

**Coherent Acoustic Phonons
in Hybrid Heterostructures Based on
van der Waals Crystals**

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Abstract

This thesis focusses on the elastic properties of the two dimensional (2D) van der Waals (vdW) crystal indium selenide (InSe) and heterostructures that combine InSe with hexagonal boron nitride (hBN) and graphene. Nanolayers and heterostructures are formed by mechanical exfoliation and dry transfer techniques, which have been developed and documented herein. Picosecond acoustics are used to probe the dynamic elastic properties of vdW nanolayers and heterostructures through the generation and detection of coherent acoustic phonons.

Coherent acoustic phonons are generated in nanolayers of InSe through the absorption of pump laser pulses leading to the generation of nanomechanical resonances whose amplitude and frequency depend upon the materials elastic properties, layer thickness and elastic coupling of InSe to its substrate and other layers of the heterostructure. Detection of these nanomechanical resonances is possible through the modulation of secondary probe pulses. A ‘spring’ model enables one to quantify the strength of interlayer coupling through the comparison of experimental and theoretical Fourier spectra of the coherent acoustic phonon spectra generated in the layers.

The data and analysis show that the vdW heterostructure interface (for InSe/hBN heterostructures and InSe/InSe homojunctions) is elastically ideal and may be described by acoustic mismatch for frequencies of up to 100 GHz. In contrast, vdW nanolayers tend to be weakly coupled to the supporting substrate (SiO_2/Si or sapphire) with a varying degree of strength described by the spring model. Picosecond acoustic imaging techniques were also used to spatially map the elastic coupling, revealing extended regions ($\sim 10 \mu\text{m}^2$) of elastically ideal and broken interfaces. This information gained on vdW interfaces could prove valuable for future development of high-quality vdW heterostructures and functional devices beyond the scope of the materials used in this study.

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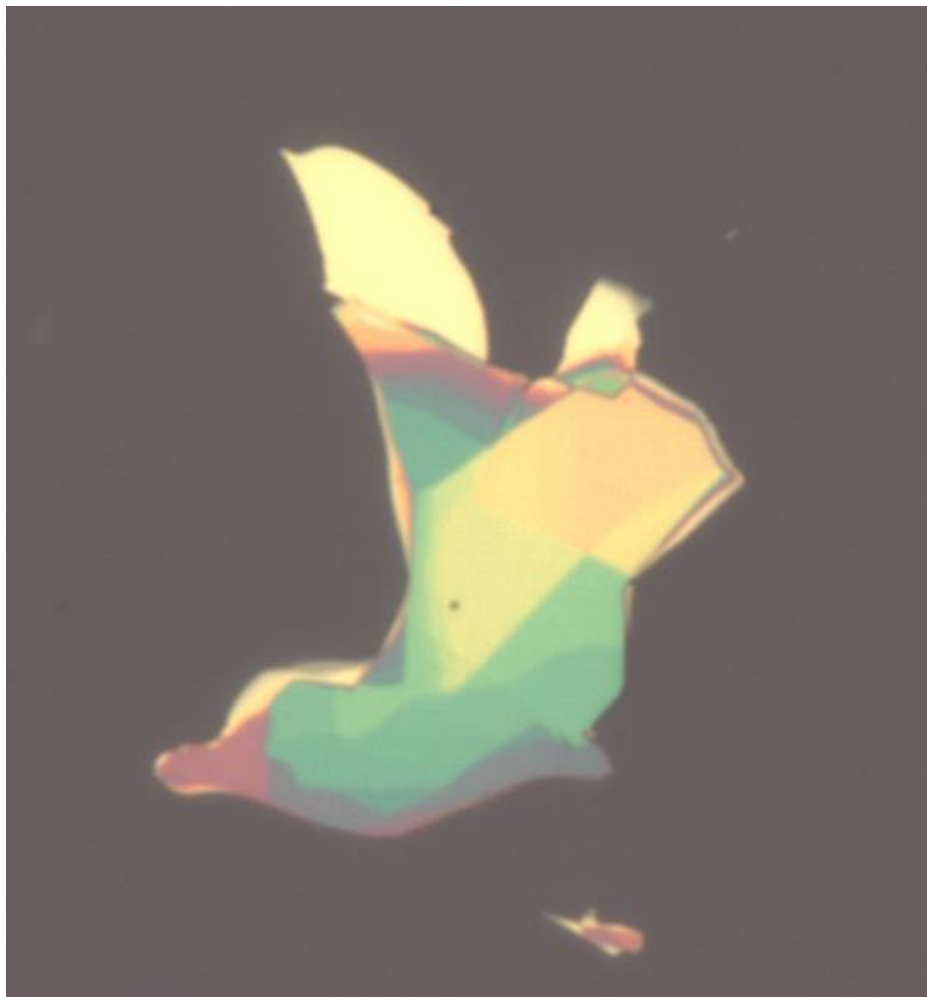
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Physical constants

Quantity	Symbol	Value	Unit
Boltzmann constant	k_B	1.38065×10^{-23}	JK^{-1}
Electron charge	e	1.60218×10^{-19}	C
Electron mass in vacuum	m_e	9.10938×10^{-31}	kg
Permittivity in vacuum	ϵ_0	8.85419×10^{-12}	Fm^{-1}
Planck constant	h	6.62607×10^{-34}	Js
Reduced Planck constant	$\hbar$	1.05457×10^{-34}	Js
Speed of light in vacuum	c	2.99792×10^8	ms^{-1}

Cloud watching

The random shape and orientation of exfoliated flakes makes finding flakes a lot like watching the clouds. For example, here is a bird.



List of Contents

1	Introduction.....	1
1.1	Thesis overview	3
2	Van der Waals crystals.....	5
2.1	Van der Waals crystals and heterostructures.....	5
2.1.1	InSe.....	8
2.1.2	hBN	14
2.1.3	Graphene	15
2.2	The rise of InSe	17
2.3	Summary	18
3	Generation of coherent acoustic phonons in van der Waals heterostructures	19
3.1	Introduction	19
3.2	Acoustic and optical phonons.....	20
3.3	Generation and detection of coherent acoustic phonons	23
3.3.1	Electron-phonon interaction and thermo-elastic effect	23
3.3.2	Photoelastic effect	26
3.4	Eigenfrequencies of phonon resonances in single layers	27
3.5	Evaluation of acoustic phonon resonances in layers and heterostructures on substrates.....	29
3.5.1	Acoustic mismatch	31
3.5.2	The spring model.....	33
4	Experimental techniques.....	36
4.1	Micro-photoluminescence and micro-Raman spectroscopy	36
4.2	Picosecond acoustics	39
4.2.1	Delay line system	41
4.2.2	Asynchronous Optical Sampling (ASOPS) system.....	42

4.2.3	Picosecond acoustic imaging.....	43
4.3	Atomic force microscopy	44
4.4	Electrical measurements	45
4.5	Device fabrication and metal deposition	47
4.5.1	Graphene patterning	47
4.5.2	Metal contacts.....	47
4.5.3	Al transducers	48
5	Mechanical exfoliation and dry transfer of van der Waals crystals .	49
5.1	Exfoliation of atomically thin uniform flakes	49
5.2	Dry transfer of thin flakes on a substrate	51
5.3	Summary	55
6	Nanomechanical probing of the layer/substrate interface of an exfoliated InSe sheet on sapphire	56
6.1	Introduction	56
6.2	InSe crystals on sapphire	58
6.3	Coherent acoustic spectra of InSe layers.....	60
6.4	The InSe/Sapphire interface: discussion of free and non-free standing layers	62
6.5	Summary	64
7	Coherent acoustic phonons in van der Waals nanolayers and heterostructures	66
7.1	Introduction	66
7.2	InSe based heterostructures and InSe nanolayers on sapphire	67
7.3	Photoluminescence and Raman spectra on InSe nanolayers and heterostructures	73
7.4	Coherent acoustic spectra of InSe nanolayers	73
7.5	Coherent acoustic spectra of InSe/hBN and hBN/InSe heterostructures	77

7.6	Coherent acoustic spectra of a thin hBN/InSe heterostructure.....	79
7.7	Coherent acoustic spectra of an InSe/InSe homojunction.....	81
7.8	Elastic properties of InSe, hBN and their interfaces	82
7.8.1	Elastic properties of InSe and hBN	82
7.8.2	Elastic properties of interfaces	84
7.8.3	Scattering and decay of coherent phonons	87
7.9	Summary	89
8	Picosecond acoustic imaging	91
8.1	Introduction	91
8.2	InSe based heterostructures and homojunctions.....	93
8.3	Picosecond acoustic imaging of single InSe layer and InSe/InSe homojunctions on sapphire.....	94
8.4	Picosecond acoustic imaging of hBN/InSe/graphene heterostructures	98
8.5	Elastic coupling at the interface of vdW layers: discussion of results.....	100
8.6	Photocurrent and photovoltage imaging of hBN/InSe/graphene heterostructures	101
8.7	Summary	105
9	Conclusions and outlook	107
9.1	Elastic coupling at the nanolayer/substrate interface	107
9.2	Elastic coupling in vdW heterostructures.....	108
9.3	Picosecond acoustic imaging.....	109
9.4	Outlook.....	110
10	Bibliography	112

Chapter 1

1 Introduction

The search for the successor, or rather successors to silicon, has been firmly focused on the two dimensional (2D) van der Waals (vdW) family of materials ever since the isolation of graphene^[1]. The vdW family comprises anisotropic crystals, with strong in plane covalent bonds and relatively weak, vdW like forces holding the layers together in a stack^[2]. Pristine graphene exhibits a range of attractive properties for technological advancements such as high carrier mobility^[3], yet is limited in its suitability due to its inherently gapless nature. Now with an abundance of exotic vdW nanolayers in the two dimensional library^[2,4,5], possessing unique optical and electronic properties with varying degrees of tuneability in their physical characteristics, novel combinations of vdW materials are increasingly likely to become the successor to overcome the limits of Si-based technologies. However, vdW materials not only provide solutions to the scaling issues of Si and the current stagnation of Moore's law, but are also furthering research in many exciting fields such as quantum optics^[6], spintronics^[7], straintronics^[8] *etc.* Prominent members of the vdW family include the wide gap insulator hexagonal boron nitride^[9] (hBN), the narrow band gap semiconductor black phosphorous^[10,11] (bP) and the large family of metal chalcogenides^[12-14]. Together these materials show promise for optoelectronic applications ranging from the infrared to the ultraviolet spectral range. Many members of the 2D library are produced with thicknesses down to the monolayer through mechanical exfoliation techniques^[15] and chemical growth techniques^[16].

An important, yet perhaps neglected, factor in the development of novel 2D devices is phonon transport through the interfaces of vdW heterostructures. Much focus has already been applied to the nature of electron transport and charge transfer at interfaces, yet it is the phonon transport at an interface that dictates the cooling rate and thus the thermal properties^[17,18]. It is the balance of electron and phonon transport between nanolayers that determines the efficiency, ZT ^[19,20], of thermoelectric devices^[19].

Many characterization techniques have the ability to probe vdW interfaces, for example, Raman spectroscopy^[21] and transmission electron microscopy^[22] (TEM), are

extensively used to evaluate the interfacial qualities of vdW materials and heterostructures^[23], and indeed are useful in assessing the quality of nanolayers and heterostructures. However, the information provided by these techniques is of a static nature, as opposed to the dynamic interfacial behaviour under the crystal perturbations caused by the generation of phonons. The fundamental aspect that controls phonon transport through an interface is the strength of elastic bonds between atoms of adjacent layers^[24], which may be evaluated through the generation and detection of coherent acoustic phonons^[25,26]. This leads to subsequent nanomechanical resonances in a sandwiched vdW heterostructure, the frequency of which depends upon the elastic properties, layer thicknesses and the strength of interfacial bonds. This information can be extracted by picosecond acoustic techniques^[25]. The picosecond acoustic technique involves the generation and detection of coherent acoustic phonons by the application of two synchronized pulsed laser sources, the pump and probe. The pump is absorbed, creating hot carriers which relax, leading to heat generation, thermal expansion and subsequent phonon generation and nanomechanical resonances^[26]. A secondary laser pulse, the probe, is periodically modulated by these resonances, and the resonant frequency is extracted from the periodic modulations. The spring model^[27,28] predicts the resonant frequencies of a heterostructure undergoing nanomechanical resonances for given thicknesses, elastic properties and interfacial coupling strength. By comparison of experimental and theoretical results, it is possible to estimate the coupling strength and identify regions of strong and weak interlayer coupling.

Motivation for the following works of this thesis is spurred in part by the prosperous research into the transition metal monochalcogenide InSe, which has generated much interest in the community due to its high degree of band gap tuneability^[29-31], sensitivity to strain^[32], high broadband photoresponsivity from the near infrared to the visible range^[33], and complementary nature as an optically active capping layer to graphene^[33-35]. These phenomena combined give great potential to InSe as a vital component of future novel devices. The success of such applications of InSe nanolayers will depend strongly upon the interfacial qualities of heterostructures, and so motivation is also provided by the suitability of picosecond acoustics as a technique able to probe the dynamic nature of interlayer coupling in multilayer heterostructures by the generation and detection of coherent acoustic phonons.

The main objective of the PhD project was to fabricate and characterize various heterostructures from InSe, hBN and graphene nanolayers with InSe as the focal component. Samples were fabricated by exfoliation of thin layers from bulk and dry transfer to form desirable heterostructures. Successful characterization of heterostructures required the refining of picosecond acoustic techniques^[25,26,36] applied to vdW heterostructures combined with the use of a spring model.

