Chapter 2

Theoretical Concepts

Abstract

In this chapter, some basic physical concepts relevant to the work presented in this thesis are explained. Starting from a general introduction to metal/semiconductor interfaces, including barrier formation and transport across the interface. The next part focuses on spintronic concepts starting from the spin-orbit coupling and the spin-Hall effect, which are relevant for understanding spin-orbit torque. The second half of the chapter introduces several relevant device fabrication techniques and explains some important measurement techniques and setups.

2.1 Schottky Barrier

When a metal comes into contact with a semiconductor, the Fermi levels of the materials at the interface have to match resulting in a bending of the conduction and valence band of the semiconductor in energy space. This gives rise to the formation of a Schottky barrier at the interface: an energy barrier that controls charge transport. In this thesis, the existence of this barrier is crucial for resistive switching in the interfacial memristors discussed in chapters 3-5 and hence, an overview of the formation and transport across metal/semiconductor interfaces is presented here.

2.1.1 Schottky-Mott Model

In Fig. 2.1(a) the band diagrams of a metal and an n-type semiconductor in equilibrium are shown. The metal is characterised by a Fermi level \( E_F \) and a work function \( \phi_m \); the minimum amount of energy required to remove an electron. Similarly, this energy is referred to as the electron affinity \( \chi_s \) for the semiconductor. The semiconductor further has a conduction \( (E_c) \) and valence \( (E_v) \) band edge. The degeneracy \( \xi = E_c - E_F \) is negative (positive) if the semiconductor is (non-)degenerate.

When the materials are brought in contact, charge is transferred between them to facilitate alignment of the Fermi levels. In the case of an n-type semiconductor, the Fermi level of the semiconductor has to be lowered by \( \phi_m - \chi_s \). This results in a positive charge in the semiconductor, balanced by a negative charge in the metal that
2.1. Schottky Barrier

Figure 2.1: Schottky barrier energy profile. (a) Energy levels when the metal and semiconductor are electrically separated. (b) When the materials are brought in contact, the Fermi levels will align resulting in a regime close to the interface where an electric field is present and the conduction and valence bands of the semiconductor are bent and a barrier is formed.

resides on the surface because the extra conduction electrons are contained within the Thomas-Fermi screening distance. The positive charge in the semiconductor is provided by the removal of conduction electrons from the surface, leaving behind a layer depleted of electrons with uncompensated positive donor ions. Because the donor concentration is significantly smaller than the concentration of electrons in the metal, this region extends over an appreciable thickness $W$, and due to the presence of an electric field in this region, the bands of the semiconductor are bent upwards[1, 2], depicted in Fig. 5.8(b). The strength of the electric field is spatially dependent and given by:

$$E(x) = \begin{cases} \frac{-qN_D}{\epsilon_s}(W - x), & \text{if } x \leq W \\ 0, & \text{otherwise} \end{cases}$$

where $\epsilon_s$ is the permittivity of the semiconductor, $q$ the electronic charge, $N_D$ the doping density and $x$ the distance from the interface. When a perfect contact is established, a barrier is formed which, in the absence of interface states, will have a Schottky barrier height given by[3, 4]:

$$\Phi_B(n) = \phi_m - \chi_{sc}$$

(2.1)

In the absence of an externally applied bias, the width of the depletion region can be
expressed as:

\[ W = \sqrt{\frac{2\epsilon_s}{qN_D}} \phi_{bi} \]  \hspace{1cm} (2.2)

where \( \phi_{bi} \) is the built-in potential: the difference between the Fermi energy of the metal and that of the semiconductor:

\[ \phi_m - \chi_s - \frac{E_c - E_{F,n}}{q} \]  \hspace{1cm} (2.3)

This model, however, is derived considering two materials that are brought in contact in a perfect vacuum and has several shortcomings. Although the theory explains and correctly predicts the bending of the bands in the semiconductor, it is typically found that it significantly overestimates the height of Schottky barriers.

### 2.1.2 Fermi Level Pinning

![Figure 2.2: Schottky barrier in extreme cases of pinning factor, \( S \). (a) \( S=1 \): barrier height controlled by the Schottky-Mott model. (b) \( S=0 \): barrier height controlled fully by Fermi level pinning at the charge neutrality level. The charge neutrality level, \( E_{CNL} \), is the energy at which the interface states transfer from donor-like (blue region) to acceptor-like (green region).](image)

In practice, it is found that the barrier height is less sensitive to \( \phi_m \) due to an effect known as Fermi-level pinning. This theory considers the effects of metal-induced gap states [5], formed because wave functions of electrons in the metal can decay...
into the bandgap of the semiconductor. These states build up charge during charge
transfer across the interface, creating a dipole that forces the bands to align in a way
that results in a zero dipole charge. This forces $E_{F(m)}$ towards the charge neutrality
level ($E_{CNL}$), the energy level within the bandgap at which the interface states transition from having a donor- to acceptor-like character[6]. If the Fermi level is fully
pinned to these intrinsic states, the barrier height does not depend on the metal work
function and is instead given by:

$$\Phi_B^{(n)} \approx \frac{1}{2} E_{bg},$$

(2.4)

where $E_{bg}$ is the bandgap of the semiconductor.

