuwe fotogeleidingstechniek om verschillende van deze aspecten in MTJs, die belangrijk zijn voor de toepassing in MRAMs, te onderzoeken.

In hoofdstuk 2 wordt eerst een theoretische achtergrond gegeven over het spingepolariseerde tunnel proces, dat uiteindelijk de grootte van het magnetoweerstandseffect bepaald. Hierna wordt het fotogeleidingsproces beschreven binnen een eenvoudig driestappen model. De fotoexcitatie, het hete elektronentransport en de barrièretunneltransmissie worden achtereenvolgens behandeld. Gebruik makend van deze beschrijving kan informatie over de barrièrevorm in tunnel juncties verkregen worden uit fotogeleidingsexperimenten. De totale efficiëntie van het fotogeleidingsproces kan zo laag zijn als $10^{-5}$ elektronen per invallend foton. Om deze reden moest extra aandacht besteed worden aan een experimentele opstelling, waarmee zulke experimenten uitgevoerd kunnen worden.

Een beschrijving van de experimentele opstelling in hoofdstuk 3, zoals gebruikt is voor de fotogeleidingsexperimenten aan MTJs, wordt vooraf gegaan door een uiteenzetting van de sample preparatie. Door gebruik te maken van een fase gevoelige detectietechniek, samen met een spanningsstabilisatiemethode, is het mogelijk gebleken fotogeleidingscurves te meten aan relatief grote ($200\times200 \, \mu m^2$) juncties. Aangezien deze juncties dezelfde magneto-elektronische eigenschappen vertonen ten opzichte van MTJs met (sub)micrometer afmetingen, wordt verondersteld dat de conclusies dezelfde zijn als die voor deze kleinere structuren, die meer relevant zijn voor toepassingen.

Voordat fotogeleiding toegepast wordt om MTJs te onderzoeken, worden eerst een aantal basis mogelijkheden van de techniek gedemonstreerd in hoofdstuk 4. Door een spanning aan te leggen over de junctie en door gebruik te maken van ver-
Schillende richtingen van het invallende licht kan informatie verkregen worden over de afzonderlijke bijdragen van de twee elektrodes. Er wordt ook aangetoond dat de vorm van de barrière niet alleen van het barrière materiaal afhangt, maar ook van het elektrode materiaal. Door de dikte van een van de elektrodes te variëren is geconcludeerd dat de meeste elektronen die bijdragen aan de fotostroom gegenereerd worden binnen de eerste paar nanometers, grenzend aan de barrière laag.

In de volgende drie hoofdstukken wordt de bulk van de verkregen experimentele resultaten van MTJs gepresenteerd. Allereerst wordt de modificatie van de grens laag tussen de onderste elektrode en de barrière in een Co$_{90}$Fe$_{10}$/AlO$_x$/Co$_{90}$Fe$_{10}$ MTJ gedurende het oxidatieproces onderzocht in hoofdstuk 5. Vanwege de extreme grens laag gevoeligheid van het spingepolariseerde tunnelproces, moet de oxidatie van de 1-3 nm dikke barrière laag zeer nauwkeurig gecontroleerd worden. Met behulp van een fotogeleidingsstudie van de oxidatie van de barrière kan de geobsereerde enige hoeveelheid bijdrage van de onderelektrode gebruikt worden om dit proces te controleren.

Om MTJs realistisch te kunnen schalen naar afmetingen beneden een micrometer, zal het oppervlak weerstandsproduct ook moeten afnemen, om geen onacceptabele elektronische ruisniveaus te verkrijgen. Een van de opties om dit te realiseren is om gebruik te maken van een barrière materiaal met een lagere barrière hoogte dan het meestal gebruikte AlO$_x$. In hoofdstuk 6 bestuderen we de mogelijke rol van TaO$_x$ als een alternatief barrière materiaal voor MTJs. De lage bandafstand van dit materiaal maakt het mogelijk om met behulp van onze fotogeleidingsexperimenten directe informatie over de scheefheid van de barrière te verkrijgen. Met toenemende oxidatietijd is een monotone toename van de scheefheid waargenomen, dat voor “negatieve” scheefheden zelfs tot een tekenwisseling leidt. Voor de optimale oxidatietijd, corresponderende met een maximum in de magnetoweerstand, is aangetoond dat deze overeenkomt met die waarvoor de barrière symmetrisch is. Vanwege een daling van de kwaliteit van de structuur met toenemende Ta dikte, neemt het maximum van de magnetoweerstandsverhouding af van 7% voor de dunst onderzochte lagen, tot 0% voor minder dan tweemaal deze dikte. Dit zal uiteindelijk de toepassing van TaO$_x$ in relevante structuren beperken.

Een van de meest bruikbare processtappen in het vervaardigen van toepassings relevante MTJs, is een temperatuurstap in de aanwezigheid van een hoog magnetisch veld. In hoofdstuk 7 laten we zien dat de bijbehorende toename in de magnetoweerstand, zowel voor AlO$_x$ als voor TaO$_x$ MTJs, correspondeert met een modificatie van het barrièrepotentiaalprofiel. Beargumenteerd wordt dat deze verandering veroorzaakt wordt door een hervordering van de zuurstof aan het grensvlak tussen de onderelektrode en de barrière laag. Om de hoogste magnetoweerstands waarde te verkrijgen zou men die juncties een temperatuurstap moeten laten ondergaan, die direct na depositie gekarakteriseerd zouden worden als licht overgeoxideerd.

Hoofdstuk 8 laat zien dat fotogeleiding niet alleen gebruikt kan worden als een karacterisatietechniek, maar dat het ook kan leiden tot nieuwe spintronicstructuren met interessante eigenschappen. Een optische spin-valve wordt geïntroduceerd, waarin de gemeten fotostroom zeer sterk afhangt van de relatieve oriëntatie van de inwendige magnetische structuur. Resultaten van berekeningen laten een significant magnetofotogeleidingseffect zien voor realistische stacks. De meest kritische
Samenvatting

parameter is de verhouding tussen de inelastische vrije weglengte en de optische indringdiepte in de bovenste laag. Door de materialen en de dikte van de lagen te optimaliseren, wordt verwacht dat relatieve effecten van boven de 100% realiserbaar zijn. Alhoewel de eerste samples geen magnetische afhankelijkheid van de fotostroom lieten zien, worden er aanbevelingen gegeven die uiteindelijk moeten leiden tot een volledig functionerende optische spin-valve.
List of publications

Journal articles

P. H. P. Koller, R. Coehoorn, and W. J. M. de Jonge, Barrier thickness dependence of the magnetoresistance in TaO$_x$ magnetic tunnel junctions, in preparation.


Oral presentations

Photoconductance study of anneal effects on the barrier shape in AlO$_x$ and TaO$_x$ based magnetic tunnel junctions, 9th joint MMM/Intermag conference, Anaheim, California, january 6, 2004.

Photoconductance as a characterisation tool for magnetic tunnel junctions, Wetenschappelijke FOM-dagen gecondenseerde materie, Veldhoven, the Netherlands, December 17, 2002.

The oxidation process of AlO$_x$-based magnetic tunnel junctions studied by photoconductance, 47th annual conference on magnetism & magnetic materials (MMM), Tampa, Florida, November 15, 2002 (finalist student award).

Photoconductance in magnetic tunnel junctions, Intermag Europe, Amsteradam, the Netherlands, May 1, 2002.

**Poster presentations**

Direct observation of barrier asymmetry in TaO$_x$ magnetic tunnel junctions, 18th International Colloquium on Magnetic Films and Surfaces (ICMFS), Madrid, Spain, July 22, 2003.


Curriculum vitae

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