Towards Nuclear Magnetic Resonance
cross-polarization of an organic monolayer from
optically pumped indium phosphide

by

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Abstract

Transferring a very large nuclear polarization from an optically pumped semiconductor to an organic overlayer is a potentially exciting solid state NMR technique. Large polarization of nuclei can be generated in $^{31}$P by irradiation of InP with circularly polarized light near the bandgap energy at low temperatures. This nuclear spin polarization should then be transferable to an organic overlayer, provided atoms in the layer are coupled to the surface $^{31}$P nuclear spins. In this way, it should be possible to observe the NMR signal from the layer, even though there are few nuclei in the organic layer. A probe was custom built for this purpose and its properties tested. The effects of laser irradiation on polarization were observed with several samples of differently doped InP. A monolayer of octadecanethiol (thiol) was bonded to the surface of InP, and XPS was used to check the surface coverage of the thiol and characterize the effects of various chemical etches. Observation of the thiol hydrogen atoms under optical pumping conditions was attempted, with no success.
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Chapter 1

Introduction

The spectroscopic technique of Nuclear Magnetic Resonance (NMR) is a powerful method for probing structure and dynamics in a wide variety of materials, but suffers from a lack of sensitivity. Typically a very small percentage of nuclear spins in a given sample contribute to the observed NMR signal (see Section (2.1)), because of the small nuclear spin polarization a sample has due to its Boltzmann distribution of spins, and the small nuclear spin Zeeman energy in available laboratory fields.

In the interest of increasing the basic signal to noise of some organic samples, this thesis investigates the possibility of transferring the very large polarization of optically pumped semiconductor nuclei, which is obtained from irradiating the semiconductors with laser light near the bandgap frequency, to an organic sample of interest. The phenomena of generating a large polarization in semiconductors from optical pumping effects will be discussed in Section (5.1). Transfer of optically pumped xenon gas polarization to an organic substance has been demonstrated by Navon et al. [1] and others, but the idea of transferring polarization from an optically pumped semiconductor originated with Tycko [2], and has not yet been demonstrated.

If successful, this technique could be useful for investigating organic materials which currently suffer from small signal to noise, such as membrane bound proteins. Membrane bound proteins are important in activating cell processes and transporting substances into and out of cells. Such materials are hard to obtain in large quantities, and cannot be probed with NMR methods in the liquid state, as the bound proteins in the membrane give very broad peaks, (usually substances in a liquid give narrow, resolved peaks) and these cannot be used to solve the structure through traditional NMR liquid techniques. Removing the protein from the membrane might make it amenable to liquid spectroscopy, but this will likely change its structure.

Molecules placed on a surface in a regularly orientated fashion also give narrow resolved peaks, but the signal from such a surface layer is usually extremely limited, because the supporting substrate occupies most of the available sample volume. Thus, successful transfer of optically pumped polarization to a bound surface molecule will make it possible to view the solid state NMR spectra, and then solve the molecular structure through a combination of orientation and distance (between atoms) constraints. The structure of the membrane bound protein gramicidin was recently solved by such measurements (in the absence of optical pumping) [3].

The relationship between InP $^{31}$P polarization and the wavelength of the
exciting laser light was investigated and is reported in Section (5.2). Measurements were taken for Fe, S and Zn doped wafers. This is in the interest of future work with InP, and to compare with previous findings for this semiconductor from Michal and Tycko [4]. Michal found that the optically pumped $^{31}$P polarization had an oscillatory behavior over a wide energy range that was not easily explained. Here a similar behavior is found and another explanation is hypothesized. A similar study [5] on the wavelength dependence of optically pumped GaAs found no oscillatory behavior, only a narrow peak.

We also seek to transfer this polarization to an organic sample, to this end we prepared and characterized InP samples with a monolayer of octadecanethiol (referred to as “thiol”) on the surface. X-ray Photoemission Spectroscopy (XPS) was used to determine if this material was in fact properly bonded to the semiconductor and to estimate the extent of the coverage (Chapter (4)). XPS is commonly used to characterize the chemical composition of surfaces and surface layers, but is not commonly used to estimate the surface coverage of a deposited layer [6]. Therefore, a few simple models had to be developed for this purpose.

Optical pumping only occurs at low temperatures ($\lesssim 20$K), as the electron spin relaxation times are otherwise too fast to allow for cross-relaxation with the nuclear spins (and thus transfer their polarization to the nuclei (see Section (5.1))). Therefore a cryogenic probe had to be obtained and modified for NMR experiments in this cold regime. In particular, the circuitry for a double resonance probe for use at cryogenic temperatures had to be constructed, which proved very challenging. Double resonance circuits are not commonly used in low temperature NMR probes (in Conradi [7], a review of standard low temperature NMR techniques, double resonance probes are not even mentioned). The probe efficiency and sensitivity was characterized over a temperature range of 293K to 5K. Details can be found in Chapter (3).

Finally, transferring the $^{31}$P optically pumped polarization to the thiol monolayer was attempted, with no success (Chapter (6)). A signal was also sought from a transfer of the low temperature $^{31}$P polarization (much higher than room temperature) to the thiol. This required multiple scans and an increase in the surface area of InP used. This attempt also met with no success. It is hoped that the lessons learned here will lead the way for a successful future endeavor.
Chapter 2

NMR

2.1 Basic theory

NMR is a spectroscopic method of detecting the composition, structure, and even physical constants of certain chemical species. The sample one wishes to investigate is placed in a large magnetic field, typically on the order of several Tesla. A solenoidal coil surrounds the sample. If an rf current of proper frequency and duration (a "pulse") is sent through the coil, causing an alternating magnetic field perpendicular to the main field, transitions of the intrinsic nuclear spin of the sample (provided it has a non-zero spin) can be excited. A superposition of spin states is created which evolves coherently, contributions from all spins in the sample sum up to create an alternating magnetic field. This field induces a voltage in the coil that alternates at the resonant frequency of the nucleus. This frequency depends mainly on the interaction of the intrinsic gyromagnetic ratio of the nucleus with the main magnetic field, and to a much lesser extent on shielding of the main magnetic field from chemical surroundings, and/or interactions with neighboring magnetic moments. This voltage signal can be amplified and detected, and typically resembles the sum of exponentially decaying sinusoidal functions, which can be Fourier transformed into a frequency spectrum. The spectrum yields information about the environment of the nuclei excited. More complicated pulse sequences, sometimes involving more than one frequency to excite different nuclear species, can yield details like distances between atoms, identification of organic substances such as amino acids, and a myriad of other information.

The basic principles of this technique can be seen by first considering the spin populations of spin 1/2 nuclei (for simplicity) in a substance. This is the familiar Boltzmann distribution for non interacting spins in a magnetic field:

\[
\frac{N_t}{N_f} = e^{-\gamma h B_0 / kT},
\]

where \(B_0\) is the NMR magnetic field in the z direction, \(\gamma\) is the gyromagnetic ratio of the nucleus, and \(T\) is the temperature. Thus there will be an excess of spin up (\(\uparrow\)) nuclei (if \(\gamma\) is positive). This produces a macroscopic magnetization of the sample in the z direction. However, this excess is normally quite small since \(\gamma h B_0 \ll kT\) even at temperatures as low as 1K. At room temperature, this excess is on the order of \(10^{-5}\) or less (for nuclei with low \(\gamma\)) in a 10 Tesla magnet. It is this excess that causes the signal detected by the surrounding coil (after a suitable pulse sequence). Thus we see immediately that NMR is not a
sensitive technique, and there is room for massive improvement, provided there is a way to make this small equilibrium excess larger (e.g. by optical pumping).

How do these excess spins create a magnetic field detectable by the coil? To see this, note that the spin is a quantum mechanical quantity, but for isolated spin 1/2 nuclei we can treat it as a classical dipole moment \( \mu \) (see Slichter ([8]) Chapter (2) for justification of this), so its motion is governed by

\[
\frac{d\mu}{dt} = \gamma \mu \times B(t)
\]  

where \( B(t) \) is the applied magnetic field, which can vary with time.

In thermal equilibrium, the Boltzmann distribution gives a net magnetization along the \( z \) axis in an applied field of \( B(t)=B_0 k \). According to equation (2.2), individual spins will precess about \( B_0 \) in a cone, but since the phase of this rotation for the different spins is random, the resulting sum yields no detectable signal. What would induce a voltage is if the net magnetization could be rotated to lie in the x-y plane. The resulting coherent precession of the spins about \( B_0 \) would produce a measurable signal.

To rotate the magnetization, we apply a time varying field at frequency \( \omega \) in the x-y plane (say pointing along the x-axis) \( B_1(t) = B_1(t)i = B_1 \cos(\omega t)i \), where \( B_1 \ll B_0 \).

So now, we must find the solution of

\[
\frac{d\mu}{dt} = \gamma \mu \times (B_0 + B_1(t))
\]  

To do this, we go into the rotating frame of the applied magnetic field, where the effect is easier to see. We first decompose it into two counter-rotating components that sum up to produce the linear \( B_1(t) \) field.

\[
B_R = B_1(i \cos(\omega t) + j \sin(\omega t))
\]  

\[
B_L = B_1(i \cos(\omega t) - j \sin(\omega t))
\]

If we jump into a coordinate frame that rotates along with \( B_1 \), \( B_L \) becomes constant, and \( B_R \) will be perceived as rotating at \( 2\omega \), and can be neglected (it is far off resonance). Also, we must express (2.3) in this rotating frame which becomes

\[
\frac{d\mu}{dt} = \mu \times [(\gamma B_0 - \omega)k + \gamma B_1 i]
\]

Since \( \gamma B_0 = \omega_0 \) we see that if we fix \( \omega = \omega_0 \) the effective field that the nucleus sees will be only \( B_1 \). Thus \( \mu \) will nutate about this field (precession in the rotating frame is referred to as nutation), no longer reacting to the large \( B_0 \) field only, even though \( B_1 \ll B_0 \). Thus we see where NMR gets its name from, since if we drive a magnetic field through our coil at the right frequency, we get a dramatic resonance effect. An intuitive way to think about this is that since we
are pushing the spin with our applied field at the same rate as we are rotating, the nucleus reacts to it to a greater extent than normal.

The angle it will nutate is given by \( \theta = \frac{\gamma B_1 t}{2} \) where \( t \) is the time we have applied the \( B_1 \) field for) since it is now precessing about \( B_1 \). If we allow the system to evolve for time \( t = \frac{\pi}{2\gamma B_1} \), then turn off our applied field, the net magnetization of the sample is now lying along the \( y \)-axis (in the rotating frame). This procedure is called applying a "90° pulse". It will now continue to precess around \( B_0 \), inducing a voltage in the surrounding coil, which we can detect. The induced voltage will drop off in less than a millisecond in many solids, longer in liquids. This is because the spins dephase in a time characterized by a parameter "\( T_2 \)" (i.e. \( \text{Signal} = A_0 e^{-t/T_2} \) where \( A_0 \) is the original amplitude), which depends on the local perturbations in the magnetic field, either from other nuclei and electrons, or the inhomogeneity in the main field. Also, the magnetization of the sample returns to thermal equilibrium in a time characterized by '\( T_1 \)', (i.e. \( M_z = A_0 (1 - e^{-t/T_1}) \) where \( M_z \) is the average magnetization of the sample along the \( z \) axis). The magnetization returns to its original state due to the spins interacting with the lattice and losing energy, hence \( T_1 \) is known as the spin-lattice relaxation time.

If we Fourier transform the time decay recorded, we get a spectrum of the element we excited. In a liquid, separate, well resolved lines for a nucleus provide information about that element's chemical bonds, though for large molecules special techniques are needed to properly assign a spectrum. Complicated series of pulses (called a pulse sequence), involving multiple nuclear species, can also yield distances between atoms, and structure of large molecules. In a solid, the absence of Brownian motion preserves internuclear couplings in the crystal, resulting in broad lines which yield some information about the substance, but less than would be immediately available from a liquid. Special techniques, such as rapidly spinning the sample at a certain angle (called the "magic angle"), can narrow these lines considerably, yielding some of the same information that is available in liquid samples. Solid samples that are regularly orientated, such as a single surface layer of bonded molecules (all orientated the same way), also yield relatively sharp, resolved spectra.

### 2.2 Hartmann-Hahn Cross-Polarization

For our purposes, we seek to transfer the large polarization of the semiconductor nuclei to a bonded organic layer. Unfortunately this cannot happen without there being a mechanism to bring the spin temperatures of the semiconductor nuclei and organic layer nuclei into equilibrium. As in equation (2.1) the number of spin up versus spin down particles depends on the gyromagnetic ratio, \( \gamma \). The value of \( \gamma \) for different nuclear species varies over three orders of magnitude. This means that different species have different populations of spin up and down nuclei. Normally, there is no mechanism by which these populations can rapidly exchange polarization, but NMR techniques (namely Hartmann-Hahn cross polarization) allow for this to occur.
These techniques have a variety of applications. One can get an increase in signal from nuclei with a low gyromagnetic ratio ($\gamma_S$) by cross polarizing from a nucleus with a high gyromagnetic ratio ($\gamma_I$). An example is cross polarizing from hydrogen to carbon (the isotope of carbon that is detectable by NMR, carbon-13, also has a low natural abundance), a useful technique in NMR of biological materials. Another application is to increase the signal from one species with a long $T_1$ time by many acquisitions in a relatively short time, since one can cross polarize it from a nucleus with a short $T_1$ time. Also, by cross polarizing, one can selectively excite nuclei within a molecule and only see a signal from those nuclei coupled to the first nucleus, allowing investigation of the specific environment of some species.

![Diagram](image)

Figure 2.1: The Hartmann-Hahn matching condition. While applying an rf field of the right frequency and power to both spins, the energy splitting between states of the nuclei are the same in the rotating frame, meaning that the same quantum of energy can cause a transition of either.

To do cross polarization, one needs to effectively match the transition energies of both species, so that

$$\omega_{II} = \gamma_I B_{II} = \gamma_S B_{I} = \omega_{IS}$$

(2.7)

in the rotating frame, (where $B_{II}$ and $B_{I}$ are the applied rf fields to the different species) and the same quantum of energy will cause a transition of either spin (see Figure (2.1)) in the doubly rotating frame. This is done by applying rf fields simultaneously to both species, at appropriate power so the above condition is satisfied. This in itself is a necessary condition for cross polarization, but not a sufficient one. One also needs a method by which their spin temperatures can equilibrate.
One scheme is to apply a 90° pulse to the $I$ spins, then quickly adjust the phase of the applied field by 90°, and continue the pulse. An rf field is applied to the other species at this time as well (Figure (2.4)). The 90° phase shift of $B_{1I}$ will "spin-lock" the magnetization to the $y$-axis of the rotating frame (the magnetization will stay constant along the $y$-axis of the rotating frame, and it will not dephase in a time characterized by $T_2$, but decay in a time on the order of $T_1$, called $T_{1p}$, the spin lattice relaxation time in the rotating frame, see Figure (2.5) and Section (2.3)). Since the same magnetization as that in the $B_o$ field is now "locked" to the $B_{1I}$ field, and $B_{1I} \ll B_o$, the spin temperature of the $I$ spins in the rotating frame is now much colder than the lattice temperature. There is now a thermodynamic reason for the spin temperature of the $S$ spins to equilibrate with the $I$ spins, and the mechanism to accomplish this efficiently (so that there is significant polarization delivered to the $S$ spins) is being provided by the $B_{1S}$ field. As shown below, the new Hamiltonian the system is evolving under provides a mechanism (the dipole coupling) by which if one $I$ spin flips, a neighboring coupled $S$ spin can also, allowing the two species to equilibrate. As this proceeds, one will be enhanced and the other will be suppressed. In the absence of the resonant irradiation, flipping mutual spins in this manner will not occur.