In practice, neither of these extremes is completely correct and the choice of metal
is found to have some effect. We can define a pinning factor, $S$, to describe how
strongly $E_{F(m)}$ is pinned[7]:

$$S = \frac{\partial \Phi_B}{\partial \varphi_m} = \frac{1}{1 + 0.1(\epsilon - 1)}$$

(2.5)

From Eq. 2.5 an effective metal work function can be calculated:

$$\varphi_{m,eff} = S \varphi_m + (1 - S) \varphi_{CNL}$$

(2.6)

The extreme cases, where $S = 1$ and $S = 0$ are illustrated in Fig. 2.2(a) and (b),
respectively. While it is clear that interface states are present in the work presented
in this thesis, where required for simulations, the Schottky barrier height will be
calculated using Eq. 2.1. We will also use transport data to extract the Schottky
barrier height as detailed in the next section.

### 2.1.3 Transport

If a potential difference, $V$ is applied across the interface, the Fermi levels will be
separated by $qV$, resulting in a net flow of electrons either from the semiconductor
to the metal side (forward bias, Fig. 2.3(a)) or from the metal to the semiconductor
(reverse bias, Fig. 2.3(b)). This process is governed by the Schottky barrier and
can happen through several mechanisms including: (i) thermionic emission (TE), (ii)
field emission (FE), (iii) thermally assisted field emission (TFE) and (iv) trap assisted
tunnelling (TAT), depicted in Fig. 2.3(c). The latter three are all forms of quantum
mechanical tunnelling.

### Thermionic Emission

Charge carriers can traverse the barrier if they have sufficient energy to overcome
the barrier height. If we assume that the barrier height is substantially larger than
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Figure 2.3: Transport through the Schottky barrier. The Schottky barrier profile when a (a) positive, (b) negative bias $qV$ is applied to the metal w.r.t. the semiconductor. (c) Possible transport mechanisms: thermionic emission (TE), field emission (FE), thermally assisted field emission (TFE) and trap-assisted tunnelling (TAT).

$k_B T$ and the net flow of current does not affect equilibrium, the current density is given by[1, 2, 8]:

$$J(V) = A^* T^2 e^{-\frac{q^2 \Phi_b}{k_B T}} (e^{\frac{q V}{k_B T}} - 1),$$  \hspace{1cm} (2.7)

where $k_B$ is the Boltzmann constant, $T$ the temperature and $A^* = \frac{4\pi q m^* k_B^2}{h^3}$ the Richardson constant ($m^*$ is the effective mass and $h$ is Planck’s constant). $n$ is the ideality factor, which is equal to unity for ideal TE and greater than one when additional transport mechanisms are present. Equation (2.7) can be used to estimate the Schottky barrier height in forward bias.

Field Emission and Thermally Assisted Field Emission

Field emission is the tunnelling of charge carriers through the barrier at energies close to the Fermi level. It is also possible for charge carriers to gain additional energy from thermal excitations allowing them to tunnel through the barrier at energies above the Fermi level. Tunnelling effects are extremely sensitive to the barrier profile and hence it is not possible to derive a generalised expression for the current, but approximate analytical expressions have been derived, for example by assuming one-dimensional Wentzel–Kramers–Brillouin (WKB) transmission through the barrier or using the Schottky-Nordheim barrier approximation\footnote{This is the barrier used for deriving the Fowler–Nordheim transmission equation.}, in which a trian-
2.2 Spin-Orbit Coupling

gular barrier rounded by an image-potential-energy term is used\[1, 2, 9, 10\]. Field emission is possible in reverse bias if the barrier is sufficiently narrow while under forward bias, tunnelling occurs only in degenerate semiconductors\[1, 11, 12\].

Trap Assisted Tunnelling

Besides direct tunnelling processes, defects give rise to tunnelling processes with two or more steps. Charge carriers tunnel via intermediate trap states. Electrons are first trapped in localised energy states within the barrier before tunnelling to the other side. It is also possible for charge carriers to hop between multiple defect states before moving to the other side. This can be an elastic process where the energy of the charge carrier is maintained or an inelastic process aided by phonons. The kinetics of TAT depends strongly on the depth of each trap, their concentration and the thermal energy\[13–17\].