Through the need to achieve high quality heterostructures, consisting of uniform nanolayers with a lateral area adequate for mapping measurements and device applications, it became a necessity that the exfoliation and dry transfer techniques employed would require development, which became an ongoing secondary objective of the PhD project.

1.1 Thesis overview

The thesis is presented in the following order:

Chapter 2 presents a background on the diverse family of 2D vdW crystals with a review of current research, technological applications and challenges in the field. Focus is on InSe, hBN and graphene with special attention applied to the attractive properties and prospects of InSe.

Chapter 3 focuses on the various physical phenomena involved in the generation and detection of coherent acoustic phonons in picosecond acoustic measurements. A derivation of the spring model, which was developed to analyse picosecond acoustic spectra, is provided.

Chapter 4 describes the various techniques and experimental setups involved in both the sample fabrication and experimental characterization.

Chapter 5 focuses on the development of exfoliation and dry transfer techniques used to fabricate vdW nanolayers or heterostructures from atomically thin, uniform flakes of large lateral area on desired substrates.

Chapter 6 investigates the elastic behaviour of exfoliated InSe nanolayers of varying thickness on sapphire substrates by picosecond acoustic techniques. The strength of interlayer coupling at the vdW nanolayer/substrate interface is assessed.

Chapter 7 investigates the elastic behaviour of InSe/hBN heterostructures and InSe/InSe homojunctions fabricated by dry transfer of exfoliated flakes, by picosecond acoustic techniques. The strongly coupled, elastically ideal behaviour of the

nanolayer/nanolayer interface and the relatively weak coupling of the nanolayer/substrate interface are discussed.

Chapter 8 investigates the elastic behaviour of InSe/hBN heterostructures and InSe/InSe homojunctions on sapphire and graphene/SiO₂ substrates fabricated by dry transfer of exfoliated flakes, with the use of picosecond acoustic imaging techniques. The presence of extended regions ($\sim 10 \mu\text{m}^2$) of both elastically ideal and broken interfaces is discussed. The implications of these findings on transport devices are also examined.

Chapter 9 concludes the thesis, providing an overview of the key findings and future research prospects.

Chapter 2

2 Van der Waals crystals

The following chapter is a general introduction to van der Waals (vdW) crystals and heterostructures. In particular, it focuses on specific materials, *e.g.* InSe, hBN and graphene, whose physical properties feature heavily in this thesis. Of particular interest is the recent development of InSe, an emerging semiconductor that is currently widely investigated.^[29,34,35]

2.1 Van der Waals crystals and heterostructures

The successful isolation of monolayer graphene^[1] in 2004 has since led to huge interest in a diverse range of anisotropic vdW crystals^[2] with strong in-plane bonds and relatively weak vdW coupling between adjacent layers. This weak interlayer coupling allows for mechanical isolation of thin layers through mechanical or liquid phase exfoliation. The resulting two dimensional (2D) crystals exhibit exciting electronic, optoelectronic, mechanical and magnetic properties different from those of the bulk due to new exotic states accessible through reduced dimensionality^[37]. The broad family of 2D vdW crystals features many materials stable in ambient conditions, including wide bandgap insulators (*e.g.* hBN^[38]) and various metal oxides^[39]; semiconductor materials, such as the III-VI compounds (*e.g.* GaS, GaSe^[13]) and transition metal dichalcogenides (TMDCs) (*e.g.* MoS₂, MoSe₂^[13]). Recent computational studies^[4] of the interatomic coupling strength of numerous experimentally known 3D layered compounds estimates a database of over 1000 potentially exfoliable materials as candidates for new 2D nanolayers. This can be seen in Figure 2-1. Here the layer binding energies of vdW crystals has been calculated computationally as a function of the relative equilibrium interlayer-distance discrepancy between one vdW and one non vdW density functional theory (DFT) model (relaxed by DF2-C09 versus revPBE functionals, see Ref. [4] for details). This allows for further identification of potential layered compounds which are characterized by dispersive interactions between layers, i.e. vdW forces^[4]. Figure 2-1 shows the largely untapped pool of potential vdW materials outside of those highlighted that may also be exfoliated into 2D layers. Perhaps the most exciting

property of the vdW family is the ability to tune the electronic band structure (and thus the physical properties) due their sensitivity to layer thickness, and external stress and strain^[40].

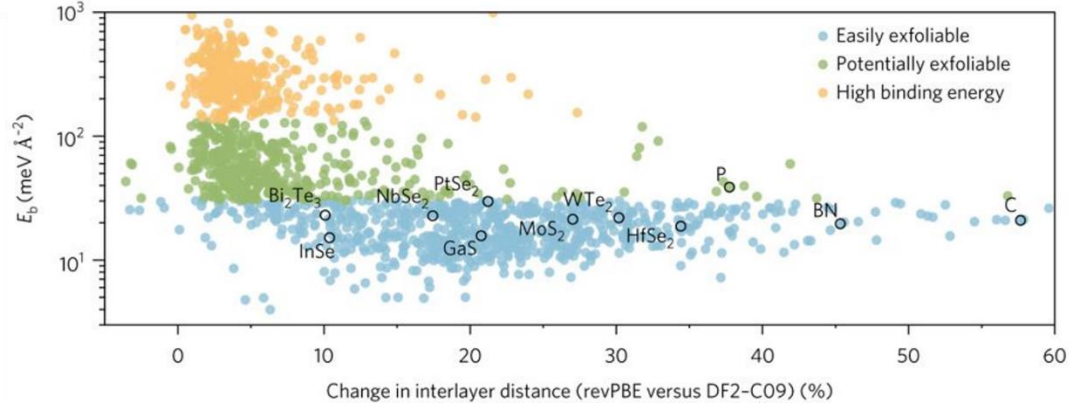


Figure 2-1. Estimated binding energies in vdW layers as a function of the interlayer-distance discrepancy between one vdW (revPBE) and one non vdW (DF2-CO9) density functional theory (DFT) model for numerous experimentally known layered compounds including many well established materials e.g. InSe, MoS₂, GaS etc. Figure taken from Ref. [4].

The successful manufacture and study of 2D materials can provide the foundation for developing new technologies and progress towards the miniaturisation of optical and electrical devices. Technologies of particular interest include broadband (IR-NIR-VIS) sources^[41], low-power consumption, high-frequency transistors^[42], multi-junction solar cells for energy^[43,44], and single photon emitters^[45] offering opportunities and solutions across several industries.

2D vdW semiconductor crystals have attracted considerable attention for digital electronics beyond Si-CMOS (Complementary metal–oxide–semiconductor) technologies^[46] due to their inherent qualities at reduced dimensionality. Despite the transformative success of Si-based devices, there are limits to their miniaturization, which ultimately compromise device performance and the progression of Moore's Law^[2]. Graphene, hBN and the family of TMDCs have all been highlighted as potential candidates for integrating 2D materials with monolithic 3D integrated circuits (M3D-IC), through vertical stacking^[47]. Materials beyond graphene have been identified for scaling to possible gate lengths < 10 nm and < 6.6 nm (MoS₂ and WSe₂ respectively^[48]), offering a greater integration density than is currently possible with

conventional materials. The family of 2D van der Waals crystals now offers a number of opportunities: these materials can retain excellent properties down to single layers of atoms^[49]; they have interfaces free of dangling bonds^[50]; furthermore, since they are bendable and stretchable^[8], and can withstand higher strain than traditional semiconductors, they are a promising candidate for flexible electronics^[32].

As well as possessing interesting intrinsic properties, vdW materials can also be combined together to form a wide range of new heterostructures, as illustrated in Figure 2-2, which depicts how vdW heterostructures can be constructed vertically through mechanical stacking in a manner similar to the building blocks of Lego. The techniques required to fabricate structures in this manner are discussed in depth in Chapter 5.

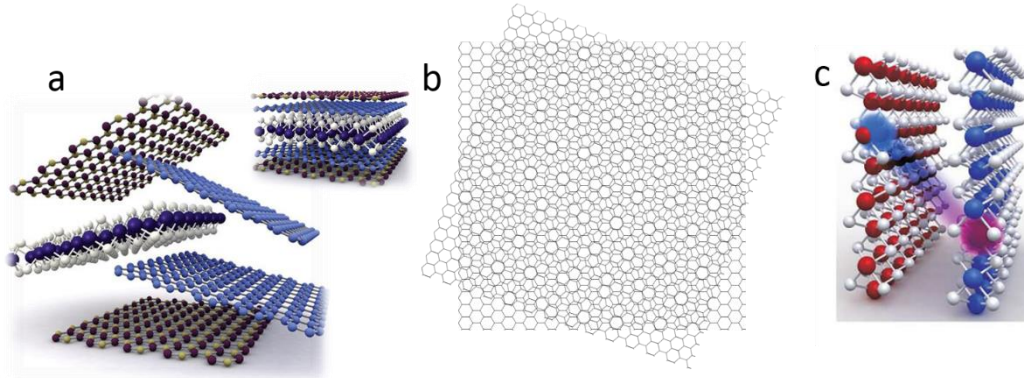


Figure 2-2. Schematics of unspecified vdW materials depicting (a) the mechanical stacking of various vdW layers to form heterostructures; (b) novel alignment of vdW layers through the introduction of a twist angle and (c) interlayer excitons (electron (blue) and hole (purple)) between the vdW layers of 2 different materials. The strong in-plane bonds of the layers are visible by solid lines while the weak interlayer vdW forces are not shown. (a) taken from Ref. [51].

Interlayer excitonic states are achievable in certain combinations of 2D materials (*e.g.* $\text{MoSe}_2\text{--WSe}_2$ ^[52,53]) where the electron and hole of a bound electron-hole pair are localized in different layers. Recent evidence^[54] suggests that these states may be further modulated by altering the rotational misalignment (twist angle) between the two layers, thus tuning the moiré potential. The corresponding strain in the structure depends on the angle and modulates the band structure. Other exotic heterostructures exploiting a twist angle in the growing field of ‘twistronics’^[55] include superconductive bilayer graphene^[56] engineered through the exploitation of a so called ‘magic angle’ ($\sim 1.1^\circ$) between the individual layers. Similarly, graphene-

hBN-graphene heterostructures have shown interesting properties, such as tuneable resonant tunnelling^[57], dependent on the twist angle of the graphene layers. Layers of MoS₂ have also been successfully strain engineered through the intentional formation of bubbles, typically a hindrance to pristine, high quality heterostructures, on the underlying substrate^[58]. The application of strain in this manner induce the diffusion of electrons and holes towards the positions of maximum strain^[58], enhancing the photoluminescence emission and creating single photon emitters.

One current challenge in the field of 2D materials is the growth and synthesis of high quality layers through a range of vdW epitaxy techniques. One of the most popular techniques to isolate 2D layers is the mechanical exfoliation of thin flakes from bulk (see Chapter 5). However, this offers little control over the thickness, shape and lateral area of the layers. Chemical vapour deposition (CVD) has seen much success growing thin films from the vdW family and is preferable to exfoliation as it allows for wafer scale growth with control over thickness and lateral area^[14]. CVD growth involves the evaporation of one or more volatile precursors onto a heated substrate in a desired configuration^[59] with the capability to produce monolayer films. The quality of CVD films is material dependent with CVD materials often being of different quality to their exfoliated counterparts^[60]. Examples of high quality vdW materials readily synthesized by CVD include graphene^[61], hBN^[9] and various TMDCs *e.g.* MoS₂^[16], MoSe₂^[62], WS₂^[63] *etc.* CVD methods for many 2D materials require further optimization before large scale synthesis is possible as their quality is often compromised compared to exfoliated films. Growth of the various polytypes and stoichiometries of InSe is being developed^[64,65], but is currently not as well developed as some of its other 2D counterparts. The exact stoichiometries and polytypes grown are difficult to predict and control^[66], with different polytypes coexisting in the same structure^[67].

2.1.1 InSe

InSe is an exciting vdW material at the forefront of research into the physics and applications of vdW materials and heterostructures^[29,34,68]. InSe is a metal chalcogenide III-VI compound and like many of the other metal chalcogenides, features a variety of polytypes,^[69] *e.g.* β , γ *etc.*, which depend upon the sequence of

layers. The studies herein focus on γ -InSe, the structure of which is discussed in this section.

Figure 2-3 shows the crystal structure of γ -InSe. The primitive unit cell consists of three tetralayers each with a thickness of $t = 0.83$ nm. Each layer consists of Se and In atoms in covalently bonded monoatomic sheets with the sequence Se-In-In-Se. The primitive unit cell has a lattice constant $c = 2.496$ nm along the c -axis. In the a - b plane, the atoms form hexagons with lattice parameter $a = 0.400$ nm^[31]. Bulk InSe has a bandgap, $E_g = 1.26$ eV (at 300 K)^[31], which can be increased up to ~ 2 eV as the crystalline sheet is reduced to a monolayer^[29]. The range of tuning with decreasing thickness is notably higher than in many other metal chalcogenides and is due to the relatively light electron mass of InSe, as is shown in Table 2-1.