The Hamiltonian for two spin species in a large magnetic field is

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_D = \gamma I B_o I_z + \gamma S B_o S_z + \mathcal{H}_{IS} + \mathcal{H}_{II} + \mathcal{H}_{SS}. \quad (2.8)$$

Where $I_z$ and $S_z$ are the spin operators of the two species and the Hamiltonian of the dipolar interaction $\mathcal{H}_D$ between different ($\mathcal{H}_{IS}$) and mutual spins ($\mathcal{H}_{SS}$ and $\mathcal{H}_{II}$) is treated as a perturbation to $\mathcal{H}_Z$. $\mathcal{H}_{IS}$ is given by

$$\mathcal{H}_{IS} = \frac{\gamma I \gamma S h^2}{r_{IS}^3} I_z S_z (1 - 3 \cos^2 \theta_{IS}) \quad (2.9)$$

where $\theta_{IS}$ is the angle between the internuclear vector and the main magnetic field, and $r_{IS}$ is the distance between them. There are more terms that arise from the dipolar interaction, but this is the only term that both commutes with $\mathcal{H}_Z$, and gives diagonal matrix elements. Hence it is the only term that contributes to the "1st order" energy shift and gives effects detectable by NMR, such as line broadening. Normally, it does not allow for coherent mutual spin flipping. However, if this Hamiltonian can be changed so that $\mathcal{H}_{IS} \propto (I_- S_+ + I_- S_-)$, then since

$$I_- S_+ \ket{\uparrow \downarrow} = \ket{\downarrow \uparrow} \quad (2.10)$$

$$I_+ S_- \ket{\uparrow \downarrow} = \ket{\uparrow \downarrow} \quad (2.11)$$

the needed mutual spin flipping can occur.

To see how we can change the Hamiltonian, we apply our two fields and move to the rotating frame on resonance. Where we have

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{II} + \mathcal{H}_{IS} + \mathcal{H}_{SS}. \quad (2.12)$$
On resonance in the rotating frame,

\[ \mathcal{H}_Z = \gamma_I B_{1I} I_z + \gamma_S B_{1S} S_z. \]  

(2.13)

So if we now quantize along the applied magnetic fields, the x-axis is now the z-axis, we replace the index x with z in equation (2.13), but the term \( I_z S_z \) in (2.9) becomes \( I_z S_z = \frac{1}{4} (I_+ S_+ + I_- S_- - I_+ S_- - I_- S_+) \). Thus we now have the desired term \( I_+ S_+ + I_- S_- \) which causes mutual spin flipping. If the system contains only two interacting spins, the spin populations will oscillate back and forth, and the spin populations will not equilibrate. However if there are more couplings such as \( \mathcal{H}_{SS} \) and \( \mathcal{H}_{II} \) and more than one \( \mathcal{H}_{IS} \) coupling in the sample, then this becomes a complicated system with competing oscillations that can be treated thermodynamically. Thus we can think of the system as two spin temperatures coming into equilibrium. The terms \( I_+ S_+ \) and \( I_- S_- \) do not commute with the new \( \mathcal{H}_Z \), and thus can be neglected.

If the \( S \) spins are much less abundant than the \( I \) spins, both spins will equilibrate at slightly less than the \( I \) spin temperature. Combining equation (2.7) and (2.1) we find that in this case the net \( S \) spin polarization is altered by a factor of \( \gamma_I / \gamma_S \). If the \( S \) spins are abundant, they have a larger effect on the intermediate spin temperature reached, and the spin polarization enhancement is somewhat less than \( \gamma_I / \gamma_S \).

### 2.3 Pulse Sequences

The most basic pulse sequence is simply to apply a 90° pulse and record the Free Induction Decay (FID) (time decay) of the signal (Figure (2.2)). The Fourier transform of the FID gives the spectrum from which the frequencies and the linewidths of the spectrum can be extracted.

As mentioned above, the nuclear spin system approaches equilibrium on a time scale of \( T_1 \). At low temperatures \( T_1 \) can become very long (minutes to hours). In order to obtain reproducible results without having to wait for full relaxation to occur, the spin system may be placed in a state of zero magnetization with a train of 90° pulses, known as a saturation train (about 30 pulses, see Figure (2.3)) The pulses in the chain are separated by a time step of about 1 ms. This is enough time for the magnetization flipped by the 90° pulse to dephase, thus the next pulse does not flip a magnetization by another 90°. In this way any magnetization along the z-axis is destroyed. If a delay of time \( \tau \) is inserted before the last pulse, the signal will grow to some level that one can record. Signals acquired after identical \( \tau \) times now become comparable in magnitude.

One can use this technique to measure the \( T_1 \) of the sample. If the time after the saturation sequence is varied, the growth of the signal can be recorded and then fit to the equation \( M_z = A (1 - e^{-t/T_1}) \), and the \( T_1 \) of the sample can be found. The sequence is also useful for comparing the amplitudes of optically pumped signals. If we saturate, then irradiate for some time, then block the laser light just before we do the final 90° pulse, we will record the optically
Figure 2.2: The most basic pulse sequence. One 90° pulse is delivered by the coil, then one acquires the resulting Free induction Decay (FID) signal.

Figure 2.3: Saturation-Recovery pulse sequence used to find the wavelength dependence of optically pumped InP. Phosphorus polarization is saturated by a series of 90° pulses, the shutter is opened to admit light, after a delay of time τ, the shutter is closed and the optically pumped signal is acquired.
pumped signal. The light is blocked to allow the electron system to return to the ground state before acquiring the NMR signal.

Figure 2.4: Cross polarization pulse sequence. A signal is generated in the $S$ spins by applying a 90° pulse to the $I$ spins. A long pulse of length “ct” (contact time, around 1ms) is then applied to both channels, then the $S$ spin signal is acquired.

We also wish to cross polarize. The basic sequence is as shown in Figure (2.4). A 90° pulse is applied to one species, and immediately afterward, the phase of the applied rf field is shifted by 90° and a field of amplitude $\gamma_I/\gamma_S$ times the first is applied to the other species. Shifting the phase of the first field spin-locks the magnetization to the y-axis in the rotating frame (see Figure (2.5)). After a long time “ct” (a few milliseconds) the signal is acquired from the second channel. The spin-lock serves to preserve the order of the I-spin magnetization. In the I-spin rotating frame the I spins are aligned along the effective field and thus do not evolve, except to equilibrate with the $S$-spins. Without the spin-lock, the I spins would dephase in a time characterized by $T_2$, and there would also be no mechanism for the two species to equilibrate.

If there are atoms in or near the coil whose signal is not desired (such as hydrogen atoms in insulation of the coil, or in the grease used to hold the sample in place) this pulse sequence should not detect it, as these nuclei are not coupled to $^{31}$P nuclei. However, after cross polarizing, there can still be a residual signal acquired (likely from atoms outside the coil), along with the cross polarization signal. The unwanted signal can be removed by a technique known as “phase cycling”. The phase of the initial 90° pulse is shifted by 180° on alternate acquisitions, this reverses the orientation of the spin-locked $I$ spins (instead of lying along the positive y-axis, they are aligned along the negative y-axis) and reverses the sign of the acquired signal. Since the phase of the $S$
Figure 2.5: Graphical representation of spin-locking on resonance in the rotating frame. (A) shows the effect of a 90° pulse. The magnetization initially aligned along the y-axis does not stay aligned, but dephases in a time characterized by $T_2$. (B) shows the effect of the spin lock. The magnetization stays aligned along the y-axis, and does not dephase.

Spin rf is unchanged, residual $S$ signal can be canceled out, leaving only the cross polarized signal. At low temperatures, this cancellation scheme can be spoiled by temperature fluctuations, as the magnitude of the residual signal will not be constant, and will thus not completely cancel out. This sequence (Figure (2.4)) was used to try to view the thiol layer by cross polarizing from optically pumped phosphorus to hydrogen (with a sufficiently long optical pumping time to build up the phosphorus polarization) in the thiol.

The cross polarization pulse sequence leaves the signal from the $I$ spins lying along the y-axis in the rotating frame, where it quickly decays after the long "ct" pulse is turned off. In trying to detect the thiol layer, we wished to make the most acquisitions in the time allotted. Since we are dealing with long $T_1$ times, it is desirable to flip the unused polarization back, give it some time to recover, then cross polarize again. Since only the $^{31}$P polarization at the surface of the InP will be transferred to the $^1$H nuclei in the thiol, flipping the polarization back will recover the polarization in the rest of the wafer. The inside polarization will diffuse closer to the surface, after which we can apply the next pulse. This will of course not work indefinitely, but should increase our signal in the time allotted. Figure (2.6) shows this pulse sequence. Figure
(2.7) shows the advantage of such a pulse sequence in a standard sample (O-phospho-L-serine, here called phosphoserine, \( \text{C}_3\text{H}_8\text{NO}_6\text{P} \)) versus not recovering the magnetization.

Figure 2.6: Cross polarization recovery pulse sequence. A pulse \((-\pi/2)\) is applied at the end to flip the phosphorus polarization back up, so it can be reused.

Finally, when attempting to see the weak signal from a stack of thiol covered wafers, the resulting change in the circuit (see section (3.5)) made cross polarization, depicted as above, difficult. Essentially, loading of the circuit by the larger conductive sample made Hartmann-Hahn cross polarization difficult and \( B_1 \) fields to match nutation frequencies at low temperatures could no longer be found. Therefore, an alternative method of cross polarization, employing an adiabatic demagnetization in the rotating frame, was attempted (Figure (2.8)). After a 90° pulse on one channel, the magnetization of that species is spin-locked, as before. However, the applied field is adiabatically (over the course of a few milliseconds) reduced to zero, after which the amplitude of the other channel adiabatically rises. This is somewhat different than the cross polarization previously described. Since the magnetization is locked to the y-axis of the rotating frame just after the 90° pulse, the order is preserved as the field is slowly (entropy=constant) reduced to zero. As the entropy is constant this order must be preserved, and it is transferred to the dipolar “reservoir”. That is, the magnetic moments become aligned along the dipolar fields of their neighbors. If we now turn on the other channel, the lower spin temperature is adiabatically transferred to the other nucleus (as it was stored in the dipolar field), and a signal is generated. Tests with phosphoserine indicated that this method actually outperformed Hartmann-Hahn polarization slightly. This was, when appropriate, used with a recovery pulse on the channel not acquired, in
order to recycle as much magnetization as possible.

**Recovery Pulse Effect on Phosphoserine Signal**

Figure 2.7: Effect of recovery pulse on phosphoserine cross polarization signal amplitude. Data plotted is phosphoserine cross polarization $^{31}$P signal from $^1$H one second after saturation of the $^1$H magnetization. The magnetization is then recovered eight times, with a varying time delay between recovery pulses. The comparison curve had no recovery pulse, but the same varying delay. Adding a recovery pulse clearly enhances the signal for small times, but once the delay is on the order of $T_1$, there is little or no enhancement, as expected.
Figure 2.8: Adiabatic cross polarization pulse sequence. Cross polarization occurs by slowly (over a few milliseconds) reducing the applied field of the one channel to zero while keeping the magnetization spin locked. The other channel slowly rises in amplitude, resulting in observable magnetization arising along the effective field.
Chapter 3

Instrumentation

3.1 The Magnet and NMR Apparatus

For NMR acquisitions an Oxford Instruments 8.4 Tesla superconducting NMR magnet was used. Resonance for $^1$H was at 363.21 MHz (for bulk thiol) and resonance for $^{31}$P (for InP) was at 147.22 MHz. The apparatus to deliver rf pulse sequences and receive the resulting signals (Figure 3.1) was constructed.
from a mixture of commercially available and home built parts assembled in the lab.

The spectrometer has a graphical user interface, Xnmr, written in C, by previous lab members. Xnmr allows programming of pulse sequences, and interactive processing of received signals. Pulse programs, written in C, and compatible with Xnmr, were written to implement the pulse sequences detailed in section (2.3).

3.2 The Cryostat Probe

Figure 3.2: The Cryostat: Helium flows through top tube, tuning of the circuit is accomplished by turning the black rotary feedthroughs. Pump is attached on right, leads to temperature sensors are attached on the left.

The cryostat (Figure 3.2) was manufactured by Janis Research with specifications from Dr. Carl Michal. It is a continuous flow cryostat, wherein helium or nitrogen gas from a pressurized dewar flows through the system, cooling the
copper sample mount ("cold finger", Figure (3.3)) to temperatures down to 4.3 K (the boiling point of helium). The transfer line uses a needle valve to regulate flow from the storage dewar. A quartz window seals off the bottom of the probe, so laser light can be admitted onto the sample. After delivery, another quartz window was installed at the bottom of the heat shield, to reduce radiative heating of the sample. The sample under investigation is attached via Apiezon type N grease to a sapphire substrate on the bottom of the cold finger, where the NMR coil is also attached. Circuitry leading to the coil is attached to the bottom of the lowest copper radiation shield (Figure 3.3). A semi-rigid copper coaxial cable delivers the rf pulses to the coil, and returns the nuclear precession signals to the preamplifier.

![Diagram of sample mount](image)

**Figure 3.3: Sample mount (cold finger).** Coil with sample on sapphire plate on bottom. Variable capacitors and copper coaxial line attached to heat shield mount, which serves as one of two radiation shields. The temperature sensor mounted on copper plate is mounted on sapphire mount. The heat shield with quartz window is also pictured.

Temperature was measured by two sensors, both ceramic oxynitride thin film Cernox (from LakeShore Cryotronics Inc. Westerville, Ohio) thin film resistors, one (CX-1050-CU) supplied with the cryostat and mounted inside the copper sample mount, the other (CX-1050-SU) added near the sample itself on a copper plate in contact with the sapphire (Figure (3.3)). Temperature was controlled by a Lakeshore 340 Temperature controller, which activated a heating coil on the copper sample mount at proper intensity to maintain the desired temperature.