2.2 Spin-Orbit Coupling

![Figure 2.4: Spin-orbit coupling. An electron orbiting around a nucleus (a) in the laboratory frame, the nucleus experiences a magnetic field due to the cyclic motion of the electron around it. (b) In the rest frame of the electron, the nucleus orbits around the electron creating a B-field, with which its spin is locked. E is the radial electric field, v is the velocity of the electron, B is the magnetic field.](image-url)

Spin-orbit coupling (SOC) describes the coupling of an electron’s magnetic moment to its orbital motion. The simplest case of this effect is illustrated by a negatively charged electron orbiting around a positively charged nucleus (Fig. 2.4(a)). The electron \((-q)\) orbiting the nucleus \((+Zq)\) with velocity, \(v\) and radial position, \(r\), will experience an electric field \((E = \frac{qr}{4\pi\varepsilon_0r^2})\) from the nucleus, where \(\varepsilon_0\) is the vacuum permittivity. This will cause a spin-orbit magnetic field, \(B\), in the reference
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frame of the electron (Fig. 2.4(b)) along ($v \times r$):

$$B = \frac{E \times v}{c^2},$$

(2.8)

where $c$ is the speed of light. Each electron has an angular momentum that is the sum of an orbital ($L$) and a spin ($S$) contribution. $S$ gives rise to a magnetic moment $\mu_s \approx -\frac{gS}{m_e}$ (where $m_e$ is the electron rest mass). The interaction of this field with the spin-orbit field results in an energy contribution $H_L = -\mu_s \cdot B$ and the electron’s spin aligns antiparallel to $B$ to minimise energy, locking the electron spin to its orbital motion. Due to this spin-orbit coupling, electrons orbiting a nucleus have preferential spin orientation, resulting in a lifting of the degeneracy between $\frac{1}{2}$ (up) and $-\frac{1}{2}$ (down)[18].

In centrosymmetric bulk crystals, two types of symmetries are present. Firstly, inversion symmetry: invariance of reflection around a point (i.e. $E(k, s^\uparrow) = E(-k, s^\uparrow)$ and $E(k, s^\downarrow) = E(-k, s^\downarrow)$). Secondly, time-reversal symmetry $E(k, s^\uparrow) = -E(-k, s^\downarrow)$

This leads to the following expression for centrosymmetric crystals:

$$E(k, s^\uparrow) = E(k, s^\downarrow),$$

(2.9)

where $k$ is the electronic wavevector and $s^{\uparrow\downarrow}$ represents the spin. This shows that atomic SOC cannot induce spin-dependent band splitting in centrosymmetric bulk crystals. To achieve a splitting in the band structure either the time-reversal or inversion symmetry has to be broken. The symmetry is inherently broken at surfaces and interfaces of heterostructures along the direction normal to the surface/interface, which is the Rashba effect. Alternatively, the spin Hall effect (SHE) can also give a non-degenerate spin dispersion.

2.3 Spin Hall Effect (SHE)

In the classical Hall effect[19], positive and negative charges move in opposite directions in a sample carrying an electric current in a magnetic field. This is due to the Lorentz force acting on the charge carriers and results in charge build-up at the boundaries, which can be measured as a transverse voltage across the sample. The SHE is an analogous transport phenomenon which gives rise to a perpendicular spin current, $j_s$, and a spin accumulation, $m$, at the boundaries of a charge current ($j_c$)-carrying sample, depicted in Fig. 2.6(a):

$$j_s = \theta_{SH} j_c \times m$$

(2.10)

This effect is purely spin-based, requiring no external magnetic field and originates from spin-orbit interaction which scales with $Z^{-4}$ (the fourth power of the effective
nuclear charge). It is therefore significant in heavy metals such as Pt and SrIrO$_3$. There are several contributing factors to this effect that are discussed below.

### 2.3.1 Extrinsic Contribution

Electrons moving through a metal under the influence of an electric field are subjected to a large number of scattering events which, other than those concerning phonons and magnons, all involve the electrostatic potential of the scatterer. Similarly to how electrons experiencing the Coulombic charge of the nucleus give rise to SOC, the interaction between conduction electrons and local potentials ($V(r)$) results in spin-dependent scattering events, inducing a favoured scattering direction for electrons depending on their spin polarisation. The interaction Hamiltonian for such a scattering event can be expressed as:

$$H_{\text{scat}} = \eta \sigma \cdot [k \times V(r)],$$  \hspace{1cm} (2.11)

where $\eta$ is the modified SOC parameter. There are two scattering mechanisms, distinguished by the relation between the initial and final direction of the $k$-vector, that make up the extrinsic contribution to the SHE.

**Figure 2.5: Contributions to the spin Hall effect.** (a) Skew scattering, (b) side jump, (c) intrinsic.

**Skew Scattering Fig. 2.5(a)**

The scattering cross-section experienced by an electron scattering with an impurity depends on its spin state, consequently scattering angles for spin-up and spin-down
electrons are different. In the rest frame of the electron, the impurity is surrounded by a magnetic field \((B')\) and approaches the electron with a velocity \((-v)\). As a result the spin \((s)\) will experience a force \(F = \nabla(s) \cdot B'\). This will cause electrons with spin-up to be scattered to the left while spin-down electrons are scattered to the right\[22-25\].