The band structure of InSe is sensitive to the number of layers (N) that constitute the crystalline sheet. The band structure of InSe has been modelled by density functional theory (DFT) calculations^[30] and is shown for different thicknesses in Figure 2-4. DFT calculations allow for a simulation of the electronic band structure in a periodic crystal through analysis of the electronic energies as a functional of the

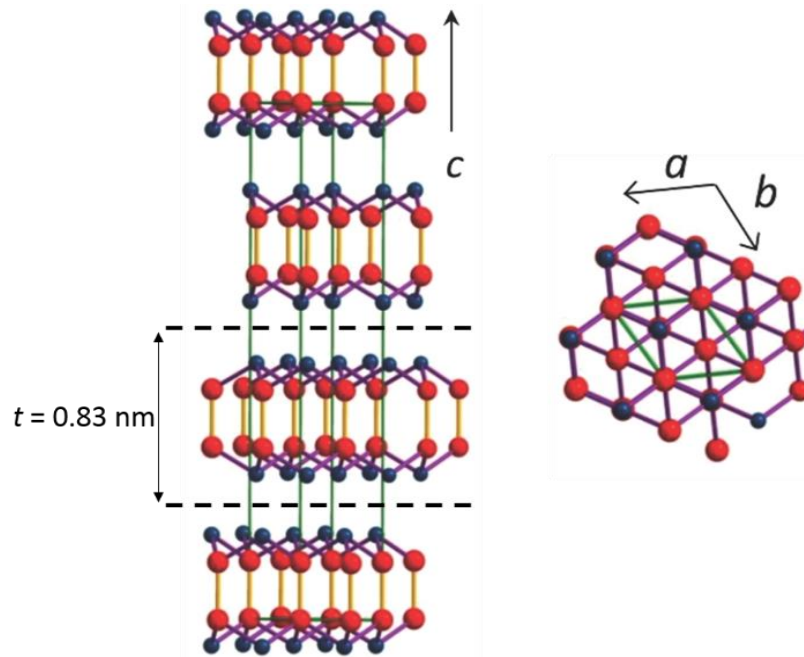


Figure 2-3. Crystal structure of γ -InSe along the c -axis (left) and in the ab -plane (right). Red and blue atoms correspond to indium and selenium atoms, respectively. Figure taken from Ref. [30].

electron density^[70]. Bulk InSe is a direct bandgap semiconductor, but it can be seen that the gap becomes indirect as the crystal becomes sufficiently thin ($\lesssim 10$ layers). The increase in the bandgap energy with decreasing N can be explained as follows. For an N -layer crystal lattice of InSe, the electronic bands of monolayer InSe are split into N sub-bands, and this reduces the energy difference between the conduction and valence states in the vicinity of the Γ point at which the bandgap is smallest^[29].

It can be seen that when the thickness L is reduced, the conduction band minimum (CBM) remains at the Γ -point and shifts to high energy; in contrast, the valence band maximum moves away from Γ towards the K-points, and the VB takes the form of an inverted “Mexican hat”. With decreasing L , the energy interval ΔE between the valence band edge at Γ and the valence band maximum (VBM) increases from 0 to ~ 70 meV; correspondingly, the VBM shifts from Γ to about 30% of the Γ -K wave-vector. Thus a direct-to-indirect band gap crossover occurs gradually with decreasing L due to a qualitative change of the VB at $L < 20$ layers.

The almost flat (though slightly inverted) saddle point in the valence band in both mono- and few-layers InSe can lead to van Hove singularities^[71], divergent points in the density of states^[72] (DOS). The inverse relation of the DOS to the gradient of the energy dispersion, $E(k)$, leads to spikes in the DOS about flat regions of the energy dispersion. These spikes in the DOS can lead to many-body effects and strongly correlated electron systems in InSe layers with p-type doping^[73]. These phenomena are still largely unexplored.

Table 2-1 shows the calculated values of the in-plane electron (m_e^Γ), hole (m_h^Γ and m_h^{VBM}) and exciton masses ($\mu_\perp^\Gamma$ and $\mu_\perp^{VBM}$) for $L = 1, 2, 5$ and 10 InSe layers. The values for bulk InSe are from the literature^[74-76]. It can be seen that the electrons are significantly lighter than holes and that the electron mass depends on the layer thickness only when L approaches 1-2 layers. The disparity in electron and hole masses is due to the large curvature about the conduction band minima and the small curvature about the valence band maxima.

L no. of layers	1	2	5	10	Bulk mass in the a - b plane
m_e^Γ/m_e	0.18	0.15	0.13	0.12	0.138 ^[74]
m_h^Γ/m_e	-0.70	-0.61	-0.68	-1.03	-0.730 ^[75]
m_h^{VBM}/m_e	2.1	1.05	0.80	1.02	
$\mu_\perp^{\text{VBM}}/m_e$	0.14	0.12	0.11	0.11	0.14 ^[76]
$\mu_\perp^\Gamma/m_e$	0.17	0.13	0.11	0.11	

Table 2-1. Relative electron, hole and reduced excitonic masses about the Γ -point and the valence band maxima (VBM), which shifts from the Γ -point with reducing thickness (approaching 1-2 layers). Masses are shown for a 1-10 layers (calculated) and for bulk (from literature).

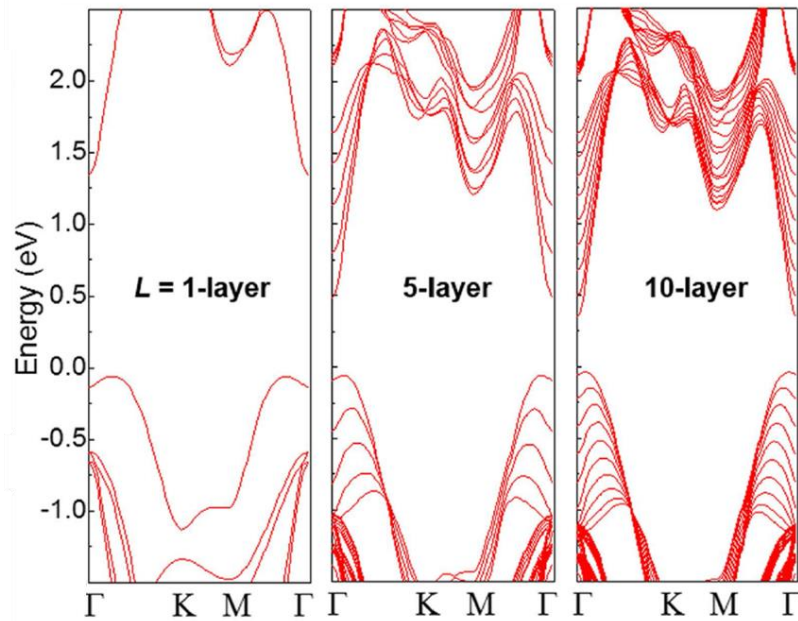


Figure 2-4. DFT of the band structure of thin InSe approaching the monolayer. Note that the energy is underestimated here as a scissor correction to the DFT has not been applied [77]. Γ , K and M are the points of symmetry along the Brillouin zone. Figure taken from Ref. [30].

A simpler empirical way of describing the effects of quantum confinement in an atomically thin semiconductor crystal is by the reduced mass quantum well model. Within this model, carriers confined in a quantum well of thickness L , can only exist in discrete quantized energy levels given by:

$$E_n = n^2 \frac{\hbar^2 \pi^2}{2mL^2}, \quad (1)$$

where n is a positive integer, $\hbar$ is the reduced Planck constant and m is the particle mass. For semiconductor systems such as InSe, under photon excitation, an electron can be excited up to the conduction band leaving behind a ‘hole’ in the valence band. The hole is treated as a charge carrier of opposite charge to the electron. Within a semiconductor the two carriers are treated to possess an ‘effective’ mass relative to that of the rest electron mass, due to interactions between carriers and the periodic crystal lattice potential^[78]. The conduction band (CB) and valence band (VB) edges are assumed to be parabolic and the effective mass, m^* , of the electron and hole is derived from the second derivative of the $E(k)$ dispersion relation in the CB and the VB along the c -axis, respectively:

$$m_{e,h}^* = \frac{\hbar^2}{(d^2E(k)/dk^2)}. \quad (2)$$

Where the subscripts e and h correspond to electron and hole, respectively. The quantized energy levels of electrons and holes are:

$$E_{e,n_1} = n_1^2 \frac{\hbar^2 \pi^2}{2m_e^* L^2}, \quad (3)$$

and

$$E_{h,n_2} = n_2^2 \frac{\hbar^2 \pi^2}{2m_h^* L^2}.$$

For InSe, m_e^* and m_h^* along the c -axis are equal to $0.08m_e$ ^[74] and $0.17m_e$ ^[79], respectively. Under the excitation of an electron from the VB to the CB, an exciton is formed. This is a bound pseudo-particle made up of the electron and hole. By first

ignoring Coulomb forces (exciton binding energies are relatively weak compared with the band gap. $E_b = 0.015$ eV in bulk InSe at 300 K^[31]), we can estimate the energy difference between the lowest electron and hole states, $n_1 = n_2 = 1$:

$$E = E_g + \frac{\hbar^2 \pi^2}{2L^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right], \quad (4)$$

where $E_g = E_{CB} - E_{VB}$ and is the band gap of the material. E_{CB} and E_{VB} are the energies of the conduction band minimum and valence band maximum, respectively. The exciton energy states within a semiconductor material are governed strongly by the thickness of the material. Absorption of photons in thin layers of InSe, for example, will require a greater energy than that of the bulk. In reality the exciton possesses a binding energy, E_b , due to the Coulomb interaction^[80]. For a 3D system^[81]:

$$E_b = \frac{R_{eh}}{n^2}, \quad R_{eh} = \frac{\mu_{//}}{2} \left(\frac{e^2}{4\pi\epsilon\hbar} \right)^2, \quad (5)$$

where R_{eh} is the exciton Rydberg energy, analogous to the Rydberg energy of the hydrogen atom, where $\epsilon = \epsilon_0\epsilon_r$ is the dielectric constant, $\epsilon_0 = 8.85 \times 10^{-12}$ Fm⁻¹ is the permittivity in vacuum and ϵ_r is the relative dielectric constant (for InSe, $\epsilon_r = 7$ ^[31]), and $\mu_{//}$ is the reduced exciton mass parallel to the c -axis,

$$\frac{1}{\mu_{//}} = \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right]. \quad (6)$$

For InSe, $\mu_{//} = 0.054m_e$ ^[82].

For 2D systems, the binding energy is modified such that,

$$E_b = \frac{R_{eh}}{\left(n - \frac{1}{2}\right)^2}. \quad (7)$$

Thus, in the 2D limit, it is expected that the binding energy of the exciton is 4 times larger than in 3D.

We can now define the energy required for the lowest energy exciton in a thin 2D semiconductor of thickness L :

$$E_{2D} = E_g - E_b + \frac{\hbar^2 \pi^2}{2\mu_{//}L^2}. \quad (8)$$

The generation of excitons in a photoluminescence experiment is discussed in Chapter 4.

2.1.2 hBN

hBN is an important material in numerous vdW heterostructures due to its inherent characteristics, which are complementary to both graphene and other 2D materials. hBN is regularly used to encapsulate vdW materials such as InSe^[29], graphene^[83] and MoS₂^[84] as a means of either improving the electronic properties of the encapsulated material, providing a tunnel barrier or protecting it from the environment. The relatively large bandgap of hBN leaves it optically transparent to the wavelengths required to probe many vdW materials and studies have shown that encapsulated crystals remain optically active for longer^[85], as they are preserved from oxidation.

Figure 2-5a shows the crystal structure of hBN. Atoms in hBN are arranged in a hexagonal lattice similar to that of InSe layers. B and N atoms form hexagons and individual layers align themselves such that B and N atoms in one layer lie directly below N and B atoms, respectively, in the layer above, *i.e* any two consecutive layers are analogues. The lattice parameters of hBN, a and c , are 2.50 Å and 6.65 Å, respectively^[86]. hBN is a wide bandgap insulator (see Figure 2-5b), with an indirect bandgap and crossover to a direct bandgap in the monolayer^[87]. There is some disagreement on the exact band structure of hBN. However, recent measurements suggest that the band gap energy of bulk hBN is $E_g \sim 6$ eV at 300 K^[87-89], which far exceeds that of bulk InSe (1.26 eV) and that of many other vdW materials.

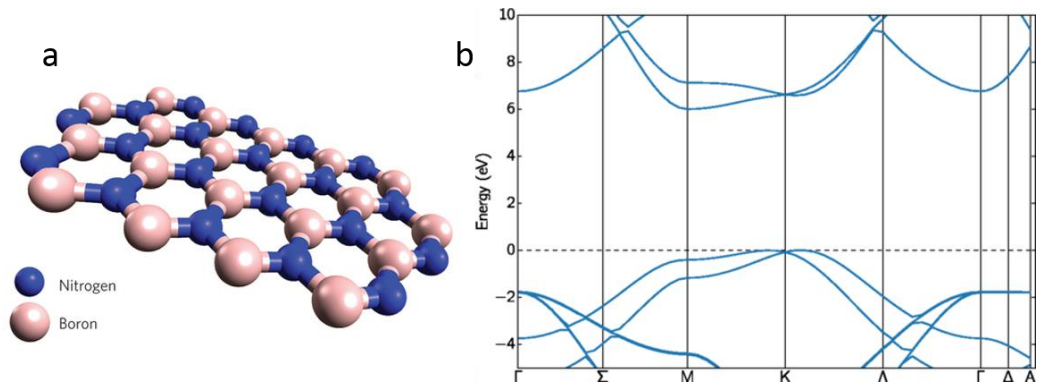


Figure 2-5. (a) Crystal structure of a monolayer of hBN. Figure taken from Ref. [90]. (b) Band structure of hBN. Figure taken from Ref. [91]. Γ , Σ , M, K and Λ are the points of symmetry along the Brillouin zone.