To operate at low temperatures, the cryostat was first pumped out over a
minimum of 12 hours with a diffusion pump. Helium was then driven through the system, the flow being adjusted as the cryostat cooled. The desired setpoint and P, I, and D control parameters were entered into the temperature controller. The system was allowed to come to equilibrium over the period of roughly an hour, at which point the circuit tuning was stabilized and data could be acquired.

In sum, the NMR probe and sample mount design is the result of a trade-off of conflicting requirements. Efficient and precise temperature control of the sample requires good thermal contact between the sample and cold finger, but cross polarization pulse sequences require good electrical isolation of the sample. To best meet these conflicting requirements, the sample is mounted on the aforementioned sapphire substrate, which has a relatively high thermal conductivity at low temperatures, but is a good electrical insulator.

Another requirement that can conflict with other desires is the need to have tuning elements in close proximity to the NMR coil. This allows for better signal to noise. Unfortunately, the geometry of the cold finger makes this difficult. Also, low impedance connections (thick wires) to the coil deliver a heat flux close to the sample. Therefore, the temperature sensor mounted inside the cold finger is not likely to represent the actual temperature of the sample. In order to best control the sample temperature, the aforementioned sensor was mounted to the sapphire.

The temperature of this sensor is that quoted for all that follows. However, this does not necessarily correspond to the sample temperature, due to local heat flux from the wires. Also, it is doubtful that the temperature was accurate when the sample was not well bonded to the sapphire, as in powder samples encased in glass vials used for testing. Since the goal of the powder sample experiments were to characterize the rf properties of the probe circuit, accurate temperature control of the sample was not critical.

3.3 Installation of Probe Components and Circuitry

First, nylon tuning rods to adjust the variable capacitors were installed, enabling the circuit to be tuned from the top rotary motion feedthroughs of the cryostat. Expansion joints were included, and plastic screwdrivers were attached at the end of the tuning rods and spring loaded to ensure contact with the variable capacitors.

Voltronics Corporation cryogenic quartz variable capacitors (NMQM22GK, range=1-22 pF and NMQM10GK, range=0.6-9.5 pF) were bolted via nylon mounts to the bottom copper radiation shield anchor. Copper coaxial cable was installed near the capacitors, the outside being soldered to both heat shield anchors. For probe tuning, American Technical Ceramics high “Q” (quality factor, see below) ceramic rf capacitors were soldered either in parallel or series to these capacitors. The receiver coil was rectangular in shape, made to house the flat InP wafers. Wire used was copper 28 gauge (smaller than usual for
an NMR probe) to minimize heat flow to the sample and thermal contraction effects that might damage the capacitors. The double resonance circuit used for optical pumping experiments can be seen in Figure (3.5), the single $^{31}$P resonance circuit in Figure (3.4).

![Diagram of the resonance circuit](image)

**Figure 3.4**: $^{31}$P resonance circuit used for optical pumping experiments:
- **C1**: Voltronics variable capacitor NMQM22GK, range=1-22 pF (match)
- **C2**: Voltronics variable capacitor NMQM10GK, range=0.6-9.5 pF (tune)
- **C3**: 2.0 pF ATC capacitor
- **L**: Receiver coil, 5 turns, dimensions= 11.4 mm (length) $\times$ 7.75 mm (width) $\times$ 2.5 mm (height) (28 gauge)

The NMR circuitry allows an AC signal from the coaxial cable to pass into the coil. In order to maximize the efficiency of the probe circuit, its impedance must be tuned to 50 $\Omega$ to match that of the transmission lines and active components (power amplifier and NMR signal preamplifier). This prevents reflections in the transmission line and maximizes the power transfer to the probe. The $B_1$ field produced by rf pulses is greatly enhanced by incorporating the coil in an LC resonance circuit similar to an LC passive filter (as in Horowitz and Hill [9] ch. 1). The $B_1$ (and the received signal) are enhanced by a factor called the quality factor (Q) of the resonant circuit, which indicates the bandwidth of frequencies the circuit is impedance matched to. Q increases as the range of allowed frequencies through the circuit gets smaller. Q must not be made too large though, as large Q's result in long "ring down" times following pulses, which obscure NMR precession signals.

Instead of one, there are two variable capacitors in the LC resonant circuit that allow for tuning to an impedance of 50 $\Omega$ at the desired frequency. One has a greater effect on the resonant frequency of the circuit (the "tune"), the other more or less adjusts the impedance at that frequency (the "match") (see Figure (3.4)).

Building a double resonant probe (for purposes of cross-polarization) on a
Figure 3.5: The Double Resonance Circuit:

- **C1**: Voltronics variable capacitor NMQM22GK, range=1-22 pF
- **C2**: Voltronics variable capacitor NMQM10GK, range=0.6-9.5 pF
- **C3**: 1 pF ATC capacitor
- **C4**: Voltronics variable capacitor NMQM22GK, range=1-22 pF
- **C5**: Voltronics variable capacitor NMQM10GK, range=0.6-9.5 pF
- **L**: Receiver coil, 4 turns, dimensions= 8.5 mm x 7.75 mm x 1.5 mm (28 gauge)
- **F1**: LC resonant filter @363 MHz C=4.7 pF, coil diameter=4.2 mm with 5 turns, coil length=11.4 mm, total length=27.9 mm.
- **F2**: LC resonant filter @147 MHz C=4.7 pF, coil diameter=11.4 mm with 7 turns, coil length=30 mm, total length=68.6 mm.

Copper sample mount to work at cryogenic temperatures is a difficult task. One has to have one channel working in the desired frequency range, then attach the other channel without affecting the first. In order to isolate the two channels, one needs a ground for at least one channel that is not a ground for the other. Hence the need for the two LC resonant filters (see Figure (3.5)). These serve as ground for one channel, but not for the other. Another method to ground one channel but not the other is to use a quarter wavelength line of coaxial cable. This was tried, but caused a greater disturbance than the LC filter approach. Finding the right LC filter is an iterative process, as the filter can affect the other channel significantly. It is also not easy to precisely predict the resonant frequency of a constructed LC filter, because at the frequencies used here, leads to the components play a significant role in the filter performance.

The $^1$H channel shown in Figure (3.5) employs a series resonant circuit, in contrast to the parallel arrangement of the $^{31}$P channel. This series arrangement
allows for tuning to higher frequencies with a given coil and variable capacitor. At these higher frequencies, this construction is prone to another problem, that of "false resonances." This is due to leads that connect various tuning elements having a parasitic impedance. As a result of these parasitics, false resonances near the $^1H$ frequency sometimes appear in the circuit. These are modes of the circuit which tune to 50 $\Omega$ and return an NMR signal, but produce pulse "widths" (length of time required to perform a 90° pulse, which are a measure of sensitivity) that are very long, and provide much smaller NMR signals.

Figure 3.6: Photograph of the large coil double resonance circuit. See Figures (3.7) and (3.3) for identification of components.

Even with this higher frequency configuration for the $^1H$ channel, the frequency may still not tune high enough. In such a case, one usually has to make a smaller receiver coil, and/or one with less turns, to reduce the inductance, and/or use thicker wire in the coil to reduce resistance, and/or shorten the circuit leads. If the circuit's resonant frequency is too high, it is easy to lower it by adding capacitance in parallel to the "tune" variable capacitor.

If the variable capacitors are strained when the circuit is cooled to cryogenic temperatures, they can crack and fracture, so one wishes to have flexible attach-
Chapter 3. Instrumentation

Copper solder wick was found to be a good solution for this problem. The resonant frequency of the circuit was found to increase as it cooled, which sometimes meant that the circuit could no longer be tuned to resonate at the desired frequency, and had to be modified. The amount of this increase is fortunately proportional to the room temperature range. That is, if there is little frequency range at room temperature, the increase in resonant frequency from cooling will be small, but for a large initial range, the increase will be large also. Typically one can deal with this by having the desired resonance near the lowest frequency attainable at room temperature.

![Diagram of the large coil double resonance circuit](image)

**Figure 3.7:** The large coil double resonance circuit:
- **C1:** Voltronics variable capacitor NMQM22GK, range=1-22 pF
- **C2:** Voltronics variable capacitor NMQM10GK, range=0.6-9.5 pF
- **C3:** Voltronics variable capacitor NMQM22GK, range=1-22 pF
- **C4:** Voltronics variable capacitor NMQM10GK, range=0.6-9.5 pF
- **C5:** 1.2 pF in series with 0.5 pF and 0.5 pF ATC capacitors
- **C6:** 3.9 pF ATC capacitor
- **L:** Receiver coil, 4 turns, dimensions= 1.5 cm length x 1.0 cm width x 0.5 cm height
- **F1:** LC resonant filter @363 MHz C=4.7 pF, coil diameter=0.18 cm with 3 turns, coil length=1.0 cm, total length=1.2 cm.
- **F2:** LC resonant filter @147 MHz C=3.9 pF, coil diameter=0.9 cm with 7 turns, coil length=1.65 cm, total length=3.3 cm.

Also built was a double resonance circuit with a much larger rectangular coil to accommodate a relatively thick stack of InP wafers (Figure 3.7 also see Chapter (6)). This required a circuit capable of higher power. Accordingly, thicker (22 gauge) wire was used for the coil, and solder wick was used for most connections. It appears that such thick wires did not create an appreciable heat load to the sample, as the temperature sensor on the sample mount approached temperatures very near or better than the setup with thin wires. New work-
able LC filters were constructed. An unexpected problem that appeared was arcing (destruction of the signal by the current discharging through air or an insulator instead of following the wire leads) of the circuit when following a high power signal. Upon investigation, it was determined that the variable capacitors themselves could not support the high voltage being delivered to them, as visible flashes were emanating from them. Hence the circuit was redesigned so that most of the voltage drop would occur through two large ceramic ATC capacitors (capacitors C5 and C6 in Figure (3.7)), which could handle a much greater load. The variable capacitors would still contribute some tuning range, but much reduced. This scheme proved very workable for the $^1$H channel, but not for $^{31}$P, where the tuning range produced was very small. Fortunately, modifying the $^1$H channel was all that was needed to eliminate this arcing problem.

It was also found that unless the coil wire used did not have insulation covering it, it was prone to arcing as well. The insulation of this wire contains hydrogen atoms, which contributed to an unwanted NMR signal. We also observed a "glow discharge" when evacuating the sample and applying a high powered signal. This purple glow results from ionization of molecules in the low vacuum and disrupted the signal received. Once in a high enough vacuum (or at 1 atmosphere of pressure) this problem went away. With very high power pulses, the only vacuum high enough to eliminate this problem occurred when the temperature was somewhere below 50 K and the remaining atmosphere was frozen to the cold finger.

### 3.4 The Laser

The Laser system used was a Verdi V-5 diode pumped laser (532 nm) to pump a Coherent 899-01 Titanium:Sapphire laser system, tunable over a range of 680 nm to 1025 nm. In the Verdi, two diode arrays emit 808 nm light to a Nd:YVO$_4$ (vanadate) gain medium. The vanadate lases at 1064 nm, emitting light to a doubling crystal within the laser cavity, resulting in 532 nm light emitted to the Titanium:Sapphire system. The Titanium:Sapphire crystal emits light over the aforementioned range, which is then passed through a birefringent filter within the lasing cavity. Adjusting the angle of the birefringent filter selects a single wavelength of light which resonates within the cavity. It is then emitted as a coherent beam at this frequency.

The light is reflected along a system of mirrors onto the bottom of the cold finger through the two quartz windows (Figure (3.8)). Before reaching the sample, the light was polarized either linearly, or circularly (left or right) by turning a quarter wave plate.

A computer controlled shutter system was constructed by fellow lab member Isaac Leung. This blocked the laser light at the desired time for acquisitions of optically pumped signal. The light was centered on the InP wafer by observing the infrared light spot with a video camera.
3.5 Probe Performance

To characterize the performance of the double resonance circuit for optical pumping, the probe performance and sensitivity were measured as the temperature was varied.

First though, we can compare the “90° pulse width” (the time it takes to flip the magnetization by 90°) and the power which is needed to do this in our probe to that of a commercially available double resonance probe from Varian (see Figure (3.1)). The rf power delivered to the probe is measured by inserting a 50 dB directional coupler in-line from the rf transmitter. A small voltage signal proportional to either the forward or reflected pulse amplitude is extracted by the directional coupler. This voltage is related to the power by $P \propto V^2$.

<table>
<thead>
<tr>
<th>Probe</th>
<th>Channel</th>
<th>Pulse Width</th>
<th>Forward Voltage (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryostat</td>
<td>$^1$H (363.7 MHz)</td>
<td>5 $\mu$s</td>
<td>340</td>
</tr>
<tr>
<td>coil volume =100 mm$^3$</td>
<td>$^{31}$P (147.2 MHz)</td>
<td>5 $\mu$s</td>
<td>720</td>
</tr>
<tr>
<td>Varian</td>
<td>$^1$H (400 MHz)</td>
<td>4.4 $\mu$s</td>
<td>283</td>
</tr>
<tr>
<td>coil volume =132 mm$^3$</td>
<td>$^{31}$P (161 MHz)</td>
<td>4.4 $\mu$s</td>
<td>466</td>
</tr>
</tbody>
</table>

Table 3.1: Pulse width and corresponding forward voltage compared with Varian probe at room temperature.
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As can be seen in table (3.1), the constructed probe is not as efficient as the Varian. This is probably attributable to the small wires used in the cryostat probe, the close proximity of the coil to a conductor (the cold finger), and the long leads needed to connect the tuning elements to the coil. However, given all these constraints, the probe seems to be doing well, and was not expected to be as good as or better than the Varian probe.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pulse Width (µs)</th>
<th>(^1\text{H} ) Voltage</th>
<th>(^{31}\text{P} ) Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>6</td>
<td>192</td>
<td>330</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>192</td>
<td>309</td>
</tr>
<tr>
<td>20</td>
<td>6</td>
<td>189</td>
<td>305</td>
</tr>
<tr>
<td>100</td>
<td>7.5</td>
<td>199</td>
<td>351</td>
</tr>
<tr>
<td>150</td>
<td>8</td>
<td>187</td>
<td>352</td>
</tr>
<tr>
<td>290</td>
<td>9.5</td>
<td>198</td>
<td>323</td>
</tr>
</tbody>
</table>

Table 3.2: Pulse width and corresponding forward voltage with temperature, while receiving on the \(^1\text{H} \) channel.

We can also test the performance of the probe as the temperature varies, at each temperature, the probe circuitry was allowed to stabilize (half an hour to a few minutes, depending on the time the probe was stable beforehand and the magnitude of the temperature change), and the probe was retuned. Table (3.2) shows that though more or less the same power was put into the probe, the pulse width decreased with temperature, meaning the efficiency of the probe increased. This was expected, since the resistance of the coil and leads decreases with temperature, increasing the Q of the probe.