Skew scattering is expected to be dominant in nearly perfect crystals in which the Bloch state transport lifetime is long enough to allow the scattering to be spin-dependent. When this is the case and Bloch electron wavepackets can coherently disperse, the skew scattering contribution to the spin Hall conductivity, \(\sigma_{SH}^{skew}\), will be proportional to the longitudinal conductivity, \(\sigma_{xx}\).

\[
\sigma_{SH}^{skew} \propto \sigma_{xx}
\]  

(2.12)

Side Jump Fig. 2.5(b)
On average, an electronic wavepacket moves in a straight line with constant velocity both before and after a collision. There is a high probability that after a scattering event in which the perturbation created by the impurity does not affect the wavevector, the electron’s trajectory will be slightly displaced. This is a completely quantum mechanical effect that happens on short timescales and results in sub-Angstrom displacements\[22, 26\].

2.3.2 Intrinsic Contribution Fig. 2.5(c)
The intrinsic contribution does not rely on the presence of scatterers. It arises from the band structure effect due to the non-equilibrium spin dynamics of the electrons when they are accelerated by a parallel electric field. In a system with Rashba spin-orbit coupling, there is a split between the spin-up and spin-down bands.

Electrons with a momentum component perpendicular to the field will have a spin component parallel to the field direction. This causes a slight distortion of the Fermi surface giving the electrons a velocity in the direction of the field and a corresponding spin polarisation perpendicular to this direction. Electrons will precess around this resulting Rashba field creating an out-of-plane spin population with opposite sign\[22, 27\].

2.4 Spin-Orbit Torque
A charge current passed through a heavy metal layer in the \(x\)-direction will generate a spin accumulation \((m)\) along \(y\) by virtue of the SHE. Here we assume the
2.4. Spin-Orbit Torque

Figure 2.6: The spin Hall effect (SHE) and spin-orbit torque (SOT). (a) When a charge current, \( j_c \), is passed through a heavy metal (HM), the SHE will convert this into a transverse spin current, \( j_s \). The deflection of electrons results in a spin accumulation, \( m \), at the boundaries of the material. (b) This spin accumulation will exert a torque on an adjacent ferromagnetic (FM) layer (magnetisation \( M \)), resulting in a field-like, \( T_{FL} \) and antidamping-like, \( T_{AD} \), torque and corresponding effective magnetic fields \( B_{FL,AD} \).

The magnetisation lies out-of-plane, along \( z \). When entering the ferromagnet, the spin accumulation \( m \) will interact with the magnetisation \( M \):

\[
\frac{\partial m}{\partial t} + D \frac{\partial j_s}{\partial z} + \frac{qJ}{\hbar} m \times M = -\frac{m}{\tau_{sf}}
\]  

(2.13)

The terms on the left-hand side represent (i) the changes in spin accumulation over time, (ii) the diffusion of \( j_s \), and (iii) the precession of the spin accumulation around the exchange field, respectively. The right-hand side of Eq. 2.13 describes the dissipation of the spin accumulation due to spin-flip mechanisms. \( D \) is the diffusion constant, \( J \) is the exchange interaction, \( \hbar \) is the reduced Planck constant and \( \tau_{sf} \) is the spin-flip relaxation time of the ferromagnet. The effect that this spin accumulation has on the magnetisation can be described by the Landau-Lifshitz-Gilbert equation\[28,29\]:

\[
\frac{dM}{dt} = -\gamma_0 M \times (H + Jm) + \alpha M \times \frac{dM}{dt}
\]

(2.14)

Here \( \gamma_0 \) is the gyromagnetic ratio, \( \alpha \) is the Gilbert damping constant and \( H \) is a term containing all additional effective fields acting on the magnetisation such as the external, anisotropy and demagnetising fields. We can separate the spin accumulation into a longitudinal \( (m || = m \cdot M) \) and a transverse \( (m \perp = m \times M) \) term. From Eq. 2.14 it can be seen that only \( m \perp \) has an effect on the magnetisation dynamics. This
allows us to express:

\[ J_{m \perp} = a m \times M + b m, \]  

(2.15)

where \( a \) and \( b \) are parameters that depend on the spin mixing conductance and the thickness of the ferromagnet. Combining Eq. 2.14 and 2.15 gives:

\[ \frac{dM}{dt} = -\gamma_0 M \times H - a\gamma_0 M \times m \times M - b\gamma_0 M \times m + \alpha M \times \frac{dM}{dt} \]  

(2.16)

The second and third terms of Eq. 2.16 capture two spin-torque effects exerted on the magnetisation by the spin accumulation:

- \( T_{AD} = -a\gamma_0 M \times m \times M \): this term describes the action of an effective field whose direction depends on the magnetisation direction, similar to the action of the Gilbert damping and is consequently known as the antidamping-like torque.