2.1.3 Graphene

Figure 2-6 shows the crystal structure and Brillouin zone of graphene. Graphene consists of a single sheet of carbon atoms arranged in a honeycomb lattice of hexagons, similar to that of hBN. Graphene is unique amongst the family of 2D materials as it possesses no band gap. The lattice parameter of graphene, a , is 2.46 Å, which is very close to that of hBN. The graphene unit cell is comprised of 2 atoms (see Figure 2-6), A (blue) and B (yellow). The unit vectors in real space for graphene are^[92]:

$$\vec{a}_1 = \left(\frac{\sqrt{3}}{2}a, \frac{a}{2} \right), \quad \vec{a}_2 = \left(\frac{\sqrt{3}}{2}a, -\frac{a}{2} \right) \quad (9)$$

and the corresponding unit vectors of the reciprocal lattice are

$$\vec{b}_1 = \left(\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a} \right), \quad \vec{b}_2 = \left(\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a} \right). \quad (10)$$

At the corners of the Brillouin zones we define the points of symmetry K and K' , also known as the Dirac points, as^[93]:

$$\mathbf{K} = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a} \right), \quad \mathbf{K}' = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a} \right). \quad (11)$$

The tight binding Hamiltonian of graphene describes the band structure^[92]

$$\hat{H}_k = \begin{pmatrix} 0 & tS_k \\ tS_k^* & 0 \end{pmatrix}, \quad (12)$$

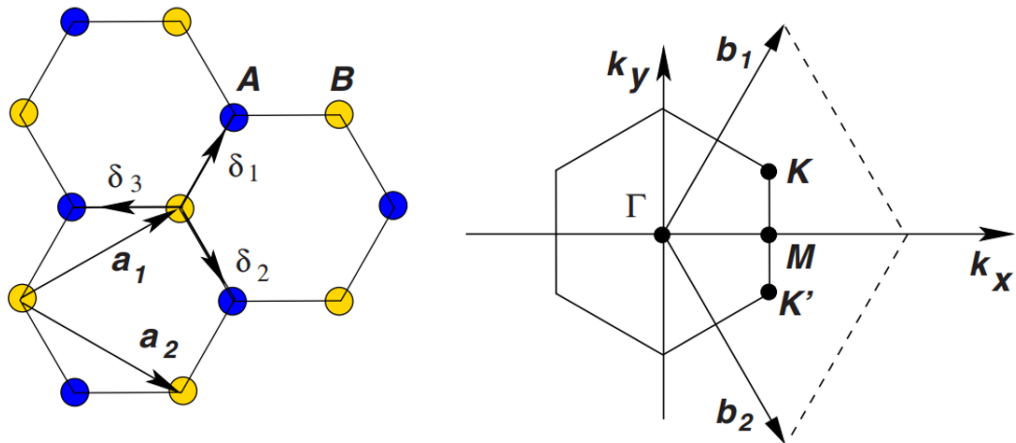


Figure 2-6. Crystal structure (left) of graphene with 2 unit cell atoms A (blue) and B (yellow). $\delta_1, \delta_2, \delta_3$ are the vectors of the nearest neighbour sites. The corresponding Brillouin zone (right). Γ and M are the points of symmetry along the Brillouin zone Figure taken from ref. [93].

where t is the nearest neighbour hopping energy ($t = 2.8 \text{ eV}$)^[93] required for electrons to hop between the two sublattices A and B , S_k is a function of the sum of nearest neighbour contributions, for a given wavevector k , given by

$$S_k = e^{i\vec{k}\cdot\vec{\delta}_1} + e^{i\vec{k}\cdot\vec{\delta}_2} + e^{i\vec{k}\cdot\vec{\delta}_3}, S_k = 2e^{-\frac{ik_x a}{2}} \cos(\sqrt{3}k_y a) + e^{ik_x a}, \quad (13)$$

where a is the nearest neighbour distance and $\delta_1, \delta_2, \delta_3$ are the vectors of the nearest neighbour sites shown in Figure 2-6. From the Hamiltonian, the energy dispersion may be described as:

$$E_k = \pm t \sqrt{3 + 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{\sqrt{3}}{2}k_x a\right)}. \quad (14)$$

From here we can see the unique band structure of graphene about the Dirac points K and K' (see Figure 2-7). About the Dirac points the energy dispersion can be approximated by the linear function:

$$E(q) = \pm v_F |q|, \quad (15)$$

where q is the electron momentum relative to the Dirac point and v_F is the Fermi velocity given by $v_F = 3ta/2 \approx 10^6 \text{ ms}^{-1}$. Many of the remarkable properties of graphene are a consequence of this unique band structure. The electrons in graphene behave as massless relativistic particles with a speed $c^* \approx 10^6 \text{ ms}^{-1}$ ^[94]. Other consequences of

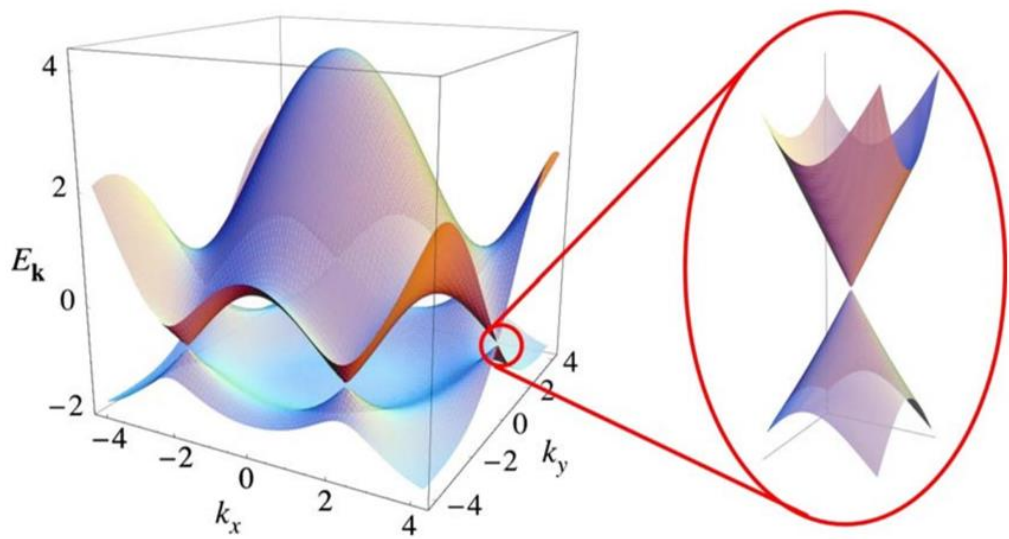


Figure 2-7. Electronic dispersion of graphene. Energy given in units of t . Inset: Energy dispersion about a Dirac point. Figure taken from ref. [93].

the unique electronic structure include high mobility ($\mu = 20 \text{ m}^2\text{V}^{-1}\text{s}^{-1}$)^[3], high thermal conductivity ($\sim 5000 \text{ Wm}^{-1}$)^[95] and high optical transmittance ($\sim 98\%$)^[96]. Also, graphene possesses a remarkably high Young's modulus ($\sim 1 \text{ TPa}$)^[97]. These qualities make graphene an ideal candidate for many studies and applications.

2.2 The rise of InSe

InSe has been earmarked as a suitable material for advancements in many emerging fields. InSe has been used to form field effect transistors^[29,98] (FETs) with high room temperature electron mobility^[29] ($\mu = 0.2 \text{ m}^2\text{V}^{-1}\text{s}^{-1}$). As well as being sensitive to layer thickness, the bandgap is also sensitive to strain^[32] adding a new dimension to the tuneable capability of InSe. Recent optical studies show that the bandgap of InSe can be reversibly reduced by $\sim 160 \text{ meV}$ through tensile strain and increased by $\sim 80 \text{ meV}$ through compressive strain^[32]. This sensitivity of the band structure to strain holds potential for electromechanical and piezoelectric applications. The combined electronic and structural qualities of InSe have potential for integration in bendable photodetectors^[99], image sensors^[100] and photon sources^[101].

InSe can be readily combined with other vdW materials (e.g. GaSe, hBN, graphene) to form heterostructures with interesting properties. For example, when InSe and graphene are combined, charge transport between the two allows for the modulation doping of graphene^[34,35], which can be further controlled by both electric and magnetic fields. InSe/graphene Hall bars have been shown to exhibit a 'giant' quantum Hall plateau^[35] by exploiting these phenomena. Here, the precise resistance quantum $h/2e^2 = 12.906 \text{ k}\Omega$ (corresponding to a Landau filling factor $\nu = 2$) has been achieved for an extended range of magnetic fields in InSe capped graphene Hall bars when compared with graphene Hall bars. This phenomenon is important for potential metrological applications, such as accurate measurements of the resistance quantum^[102]. Devices that showed such phenomena and their fabrication are discussed further in Chapter 5. Combining the high mobility of graphene with InSe as a optically active capping layer has been shown to demonstrate broadband photoresponsivity^[99] superior to that of many other 2D crystals (up to $\approx 10^5 \text{ AW}^{-1}$ at $\lambda = 633 \text{ nm}$)^[33] with a spectral response spanning the visible to the near infra-red range. Similar levels of photoresponsivity were reported on both rigid and flexible substrates^[99] showcasing InSe as a candidate for versatile future photodetectors. Other heterostructure

applications include p -InSe/ n -InSe and p -GaSe/ n -InSe junctions as emitters of room temperature electroluminescence^[101]. Similarly InSe/In₂O₃ may be purposely formed by photo- or thermal-annealing of InSe forming an oxide layer and subsequent heterostructure^[85]. Such oxidation reduces the InSe thickness which can be exploited to induce confinement effects. Such InSe/In₂O₃ p - n junctions were also seen to produce room temperature electroluminescence^[85]. Despite this surge of interest in InSe, there are several aspects that require further studies ranging from the controlled growth to the investigation of phenomena of fundamental and applied interest.

2.3 Summary

Here it is shown that the vast interest and focus afforded to vdW materials and heterostructures is justified. The unique structural and electronic properties of the diverse family 2D vdW materials, combined with their exciting potential to be electronically and optically tuned, make them an ideal candidate for a range of novel technological applications.

The inherently attractive physical phenomena of graphene has kept it at the forefront of research into 2D materials since its successful isolation. However, in order to achieve the ambitious technological goals of the scientific community, graphene must be combined with many other exciting 2D materials such as the TMDCs or hBN in a complimentary fashion. It has been shown that one such candidate, InSe, has great potential to fulfil many functions from both a technological and research standpoint.

Chapter 3

3 Generation of coherent acoustic phonons in van der Waals heterostructures

The following chapter describes phonons in a crystal lattice and the various phenomena considered in both the generation and detection of coherent acoustic phonons in picosecond acoustic measurements.

3.1 Introduction

In picosecond acoustic measurements, two femtosecond laser sources (pump and probe) are used for the generation (pump) and detection (probe) of coherent phonons. For given photon wavelengths, the pump beam is absorbed by the crystal, which causes rapid heating of the sample and produces stress due to the thermoelastic effect^[36]. Dynamical stress also appears during the generation of electron-hole pairs via deformation potential mechanisms. As a result of this stress, a strain pulse is generated^[25], the amplitude and temporal shape of which depend on the boundary conditions and elastic properties of the material. The generated strain pulse may be considered as a wavepacket of coherent acoustic phonons, generated with the same phase, travelling parallel to one another, perpendicular to the incident surface of the pump beam. It is detected by measuring the intensity of the transmitted or reflected optical probe pulse versus the time difference between pump and probe pulses. The arising intensity changes of the reflected or transmitted probe beams are due to the photoelastic effect (see Section 3.3.2). The excitation of vdW flakes with thickness d , comparable with the wavelength of the generated acoustic phonons, results in the resonant vibrations of the vdW nanolayers with the frequency dependent on the thickness d and the boundary conditions at the interfaces. A ‘spring’ model which describes in detail the frequency dependence of acoustic resonances in vdW nanolayers on the strength of elastic coupling at the van der Waals (vdW) interface of heterostructures is presented in Section 3.5.

The experimental techniques and apparatus that utilize the phenomena described here are discussed in Chapter 4 and the experimental results are discussed in Chapters 6, 7 and 8.

3.2 Acoustic and optical phonons

Phonons are the quanta of elastic vibrations of the lattice in a crystal as atoms are perturbed from their equilibrium positions. The atoms in a crystal lattice may vibrate in one of two ways: longitudinal modes where the displacement is parallel to the direction of wave propagation (see Figure 3-1a) and transverse modes where the displacement of the atoms is perpendicular to the direction of wave propagation (see Figure 3-1b).

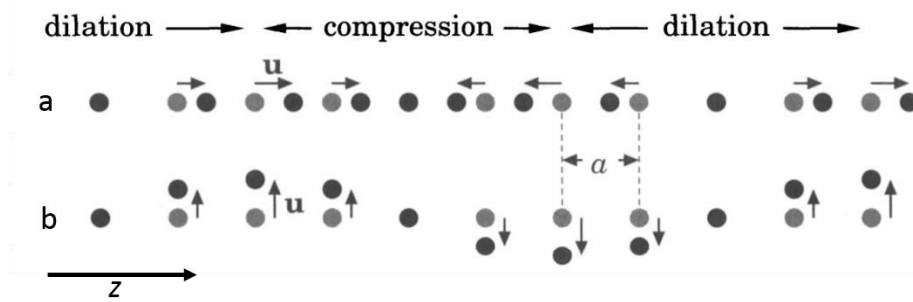


Figure 3-1. Motion of atoms in (a) longitudinal and (b) transverse phonon modes in a one dimensional monatomic chain. Equilibrium positions are shown in light grey with displaced positions in dark grey. Here a is the equilibrium atomic separation distance and u is the displacement from equilibrium. Figure taken from Ref. [81].

For a lattice consisting of different atoms, there exists two types of vibration with different dispersion relations. These are acoustic and optical phonons. The simplest model that describes the origin of the different types of phonon vibration is that of a one-dimensional diatomic chain of atoms with masses m and M along x separated by a repeat distance a and connected by springs of force constant K (see Figure 3-2).