For both the large and small coil configurations, rf field strengths for efficient cross polarization at various temperatures were found using phosphoserine samples. This gave parameters to use in attempts to observe the thiol signal from covered wafers.

S-doped InP was used to find the signal to noise (and \(T_1 \) for S-doped InP) as a function of temperature, as shown in Figure (3.9). We can predict the behavior of this curve; since \(\gamma hB_0 \ll kT \) we can use equation (2.1) to derive

\[
\frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} = \frac{N_{\text{polarized}}}{N_{\text{total}}} \approx \frac{\gamma hB_0}{2kT}
\]

Therefore, \(A \propto \frac{1}{T} \) where \(A\) is the amplitude of the signal. Hence Figure (3.9) should show a linear relation. While the linear relation holds for 20 K<\(T<300 \) K, the signal does not increase as predicted below about 20 K for both channels. We attribute this to the heat flux from the leads to the coil. It could be due to radiation also, testing after inclusion of the quartz window in the heat shield indicated that it reduced the sapphire mounted temperature sensor reading from 11 K to 5.5 K, when the internal sensor read 5 K. One might expect that the signal increase would be better than linear, given that the Q of the coil increases in this way. However, due to the retuning of the probe circuit
at low temperatures, the increase in signal with $\frac{1}{T}$ for the entire circuit should be linear. Also, since the thermal noise decreases with temperature, one would expect that the signal to noise increases more at lower temperatures than the signal amplitude. Indeed, Figure (3.9) does show this behavior. However, noise contributions from the preamplifier prevent the larger increase. In any event, these results indicate that the recorded temperature was not equal to the sample temperature at low temperatures.

Indeed, we fall short of our expected increase in signal amplitude. Since $A \propto \frac{1}{T}$ we would expect to increase our signal by a factor of 53 by reducing the temperature from 293 K to 5.6 K, instead it is increased by a factor of about 30 in the $^{31}P$ channel, indicating that the sample was actually at around 10 K. $T_1$ measurements of the S-doped InP made under the same conditions are also shown in Figure (3.9) and show a similar behavior. Over 20 K $< T < 300$ K, the $T_1$ shows a linear dependence on $\frac{1}{T}$, as expected for a heavily doped semiconductor, but again levels off for lower temperatures. This again implies that the sample temperature deviates from that of the sensor.

The sensitivity of the probes can be expressed by the signal to noise per atom, calculated from the number of atoms in the phosphoserine samples and InP samples. Table (3.3) shows us that the larger coil configuration is only a little less sensitive (1.5 times less for $^{31}P$ and 2.1 times less for $^1H$) than the small coil configuration. The volume change in the coil should reduce the signal by $(\text{Volume})^{1/2}$, that is by a factor of 2.7. The fact that the large coil exceeds this expectation is probably due to the thick wires used in the coil, which increase the coil Q value, and increase the coil inductance, which reduces the effects of the lead inductances.

<table>
<thead>
<tr>
<th>Circuit</th>
<th>SN per atom $^1H$ Channel</th>
<th>SN per atom $^{31}P$ Channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large Coil</td>
<td>$3.3 \times 10^{-20}$</td>
<td>$2.6 \times 10^{-20}$</td>
</tr>
<tr>
<td>coil volume =750 mm$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small Coil</td>
<td>$7 \times 10^{-20}$</td>
<td>$4 \times 10^{-20}$</td>
</tr>
<tr>
<td>coil volume =100 mm$^3$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3: Signal to noise per atom comparison of large and small coil configurations at room temperature.

It should be noted that the above measurements for signal to noise per atom were made for phosphoserine, which has its own particular line width (FWHH $\approx 15$ kHz for phosphorus, FWHH $\approx 45$ kHz for hydrogen). Since the hydrogen peak is so wide, SN per atom measurements on hydrogen from phosphoserine were made from the raw time decay signal, which is sharper. A smaller line width makes it easier to see the signal. These line widths, though, should be similar to the thiol linewidths.

When the large stack of S-doped InP wafers was placed in the larger coil, the shortest pulse width achievable on the phosphorus channel became 15 $\mu$s,
Figure 3.9: Integrated signal and the signal to noise behavior with temperature of the phosphorus channel. The phosphorus channel data was taken from a sample of S-doped InP. It follows a linear relation over 20 K < T < 300 K as expected, but deviates from this at smaller temperatures. Greatest signal to noise value suggests a sample temperature of 10.2 K, greatest amplitude suggests 12 K. Also included are measurements of T1 times of the wafer, which show a similar behavior.

whereas with phosphoserine it was 6 μs. The pulse width stayed at 15 μs upon lowering the temperature to 5.5 K (about 10 K according to NMR data). This is probably due to the conductivity of the wafers. If the sample is conductive, much of the power put into the coil will be dissipated by the coil induced magnetic field moving electrons about. Our S-doped wafers have a reported carrier concentration of about $5 \times 10^{18}$ cm$^{-3}$. The ionization energy of the donor atoms is about 5.7 meV, whereas $k_B T = 25$ meV at room temperature and 0.863 meV...
at 10 K. One might hope that since the ionization energy is somewhat bigger than $k_B T$ at 10 K that the number of charge carriers would be significantly reduced and the sample would be much less conductive. However, for a non-degenerate (where there are many less conduction electrons than in a metal, or $E_c - \mu \gg k_B T$ where $E_c$ is the energy level of the conduction band and $\mu$ is the chemical potential) semiconductor, the rough temperature where the semiconductor is no longer conductive is when $k_B T \ln \frac{N_c}{N_d} \approx E_b \ (\text{as in Marder [10] ch. 19}).$ Here $E_b$ is the ionization energy (5.7 meV) and $N_c (10^{22} \text{ cm}^{-3})$ is the density of states in the conduction band, and $N_d$ is the density of donors. For the S-doped wafers, this number is nearly equal to $E_b$ at 10 K, meaning we are still in the conducting region, but just barely. However, at high doping concentrations, as in this sample, the dopants themselves can form impurity bands, leading to a high conductivity at low temperatures.
Chapter 4

XPS

4.1 Theory

X-ray Photoemission Spectroscopy (XPS) is a method of investigating surface composition and chemistry of solid materials, sensitive to elements in the first ~50 Å of the surface. The surface is bombarded by X-rays, usually from either Mg (1253.6 eV) or Al (1486.6 eV) causing excitation and emission of electrons from the sample being investigated. These electrons then go through a hemispherical structure containing an electric field, which selects electrons of certain kinetic energies. Sweeping through all kinetic energies and recording the intensities yields a spectrum, from which the surface composition can be determined. Small shifts in spectrum peaks are indicative of chemical bonds. The method is not sensitive to hydrogen or helium.

XPS was used to determine if a successful octadecanethiol (\(\text{CH}_3(\text{CH}_2)_{17}\text{SH}\)), a saturated carbon chain terminated with a thiol group (-SH), hereafter called 'thiol') monolayer was deposited on the InP wafers. Also, a determination of the surface coverage was desired. One method of doing this is to compare the indium or phosphorus peak intensity of a freshly etched sample with intensities from a thiol coated wafer. A separate method is to compare the intensities of different element peaks. Knowing the comparative sensitivity of the element peaks should yield the quantity of each element.

4.1.1 Surface Coverage from Extinguishment

We can calculate the expected intensity of an XPS signal [6] from an element \(i\) through

\[
I_i^{\text{pure}} = \frac{\beta' \sigma_i J_o}{K E_i} \int_0^\infty N_i \exp\left(-\frac{z}{\lambda_{is} \cos \theta}\right) dz
\]

where \(I_i^{\text{pure}}\) is the signal from the element with no surface covering, \(\beta'\) is the spectrometer constant, \(\sigma_i\) is the x-ray photoionization cross section for the element, \(J_o\) is the primary x-ray current, \(K E_i\) is the kinetic energy of the element electron peak, \(N_i\) is the number density of the element in the sample, \(\theta\) is the angle of the receiving lens relative to the normal of the sample, \(\lambda_{is}\) is the inelastic mean free path (IMFP) of electrons from the element passing through the sample \(S\), and we integrate over the depth of the sample, \(z\).

However, if the electrons pass through a monolayer of some substance, we
must modify the intensity we receive by

\[ I_i^M = I_i^{\text{pure}} \exp\left(\frac{-t}{\lambda_{iM} \cos \theta}\right) \]  

(4.2)

where \( I_i^M \) is the intensity of element peak \( i \) (indium or phosphorus), after going through monolayer \( M \). \( I_i^{\text{pure}} \) is the intensity of peak \( i \) if it goes through no layer. The thickness of the layer is \( t \), and \( \lambda_{iM} \) is the IMFP of electron from element peak \( i \) of a specific energy, in the layer \( M \).

Assuming that the coverage of the wafer is 'spotty' i.e. that there are islands of thiol all of thickness \( t \) making up a fraction \( f \) that covers the surface, then we would expect

\[ I_{i}^{\text{sig}} = fI_i^M + (1 - f)I_i^{\text{pure}} \]  

(4.3)

Where \( I_{i}^{\text{sig}} \) is the signal received. Substituting in our expression for \( I_i^M \) and solving for \( f \), we obtain

\[ f = \frac{I_{i}^{\text{sig}} - I_i^{\text{pure}} - 1}{\exp\left(\frac{-t}{\lambda_{iM} \cos \theta}\right) - 1} \]  

(4.4)

Thus with XPS data from a freshly etched sample and from a thiol covered sample, one can estimate the surface coverage, provided the thickness \( t \) is known. Gu et al. [11] found the thickness of the octadecanethiol layer on InP to be 18 Å through ellipsometry measurements. Seah and Dench [12] give the empirical formula

\[ \lambda_{KE} = \frac{31}{KE^2} + 0.087\sqrt{KE} \]  

(4.5)

for organic IMFP’s, where \( \lambda_{KE} \) is the IMFP in nanometers and KE is the Kinetic Energy of the electron in eV. However, equation (4.5) has an RMS scatter factor of 2.12, meaning that the formula result has error bars of more than ±200%. Thus eq. (4.5) is quite uncertain, but appears to be the only equation available.

Equation (4.4) was derived assuming that there are “islands” of thiol on the surface of the wafer surrounded by bare wafer. It is much more likely that, instead of bare wafer, the thiol islands are surrounded by an InP oxidation layer of some average thickness \( t_{ox} \). Gu et al. [11] reports that the oxidation layer is around 7 Å, but is seems likely that the average thickness is somewhat less after etching. Active controversy exists as to the composition of the InP oxide layer [13], and no measurements of IMFP’s are forthcoming. Guivarc’h et al. [14] report that the major components of the oxidation layer are InPO₄ and hydrocarbons. Powell and Joblonski [15] give best fits IMFP’s for aluminum oxide and silicon dioxide which average over our relevant energy range (range of peaks used in this study) to 1.98 nm and 2.82 nm, respectively. Organic IMFP’s average to 2.62 nm over this range. Since organic IMFP’s are similar to those of related oxides, we assume that the IMFP of an oxidation layer is similar to that of an organic layer. It may also be the case that the thiol bound to the
oxidation layer itself, and not the InP surface. In this case, the attempt to form a monolayer for purposes of cross-polarization from optical pumping would be a failure. However, evidence that the thiol is not binding to the oxidation layer is presented below.

Assuming that we do have islands of thiol and islands of oxidation, equation (4.4) can be modified by considering that

\[ I_{t}^{\text{sig}} = f I_{t}^{M} + (1 - f) I_{t}^{\text{ox}} = f I_{t}^{\text{pure}} \exp\left(\frac{-t}{\lambda_{IM} \cos \theta}\right) + (1 - f) I_{t}^{\text{ox}} \]  

(4.6)

and since \( I_{t}^{\text{ox}} = I_{t}^{\text{pure}} \exp\left(\frac{-t_{\text{ox}}}{\lambda_{IM} \cos \theta}\right) \) we can eliminate \( I_{t}^{\text{pure}} \) and get

\[ f = \frac{I_{t}^{\text{sig}} - 1}{\exp\left(\frac{t_{\text{ox}}}{\lambda_{IM} \cos \theta}\right) - 1} \]  

(4.7)

An alternative was given by Bramblett et al. [6], who used XPS to estimate surface coverage of porphyrins (larger molecules also terminated with a sulphur group) on gold. They give the equation

\[ t = -\lambda_{IM} \cos \theta \ln \left(\frac{I_{t}^{\text{sig}}}{I_{t}^{\text{pure}}}\right) \]  

(4.8)

where \( i \) is a substrate element such as phosphorus or indium.

This equation is just the solution for \( t \) from equation (4.2). They then convert this thickness into a surface concentration,

\[ \Gamma_{\text{monolayer}} \text{(molecules/cm}^2) = \frac{t(\text{nm}) \times \rho(\text{g/cm}^3) \times 10^{-7}(\text{cm/nm}) \times N_{AV} \text{(molecules/mol)}}{MW(\text{g/mol})} \]  

(4.9)

where \( \Gamma_{\text{monolayer}} \) is the surface concentration of the monolayer, \( \rho = 1.275 \text{ g/cm}^3 \) is the density of tetraphenylporphinatozinc(II) toluene, an organic substance assumed to have a similar density to our thiol. \( N_{AV} \) is Avogadro's number, and \( MW \) is the molecular weight of the thiol. This can be compared to the theoretical surface concentration \( \Gamma_{\text{unitcell}} \) which is calculated from assuming one thiol molecule per indium atom.

So our surface fraction will be

\[ f = \frac{\Gamma_{\text{monolayer}}}{\Gamma_{\text{unitcell}}} \]  

(4.10)

This derivation of surface fraction suffers from the fact that it is not clear how the thickness \( t \) calculated from the extinguishment ratio of an element is related to a value of \( t \) that will yield the actual surface concentration through equation (4.9). It also makes no attempt to account for an oxidation layer.
4.1.2 Surface Coverage from Comparative Intensities

As an alternative method to find the surface fraction, one can measure the intensities of different element peaks and, knowing the intrinsic photoionization cross sectional intensity of each peak, one can estimate the surface concentration. For phosphorus (similarly for indium) with no surface covering, the signal should be given by (from equation (4.1))

\[ I_{p}^{\text{pure}} = \frac{\beta' \sigma_{p} J_{0}}{K E_{p}} \int_{0}^{\infty} N_{P} \exp\left(\frac{-z}{\lambda_{PInP} \cos \theta}\right) dz \]  

(4.11)

Where \( I_{p}^{\text{pure}} \) is the signal from phosphorus with no surface covering, \( \sigma_{p} \) is the x-ray photoionization cross section for phosphorus, \( K E_{p} \) is the kinetic energy of the phosphorus electron peak, \( N_{P} \) is the number density of phosphorus atoms, \( z \) is the depth, and \( \lambda_{PInP} \) is the IMFP of electrons from phosphorus passing through InP. If the signal passes through a layer \( (M) \) of IMFP \( \lambda_{PM} \) of thickness \( t \) we get, (after integration)

\[ I_{p}^{M} = \frac{\beta' \sigma_{p} J_{0}}{K E_{p}} N_{P} \lambda_{PInP} \cos \theta \exp\left(\frac{-t}{\lambda_{PM} \cos \theta}\right) \]  

(4.12)

This can be compared to an atom in the monolayer, in our case, sulphur or carbon. Gu et al. [11] found that sulphur atoms bond directly to the indium atoms and hence are a single layer at the top of the InP whose signal passes through a layer of carbon and hydrogen (thiol, the same thickness as before), thus we expect

\[ I_{S}^{M} = \frac{\beta' \sigma_{s} J_{0}}{K E_{s}} n_{S} \cos \theta \exp\left(\frac{-t}{\lambda_{SM} \cos \theta}\right) \]  

(4.13)

Where \( n_{S} \) is the number of sulphur atoms per unit area at the surface of InP, \( K E_{s} \) is the kinetic energy of the sulphur peak, and \( \lambda_{SM} \) is the IMFP of sulphur electrons through the monolayer.