- \( T_{FL} = -b\gamma_0 M \times m \): this term describes the action of an effective field in the direction of the spin accumulation and has the effect of aligning the magnetisation with the spin accumulation direction and is consequently referred to as the field-like torque.

The torque can also be viewed as a magnetic field acting on the magnetisation [26, 30–32]. These torques and their respective effective fields are illustrated in Fig. 2.6(b).

\[ B_{AD} \propto M \times T_{AD} \quad B_{FL} \propto M \times T_{FL} \]  

(2.17)

2.4.1 Transport

The SOT induced by an alternating current (AC) results in periodic oscillations of the magnetisation around its equilibrium position. Injecting an AC \( I_0 \sin(\omega t) \) gives rise to a time-dependent oscillating voltage:

\[ V(t) = I_0 \sin(\omega t)R(t) \]  

(2.18)

To explicitly separate the static and dynamic contributions, we can express the resistance \( R \) as:

\[ R(t) = R(B_0 + B_1(t)), \]  

(2.19)

where \( B_0 \) is an effective field in the equilibrium direction of the magnetisation and \( B_1(t) \) comprises the fields induced by current described in Eq. 2.17 as well as the Oersted field. Eq. 2.19 can be expanded to the first order as:

\[ R(t) \approx R(B_0) + \frac{dR}{dB_1} \cdot B_1 \sin(\omega t) \]  

(2.20)
2.4 Spin-Orbit Torque

\[ V(t) \approx I_0 [R_0 + R_\omega \sin(\omega t) + R_{2\omega} \cos(2\omega t)] \] (2.21)

\[ R_0 = \frac{1}{2} \frac{dR}{dB} \cdot B_I \]
\[ R_\omega = R(B_0) \]
\[ R_{2\omega} = -\frac{1}{2} \frac{dR}{dB} \cdot B_I \] (2.22)

The derivation above does not consider the measurement geometry and holds for both the longitudinal and transverse (Hall) signals shown in Fig. 2.11(a). The first and second harmonic signals in these directions can be written as:

\[ R_\omega = R^2 + (R^x - R^z) \sin^2(\theta) \cos^2(\varphi) + (R^y - R^z) \sin^2(\theta) \sin^2(\varphi) \] (2.23)

\[ R_{2\omega} = [(R^x - R^z) \cos^2(\varphi) + (R^y - R^z) \sin^2(\varphi)] \frac{d\sin^2(\theta)}{dB} \cdot B_I + (R^x - R^y) \sin^2(\theta) \frac{d\cos^2(\varphi)}{dB} \cdot B_I \] (2.24)

\[ R_H^2 = R_{AHE} \cos(\theta) + R_{PHE} \sin^2(2\varphi) \] (2.25)

\[ R_{2\omega}^H = (R_{AHE} - 2R_{PHE} \cos(\theta) \sin(2\varphi)) \frac{d\cos(\theta)}{dB} \cdot B_I + R_{PHE} \sin^2(\theta) \frac{d\sin(2\varphi)}{dB} \cdot B_I \] (2.26)

where \( \theta \) and \( \varphi \) are the polar and azimuthal angles of the magnetisation vector, respectively (Fig. 2.11(a)), and \( R^{x,y,z} \) is the resistance when \( M \) is aligned with the \( x, y \) and \( z \) axis.

The current-induced fields scale quadratically with voltage and are as a result captured in the second harmonic components of the resistance. Hence, we can probe the SOT signals by measuring the second harmonic voltage and performing angle sweeps where a fixed magnetic external magnetic field, \( B_{ext} \), is rotated around the sample. The subscript \( B \) in the following equation refers to the angle of this field[32-35].

\[ R_{2\omega}^{SOT} = [(R^x - R^z) \cos^2(\varphi) + (R^y - R^z) \sin^2(\theta)] \frac{d\sin^2(\theta_B)}{d\varphi} \frac{B_1^\theta}{B_{ext} \cos(\theta_B - \theta)} + (R^x - R^y) \sin^2(\theta) \frac{d\cos^2(\varphi)}{d\varphi_B} \frac{B_1^\varphi}{B_{ext} \sin(\theta_B) \cos(\varphi_B - \varphi)} \] (2.27)

\[ R_{2\omega}^{H,SOT} = (R_{AHE} - 2R_{PHE} \cos(\theta) \sin(2\varphi)) \frac{d\cos(\theta)}{d\theta_B} \frac{B_1^\theta}{B_{ext} \cos(\theta_B - \theta)} + R_{PHE} \sin^2(\theta) \frac{d\sin(2\varphi)}{d\varphi_B} \frac{B_1^\varphi}{B_{ext} \sin(\theta_B) \cos(\varphi_B - \varphi)} \] (2.28)
This is usually done by scanning the field along Cartesian planes, either in-plane ($xy$) or out-of-plane ($xz$ and $yz$). In ferromagnetic layers with perpendicular magnetic anisotropy, it is best to probe SOT along the energetically favourable perpendicular orientation of the magnetisation, and hence in this work, we focus on scans in the $xz$ ($yz$) plane, where $\varphi_B = 0^\circ$ ($\varphi_B = 90^\circ$) and $\theta_B$ is varied.