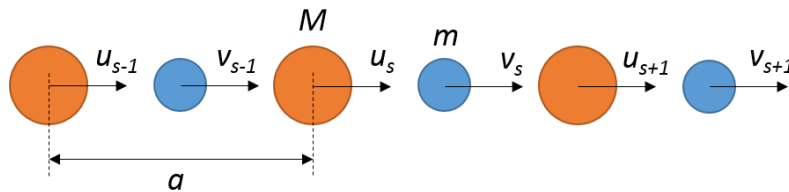


Figure 3-2. A diatomic crystal structure of masses M and m connected by a force constant K . The displacements of consecutive atoms M and m are described by u_{s-1} , u_s , $u_{s+1} \dots$ and v_{s-1} , v_s , $v_{s+1} \dots$, respectively, while s is the loop variable, which is used to count successive unit cells in the diatomic basis.

The equations of motion for the two atoms, under the assumption of only nearest neighbour interactions, are described by Hooke's law. The displacement of atoms of mass m (v_s) and M (u_s) are described by^[80]:

$$m \frac{d^2 u_s}{dt^2} = K(v_s + v_{s-1} - u_s), \quad (16)$$

and

$$M \frac{d^2 v_s}{dt^2} = K(u_s + u_{s-1} - v_s), \quad (17)$$

with solutions of the form

$$u_s = u \exp(iska) \exp(-i\omega t), \quad (18)$$

and

$$v_s = v \exp(iska) \exp(-i\omega t), \quad (19)$$

where u and v are the vibration amplitudes of M and m , respectively, k is the wavevector, and s is the loop variable, which is used to count successive unit cells in the diatomic basis. On substitution of Eqs. (18) and (19) into (16) and (17), respectively, we have

$$-\omega^2 M u = K v [1 + \exp(-ika)] - 2K u, \quad (20)$$

and

$$-\omega^2 m v = K u [\exp(-ika) + 1] - 2K v.$$

The unknowns u and v can then be found by taking a determinant of their relative coefficients:

$$\begin{bmatrix} 2K - M\omega^2 & -K[1 + \exp(-ika)] \\ -K[1 + \exp(ika)] & 2K - m\omega^2 \end{bmatrix} = 0, \quad (21)$$

or

$$M m \omega^4 - 2K(M + m)\omega^2 + 2K(1 - \cos ka) = 0, \quad (22)$$

which has solutions of the form

$$\omega^2 = K \left(\frac{1}{m} + \frac{1}{M} \right) \pm K \sqrt{\left(\frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4}{mM} \sin^2 \frac{ka}{2}}. \quad (23)$$

The two solutions are the basis for the acoustic and optical branches of phonons. In the acoustic branches, all atoms in the unit cell oscillate in phase (Figure 3-3a), as for sound waves in air, hence the name acoustic phonon. In the optical branches, oscillations of the two atoms are out of phase and the atoms in the unit cell vibrate against one another in opposing directions (Figure 3-3b). Such oscillations can be excited by the electric field of a light wave if the atoms possess a dipole, hence the name optical phonon. The dispersion relations of optical and acoustic phonons are plotted in Figure 3-4.

As k approaches 0, the two branches exhibit a different behaviour. In the acoustic branch, longer wavelengths correspond to $\omega \rightarrow 0$ and reduced differences in amplitude between adjacent atoms. Molecules will then behave like a rigid body in the limit $k = 0$. For optical phonons, as k approaches 0, the two atoms are in antiphase with a fixed centre of mass. In this case, the spring distortion is at its maximum with the frequency approaching a maximum.

The work discussed further, both in this section and others, only concerns the generation and detection of longitudinal acoustic (LA) phonons perpendicular to the plane in layered vdW crystals, such as InSe and hBN.

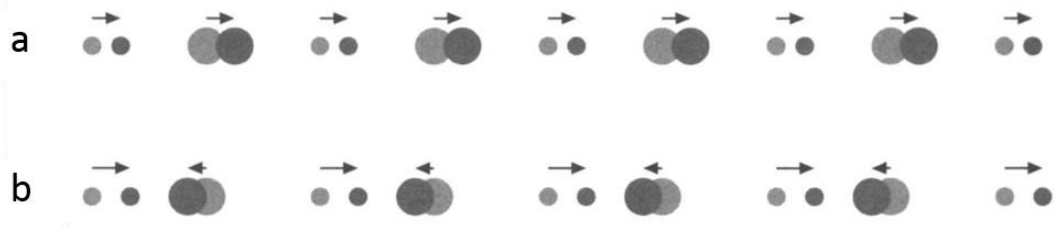


Figure 3-3. Motion of atoms in both acoustic (a) and optical (b) modes of a diatomic crystal. Equilibrium positions are shown in light grey with displaced positions in dark grey^[81].

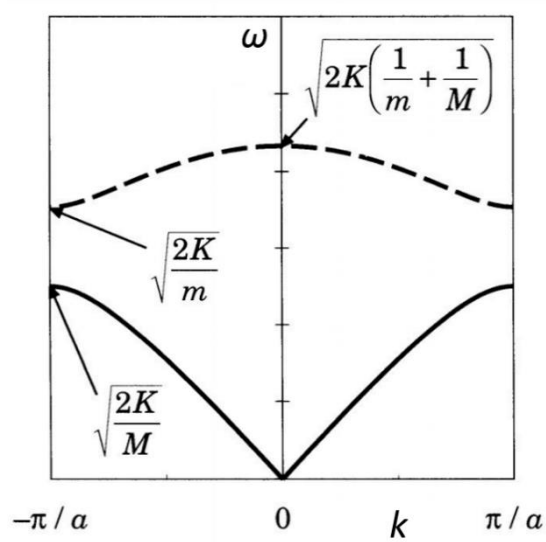


Figure 3-4. Dispersion relation of both the optical (dashed line) and acoustic (solid line) branches of longitudinal phonons for a 1D diatomic chain of atoms with masses M and m in a one dimensional lattice. Arrows show the respective maxima and minima of the two branches. Figure taken from Ref. [81].

3.3 Generation and detection of coherent acoustic phonons

Laser light is capable of generating dynamical stress in a crystal through absorption of photons. There are two main mechanisms responsible for the generation of stress in vdW semiconductors: (i) the deformation potential and (ii) the thermoelastic effect.

3.3.1 Electron-phonon interaction and thermo-elastic effect

Electrons and phonons in a crystal lattice can interact through a deformation potential $U^{[36]}$ (see Figure 3-5). Generated stress modifies the interatomic forces leading to dynamical strain and the generation of longitudinal acoustic phonons.

The relation between the strain and the deformation potential can be described as^[36]

$$\varepsilon = \frac{dU}{d_{eh}}, \quad (24)$$

where ε is the strain, dU is the incremental change of electronic energy, U , and d_{eh} is the deformation potential coefficient. The deformation potential coefficient describes the strain-induced linear shift of electronic energy levels. As atoms in the crystal are

displaced through stress, the orbital overlapping is modified since the distance or angle between atoms changes and consequently, the electronic levels are shifted. When the electronic energy levels in the lattice shift, electron populations are modified, thus changing the carrier density. The generation of electron-hole pairs also alters the local carrier density, consequently changing the strength of atomic bonds and leading to the generation of phonons (Figure 3-5b). The contributions of photo-induced electron-hole pairs to the deformation potential and thermal stress is expressed as^[36]

$$\sigma_{DP} = -d_e n_e - d_h n_h = -d_{eh} N, \quad (25)$$

where d_e and d_h are the deformation potential coefficients of electrons and holes, respectively. The corresponding carrier concentrations at the conduction band minimum and valence band maximum are given by d_e and d_h , respectively.

The thermo-elastic effect describes a volume change induced in a crystal by a change in temperature^[36]. For a thermal expansion of a crystal lattice to occur, lattice anharmonicity must be present. For a harmonic potential, an increase in potential energy, *i.e.* an increase in atomic spacing through a temperature and phonon population increase (see Figure 3-6), results in the average interatomic spacing, r_0 , to remain at the same value and hence no thermal expansion of the solid would be possible. In an anharmonic potential however, an increase in the atomic spacing

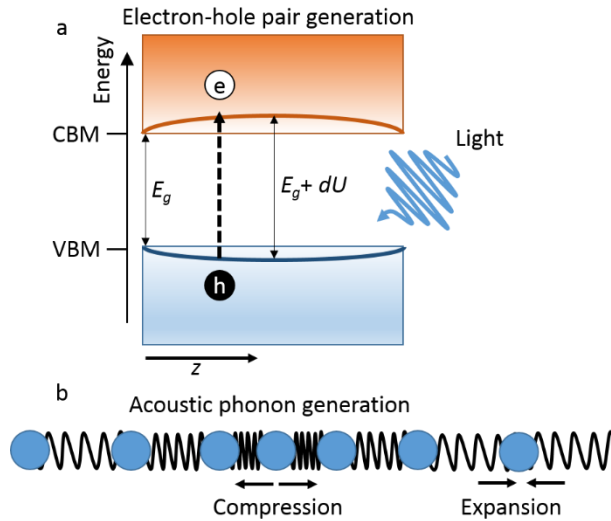


Figure 3-5. (a) Deformation potential according to a band structure description. Electron-hole pairs generated in the conduction band (CB) and valence band (VB) create a stress via the deformation potential, U . This leads to the generation of acoustic phonons (b) as the induced stress leads to compression and expansion of the interatomic spacing. Here CBM and VBM refer to the conduction band minimum and valence band maximum, respectively.

through a temperature increase results in a change of the average interatomic spacing r_0 .

Ultrafast lattice heating is due to intraband relaxation of electrons and holes in the conduction and valence bands, respectively^[25]. If we assume complete transfer of intraband relaxation energy from the generated hot electron-hole pairs in a semiconductor material to phonons, we can calculate the incremental change in the lattice temperature dT_L as

$$dT_L = N(h\nu - E_g)/C_L, \quad (26)$$

where N is the carrier concentration, E_g is the bandgap and C_L is the lattice heat capacity^[36]. In the case of metals, assuming complete energy transfer of the carrier relaxation energy to phonons, the incremental change in the lattice temperature is

$$dT_L = Nh\nu/C_L, \quad (27)$$

The ultrafast rise in temperature as a result of pump excitation leads to the generation of thermo-elastic stress^[25,26,36]

$$\sigma_{TE} = -3B\beta\Delta T_L. \quad (28)$$

where β is the linear thermal expansion coefficient, B is the bulk modulus and ΔT_L is the lattice temperature increase.

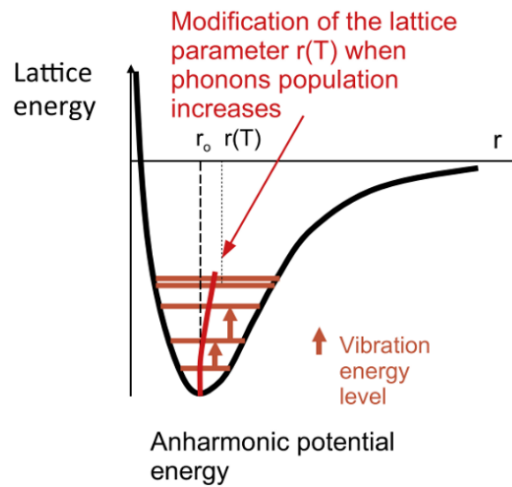


Figure 3-6. Modification of the mean interatomic distance r_0 when the vibrational energy increases in an anharmonic potential. Figure taken from Ref. [36].

The stress generated as a result of the thermo-elastic effect leads to the generation of dynamical strain. In the case of vdW nanolayers, where there is acoustic mismatch at the interfaces (underlying substrate or air), this leads to resonant vibrations of the layer with frequency defined by its thickness, elastic constants and boundary conditions. This case will be discussed in Section 3.4.

3.3.2 Photoelastic effect

Pressure variations and subsequent induced strain in a crystal lattice can alter the refractive index of the material. This is a well-known effect, which has been experimentally demonstrated in many semiconductors including InSe^[103]. Coherent acoustic phonons propagating through the crystal cause a dynamical strain, which alters the refractive index of the material, and in turn varies the reflection and transmission of light^[25,26]. In the simple case of one-dimensional longitudinal acoustic phonons, changes in the refractive index of a material due to strain, $\varepsilon(x, t)$, in the direction parallel to the c -axis (x) are expressed as^[26]

$$\Delta\tilde{n}(x, t) = \frac{\partial\tilde{n}}{\partial\varepsilon}\varepsilon(x, t), \quad (29)$$

where $\tilde{n} = n + i\kappa$ is the complex refractive index, n and κ are the real and imaginary components and $\partial\tilde{n}/\partial\varepsilon$ is the photo-elastic constant, which determines the magnitude of change in refractive index with respect to the strain.

The effect of a strain pulse on the reflection of light in a bulk material is shown in Figure 3-7a. Here a probe beam is incident on a crystal lattice. A strain pulse induced by absorption of a pump beam travels parallel to the c -axis, inducing a spatial and time dependent strain $\varepsilon(x', t)$ and subsequent perturbations of the refractive index $\Delta\tilde{n}(x', t)$. The relative temporal change in the reflection coefficient (R) is given by^[26]

$$\frac{dR(t)}{R_0} = \frac{4ik\tilde{n}}{1-\tilde{n}^2} \int_0^\infty \Delta\tilde{n}(x', t) e^{2ik\tilde{n}x'} dx', \quad (30)$$

or

$$\frac{dR(t)}{R_0} = \frac{4ik\tilde{n}}{1-\tilde{n}^2} \frac{\partial\tilde{n}}{\partial\varepsilon_{33}} \int_0^\infty \Delta\varepsilon_{33}(x', t) e^{2ik\tilde{n}x'} dx', \quad (31)$$

where k is the probe wavevector, R_0 is the unperturbed reflection coefficient and ε_{33} is the strain parallel to the c -axis (x). A similar modulation will occur on the transmission of the beam.