To derive a theoretical expression for carbon, we assume that the carbon atoms are evenly distributed throughout the thiol layer, so we have

\[ I_{C}^{M} = \frac{\beta' \sigma_{c} J_{0}}{K E_{c}} \int_{0}^{t} N_{C} \exp\left(\frac{-z}{\lambda_{CM} \cos \theta}\right) dz \]  

(4.14)

Where \( N_{C} \) is the number of carbon atoms per unit volume in the thiol, \( K E_{c} \) is the kinetic energy of the carbon peak, and \( \lambda_{CM} \) is the IMFP of carbon electrons through the monolayer. Upon integrating, this becomes

\[ I_{C}^{M} = \frac{\beta' \sigma_{c} J_{0}}{K E_{c}} N_{C} \lambda_{CM} \cos \theta \left[1 - \exp\left(\frac{-t}{\lambda_{CM} \cos \theta}\right)\right] \]  

(4.15)

We can now use the various ratios of these predicted intensities to calculate the surface fraction.
For instance, the sulphur to carbon peak ratio should be predictable. If we assume that both signals only come from the thiol, then we have

\[ \frac{I^S}{I^C} = \frac{\sigma_S K E_S N_C \lambda_C \exp\left(\frac{-t}{\lambda_S \cos \theta}\right)}{\sigma_C K E_C N_C \lambda_C \cos \theta [1 - \exp\left(\frac{-t}{\lambda_C \cos \theta}\right)]} \]  

(4.16)

A deviation from this ratio serves as a check to see if there is excess carbon on the surface. Assuming that islands of oxidation are contributing an excess carbon signal, then we should have \( \frac{I^S}{I^C} = \frac{I^S_{\text{pure}}}{N_C^2} \left[ 1 - \exp\left(\frac{-t}{\lambda_C \cos \theta}\right) \right] \), which leads to

\[ f = \left( \frac{N_C^2 I^S_{\text{pure}}}{I^S_{\text{pure}}} \right) \left( 1 - \exp\left(\frac{-t}{\lambda_C \cos \theta}\right) \right) \]

(4.17)

Where \( \gamma_{SC} = \frac{\sigma_S K E_S N_C}{\sigma_C K E_C N_C} \) and \( N_C^2 \) is the number density of carbon atoms in an oxidation layer (see Appendix (A.3)).

Other ratios include the sulphur to phosphorus, assuming no islands of oxidation interspersed with islands of thiol, which results in

\[ \frac{I^S}{I^P} = \frac{f I^M}{N_C^2 (1 - f) P_{\text{pure}}} = \frac{\sigma_S N_C K E_P}{\sigma_P P_{\text{pure}} \cos \theta K E_S} \frac{I^S_{\text{pure}}}{I^P} \]  

(4.18)

Setting \( \gamma_{SP} = \frac{\sigma_S K E_S}{\sigma_P P_{\text{pure}} \cos \theta K E_S} \) and rearranging, we arrive at

\[ f = \left( \frac{I^S_{\text{pure}}}{I^P_{\text{pure}}} \right) \left( \gamma_{SP} I^S_{\text{pure}} - I^P_{\text{pure}} (e^{\lambda_S \cos \theta} - 1) \right)^{-1} \]  

(4.19)

We can also derive expressions for \( f \) from S/In, C/P, and C/In, assuming an oxidation layer or not. These are presented in Appendix (A).

Bramblett et al. [6] also give a formula to calculate surface fraction coverage from comparative intensities of elements. Again it is based upon solving for \( t \) with no regard for how exactly this relates to surface concentration. The formula

\[ 0 = 1 - \exp\left(\frac{-t}{\lambda_I \cos \theta}\right) - \gamma_{iP} \exp\left(\frac{-t}{\lambda_P \cos \theta}\right) \]  

(4.20)

with

\[ \gamma_{iP} = (I_i K E_i \sigma_{iP} N_i \lambda_{iP}) / (I_P K E_P \sigma_i N_i \lambda_i) \]  

(4.21)

must be solved numerically for \( t \), after which we can apply (4.9) and (4.10) to find \( f \). Here \( i \) is an element such as carbon, and the subscript \( P \) stands for phosphorus but can easily be substituted for indium. Derivation of this equation can be found in Bramblett et al. [6]. The equation assumes that the element \( i \) is uniformly distributed throughout the monolayer. As already noted, this is not true for sulphur. An equation of this style for sulphur is derived in Appendix (A).
4.2 Thiol deposition

Deposition of a Self-Assembled Monolayer of thiol on InP wafers was first demonstrated by Gu et al. [11]. The procedure is to chemically etch the sample to clean off the native oxidation layer of the InP, then to immerse it in 140 °C molten thiol for 12 hours. To prevent oxidation during the deposition of the layer, nitrogen gas should be cycled through the apparatus.

Instead of using HF to etch the InP, as in Gu et al. [11] A bromine-methanol solution was used. A 1:10 HCl:H₂O solution was later tried, as it was recommended by Whaley et al. [16] where it gave the best results out of a variety of etching mechanisms for their peptide binding purposes. Samples were left in a 1% Br-Meth solution for 5 to 10 minutes. They were then cleaned with methanol, rubbed with lens paper for 1 minute, then immersed again in Br-Meth(0.05%) for 1 minute. Finally, they were cleaned again with methanol, dried with nitrogen gas, and immersed in the molten thiol. After removal, samples were rinsed in acetone and then methanol to remove the excess thiol. For the HCl etch, wafers were immersed in the 1:10 HCl:H₂O for 1 minute, rinsed in deionized water for 1 minute, dried with nitrogen gas, then placed in the molten thiol. XPS measurements were also taken of samples etched in these ways but not immersed in the thiol. These were stored in a nitrogen atmosphere until the measurements were made.

4.3 XPS data

XPS measurements were taken by a Leybold MAX 200 X-ray Photoelectron Spectrometer at the UBC Interfacial Analysis and Reactivity Laboratory by Dr. Kin Chung Wong. A Mg (1253.6 eV) X-ray source was used and θ for this spectrometer was 0°.

As can be seen in Figure (4.2) substantial amounts of carbon and some oxygen were removed by the Br-Meth etching process. With HCl there is reduction of oxygen, but an actual increase in carbon. It should be noted that the etched samples were exposed to air while being prepared for XPS analysis. Of course the time of exposure was kept to a minimum. Somehow, this may have greatly increased the carbon content on the HCl etched wafer. From this analysis it was decided that, for future thiol deposition, an HCl followed by a Br-Meth etch would probably get best results. Indeed, doing this resulted in the highest attained surface fraction values.

Evidence from XPS data of a monolayer of thiol being formed on the wafer surface can be seen in Figure (4.1). The thiol covered wafer has a small sulphur signature, an enhanced carbon peak (even over the unetched sample), and all indium and phosphorus peaks are significantly reduced. The effects of etching are also seen as a reduction of the oxygen and carbon peaks, and an enhancement of the the phosphorus and indium peaks.

A high resolution scan of the sulphur S(2p) peak reveals a peak centered at around 163 eV (Figure (4.3)). According to Tao et al. [17] this is right where
Figure 4.1: XPS spectra of untreated, etched and thiol covered wafers with peaks labeled.

one would expect an S-In bond to occur. An S-O bond would occur at 168 eV. An S-In bond should also be revealed by a shift of about 0.45 eV of the In(3d$_{5/2}$) peak. However, the vast majority of the indium signal should be from atoms not bound to the thiol, translating into a very small shift in the peak, probably beyond the capabilities of the spectrometer. Indeed, no shift can be seen.

Since these signatures are seen, and the procedure from Gu et al. [11] was followed, it was assumed that a monolayer was formed on the wafer. However the surface coverage may not be ideal.

To estimate the surface coverage of the thiol, the In(3d), P(2p), C(1s), and S(2p) peaks of the thiol covered and etched samples were scanned on a finer scale,
Figure 4.2: Effects of Br-Meth and HCl etching on XPS O(1s) and C(1s) peaks. Br-Meth etch was performed on a Fe-doped sample, HCl etch on an S-doped sample.

Figure 4.3: XPS narrow scan of S(2p) peak from thiol covered wafer.
and integrated. The following tables ((4.2) to (4.6)) represent the results of the various formulas derived. For these calculations, the number of phosphorus (or indium) atoms per unit area were calculated from the lattice spacing of InP, (a cubic zinc-sulfide structure) which is 5.87 Å. Therefore, \( N_P = N_{In} = 4 \times (5.87\text{Å})^{-3} = 1.98 \times 10^{28} \text{atoms/m}^3 \). Assuming that each sulphur atom is bonded to a surface indium atom, and there are two surface indium atoms per square cell spacing, we can calculate \( n_S = 2 \times (5.87\text{Å})^{-2} = 5.8 \times 10^{18} \text{atoms/m}^2 \).

Also, we can calculate \( N_C = 18 \times 2/((5.87\text{Å})^{-2} \times 18\text{Å}) = 5.8 \times 10^{28} \text{atoms/m}^3 \) since there are 18 carbon atoms emerging from the sulphur atoms, and the thiol thickness is 18 Å. The IMFP for indium or phosphorus electrons traveling through InP was taken to be \( \lambda_{P(In,P)} = 19\text{Å} \) and \( \lambda_{P(In,P)} = 16\text{Å} \) (Zommer et al.[18]). The thickness of the oxide layer was assumed to be 6 Å.

The cross sectional intensities, kinetic energies and corresponding IMFP’s for each peak are given in Table (4.1).

<table>
<thead>
<tr>
<th>peak</th>
<th>In(3d5/2)</th>
<th>In(3d3/2)</th>
<th>P(2p)</th>
<th>C(1s)</th>
<th>S(2p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross Section ((\sigma))</td>
<td>5.44</td>
<td>3.66</td>
<td>0.61</td>
<td>0.34</td>
<td>0.84</td>
</tr>
<tr>
<td>Kinetic Energy (eV)</td>
<td>808.6</td>
<td>801.1</td>
<td>1124.6</td>
<td>968.4</td>
<td>1091.2</td>
</tr>
<tr>
<td>Organic IMFP (nm)</td>
<td>2.474</td>
<td>2.462</td>
<td>2.918</td>
<td>2.707</td>
<td>2.874</td>
</tr>
</tbody>
</table>

Table 4.1: Relative cross sectional intensity, kinetic energy, and organic IMFP (equation (4.5)) of various peaks. Relative cross sectional intensities are relative dimensionless ratios from the Leybold Max 200 DS100 User’s Guide [19], and are specific to the XPS system used. They are not the photoionization cross section, but can be used as such for the equations used here, which are only concerned with the ratio of intensities.

<table>
<thead>
<tr>
<th>f (HCl etch In(3d5/2))</th>
<th>eq. (4.4)</th>
<th>eq. (4.7)</th>
<th>eq. (4.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.27</td>
<td>1.10</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>f (HCl+Br etch In(3d5/2))</td>
<td>1.55</td>
<td>1.82</td>
<td>1.86</td>
</tr>
<tr>
<td>f (HCl etch In(3d3/2))</td>
<td>1.29</td>
<td>1.30</td>
<td>1.26</td>
</tr>
<tr>
<td>f (HCl+Br etch In(3d3/2))</td>
<td>1.50</td>
<td>1.72</td>
<td>1.71</td>
</tr>
<tr>
<td>f (HCl etch P(2p))</td>
<td>1.47</td>
<td>1.51</td>
<td>1.52</td>
</tr>
<tr>
<td>f (HCl+Br etch P(2p))</td>
<td>1.70</td>
<td>1.97</td>
<td>2.07</td>
</tr>
</tbody>
</table>

Table 4.2: Surface coverage fraction calculated from extinguishment of In(3d) and P(2p) peaks.

Of the four thiol covered samples that XPS analysis was performed on, the HCl+Br etch performed on an S doped wafer seemed the most successful. Carbon and sulphur peaks appeared the most enhanced, indium and phosphorus peaks were the most suppressed, and the oxygen peaks were the lowest seen.
Table 4.3: Surface coverage fraction from intensity ratios, assuming no islands of oxidation.

<table>
<thead>
<tr>
<th></th>
<th>eq. (4.19) $I_S/I_{P(2p)}$</th>
<th>eq. (A.1) $I_S/I_{Pn(3d_{5/2})}$</th>
<th>eq. (A.2) $I_S/I_{P(2p)}$</th>
<th>eq. (A.3) $I_S/I_{Pn(3d_{5/2})}$</th>
<th>eq. (A.5) $I_S/I_{P(2p)}$</th>
<th>eq. (4.20) $I_S/I_{Pn(3d_{5/2})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>f (HCl etch)</td>
<td>1.10</td>
<td>1.07</td>
<td>1.05</td>
<td>1.14</td>
<td>1.07</td>
<td>1.05</td>
</tr>
<tr>
<td>f (HCl+Br etch)</td>
<td>1.70</td>
<td>1.56</td>
<td>1.51</td>
<td>1.49</td>
<td>1.38</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Table 4.4: Surface coverage fraction from intensity ratios, assuming islands of oxidation.

<table>
<thead>
<tr>
<th></th>
<th>eq. (A.2) $I_S/I_{P(2p)}$</th>
<th>eq. (A.3) $I_S/I_{Pn(3d_{5/2})}$</th>
<th>eq. (A.5) $I_S/I_{P(2p)}$</th>
<th>eq. (4.20) $I_S/I_{Pn(3d_{5/2})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>f (HCl etch)</td>
<td>1.12</td>
<td>1.15</td>
<td>-14.94</td>
<td>-0.98</td>
</tr>
<tr>
<td>f (HCl+Br etch)</td>
<td>2.02</td>
<td>1.71</td>
<td>-126.367</td>
<td>-1.49</td>
</tr>
</tbody>
</table>

Table 4.5: Surface coverage fraction from Bramblett et al. comparison equations.