Joule heating by current has a quadratic dependence ($T \propto I^2 R$). The resulting thermal gradient, $\Delta T$, can give rise to various effects such as (spin) Seebeck; the conversion of $\Delta T$ into a potential difference (spin current), (anomalous) Nernst; creation of an electric field orthogonal to $\Delta T$ and $B_{ext}$ ($M$), and magneto-thermopower effects. These contributions can also be picked up and their angle variation needs to be considered to eliminate them\cite{36}.

2.5 Lithography

![Lithography and ion beam etching](image)

**Figure 2.7: Lithography and ion beam etching.** (a) UV lithography; a photosensitive resist is exposed to UV light through a mask that selectively blocks part of the light. (b) Electron beam lithography; an electron beam is used to pattern a resist. (c) Ion beam etching; Ar ions are used to remove material from the surface of a sample.

2.5.1 Optical Lithography

Optical lithography is a technique suitable for recreating patterns with dimensions greater than several microns. In this thesis, optical lithography was used for two
purposes: either the photoresist served as a hard mask during ion beam etching or as a medium for realising lift-off. The substrate is coated with a UV-sensitive resist and a manual mask aligner with a UV light source from Suss MicroTec is used to selectively expose the resist, as shown in Fig. 2.7(a). When used for ion beam etching, a hard bake is carried out at 120° to ensure that all solvent has evaporated and provide resistance to the impeding ions.

2.5.2 Electron Beam Lithography

Electron beam lithography offers a greater ability to fabricate smaller structures than UV lithography. In addition, it is also more flexible as it allows for patterns to be readily designed using the eLiNE software. Electron beam lithography (EBL) is a direct writing technique where a focused beam of electrons is used to pattern an electron-sensitive resist. It is possible to pattern features down to sub-10 nm on substrates that have been coated with an electron beam-sensitive resist. Exposure to the electron beam changes the solubility of the resist, enabling selective removal of either the exposed or non-exposed regions, depending on the tone of the resist. The system used in this thesis was a RAITH EBL setup equipped with a field emission electron source, a beam blanker, an aperture, a deflector and several lenses for focusing and deflecting the beam, as shown in Fig. 2.7(b).

2.5.3 Ion Beam Etching

Ion beam etching (IBE) uses a directed beam of Ar ions to remove material from the surface of the sample. During the etching, a neutraliser provides low-energy electrons that neutralise the positively charged ions in the beam, preventing beam divergence and aiding in dissipating charge build-up on the substrate. The process is carried out with the sample at an angle of 20° w.r.t. the normal beam incidence and rotating. These factors aim to prevent edge redeposition.

2.6 Deposition Techniques

2.6.1 Thermal Evaporation

Materials such as Co, Ni, Au, Ti, AlOx were thermally deposited thermally under high vacuum (10⁻⁷-10⁻⁶ mbar). The target materials are stored in a carousel with tungsten crucibles. A magnetic field-directed electron beam is utilised to melt the materials. The electron gun is positioned below the targets so that it does not become contaminated by the vapour. The evaporation rate is controlled by the current of the
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electron gun and was typically between 1-3 Ås\(^{-1}\). The chamber utilises a quartz crystal microbalance to measure the rate and give the thickness in situ.

Atoms leave the target with low kinetic energy and, due to long mean free paths, in straight lines. The separation between substrate and source is around 0.5 m. Finally, the deposition is very directed, making this a favourable technique for when lift-off is required.

2.6.2 Pulsed Laser Deposition

![Figure 2.8: Pulsed laser deposition. (a) Schematic of PLD chamber. (b) RHEED intensity oscillations as a function of coverage, θ; when the coverage is 0, the intensity will be maximum as the coverage increases, the roughness will increase and the intensity will go down until θ=0.5 (maximum roughness and minimum intensity). The intensity will then increase until a full layer is grown.](image)

Epitaxial growth of high-quality complex oxide films can be realised using pulsed laser deposition (PLD). PLD is a physical vapour deposition technique where energetic laser pulses are used to transfer material from a target onto a substrate while maintaining stoichiometry. The main parts of the setup are shown in Fig. 2.8(a). The deposition process is separated into stages. Firstly, laser ablation of the target material removes surface atoms and creates a plasma plume composed of high-energy ions, electrons and neutral species. The plume then propagates through the chamber towards the sample during which it interacts with background gases. To preserve the stoichiometry of complex oxides and compensate for the loss of highly volatile oxygen, the deposition is carried out under high oxygen pressure region where the ablated material is expanded in a diffused way. The background gas also reduces
the kinetic energy of the ions in the plasma, which ensures that the deposited atoms do not damage the growing film. When the material reaches the surface, it is deposited. Due to the elevated temperature and time between pulses, the material is given enough time to nucleate and diffuse. This allows the atoms to reach local energy minima, which are typically sites with high atomic coordination. On a defect-free surface, this is typically a step edge or another atom. By optimising parameters such as the laser fluence (energy per surface area), deposition rate, substrate temperature, background pressure and substrate surface roughness, we aim to realise a two-dimensional growth where one layer is completed before the next layer starts to grow. The growth can be monitored in situ using reflection high-energy electron diffraction (RHEED).