This however, is a general case for a bulk object with a thickness that far exceeds the wavelength of the probe light. For the case of vdW layers, we consider films that are relatively thin (Figure 3-7b) compared with the probe wavelength^[104]. The modulation of the reflection coefficient r in sufficiently thin layers of thickness d is expressed as^[25]

$$R = R_0 + \frac{ik_0^2}{2k} t_0 t_1 \int_0^d \Delta \varepsilon(x', t) e^{2ikx'} dx' = R_0 + \Delta R, \quad (32)$$

where R_0 and ΔR are the unperturbed reflection coefficient and induced contribution to the reflection coefficient, respectively; t_0 and t_1 are the transmission coefficients at the air/layer and layer/air boundaries, respectively, and k_0 and k are the wavevectors in air and layer, respectively.

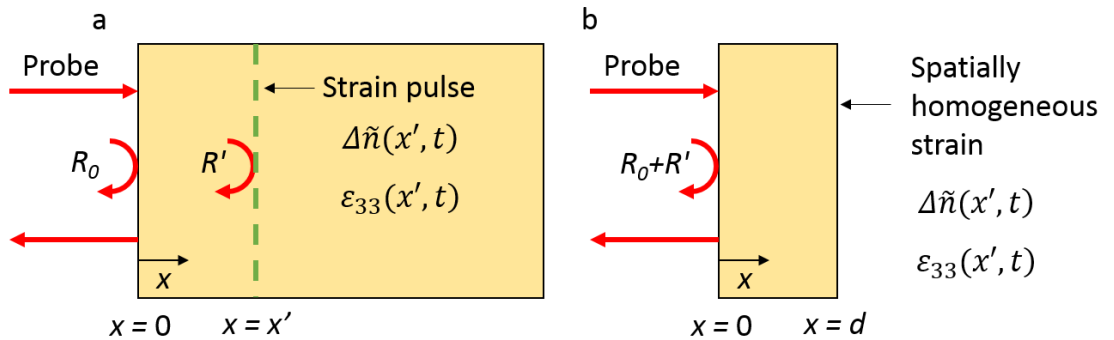


Figure 3-7. A schematic describing the effect of the strain pulse on the reflection of the probe beam in a crystal lattice in bulk (a) and thin films (b).

3.4 Eigenfrequencies of phonon resonances in single layers

For single layers undergoing nanomechanical resonances induced by the absorption of a pump beam, it is possible to extract the expected resonant frequencies through solutions of the elastic equation. We consider two extreme cases with different boundary conditions: (i) boundary conditions are set for the case of free standing layers (see Figure 3-8a) and (ii) layers supported by a semi-infinite solid substrate (see Figure 3-8b). We assume that the pump excitation through the layer in the x -direction is homogeneous and instantaneously generates homogeneous stress.

To calculate eigenfrequencies for LA phonons propagating along the x direction, perpendicular to the plane of the vdW layers, the elastic equation for displacement, u , without external force is^[36]

$$\rho \frac{\partial^2 u}{\partial t^2} = c \frac{\partial^2 u}{\partial x^2}, \quad (33)$$

where ρ is the density and c is the elastic constant. For comparison with the experiment, it is convenient to present the results in a spectral domain for the Fourier components of displacement $\tilde{u}(\omega, x)$ and strain $\tilde{\epsilon}(\omega, x) = d\tilde{u}/dx$. In the spectral domain, Eq. (33) may be written as

$$\frac{\partial^2 \tilde{u}(\omega, x)}{\partial x^2} + \frac{\omega^2}{s_{LA}^2} \tilde{u}(\omega, x) = 0, \quad (34)$$

where $s_{LA} = (c/\rho)^{1/2}$ is the sound velocity LA phonons in the layer.

The solution of the elastic equations for the Fourier component ω in the i^{th} layer is

$$\tilde{u}(\omega, x) = A \cos(kx) + B \sin(kx), \quad (35)$$

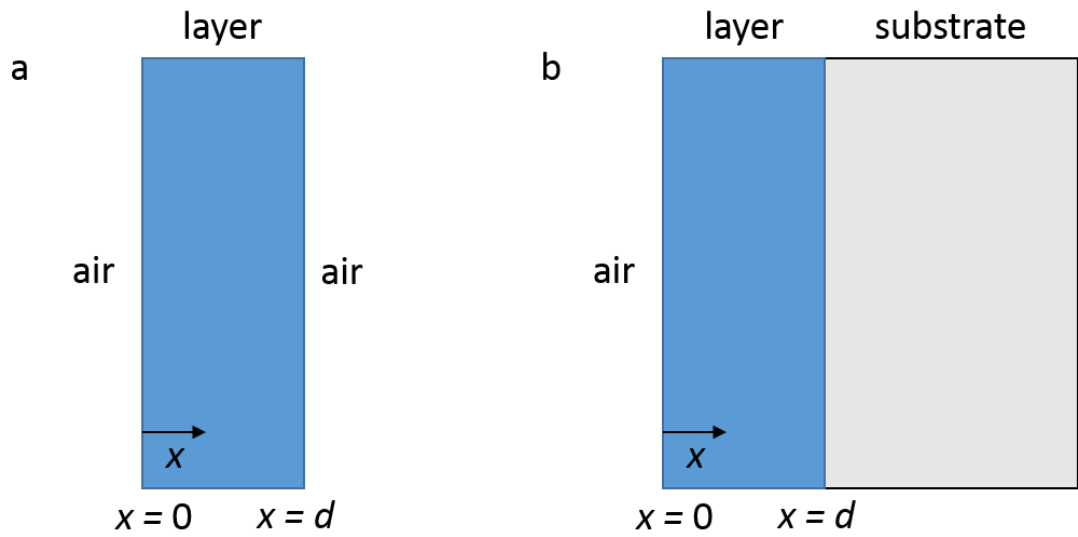


Figure 3-8. Schematics for the two cases where layers are (a) free standing and (b) supported by an infinite substrate with an ideal interface.

where $k = \omega/s_{LA}$ is the phonon wavevector, s_{LA} is the sound velocity in the layer and A and B are coefficients which depend on the boundary conditions.

For the free-standing case (Figure 3-8a) the stress at each boundary is equal to zero. Therefore at $x = 0$

$$c \frac{\partial \tilde{u}}{\partial x} = 0 \text{ and } -Akc \sin kx + Bkc \cos kx = 0. \quad (36)$$

From this, one can deduce that the coefficient $B = 0$. For the other boundary at $x = d$

$$c \frac{\partial \tilde{u}}{\partial x} = 0 \text{ and } Akc \sin kx = 0. \quad (37)$$

This relation is satisfied under the condition $kx = n\pi$, where n is an integer. By taking into account that $k = \omega/s_{LA}$ where ω is the angular frequency ($\omega = 2\pi f$) and s_{LA} is the sound velocity of the layer, it can be shown that the eigenfrequencies can be expressed as

$$f_n = \frac{n s_{LA}}{2d}. \quad (38)$$

For a layer supported by a semi-infinite solid substrate (Figure 3-8b), the boundary conditions at $x = 0$ are the same as for the free standing case and the coefficient $B = 0$. However, at $x = d$ there is now zero displacement due to the semi-infinite solid substrate:

$$u = 0 \text{ and } A \cos(kx) = 0. \quad (39)$$

This relation is satisfied under the condition $kx = (2n-1)\pi/2$ and it can be shown that eigenfrequencies are expressed as

$$f_n = \frac{(2n-1)s_{LA}}{4d}. \quad (40)$$

3.5 Evaluation of acoustic phonon resonances in layers and heterostructures on substrates

In the following section we discuss two possible approaches for calculating the expected resonant frequencies in a heterostructure, which consists of two layers on a substrate (see Figure 3-9). The acoustic mismatch model assumes ideal interfaces

between the different layers while the spring model is used to describe phonon transport and nanomechanical resonances in the case when the contact between the layers or layer and substrate is not ideal and may be modelled by springs^[27,28]. The notation is similar to that for the case of single layers. However, we introduce the subscript i to describe the behaviour of the i^{th} layer in the heterostructure.

We describe coherent phonons as classical wave packets of acoustic waves with displacement vector $\mathbf{u}$, wavevector $\mathbf{k}$ and given strain, ε , and stress, σ , tensors. For propagation of longitudinal acoustic phonons along the x direction, perpendicular to the plane of the vdW layers, the elastic equation is^[36]

$$\rho_i \frac{\partial^2 u_i}{\partial t^2} = c_i \frac{\partial^2 u_i}{\partial x^2} + \frac{\partial \sigma_0}{\partial x}, \quad (41)$$

where the index (i) defines the vdW layer or the substrate (S) with density ρ_i and elastic constant c_i , and σ_0 is the stress generated by the optical pump pulse. In our experiments, the pump pulse is absorbed in a thin InSe layer or Al transducer and with good approximation we may consider the excitation as spatially homogeneous due to fast transport of photoexcited carriers and heat in the layer^[104]. Then σ_0 does not depend on x except at the interfaces at which the second term in the right part of Eq. (41) is equal to zero. For comparison with the experiment, it is convenient to present

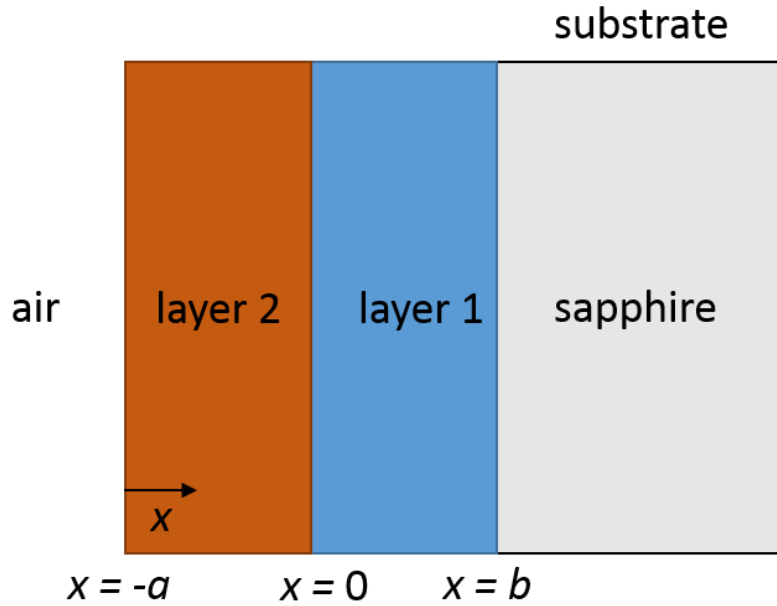


Figure 3-9. Schematic of a two-layer InSe/hBN heterostructure on an infinite substrate with ideal interfaces. For this model, layer 1 or layer 2 can be InSe or hBN.

the results in a spectral domain for the Fourier components of displacement $\tilde{u}(\omega, x)$ and strain $\tilde{\epsilon}(\omega, x) = d\tilde{u}/dx$. In the spectral domain, Eq. (41) may be written as

$$\frac{\partial^2 \tilde{u}_i(\omega, x)}{\partial x^2} + \frac{\omega^2}{s_i^2} \tilde{u}_i(\omega, x) = 0, \quad (42)$$

where $s_i = (c_i/\rho_i)^{1/2}$ is the sound velocity in the i^{th} layer or substrate.

3.5.1 Acoustic mismatch

In the acoustic mismatch (AM) model, the displacement and stress are continuous at each interface. An example of a multilayer InSe/hBN heterostructure on a substrate is schematically shown in Figure 3-9. There are two vdW nanolayers, layer 1 and layer 2 (InSe or hBN) with thicknesses a and b , respectively, on a sapphire substrate (S). There are three interfaces at $x = -a$, $x = 0$, and $x = b$.

The solution of the elastic equations for the Fourier component ω in the i^{th} layer is

$$\tilde{u}(\omega, x) = A_i \cos(k_i x) + B_i \sin(k_i x), \quad (43)$$

where $k_i = \omega/s_i$ is the phonon wavevector and s_i is the sound velocity in the i^{th} layer. The solution for the elastic wave in a semi-infinite substrate (S) is

$$\tilde{u}_S(\omega, x) = A_S \exp(-ik_S x). \quad (44)$$

The simplest, most common case for the boundary conditions is the acoustic mismatch (AM) model, *i.e.*, the displacement and stress are continuous at each interface^[105]. This approximation works for relatively thick layers and perfect, atomically flat interfaces. Here, the elastic coupling between the boundary atoms in the two materials is assumed to be absolutely rigid.