<table>
<thead>
<tr>
<th></th>
<th>eq (4.16) theoretical $I_S/I_C$</th>
<th>measured $I_S/I_C$ (with oxide)</th>
<th>eq. (4.17) $f$ from $I_S/I_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl etch</td>
<td>0.089</td>
<td>0.074</td>
<td>0.74</td>
</tr>
<tr>
<td>HCl+Br etch</td>
<td>0.089</td>
<td>0.131</td>
<td>2.19</td>
</tr>
</tbody>
</table>

Accordingly, the values for fractional coverage for this sample were the highest amongst almost all equations. For comparison, coverage values for an HCl etched S-doped wafer are shown beside these values.

The sulphur to carbon ratios in Table (4.6) deviate from those predicted. If there is excess carbon on the surface from the oxidation layer, one would expect the measured ratios to be less than the predicted. This did not occur for the HCl+Br etch, perhaps due to inaccuracies in the variables used. The surface fraction from the sulphur to carbon ratios is highly dependent on the calculated value of $N_C$ (8.6x10$^{28}$ atoms/m$^3$, see Appendix A.3). This had to be calculated from XPS data, as it is basically unknown. It is similar in value
to the carbon number density of thiol \(N_C=5.8 \times 10^{28}\) atoms/m\(^3\). The carbon signal in the oxidation layer originates from hydrocarbon molecules (Guivarc'h et al. [14]). In calculating \(N_{C2}\) from XPS data, it was assumed that the IMFP of the oxide layer was the same as that for an organic substance, something which we cannot justify. This, and not knowing exactly how thick the native oxidation layer is, make \(N_{C2}\) uncertain. Therefore, less stock should be placed in this value than others presented.

As can be seen, the equations from Bramblett et al. [6] yield values similar to those obtained with the derived equations, with the exception of those calculated from the ratio of sulphur to indium or phosphorus. These vary to extremes, and in the case of phosphorus and sulphur, we get a meaningless negative ratio. The behavior of the function (eq. A.4) is varying wildly in the range of values used here. Otherwise, despite the simplicity and unclear features of the model used to derive these equations, the equations yield similar values to the derived equations.

Most values given exceed 100%. It is hard to believe that we are in fact covering 100% of the surface when there is a noticeable oxygen peak on the thiol covered wafer spectrum. Also, Gu et al. [11] found no evidence of multiple thiol layers. As noted above, there is a large uncertainty in the organic IMFP. If we reduce the calculated values to the lowest values within these error bars (a factor of 2.12), we can reduce the coverage values given for the HCl+Br etch from an average of 168% to 122% for the comparison equations (excluding the Bramblett equations and sulphur to carbon equation, which goes up) and from an average of 171% to 105% for the extinction equations (excluding the Bramblett equations). To get an HCl+Br etch fraction average of 100% for the comparison equations, we must reduce the organic IMFP’s by a factor of four. Further reduction does not reduce this percentage by much more. Other uncertainties may be in the values \(\lambda_{PInP}\) and \(\lambda_{InInP}\) (reducing these also brings fraction values down), the value of monolayer thickness \(t\) (increasing this by some factor reduces values by about the same factor) the value of the oxidation layer thickness \(t_{ox}\) (reducing this to zero brings all equations to values equal to where we assume no oxidation layer) and the value of \(N_C\). The value of \(N_C\) is dependent on \(t\), which in itself is somewhat uncertain, probably to within a few angstroms (let us assume 10%). The uncertainty of \(\lambda_{PInP}\) and \(\lambda_{InInP}\) is unknown, but probably have similar error bars to the organic IMFP’s, since compound IMFP’s in Seah and Dench [12] have a similar RMS scatter to organic IMFP’s. Varying these variables between their estimated extreme values varies the fractional coverage values by about 40% for the comparison and extinction equations. This puts our average coverage fraction for the HCl+Br etch to about 100% for both sets of equations (71% for comparison and 82% for extinction equations for the HCl etch).

New formulas, not included here, were derived for the assumption that there is a 6 Å oxidation layer covering the entire surface, with some fraction of the surface covered by thiol bound to the oxidation layer, instead of the bare InP surface. Adding this assumption reduces the above numbers by about 10%. As above, we do not believe this coverage scenario is the case, due to the placement
of the S(2p) peak. Nevertheless, it is interesting to note what the addition of this assumption does to the quoted numbers.

Overall, as long as the value of organic IMFPs used for the monolayer are so uncertain, surface fraction values from XPS data will have to be treated with some suspicion. These equations do however, give some idea as to how successful a given monolayer deposition was in comparison with previous trials.
Chapter 5

Optical Pumping of InP

5.1 Theory of Optical Pumping

Figure 5.1: Band structure of a III-V type semiconductor. The bands are: the conduction band, where electron spin is $\pm \frac{1}{2}$, the heavy hole band, where the hole spin can be $\pm \frac{3}{2}$, the light hole $(\pm \frac{1}{2})$ and the split off electron band $(\pm \frac{1}{2})$. For InP, the energy gap $E_g = 1.421$ eV at 5 K and the split off band energy gap is $\Delta = 0.108$ eV.

Optical pumping of the InP nuclear spin polarization arises from the cross relaxation of the nuclear spins with excited electrons polarized by laser light. To
see in detail how these excitation effects arise, we begin with the band structure of a III-V type semiconductor (e.g. GaAs, InP) as shown in Figure (5.1) (from [20] ch. 1). It consists of a conduction band (CB), a heavy hole (HH) (spin=±\(\frac{3}{2}\)) and light hole (LH) (spin=±\(\frac{1}{2}\)) band, and a split off (SO) (spin=±\(\frac{3}{2}\)) band. The energy surfaces of the bands are actually non-parabolic due to interactions amongst themselves, but are approximately parabolic near \(k=0\). We will not consider the split off band here, as we are interested in the behavior under excitation with light tuned to the bandgap energy.

The following presentation is drawn from Optical Orientation [20] ch. 1. Here we will not consider the non parabolicity of the energy bands (where parabolicity implies that the energy spectrum is given by \(\epsilon_i = \frac{n_i^2 k^2}{2 m_i}\) where \(m_i\) is the effective mass of particle \(i\)).

The wavefunction of an electron in the conduction band is simply

\[
\psi_m = u_m e^{ikr}, \quad m = \pm \frac{1}{2}
\]

where \(u_m\) is the Bloch amplitude and spin function corresponding to different spin directions, i.e. \(u_{\frac{1}{2}} = S\uparrow\) and \(u_{-\frac{1}{2}} = S\downarrow\). \(\uparrow\) or \(\downarrow\) denote the direction of spin and S is the coordinate function invariant under symmetry transformations in the crystal. S has the same symmetry properties as atomic s functions (for example, the spherical harmonic function \(Y_{00}\)).

To find the heavy and light hole band wavefunctions, consider that the degenerate p-states are split by spin orbit coupling into one group of four (the light and heavy hole bands with \(J=3/2\)) and one group of two (the split off band with \(J=1/2\)). Dealing here only with \(J=3/2\), we must then find solutions to the following simplification of Luttinger’s Hamiltonian [21]

\[
\mathcal{H} = \frac{\hbar^2}{2 m_o} (\gamma_1 + \frac{5}{2} \gamma) k^2 - \frac{\hbar^2}{m_o} \gamma (k \cdot J)^2, \quad \gamma = (2 \gamma_2 + 3 \gamma_3)/5
\]

where \(m_o\) is the free electron mass, \(\gamma_1, \gamma_2, \gamma_3\) are Luttinger’s parameters, and \(J = (J_x, J_y, J_z)\) are the components of \(J\), and are \(4\times4\) total angular momentum matrices for angular momentum of \(3/2\). The \(4\times4\) nature of the Hamiltonian originates from the addition of of the orbital angular momentum (\(L=1\)) and the electron spin (\(S=1/2\)).

The complete wavefunction that gives the energy spectrum for this Hamiltonian is

\[
\psi_{kM}^{\text{hole}} = e^{ikr} \sum_{\mu} \Omega_{M\mu}(k) u_{\mu}^{(3/2)}, \quad M = \pm \frac{1}{2}, \pm \frac{3}{2}
\]

Where \(u_{\mu}^{3/2}\) is a given Bloch amplitude that transforms as an eigenfunction of the total angular momentum. Respectively, they are

\[
\psi_{3/2}^{(3/2)} = -\frac{1}{\sqrt{2}} (X + iY) \uparrow
\]
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\[ u^{(3/2)}_{1/2} = \frac{1}{\sqrt{3}} \left[ -\frac{1}{\sqrt{2}} (X + iY) \downarrow + \sqrt{2} Z \uparrow \right] \quad (5.5) \]

\[ u^{(3/2)}_{-1/2} = \frac{1}{\sqrt{3}} \left[ \frac{1}{\sqrt{2}} (X - iY) \uparrow + \sqrt{2} Z \downarrow \right] \quad (5.6) \]

\[ u^{(3/2)}_{-3/2} = \frac{1}{\sqrt{2}} (X - iY) \downarrow . \quad (5.7) \]

Where \( X, Y \) and \( Z \) are the coordinate parts of the Bloch amplitudes which transform as the coordinates \( x, y, \) and \( z \). These are functions with the same symmetry properties as atomic \( p \) functions. (i.e. \( X \propto (Y_{1-1} - Y_{1+1}), Y \propto i(Y_{11} + Y_{1-1}) \) and \( Z \propto Y_{10} \))

The Hamiltonian operates directly on the coefficients \( \Omega_{M\mu} \) to give

\[ \mathcal{H} \Omega_{M\mu} = \epsilon_{M\mu} \Omega_{M\mu}. \quad (5.8) \]

The \( \Omega_{M\mu} \) which determine \( \epsilon_{M\mu} \) (where \( \epsilon_{3/2} = \epsilon_{HH} = \frac{\hbar^2 k^2}{2m_{HH}}, \quad m_{HH} = \frac{m_e}{\gamma_{1-2}}, \quad m_{LH} = \frac{m_e}{\gamma_{1+2}} \)) from operations of our Hamiltonian are dependent only on the direction of \( \mathbf{k} \) and are equal to the spin 3/2 finite rotation matrices (see Edmonds [22])

\[ \Omega_{M\mu} = D^{(3/2)}_{\mu\lambda}(\phi, \theta, \psi), \quad (5.9) \]

where \( \phi \) and \( \theta \) are the polar angles of the vector \( \mathbf{k} \) with respect to some fixed coordinate frame, and \( \psi \) is an arbitrary angle defining the phase of the wavefunction.

Now, we can use equations (5.1) and (5.3) to derive the optical transitions inherent to InP and the polarization of light that drives these transitions. Application of Fermi's Golden Rule tells us that the transition rate \( (R_{i \to f}) \) between initial \( (i) \) and final \( (f) \) states of an electron is proportional to the square of the matrix elements of the dipole operator \( (\mathbf{e} \cdot \mathbf{r}) \) where \( \mathbf{e} \) is polarization and \( \mathbf{r} \) is the electron position vector) operating on states, i.e.

\[ R_{i \to f} \propto |\langle i | \mathbf{e} \cdot \mathbf{r} | f \rangle|^2. \quad (5.10) \]

Therefore, by taking the initial state to be in the heavy or light hole band, and the final state to be in the conduction band, we can derive the relative intensities of each transition. For instance, for the transition HH (3/2) to CB (1/2) we need to evaluate

\[ (e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{\mu} D^{(3/2)}_{\mu\lambda}(\phi, \theta, \psi) u^{(3/2)}_{\mu} | \mathbf{e} \cdot \mathbf{r} | u^{(1/2)}_{\lambda} e^{i\mathbf{k} \cdot \mathbf{r}}). \quad (5.11) \]

The explicit values of \( D^{(3/2)}_{\mu\lambda}(\phi, \theta, \psi) \) are:

\[ D^{(3/2)}_{\frac{1}{2}, \frac{3}{2}} = e^{-\frac{i}{2}(\phi + \psi)} \cos^3 \left( \frac{\theta}{2} \right), \quad D^{(3/2)}_{\frac{3}{2}, \frac{1}{2}} = \sqrt{3} e^{-\frac{i}{2}(\phi + \psi)} \cos^2 \left( \frac{\theta}{2} \right) \sin \left( \frac{\theta}{2} \right) \]
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\[ D^{(3/2)}_{\pm \frac{1}{2}}(\pm \frac{1}{2}, \pm \frac{1}{2}) = \sqrt{3} e^{\frac{i}{2} \phi} \cos(\theta) \sin(\theta) \]
\[ D^{(3/2)}_{\pm \frac{1}{2}}(\pm \frac{1}{2}, \pm \frac{1}{2}) = e^{\frac{i}{2} \phi} \sin(\theta). \]

(5.12)

Thus, if we rotate our reference frame so that it is along our wavevector \( \mathbf{k} \), \( \theta = 0 \). The only surviving term is \( D_{\pm \frac{1}{2}}^{(3/2)} \), and \( \psi^{(3/2)} \) is the wavefunction we are left with. All other transitions simplify this way, so that \( \psi^{\text{hole}} \propto \psi^{(3/2)} \) in this frame.

Taking \( r = (x, y, z) \) and \( \mathbf{e} = (e_x, e_y, e_z) \), (5.11) now simplifies to
\[ \left( -\frac{1}{\sqrt{2}} (X + iY) \right) \psi = e_x x + e_y y + e_z z \]
\[ \| S \| = \frac{1}{\sqrt{2}} K (e_x + i e_y). \]

(5.13)

Where \( K = (X|x|S) = (Y|y|S) = (Z|z|S) \). These are equal by symmetry, all other matrix elements are zero. We can see this, for example, by noting that \( (x|z|S) \propto (Y_{11} - Y_{10})/Y_{10} = 0 \), and so on. We have also used the fact that spin functions are orthogonal for different spin directions.

Continuing in this manner, we find the matrix elements in Table (5.1) (suppressing \( K \) for simplicity):

<table>
<thead>
<tr>
<th>Conduction Band 1/2</th>
<th>Conduction Band -1/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy Hole +3/2</td>
<td>-\sqrt{\frac{3}{2}} (e_x + i e_y)</td>
</tr>
<tr>
<td>Heavy Hole -3/2</td>
<td>0</td>
</tr>
<tr>
<td>Light hole +1/2</td>
<td>\sqrt{\frac{3}{2}} e_z</td>
</tr>
<tr>
<td>Light hole -1/2</td>
<td>\sqrt{\frac{3}{6}} (e_x - i e_y)</td>
</tr>
</tbody>
</table>

Table 5.1: Matrix elements of the dipole operator. \( e_z \) is the z component of the light polarization, \( e_x \) and \( e_y \) are in the plane perpendicular to the electron momentum.