**RHEED**

During the growth, an electron gun providing high-energy electrons is incident on the substrate at a grazing angle. After being diffracted by atoms in the sample, the electrons interfere constructively at specific angles determined by the crystal structure and spacing of the atoms at the sample surface. Some of these electrons are collected on a phosphorescent screen, resulting in a diffraction pattern. By monitoring the intensity of the diffraction spots, the film growth can be monitored in situ. The intensity will be maximum when the surface is atomically flat due to minimal scattering of the beam. During growth, the layer roughness will increase, resulting in an increase in scattering and a reduced intensity. This will be maximised when the atomic coverage ($\theta$ in Fig. 2.8(b)) is 0.5, resulting in an intensity minimum. The intensity will increase as the layer becomes smoother until a full layer has formed and another peak in intensity is reached.

### 2.7 Magnetic measurements

Magnetic measurements were conducted utilising a Quantum Design Magnetic Property Measurement System (MPMS) XL-7T, which employs Superconducting QUantum Interference Device (SQUID) magnetometry (Fig. 2.9(b)). This technique uses a superconducting loop, in which there are two Josephson junctions in parallel separated by a non-superconducting material. The current that flows through the weak electric contact between two loops depends on the phase difference ($\Delta \phi$) between their wave functions. In a superconducting ring containing a Josephson junction, the magnetic flux enclosed in the ring influences $\Delta \phi$ and its time derivative ($\frac{d\Delta \phi}{dt}$) depends on the voltage across the contact. To measure the moment of a film, a straw containing the sample is connected to a transport rod which is controlled by a
stepper-motor that moves it through the coil. We used reciprocating sample (RSO) mode, where the sample rapidly oscillates over a distance of 5 cm. The changing position of the sample in the coil induces a change in the flux and consequently a change in the current. The SQUID voltage signal and the position of the sample are measured simultaneously. This is repeated three times to improve accuracy. The expected voltage signal as a function position is shown in Fig. 2.9(a). From this signal the magnetic moment is extracted from the software by a regression fit.

The substrate, straw and Kapton tape used to mount the sample are diamagnetic and constitute a background signal superimposed onto the magnetic signal of the film. When the magnetic response of the film reaches saturation, it is expected to be constant with increasing magnetic field. The raw data, however, show a decrease in the magnetisation with increasing the magnetic field in this regime (Fig. 2.9(c)). By fitting a straight line with a constant, negative slope the diamagnetic contribution can be estimated (blue line). To subtract this contribution, a straight line with this slope is removed from the raw data (red line).
2.8 Electrical Characterisation

One of the most important characterisation methods in this thesis is electrical measurements. These measurements provide an understanding of the performance and functionalities of the fabricated devices.

2.8.1 Keysight B1500A

The Keysight B1500A Semiconductor Device Analyzer (SDA) consists of a mainframe with a ground unit, a graphical user interface (GUI) and ten slots in which different measurement units can be integrated. All units can be controlled through the EasyEXPERT group+ software. The system is equipped with two remote sense and switch units (RSUs), each connecting a source measurement unit (SMU) and one of the channels of a waveform generator/fast measurement unit (WGFMU) so that it is possible to switch between the different modules without having to change connections. This is realised through the configuration shown in Fig. 2.10. The output of each of the RSUs is connected to a probe that can directly be contacted to a device. The SDA has two SMUs. During voltage-controlled sweeps, the voltage is ramped in a quasi-static manner where the input signal has an incremental nature: it is a stepwise rather than a continuous function. Each step has a delay, which should be large enough to bring the sample to a static state after the voltage jump, and integration time which determines how the averaging is carried out to reduce noise. Due to the wide range of current values measured during the I-V measurements in this

Figure 2.10: Probe station setup. Schematic of the Keysight B1500A Semiconductor Device Analyzer used for electrical measurements with the probe station.
thesis, we typically used auto-ranging for sweeping measurements. When operating
in this mode, the software has several range change rules available. For the measure-
ments in Chapter 4, a normal auto-ranging operation setting was used, giving rise to
step-like features in the loops whenever the range changes. For the measurements
in Chapter 5, the go up and down ahead rule was used, which changes the sweeping
rate when a range boundary is approached and reduces the previously mentioned
artefact.