The frequency dependent coefficients A_i , B_i , and A_S define the coherent phonon spectrum and can be found by applying boundary conditions to the displacement and stress at each interface. The stress σ_0 induced by the optical pump pulse is generated only in the InSe nanolayer. In contrast, $\sigma_0 = 0$ in the hBN layer and the sapphire substrate, which do not absorb the pump light. The boundary conditions in the case of ideal interfaces and AM, where InSe is layer 1 and hBN is layer 2, may be written as

$$A_1 k_1 \sin k_1 a + B_1 k_1 \cos k_1 a + \tilde{\sigma}_0 = 0 \quad \text{at } x = -a \quad (45)$$

$$\begin{cases} A_1 = A_2 \\ B_1 c_1 k_1 + \tilde{\sigma}_0 = B_2 c_2 k_2 \end{cases} \quad \text{at } x = 0 \quad (46)$$

and

$$\begin{cases} A_2 \cos k_1 b + B_2 \sin k_2 b = A_s \exp(-ik_s b) \\ -A_2 c_2 k_2 \sin k_2 b + B_2 c_2 k_2 \cos k_2 b \\ = -iA_s c_s k_s \exp(-ik_s b) \end{cases} \quad \text{at } x = b \quad (47)$$

Solving Eqs. (45), (46), and (47), we find five complex amplitudes A_1 , A_2 , B_1 , B_2 , and A_s , and substituting them into Eqs. (43) and (44), we get the Fourier spectrum of coherent phonons at the coordinate x . To understand the behaviour of phonon dynamics on a qualitative level and estimate the finesse of phonon resonances (see Chapter 7), it is useful to consider the phonon reflection, R , at the interface. For a wave propagating in a medium (i) and reaching the interface with another medium (j), the amplitude reflection coefficient R_{ij} for the strain is

$$R_{ij} = \frac{Z_j - Z_i}{Z_j + Z_i}, \quad (48)$$

where Z_i and Z_j are the acoustic impedances ($Z = \rho s_{LA}$, where ρ is the density and s_{LA} is the sound velocity) of the materials. For phonons propagating from a high to a low impedance material ($Z_i > Z_j$), $R_{ij} < 0$ and the phase for the strain wave of the reflected beam is changed by π . In the opposite case ($Z_i < Z_j$), $R_{ij} > 0$ and the phase does not change on reflection. The case $Z_i = Z_j$ corresponds to $R_{ij} = 0$ and no phonon resonances take place. As discussed in Section 3.4, for a single layer of thickness a on a substrate with acoustic impedance Z_s , the phonon frequencies are given by Eq. (40) for $Z_i < Z_s$ and Eq. (38) for $Z_i > Z_s$.

In general, the AM model may not be valid when the phonon dispersion plays a role, *e.g.* at high phonon frequencies or when the interface between the layers is not elastically perfect. The maximum phonon frequency studied in this work is 120 GHz, which is much smaller than the frequency at which phonon dispersion effects become important^[106] (~ 1 THz). Thus the main limitation to the validity of the AM model to our structures is the imperfectness of the interfaces.

3.5.2 The spring model

To account for the elastic properties of an imperfect interface, we use the spring model^[27,28]: the adjacent layers of two materials, i and j , are coupled by effective “springs” with stiffness η_{ij} . Figure 3-10b shows the scenario in which an InSe/hBN heterostructure on sapphire has AM between the layers, but is weakly coupled to the substrate by an effective spring of stiffness η_s . Figure 3-10c shows the scenario in which both interfaces are imperfect, *i.e.* there is also a spring of stiffness η_H at the InSe/hBN interface. The boundary conditions in the spring model include the continuity of the stress at the interfaces with springs, from which the coefficients A_i , B_i , and A_s can be derived. The parameter η characterizes the force F per unit area, which appears during the modulation of the distance x between the boundaries of the neighbouring materials, denoted as Δx . In the linear approximation, according to Hooke’s law, we can write

$$\Delta F = \eta \Delta x. \quad (49)$$

The boundary conditions for stress at the free surface, $x = -a$, are the same as Eq. (45). For the interface at $x = 0$ and $x = b$, the conditions for the continuity of the stress can be written, respectively, as

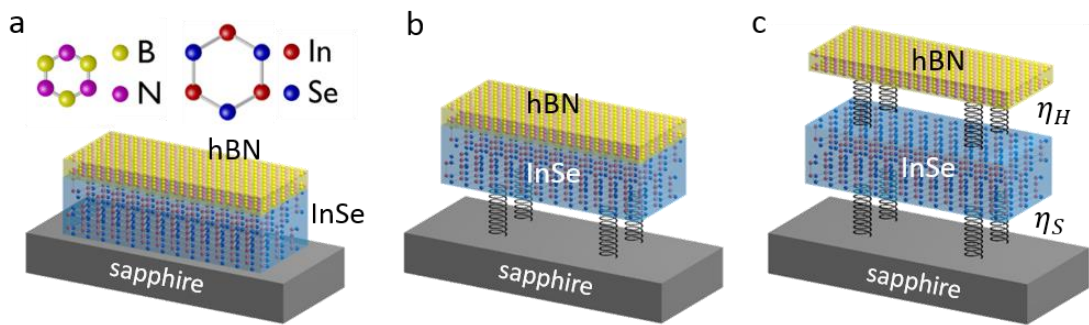


Figure 3-10. Schematics showing different strengths of elastic coupling between van der Waals layers (e.g., InSe and hBN) and between a van der Waals layer and a sapphire substrate. (a) Rigid interface between InSe and hBN, and between InSe and sapphire. The elastic properties of the rigid interfaces are described by the acoustic mismatch model. (b) Rigid interface between InSe and hBN, but weak elastic coupling between InSe and sapphire. (c) Weak elastic coupling for both InSe/hBN and InSe/sapphire interfaces, as described by springs with stiffnesses η_H and η_s , respectively.

$$\begin{cases} B_1 c_1 k_1 + \tilde{\sigma}_0 = \eta_H (A_2 - A_1), \\ B_2 c_2 k_2 = \eta_H (A_2 - A_1), \end{cases} \quad (50)$$

and

$$\begin{cases} A_2 c_2 k_2 \sin k_2 b + B_2 c_2 k_2 \cos k_2 b = \\ \eta_S [A_S \exp(-ik_S b) - A_2 \cos k_2 b - B_2 \sin k_2 b] \\ -A_S i c_S k_S \exp(-ik_S b) = \\ \eta_S [A_S \exp(-ik_S b) - A_2 \cos k_2 b - B_2 \sin k_2 b] \end{cases} \quad (51)$$

Eqs. (50) and (51) give the solution for the coefficients A_i and B_i .

Similarly to the AM model, the spring model reveals nanomechanical resonances in the heterostructure. However, the resonance frequencies f_n differ from those predicted by the AM model; also, due to the weaker coupling at the interfaces, these resonances can be narrower (see Chapters 7 and 8).

For acoustic phonons propagating from material i to material j and back from j to i , it is convenient to use parameters G_{ij} and G_{ji} , respectively, related to $\eta_{ij} = \eta_{ji}$:

$$G_{ij} = G_{ji} = \eta_{ij} \frac{Z_j + Z_i}{2\pi Z_j Z_i}. \quad (52)$$

Since in our work we use no more than two vdW nanolayers, we consider two parameters G_H and G_S , which characterize the coupling between the vdW nanolayers at the heterostructure interface (G_H) and the substrate interface (G_S):

$$G_H = \eta_H \frac{Z_1 + Z_2}{2\pi Z_1 Z_2}, \quad (53)$$

and

$$G_S = \eta_S \frac{Z_S + Z_2}{2\pi Z_S Z_2}, \quad (54)$$

where Z_1 , Z_2 , and Z_S are the acoustic impedances of the outer, inner nanolayers, and substrate, respectively. The parameters G_H and G_S have the dimension of frequency. In the extreme case of a single layer weakly coupled to the substrate, *e.g.*, $G_S \ll f_n$, the resonance frequencies are given by Eq. (38). One of the main aims of the present work is to obtain the values of G_S or G_H , which are directly related to the coupling parameters η_S and η_H , respectively. To obtain these parameters, first, we obtain the frequencies f_n of the phonon resonances from the measured phonon spectra and

compare them with the theoretical values of f_n obtained from the calculated spectra for various G_S and G_H . To make this comparison, we calculate the modelled strain spectrum as

$$S(f) \approx f \sqrt{\sum_i (|A_i|^2 + |B_i|^2)}. \quad (55)$$

For strain waves incident from i to j , the equation for the reflection coefficient at the interface is

$$R_{ij} = \frac{\eta_{ij}(Z_j - Z_i) - iZ_j Z_i \omega}{\eta_{ij}(Z_j + Z_i) + iZ_j Z_i \omega} = \frac{G_{ij} R_{ij}^{AM} - if}{G_{ij} + if}, \quad (56)$$

where R_{ij}^{AM} is the reflection coefficient given by Eq. (48). For $G_{ij} = 0$, $R_{ij} = -1$ as for a free surface. For $G_{ij} R_{ij}^{AM} \gg f$, $R_{ij} \approx R_{ij}^{AM}$. In contrast to the scenario of AM, in this case R_{ij} depends on f and has a complex value, thus implying that the phase change at the interface depends on η . This is also responsible for the difference in the values of f_n in the spring and AM models. In particular, an important difference between the spring and AM models is that R_{ij} depends on f in the spring model while R_{ij} is the same for all frequencies for AM. Thus it may happen that for frequency independent values of η , the fundamental resonance mode with $n = 1$ behaves as in the case of AM while for higher modes, f_n is close to the spectrum for free standing films. The spring model is further complicated if the spring stiffness depends on f ^[107] or if springs have finite mass^[108], which is not considered in this work.

Chapter 4

4 Experimental techniques

The following chapter describes the various techniques employed in the fabrication and characterization of samples. The specific techniques used for the exfoliation and dry transfer of flakes on a substrate are discussed in Chapter 5.

4.1 Micro-photoluminescence and micro-Raman spectroscopy

Micro-photoluminescence (μ -PL) and micro-Raman (μ -Raman) spectroscopy techniques are commonly used in assessing sample quality^[109], and optical^[110] and vibrational^[111] properties. The PL and Raman experiments are conducted within the same optical confocal microscope. A schematic of the setup is shown in Figure 4-1. The apparatus consists of 2 laser sources: a 633 nm He-Ne laser and a 532 nm frequency doubled Nd:YVO4 laser. Laser light is passed through an adjustable pinhole aperture and then through a beam splitter. The laser is then focused onto the sample through an adjustable objective. A laser spot of diameter $\sim 1\ \mu\text{m}$ can be achieved allowing for the accurate measurement of distinct areas on a flake or heterostructure. Light from the sample is returned through the objective and is reflected from the beam splitter into a second pinhole aperture before passing through a filter to remove unwanted light from the sample. The light is then monochromated by the grating

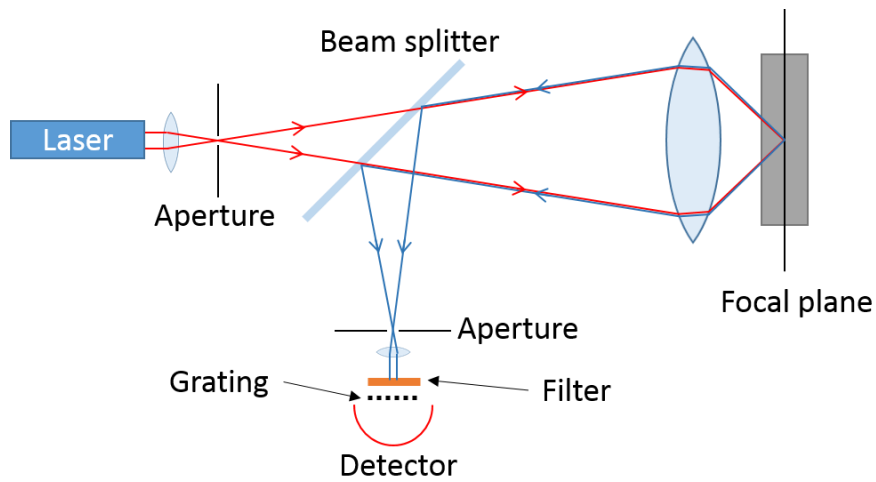


Figure 4-1. (a) Schematic of the confocal microscope system. The red and blue lines denote incident laser light and the light detected in a μ -PL or μ -Raman measurement, respectively.

before finally reaching the detector. The second aperture blocks unwanted light from sources other than the sample area excited by the focused laser beam. Two types of detector are available. A Charge-Coupled Device (CCD) detector and an indium gallium arsenide (InGaAs) array detector are used depending on the spectral range of interest: The CCD detector covers the range 350 to 800 nm and the InGaAs detector covers the range 800 to 1600 nm. A series of filters are used to reduce the power of the laser. Typically 1% of full power ($P = 15$ mW) is used for PL and Raman experiments to achieve a good signal without overheating and damaging the flakes. The grating of the detector can be set to either 150 or 1200 g/mm (grooves per mm) in order to alter the spectral resolution. For PL experiments, broad emission peaks are generally observed so the 150 g/mm grating is favourable. For Raman, narrow peaks are observed with over a small spectral range so the 1200 g/mm grating is preferred. The sample to be measured is placed upon a motorized xy stage allowing for sub-micron scale adjustments of the laser spot position. PL or Raman mapping of the sample is also possible via use of the stage.

In a PL experiment, a system is excited to a higher energy state via absorption of a photon from a laser light source. The incident photon of energy $E = \hbar\omega$ can excite an electron from the valence band (VB) into the conduction band (CB), provided that the photon energy exceeds the band gap, E_g , of the material. This excitation results in an electron-hole pair, bound by the attractive Coulomb force^[110]. Electrons and holes relax into lower energy states and recombine (see Figure 4-2). If the excitonic

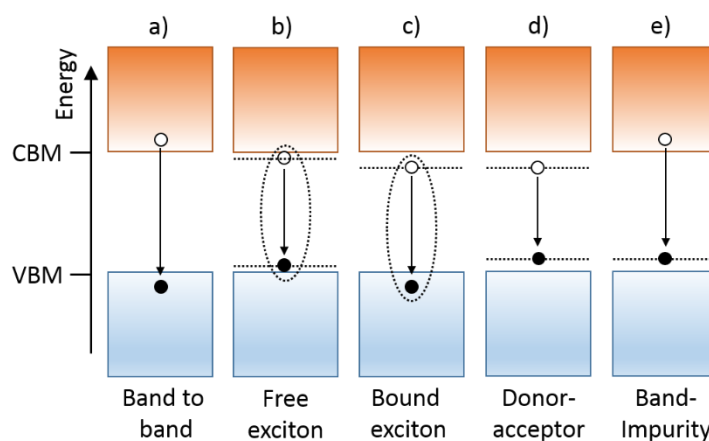


Figure 4-2. Depiction of electron-hole recombination in the case of various scenarios including (a) band to band transitions; (b) free excitons; (c) bound excitons; (d) donor-acceptor transitions and (e) band-impurity transitions. CBM and VBM denote the conduction band minima and valence band maxima, respectively.