The terms \( (e_x + i e_y) \), \( (e_x - i e_y) \) and \( e_z \) in Table (5.1) signify that the transition is excited by left or right circularly polarized light or linearly polarized, respectively. Upon squaring these terms, we can find the relative probabilities of each transition, and thus the rate at which they will be excited upon stimulation. Setting the magnitude of transition rate \( \langle HH -3/2 \rangle \Rightarrow (C 1/2) \rangle = K^2 = 1 \), we can see pictorially the relative intensities of each transition and the polarization that excites them in Figure (5.2)

Thus, if we irradiate with left circularly polarized light, we excite both the HH \(-3/2 \rangle \Rightarrow \langle C 1/2 \rangle \rangle and the LH \(-1/2 \rangle \Rightarrow \langle C 1/2 \rangle \rangle. However the rate at which the HH excitation occurs will be three times that of the LH. Therefore, in equilibrium we will build up an excess of spin -1/2 conduction electrons. We can also get an excess of spin 1/2 electrons by exciting with right circularly polarized light.
Table (5.1) applies to electrons with momentum along the direction of propagation of the incident light. Averaging over all directions, $k$, we find (see Optical Orientation [20] p.24-25) the average angular momentum of the excited electrons will be $\pm \frac{1}{2}$, or 50% polarization for circularly polarized light. This is coincidentally the same polarization one would expect for electrons at 10 K in our 8.4 Tesla magnet. The polarization of electrons in a sample is much higher than that of nuclei, due to the much higher electron gyromagnetic ratio.

This analysis applies to InP in zero magnetic field. Our optical pumping experiments are performed in a high magnetic field where the spin orbit coupling is modified and the selection rules become more complicated than presented here.

An excess of spin 1/2 conduction electrons corresponds to a very low spin temperature, which under favorable conditions will be transferred to the nuclei. As in section (2.2) there must be a mechanism by which this can happen. This is provided by the hyperfine coupling, which allows for cross relaxation between the nucleus and the electron. This cross relaxation takes place most rapidly in the vicinity of defects and shallow donors (Paget, [23]), where a fluctuating hyperfine field causes polarization of the nuclear spins. Nuclear spin polarization diffuses slowly away from the “pumping sites.” In a large magnetic field, we
have
\[ H = \gamma_e \hbar B_0 S_z - \gamma_n \hbar B_0 I_z + H_{IS} \]  
(5.14)
Where \( \gamma_e \) and \( \gamma_n \) are the gyromagnetic ratios for the electron and the nucleus, respectively. \( S_z \) and \( I_z \) are the spin operators for the electron and nucleus, respectively. \( B_0 \) is the main NMR magnetic field and \( H_{IS} \) is the hyperfine coupling term between the nuclear and electron spin:
\[ H_{IS} = A(t)I \cdot S = A(t)(I_z S_z + I_y S_y + I_x S_x), \]  
(5.15)
where \( A \) is the hyperfine coupling constant. Therefore, as in (2.2) we will have terms \((I_z S_z + I_y S_y + I_x S_x)\) which can cross relax the electron and nuclear spins. However, because this mutual spin flip does not conserve energy as it did in Hartmann-Hahn cross polarization, the mechanism by which the spin temperatures equilibrate requires fluctuations in \( H_{IS} \), and therefore is dependent on the average time the electron spends near the nucleus (electron correlation time, \( \tau_c \)). The rate at which this cross relaxation occurs, for times \( \gg \tau_c \), is given by
\[ R_{e\rightarrow n} \propto \int_{-\infty}^{\infty} \langle e_{\uparrow} n \mid \mathcal{H}_{IS}(t) \mid e_{\downarrow} n \rangle \langle e_{\downarrow} n \mid \mathcal{H}_{IS}(t') \mid e_{\uparrow} n \rangle e^{\frac{i}{\hbar} (E_{e\uparrow} - E_{e\downarrow})(t-t')} \]  
(5.16)
(From Slichter [8] ch.5, eq. 5.270). That is, the rate at which the flipping occurs from \( |e_{\uparrow} n\rangle \) to \( |e_{\downarrow} n\rangle \), \( (R_{e\rightarrow n} \rightarrow e\rightarrow n) \) is dependent on the spectral density of the hyperfine coupling. Equation (5.16) comes from NMR relaxation theory of metal nuclei through interactions with electrons, a situation similar to what we are considering. Also, the rates of the “forward” and “reverse” processes are related by \( R_{e\rightarrow n} = e^{(E_{e\uparrow} - E_{e\downarrow})/kT} \approx 1 \) (Slichter [8] ch.7).

What conditions must be met to have an efficient transfer of electron spin polarization to the nuclei? To answer, let us assume that the electron polarization difference from thermal equilibrium, \( P_e \), is contributing some polarization to the nuclei, \( P_n \) (which is the nuclear polarization difference from thermal equilibrium), through hyperfine contact, we should have
\[ \frac{dP_n}{dt} = P_e R_{e\rightarrow n} - P_n R_{n\rightarrow e} - P_n R_{n\rightarrow L} \]  
(5.17)
where \( R_{e\rightarrow n} = R_{e\rightarrow \uparrow n \rightarrow e\downarrow n} \) is the rate at which nuclei are polarized due to cross relaxation with the electrons, \( R_{n\rightarrow e} = R_{e\downarrow n \rightarrow e\uparrow n} \) is the rate at which nuclear polarization is transferred to the electrons, and \( R_{n\rightarrow L} \) is the rate at which nuclei are relaxed by the lattice.

Now, \( R_{e\rightarrow n} \approx R_{n\rightarrow e} = R_{hf} \propto \frac{1}{T_{hf}} \) where \( T_{hf} \) is the \( T_1 \) relaxation time of the nuclei due to the hyperfine coupling. Also, \( R_{n\rightarrow L} \propto \frac{1}{T_L} \) where \( T_L \) is the \( T_1 \) relaxation time of the nuclei due to the lattice.

If we assume steady state, \( \frac{dP_n}{dt} = 0 \), and we can solve for \( P_n \), yielding
\[ P_n = P_e \frac{T_L}{T_L + T_{hf}}. \]  
(5.18)
So if $T_L \gg T_{hf}$ or equivalently, $R_{n \rightarrow L} \ll R_{hf}$, the dominant relaxation mechanism is through the electrons, and the transfer of electron polarization to the nuclei should be very efficient. Thus, we should see a dramatic enhancement of the NMR signal. Note that we get a very significant enhancement from the fact that we are exciting electron transitions (Slichter [8] ch.7), since $P_e \sim \gamma_e B_0/kT$ and $P_n \sim \gamma_n B_0/kT$ so $\frac{P_e}{P_n} \sim \frac{2\gamma_e}{\gamma_n}$, and this ratio is $\sim 1600$ for $^{31}P$. If, instead, the rate at which the nucleus relaxes is dominated by relaxation to the lattice, as for indium in InP, we see little enhancement.

By considering the lifetime of the electrons and their relaxation time, we can derive a similar equation for $P_e$, yielding

$$P_e = P_{eo} \frac{T_{relax}}{T_{relax} + T_{ife}}.$$  \hspace{1cm} (5.19)

Where $P_{eo}$ is polarization at the moment of excitation, $T_{relax}$ is the $T_1$ relaxation time of the electrons, and $T_{ife}$ is the time that characterizes the lifetime of the electrons in the conduction band. If then $T_{relax} \gg T_{ife}$ the steady state electron polarization will be large, and transferable to the nuclei. The relaxation time can only be larger than electron lifetime if the semiconductor is at low temperatures, thus optical pumping of InP at room temperature will not work.

Throughout, we have ignored the presence of holes since holes are composed of p-type functions that have $|\Psi|^2 \approx 0$ at the position of the nucleus. Thus they have no hyperfine coupling. We have also ignored the presence of electrons in the conduction band not generated by light absorption. Such thermally polarized electrons will dilute the electron spin polarization generated by optical pumping.

### 5.2 Observation of Optical Pumping in InP

Optical pumping of InP was attempted on three differently doped wafers (all orientated (100)), iron doped (semi-insulating), zinc doped (p-type), and sulphur doped (n-type). Wafers were bought from Wafer Technology Limited (Tongwell, U.K.). Samples were cleaved to the desired size and attached with Apiezon grease to a sapphire mount at the base of the cold finger (Figure (3.3)). The temperature was brought down to 5.5 K. Laser light was emitted through the base of the cryostat onto the wafer. This caused a temperature increase recorded by the temperature sensor mounted on the sapphire (from 5.5 K to about 12 K with 300 mW of laser light). In recording the dependence of signal amplitude with wavelength, this temperature was kept relatively constant (± 0.1°C) with the temperature controller.

The pulse program used to find the Phosphorus NMR signal amplitude dependence on wavelength is diagrammed in Figure (2.3). As in section (2.3) the polarization must first be reduced to zero by a series of 30 or more 90° pulses, as the $T_1$ at low temperatures becomes very long (Table (5.2)). Thus the signal is reproducible in a convenient time.

The InP $^{31}P$ NMR signal received from optical pumping is shown in Figure (5.3). As expected, one can cause a negative amplitude signal by simply turning
### Table 5.2: $T_1$ times, thickness, and carrier concentration (as quoted by the manufacturer) for each type of InP wafer.

<table>
<thead>
<tr>
<th>Material</th>
<th>Room Temp. Carrier Concentration ($\text{cm}^{-3}$)</th>
<th>$T_1$ @293 K (sec)</th>
<th>$T_1$ @5 K (sec)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe doped</td>
<td>$(0.3-5)\times10^8$</td>
<td>311</td>
<td>&gt; 2 hours</td>
<td>0.23</td>
</tr>
<tr>
<td>Zn doped</td>
<td>$(6-20)\times10^{16}$</td>
<td>150</td>
<td>432</td>
<td>0.38</td>
</tr>
<tr>
<td>S doped</td>
<td>$(3-10)\times10^{18}$</td>
<td>1.5</td>
<td>65</td>
<td>0.52</td>
</tr>
</tbody>
</table>

- **Figure 5.3:** Fourier transformed $^{31}$P NMR signal of optically pumped InP (at 880 nm), 200 seconds after saturation. Top signal is from linearly polarized light, middle is induced by $\sigma^+$ circularly polarized light, bottom is from $\sigma^-$ circularly polarized light.

- **Figure 5.4:** Results of the wavelength dependence of optically pumping the various samples of InP are shown. Data was taken with linear, $\sigma^+$, and $\sigma^-$ laser light polarization, after an optical pumping time of 70 seconds for Fe-doped wafers, and 30 seconds for the other two types, as their $T_1$ times were much less. Note that the amplitude of the signal comes from both the optically pumped region (about 1 $\mu$m thick) and the rest of the wafer ($\approx$ 200-500 $\mu$m).

As can be seen, the most dramatic signal comes from the Fe-doped wafer (semi-insulating). The Zn-doped (p-type) wafer shows definite optical pumping, though it is much smaller. The S-doped (n-type) appears to show some behavior close to the bandgap, but this is within estimated error bars. Non reproducible changes in temperature due to heating of the sample by the laser are by far the most likely cause of the point scatter. That there is no signal is not surprising, given the carrier concentration of the wafers (Table 5.2). A low carrier concentration means there are few electrons intrinsically in the
Chapter 5. Optical Pumping of InP

Conduction band, thus the majority in the conduction band after irradiation are from optical pumping effects, and thus the majority of the cross relaxation is between the optically pumped electrons and the nuclei. As the intrinsic number of electrons in the conduction band goes up, less and less of the cross relaxation involves optically pumped electrons.

As was found by Michal et al. [4] (see also Figure (5.5)) the Fe-doped pumped signal shows an oscillatory behavior at lower wavelengths, and the Zn-doped signal seems to as well. At higher energies, there is a qualitative match between the oscillatory behavior of the Fe-doped and Zn-doped measurements, though the pattern is less pronounced in the Zn-doped data. Measurements of Zn-doped were taken twice on different days, Figure (5.5) shows data for one day. Both sets of data show the same general behavior, though there is some scatter.

Michal [4] found a different behavior for the Fe-doped optically pumped signal. This suggests either a doping dependence on signal behavior (Michal's sample was Fe-doped, but to what extent is not known, and the doping strength is assumed to be different), or a dependence on the magnetic field, since Michal's data was taken in a 9.4 Tesla magnet (as opposed to our 8.4 Tesla magnet). As was mentioned above, placing the semiconductor in a magnetic field causes a modification of the electron spin-orbit splitting, and thus a complicated modification of the selection rules previously presented. Further, theory of optical magnetoabsorbption data of semiconductors (see Roth et al. [24]) predicts an oscillatory behavior as wavelength is varied for a semiconductor in a high magnetic field. Detailed calculations (Madelung [25]) reveal a qualitative similarity between data and theory for a variety of semiconductors as the magnetic field is varied. Using this theory to predict the qualitative behavior of our data as the magnetic field is varied is a subject of future work. The hypothesis that the difference in oscillatory behavior observed depends on the strength of the magnetic field makes more sense than the hypothesis that it depends on the doping, since we see similar qualitative behavior for Fe-doped and Zn-doped data. The oscillations would then represent an interference effect between Landau levels in the conduction and valence bands. This could explain the dramatic change observed with the relatively modest change in $B_0$ (Figure (5.5)).

The wavelength dependence of $^{31}$P for etched and thiol covered Fe-doped samples was also found (Figure (5.6)). Samples were very close to the same size, were irradiated with 300 mW of laser light, and kept at the same temperature. As expected, the etched sample shows a bigger signal as the light does not go through an oxidation or thiol layer. The thiol covered wafer has more or less the same amplitude as the unetched sample. Inexplicably, the etched sample signal deviates in its oscillatory behavior from the other two samples in the region of 840 nm to 860 nm. This effect is not understood, but appears to indicate a dependence of optical pumping effects on the surface treatment, not included in section (5.1).
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Fe doped

Wavelength (nm)

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Amplitude (Arb. units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>894.3</td>
<td>3000</td>
</tr>
<tr>
<td>897.9</td>
<td>2000</td>
</tr>
<tr>
<td>891.6</td>
<td>1000</td>
</tr>
<tr>
<td>885.4</td>
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</tr>
<tr>
<td>877.5</td>
<td>-3000</td>
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Zn doped

Energy (eV)

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Amplitude (Arb. units)</th>
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<tbody>
<tr>
<td>1.39</td>
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<td>1.47</td>
<td>+</td>
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<tr>
<td>1.48</td>
<td>+</td>
</tr>
</tbody>
</table>

S doped

Figure 5.4: Amplitude of Phosphorus NMR signal received versus wavelength of (σ⁺ and σ⁻) circularly polarized light for Fe, Zn and S-dopings. Semi-insulating (Fe) and p-type (Zn) show some wavelength dependence, n-type (S) shows none. Note the different vertical scales, optical pumping effects in the Fe-doped sample were so extreme that the polarization was reversed in some instances.
Figure 5.5: Comparison of InP $^{31}$P wavelength dependent signal with previously published data. Discrepancy suggests dependence of signal on doping or main magnetic field.
Figure 5.6: Amplitude of $^{31}$P NMR signal received versus wavelength for un-etched, etched, and thiol covered wafers.
Chapter 6

Thiol Monolayer

The surface area of the wafer for a typical attempt to see the thiol monolayer was 0.65 cm$^2$, which translates into $3.8 \times 10^{14}$ molecules of thiol if there is 100% coverage of 2 molecules per square lattice constant. Since there are 38 hydrogen atoms in the thiol chain this means there are $1.43 \times 10^{15}$ protons to find a signal from. As in Section (3.5) the signal to noise per atom of the Hydrogen channel was measured to be $7 \times 10^{-20}$. This is at room temperature without optical pumping, so if we increase it by a factor of $293K/10K$ (assuming we reached 10K, as is indicated in Section (3.5)) we need $5 \times 10^{17}$ atoms to get a signal to noise of 1. However, with $5 \times 10^{17}$ atoms at 10K, only $4.2 \times 10^{14}$ atoms are polarized (by eq. (3.1)), many less than we have on our thiol layer. If we make a conservative estimate that we are covering only 50% of the surface and 1/3 of the hydrogen atoms are close enough to the surface to have a significant dipole coupling to the phosphorus atoms, this leaves us with $2.38 \times 10^{15}$ atoms to find a signal from. To get a signal to noise of 1 at 10K, we need to enhance the polarization of these atoms by $\approx 200$ times.