The WGFMU module allows for pulsed measurements; it combines arbitrary lin-
ear waveform generation (ALWG) and current and voltage measurements with a
timing resolution of 10 ns. The waveforms are output through one of the RSUs and
the current/voltage measurement is carried out through the other terminal. The
WGFMU can operate in one of two modes. Firstly, pulse generator (PG) mode, which
can perform fast voltage measurements and has a 50 Ω output impedance to reduce
waveform reflections. Secondly, the fast IV mode can measure both voltage and cur-
rent but is slightly slower than the PG mode.

Each WGFMU module has two channels that both need to be controlled. Pulse mea-
surements in this thesis are typically done by setting channel 1 to PG $V_{meas}$ to supply
the pulse, while also recording the pulse shape from the positive terminal. Channel
2 is usually set to Fast IV $I_{meas}$ and supplies 0 V throughout the measurement; note
that sign of the current should be inverted.

To define a waveform, a 2D vector is defined for each channel specifying the voltage
at different time points ($t_w$). Secondly, the measurement event(s) are specified with
another vector. This vector contains the start time of each measurement event ($v_{m}$),
the total number of measurements taken during the measurement event (points), the
interval, and averaging. The interval, the time between two measurement points, is
divided into two parts, during the latter part of the interval no measurements are
taken. A measurement is taken during the averaging portion. Averaging is done to
reduce the noise in the measurement and is done by taking the average current over
a number of measurements spaced by 5 ns.

2.8.2 Cryostat

To perform electrical measurements inside a cryostat the chip is stuck to a 44-pin chip
carrier with Ag paste. By ultrasonic wire bonding, electrical connections are made
from the pins on the chip carrier to different devices. The chip carrier was inserted
in a holder on a dipstick, which is subsequently placed in a cryostat. The chip holder
is connected to a pair of 22-pin connectors via twisted pair wires and subsequently
connected to a switch box via a shielded cable.

For the measurements in Chapter 3, a setup is used where the base pressure in
the sample space is $\sim 10^{-7}$ mbar. The sample space is equipped with a heater and
can be cooled using a transfer line that can be inserted into either liquid Ni or liquid He so that the temperature can be varied from around 4-400 K.

The measurements described in Chapters 5 and 7 were carried out using a Cryogenic Limited 4He variable temperature insert (VTI). The sample space is placed between the coil of a superconducting magnet coil, which can apply fields up to 7 T. The sample can be rotated in the field in either the in-plane or out-of-plane direction using a stepper motor connected to the dipstick.

In both setups, the sample can be connected to various measurement apparatuses for either direct current (DC) electrical measurements using a Keithley 2410 SMUs via a LEMO to coaxial connection or AC measurements using lock-in amplifiers via LEMO to LEMO connections.

2.8.3 Lock-in Amplifiers

The device is subjected to a sinusoidal signal and the output is measured with respect to a reference signal. The output signal from the device and the reference signal are put into a frequency mixer:

$$V_s(t) \ldots V_R(t) = R \cos(\omega_s t + \theta_s) \ldots \cos(\omega_r t)$$  \hspace{1cm} (2.29)

Resulting in components with frequencies $\omega_s - \omega_r$ and $\omega_s + \omega_r$. Usually, $\omega_r = \omega_s = \omega$ so that there are two components with frequencies 0 Hz and 2$\omega$. The DC component is separated from the 2$\omega$ part using an adjustable low pass filter. According to the Fourier theorem, every periodic function can be written as:

$$V_s(\omega) = \sum x_n \cos(n \cdot \omega_0 + \theta_n) + i \cdot y_n \sin(n \cdot \omega_0 + \theta_n)$$  \hspace{1cm} (2.30)
Selecting only frequencies within one filter bandwidth of the reference signal removes higher harmonics and reduces the signal to:

\[ V_s(t) = R \cdot \cos(\omega_0 \cdot t + \theta) + R \cdot \sin(\omega_0 \cdot t + \theta) \]  \hspace{1cm} (2.31)

The signal originating directly from the low pass filter corresponds to the cosine term in Eq. 2.31 and is known as the \( x \) component. By delaying the reference signal by +90°, the sine term can be obtained, which is known as the \( y \) component. The \( x \) and \( y \) components, in Cartesian coordinates, can be expressed in polar coordinates using:

\[ R = \sqrt{X^2 + Y^2} \]  \hspace{1cm} (2.32)

By means of this phase-sensitive detection, a particular frequency can be filtered and other components are removed so that a small signal can be extracted from a comparable noise level, as shown in Fig. 2.11(b). Additionally, the higher-order harmonic terms \((n > 1)\) can be measured\cite{37,38}. 

Bibliography

2. Theoretical Concepts


[37] About lock-in amplifiers. URL: https://web.physics.indiana.edu/courses/p451/background_info/SRS_Lock-In_Amplifiers.pdf