The first attempt to see the thiol monolayer was made using a thiol covered Fe-doped wafer, which showed the strongest optical pumping enhancement of $^{31}$P. Laser light was circularly polarized $\sigma^-$ at a wavelength of 871.5 nm. This wavelength was chosen as it was determined to be a wavelength where surface absorption was strong by Michal et al. [4]. Eight cross polarization acquisitions were made, after optically pumping for 1000 seconds each time to let the polarization build up very strongly (the signal to noise grows by $\sqrt{N}$, where $N$ is the number of acquisitions). No visible signal emerged. Parameters for cross polarization used were the same as for phosphoserine at temperatures of 5K to 20K, except the phosphorus frequency was resonant for InP, and not for phosphoserine, which is 12.7 kHz different.

Therefore, the polarization of the protons under optical pumping conditions while cross polarizing from phosphorus is less than 18% (less than 9% if we are covering the entire surface, and less than 5% if all the protons in the thiol chain participate). For comparison, at room temperatures the polarization of hydrogen in our magnet is 0.0029% and is 0.09% at 10K (equation (3.1)) (wheras electrons are at 1.9% and 50.5% respectively).

There are then two possible reasons why there was no observed signal. Either the surface phosphorus atoms do not get highly polarized through optical pumping, and/or the transfer of polarization from phosphorus to thiol through cross polarization is not efficient, perhaps due to poor coupling between the thiol protons and the InP phosphorus nuclei.
Next, it was thought that more signal to noise could be produced if the recovery pulse sequence, as in Figure (2.6), was used. This was run for 4 (with eight recovery pulses) acquisitions and then terminated, as the supply of helium was running out. No signal was seen, and since recovery pulses were used, there should be somewhat more signal to noise than the previous attempt. Assuming the recovery pulse recovers 80% of the original $^{31}\text{P}$ polarization (a rough guess), the 8 recovery pulses increase the original signal to noise for one acquisition by a factor of 2.1. This makes this experiment 1.5 times more sensitive than the previous, thus the upper bound of thiol proton polarization is less than 12%.

This experiment was not repeated as it was felt that detailed measurements of the probe sensitivity with temperature was warranted at this time, to better understand the chances of observing the thiol monolayer. It should be noted that keeping the cryostat temperature stable so these acquisitions can be taken for more than a few hours is rather difficult, as the flow rate of helium from the dewar changes with the pressure of the dewar. Slight changes in flow lead to temperature fluctuations not correctable by the temperature controller, meaning that unwanted signal cannot be canceled out.

Since an optical pumping observation of the thiol layer seemed unsuccessful, it was decided to attempt to observe the thiol signature through many scans and no optical pumping. To get the best signal to noise, an entire wafer of S-doped InP was etched and a thiol layer deposited on it, then cleaved into smaller wafers. This increased the surface area observed as compared to the optical pumping transfer experiments by about 62 times (helped by using both sides of the wafer). A new double resonance circuit was built with enough width to accommodate this stack of wafers, as in Section (3.3). Also, this arrangement was brought to an internal sensor reading of 4.5 K, to increase the signal to noise still further due to the low temperature. S-doped InP was used, as the $T_1$ of S-doped wafers is around 60 seconds at 5 K, much shorter than the thiol $T_1$, or any other type of wafer, leading to more acquisitions in a given time. The short $T_1$ time is due to the presence of many more mobile electrons than any other sample, which unfortunately also degrades the probe performance. The adiabatic recovery sequence (Figure (2.8)) from phosphorus to hydrogen was used in 8 three second intervals after a long wait of 100 seconds. 100 scans (with eight recoveries each) were accumulated this way, with no signal seen.

Assuming 100% coverage and all thiol protons contributing a signal in the wafer stack, we are looking for a signal from $8.87 \times 10^{17}$ atoms. As in Table (3.3) the signal to noise per atom of the $^1\text{H}$ channel for the large coil is $3.3 \times 10^{-20}$, which decreased upon placing the wafer stack in the coil to about $2 \times 10^{-20}$, which is increased to about $5.86 \times 10^{-19}$ due to our temperature factor, so the signal to noise of our stack for full coverage and all thiol protons participating should be 0.52, but is 0.09 with the 50% coverage and 1/3 $^1\text{H}$ participation in cross polarization assumed above. After 100 acquisitions, the expected signal to noise increases to 10.8 and 1.8 respectively due to our recovery acquisitions. Thus even with our pessimistic assumptions, the thiol monolayer should still be visible. This leads to the conclusion that the cross polarization between the phosphorus and the protons is not efficient, or the thiol layer is not intimately
bound to the InP surface.

A room temperature attempt to observe the thiol was made with this wafer stack. Over 100,000 scans were made, and no signal seen. The predicted signal to noise after all these scans for the optimistic coverage assumption is 5.6 and 0.94 for the pessimistic. Thus the signal should be more or less visible. Again this suggests an inefficiency in cross polarization, or poor contact between the surface $^1\text{H}$ and bulk $^{31}\text{P}$. 
Chapter 7

Conclusions and Recommendations

7.1 Conclusions

The results above seem to indicate cross polarization form the phosphorus to the nuclei is not efficient. This contradicts recent studies by Lucas Goering [26], where cross polarization from 4-trifluoromethylbenzylbromine to powdered InP (with a much greater surface area) was observed. The efficiency appeared to be quite high in these experiments, but is difficult to quantify due to uncertainties in the InP powder surface area and coverage. The inefficiency of cross polarization may be due to a weak coupling between the surface $^{31}$P and the thiol hydrogen atoms.

Though the goal of demonstrating polarization transfer from single-crystal InP to an organic overlayer was not successful, a number of achievements were made. Two working double resonance circuits were built that worked over a range of 300 K to 4.3 K, a difficult task. The performance of the circuits was characterized. Optical pumping of $^{31}$P in InP was observed, as well as the optical pumping signal dependence on wavelength. The similarity of the Fe-doped and Zn-doped wavelength dependence suggests that the behavior of signal with laser wavelength is not dependent on the doping, but on the magnetic field. The effects of etching and thiol deposition on the optically pumped $^{31}$P signal was found, but not completely understood. Techniques were developed to deposit thiol on an InP surface and measure the surface concentration of the thiol using XPS.

In all, though the the thiol layer was not observed, this thesis has laid the groundwork for eventual success in this endeavor.

7.2 Recommendations

Observing a weak NMR signal at low temperatures is quite difficult. It is complicated by the fact that there may exist unwanted signals from atoms not in the sample, such as hydrogen atoms in the insulation of the coil. If the temperature varies for some reason during an acquisition, then there will be a mismatch in amplitudes of the background that does not properly phase out. This can lead to false signals. Close attention must be paid to this factor.
Another difficulty is that one is never sure if the parameters being used are optimal. It is not certain that the $^{31}$P on the surface of the InP resonates at the same frequency as the internal $^{31}$P, though the experiments performed by Goering [26] suggest that the two are close.

It is recommended that future work in this area should lead to first observing the bonded thiol signature without optical pumping. Better techniques for thiol (or other materials) deposition should be investigated, and using a wafer stack with more surface area (from thinner wafers) will probably be successful. Instead of etching the surface, cleaving the InP in a nitrogen atmosphere should make for an oxidation free surface. It will also allow for a thinner wafer stack. Thiol treatment could also be applied to a freshly grown wafer. Also, if the wafers could be made semi-insulating with a thin top layer of S-doped material, the problems of probe inefficiency that placing the stack of S-doped wafers in the coil would likely be reduced or eliminated.

Observation of the thiol without optical pumping will give an unambiguous determination of the frequency needed to observe it with optical pumping, and give an idea of the efficiency of the cross polarization. If it can be made efficient, then it will be clear that the problem lies in building up enough of a polarization at the surface of the InP. Perhaps using a bonded molecule that includes fluorine, an element which should not be contained in any substances near the coil, will make observation of cross polarization clearer and unambiguous.

Another goal of future work can be to increase the wavelength range over which the optically pumped $^{31}$P signal is observed. If this reveals more oscillations, and the data can be matched to theoretical predictions based on modification of the spin orbit splitting, this will reveal the cause of the oscillatory behavior.
References


References


Appendix A

Further surface fraction equations

A.1 Further Comparison Equations

Further expressions which can be used to calculate the fraction of surface coverage are as follows.

For carbon and phosphorus, assuming no oxidation layer, we have \( \frac{I_{C}^{\text{sig}}}{I_{P}^{\text{sig}}} = \frac{f_{M}}{f_{P} + (1-f)I_{P}^{\text{corr}}} \), therefore

\[
f = \frac{I_{C}^{\text{sig}}}{I_{P}^{\text{sig}}} \left[ \gamma_{CP} \left( 1 - e^{\frac{-1}{\chi_{C} \cos^{2}}(1-e^{\frac{-1}{\chi_{C} \cos^{2}}})} \right) - \frac{I_{C}^{\text{sig}}}{I_{P}^{\text{sig}}} \left( e^{\frac{-1}{\chi_{P} \cos^{2}}} - 1 \right) \right]^{-1} \quad \text{(A.1)}
\]

where \( \gamma_{CP} = \frac{\sigma_{C} N_{C} \lambda_{CM} K_{EP}}{\sigma_{P N_{P} \lambda_{P}} K_{EC}} \).

For sulphur and phosphorus, assuming an oxidation layer, we have \( \frac{I_{S}^{\text{sig}}}{I_{P}^{\text{sig}}} = \frac{f_{M}}{f_{P} + (1-f)I_{P}^{\text{corr}}} \), therefore

\[
f = \frac{I_{S}^{\text{sig}}}{I_{P}^{\text{sig}}} e^{\frac{-\tan \phi}{\cos \phi}} \left[ \gamma_{SP} e^{\frac{-1}{\chi_{S} \cos^{2}}} - \frac{I_{S}^{\text{sig}}}{I_{P}^{\text{sig}}} \left( e^{\frac{-1}{\chi_{P} \cos^{2}}} - 1 \right) \right]^{-1} \quad \text{(A.2)}
\]

where \( \gamma_{SP} = \frac{\sigma_{S} \lambda_{SM} K_{EP}}{\sigma_{P N_{P} \lambda_{P}} K_{ES}} \).

For carbon and phosphorus, assuming an oxidation layer, we have \( \frac{I_{C}^{\text{sig}}}{I_{P}^{\text{sig}}} = \frac{f_{M}}{f_{P} + (1-f)I_{P}^{\text{corr}}} \), therefore

\[
f = \left( \frac{\gamma_{CP} N_{C} \left( 1 - e^{\frac{-1}{\chi_{C} \cos^{2}}} \right) - \frac{I_{C}^{\text{sig}}}{I_{P}^{\text{sig}}} e^{\frac{-1}{\chi_{C} \cos^{2}}} + 1}{-\gamma_{CP} N_{C} e^{\frac{-1}{\chi_{P} \cos^{2}}} + \frac{I_{C}^{\text{sig}}}{I_{P}^{\text{sig}}} e^{\frac{-1}{\chi_{P} \cos^{2}}} + 1} \right)^{-1} \quad \text{(A.3)}
\]

where \( \gamma_{CP} = \frac{\sigma_{C} \lambda_{CM} K_{EP}}{\sigma_{P N_{P} \lambda_{P}} K_{EC}} \).

Fractions calculated using an indium peak are the same as those with phosphorus, with only a change in the labels.
A.2 Bramblett-type Sulphur Equation

As noted in Section (4.1.2) equation (4.20) from Bramblett et. al [6] is only useful for an element uniformly distributed throughout the monolayer. Sulphur is only located at the end of the thiol bonded to the InP.

Taking this into account to solve for the thickness, we use

\[
\frac{I_{S}^{M}}{I_{P}^{M}} = \frac{\sigma_{S}n_{S}K_{P}\cos \theta}{\sigma_{P}N_{P}\lambda_{P}K_{E_S}}
\]

Solving for \( t \), we get

\[
t = \left( \frac{\lambda_{PM}}{\lambda_{SM} - \lambda_{PM}} \right) \ln \left( \frac{I_{S}^{M}\sigma_{P}N_{P}\lambda_{P}K_{E_S}}{I_{P}^{M}\sigma_{S}n_{S}K_{P}} \right)
\]

We can then insert this thickness into equation (4.9) to find our fractional thiol coverage.

A.3 Value of \( N_{C}^{\text{ox}} \)

Since we have no idea for the value of \( N_{C}^{\text{ox}} \), we must calculate it from XPS data from an untreated sample. To find this, we can take the intensity ratio of the untreated carbon peak with that of any other element, such as phosphorus, and solve for \( N_{C}^{\text{ox}} \).

\[
N_{C}^{\text{ox}} = \frac{\sigma_{P}N_{P}\lambda_{P}K_{E_C}}{\sigma_{C}\lambda_{C}K_{E_C}I_{C}^{\text{ox}}} \exp \left( \frac{-I_{C}^{\text{ox}}}{\lambda_{C}K_{E_C}} \right) \frac{\exp \left( \frac{-I_{P}^{\text{ox}}}{\lambda_{P}K_{E_P}} \right)}{1 - \exp \left( \frac{-I_{P}^{\text{ox}}}{\lambda_{P}K_{E_P}} \right)}
\]

the results of this calculation averages to \( 8.6 \times 10^{28} \) atoms/m³.