Coulomb interaction is negligible, this leads to a band to band transition and an emitted photon of energy equal to the band gap E_g (see Figure 4-2a). However, in most cases the excitonic Coulomb interaction is not negligible and the transition is that of a free or a bound exciton (see Figure 4-2b-c). For a free exciton, the emitted photons have energy equal to the band gap minus the exciton binding energy E_b . The presence of crystal defects or impurities can lead to states inside the ‘forbidden’ gap, which can contribute to the recombination process and also be detected by PL (see Figure 4-2c-e). Thus PL is an ideal technique for the study of semiconductors such as InSe (see Chapter 2). Our studies focus on the PL properties of InSe flakes at room temperature.

In a Raman experiment, inelastically scattered light from the sample is analysed to give information about the vibrational modes of the crystal^[111]. Atoms in crystal structures are able to vibrate in different ways. Figure 4-3 shows a selection of the Raman modes of InSe, which will be discussed further in Chapter 2.

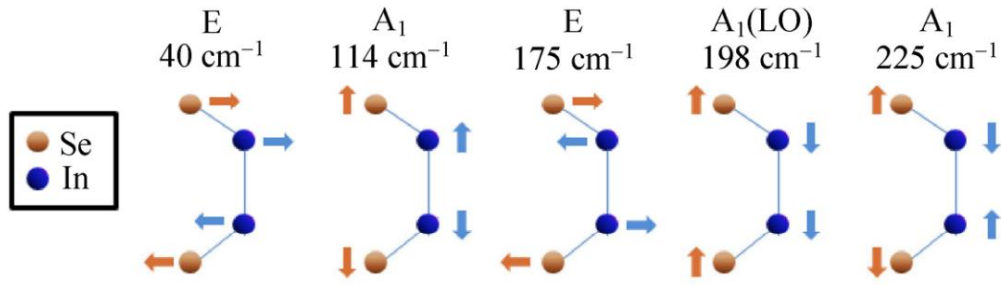


Figure 4-3. Example of five Raman modes of InSe and their respective Raman shift. Figure reproduced from Ref. [109].

Raman techniques are commonly used to analyse two dimensional layers such as graphene whose vibrational mode intensities and peak positions differ from those of graphite^[112]. A photon of energy $E_i = \hbar\omega_i$ and wave vector $\mathbf{k}_i$ interacting with a sample can be scattered by a phonon of energy $E_q = \hbar\omega_q$ and wave vector $\mathbf{q}$, which is either excited or absorbed. Since energy and momentum are conserved, the energy and wave vector of the scattered photon are:

$$\hbar\omega_s = \hbar\omega_i \pm \hbar\omega_q, \quad (57)$$

and

$$\hbar\mathbf{k}_s = \hbar\mathbf{k}_i \pm \hbar\mathbf{q}. \quad (58)$$

Here the positive and negative signs refer to phonon absorption (anti-Stokes component) and phonon emission (Stokes component), respectively. Scattered light is detected by the detector and the Raman shift is expressed as a function of the wavenumber difference between incident and scattered light. Our setup enables us to study only the Stokes component of the Raman spectra due to the interferential filter used to stop laser light being detected. Anti-Stokes processes occur less frequently since a phonon population must already exist before a phonon can be absorbed by an incident photon.

Raman spectra can be affected by any strain applied to the crystal, which can be identified by shifts in the Raman modes and/or variations in peak intensity^[113,114]. In vdW heterostructures fabricated by dry transfer techniques, many interfacial defects, such as folds or bubbles can be present, resulting in strained layers. The ability to assess strain by Raman spectroscopy makes it useful for assessing sample quality, and was routinely used in experiments to characterize InSe and hBN/InSe heterostructures, as discussed in Chapter 7.

4.2 Picosecond acoustics

The following section describes the various setups used for picosecond acoustic measurements. Two similar systems (see Sections 4.2.1 and 4.2.2) were used for measurements at the University of Nottingham (see Chapters 6 and 7) with the main difference being the mechanism of how temporal scans are acquired. A third system (see Section 4.2.3) was used for measurements at Le Mans University, where a smaller laser spot ($d \sim 1 \mu\text{m}$) was used for picosecond acoustic imaging studies (see Chapter 8).

Picosecond acoustics, first proposed by Thomson *et al.*^[25] in the 1980s, is well developed nowadays and is described in several reviews^[26,115]. In this technique, an optical pump pulse from a femtosecond laser excites the sample directly or through an optoelastic transducer (e.g., a thin metal film), which absorbs light. As a result, a stress is generated in the sample due to a rapid, almost instantaneous (~ 100 fs) electron and lattice temperature rise^[25,104,116]. The stress causes dynamical strain and, correspondingly, generates a coherent wave packet of longitudinal acoustic phonons. These phonons are generated with the same initial phase and are distinct from the thermal phonons which have random phase. The spectrum of these sub-THz phonon

pulses depends on the absorption length and the thickness of the layer. The spatial and temporal evolutions of the coherent phonons are governed by the elastic properties of the sample and its interfaces, and can be probed by the reflection or transmission of a second probe optical pulse. The pump and probe pulses may be generated by the splitting of a single laser or through two lasers (see sections 4.2.1 and 4.2.2, respectively). A schematic of a general pump-probe beam system is shown in Figure 4-4.

The laser wavelengths ($\lambda = 400$ and 515 nm) chosen for our experiments enable a strong absorption of the pump beam by the InSe flake, thus generating hot electron-hole pairs. These non-equilibrium carriers are coupled to the lattice via electron-phonon interactions and thermoelastic effects, causing a local stress in the flake^[117]. As a result of this stress, the InSe nanolayer starts to vibrate at its resonant frequency, which is determined by elastic properties of the layer and interfaces and layer thickness d . We monitor such vibrations by measuring the intensity variation of the transmitted or reflected probe beam, arising due to changes in the thickness of the nanolayer and the photoelastic effect^[118]. Scanning the time delay between pump and probe pulses makes it possible to monitor the temporal evolution of the wave packet of coherent acoustic phonons generated in the sample. The time delay between pump and probe can be controlled in two ways. Firstly, by using a delay line to alter the optical path

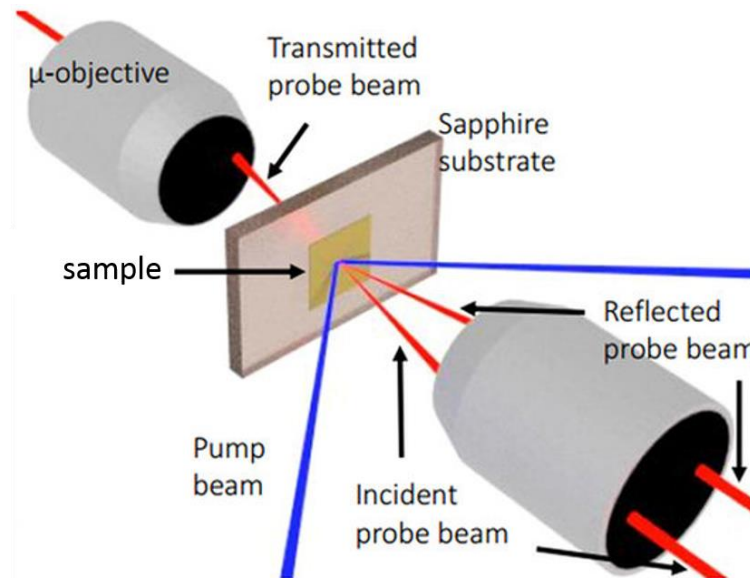


Figure 4-4. Schematic of the laser set up for picosecond acoustic measurements. The sample may be a single semiconductor flake, heterostructure and may also be coated in a thin Al transducer layer.

length of the pump (section 4.2.1) and secondly, by application of an asynchronous optical sampling (ASOPS) system (section 4.2.2). In ASOPS a small difference in the pulsing frequency of the two pump and probe lasers is applied. As a result, the relative time delay of the two lasers is varied, allowing for temporal scanning. Resonant frequencies are extracted from the temporal scans through removal of the background signal and use of fast Fourier transform (FFT), as discussed in Chapter 7.

4.2.1 Delay line system

Single 120 fs pulses are emitted from a Ti:Sapphire laser at a wavelength $\lambda = 800$ nm and a pulsing frequency of 80 MHz (see Figure 4-5, red lines). The laser beam is partly reflected by a beam splitter to form the pump and probe paths. The probe beam is directed into a confocal microscope, consisting of two micro-objectives and a microscope head that can be removed from the beam path during the measurement. A removable mirror positioned before the detector allows the system to detect the probe beam that is either transmitted or reflected from the sample. The pump beam passes through an acousto-optic modulator, a frequency doubler and through a variable delay

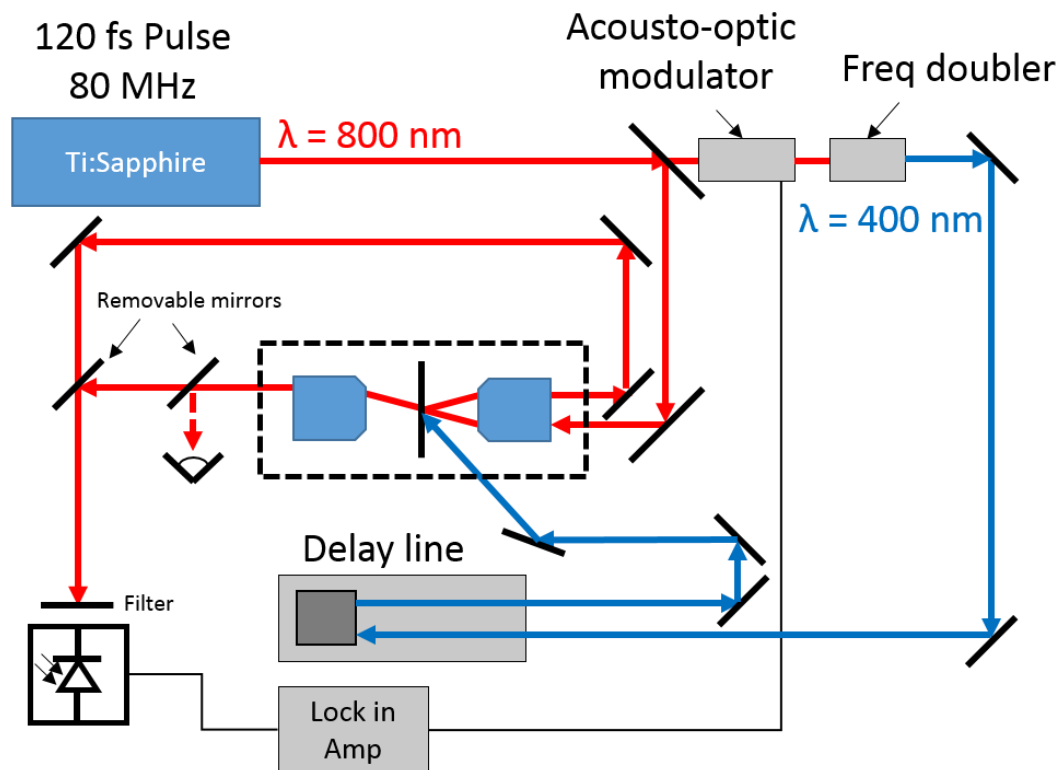


Figure 4-5. Schematic of the delay line system. Red and blue lines correspond to probe and pump beams respectively.

line to deliver pulses with a central wavelength of $\lambda = 400$ nm (see Figure 4-5, blue lines) to the sample, and allows for the stroboscopic measurement.

The acousto-optic modulator contains a transparent crystal and piezoelectric transducer. Sound waves are generated in the crystal which in turn applies a periodic modulation to the beam as the refractive index of the crystal is altered. The pump and probe beams are focused to diameters of ~ 50 μm and ~ 5 μm , respectively, at the sample surface. The power of the pump and probe beams was kept below 5 and 0.5 mW, respectively, to avoid overheating and photo-oxidation of the InSe layers.^[85] We use a band pass filter to prevent the detection of any photoluminescence ($\lambda > 950$ nm) from entering the detector. The photodiode signal is read by a lock-in amplifier locked to the frequency of the pump beam modulation as a reference. The lock-in amplifier amplifies signals that match the frequency of the reference signal, allowing them to be better distinguished from noise.

4.2.2 Asynchronous Optical Sampling (ASOPS) system

Two 120 fs pulses are emitted from two Ti:Sapphire lasers at a wavelength $\lambda = 800$ nm and pulsing frequencies of $f \sim 80$ MHz (see Figure 4-6, red lines). A small difference in pulsing frequencies ($\Delta f \sim 500$ Hz) is applied between the two lasers. This allows the time delay between pump and probe to be varied with each consecutive laser pulse without the need of a delay line, as shown in Figure 4-7b. The incremental time delay between consecutive pump and probe pulses, and subsequent resolution of measurements, can be expressed as $\Delta\tau = \Delta f / (f_{\text{pump}} f_{\text{probe}})^{[119]}$. The pump beam passes through a frequency doubler to deliver pulses with a central wavelength of $\lambda = 400$ nm (see Figure 4-6, blue lines). ASOPS is less noisy than the delay line and so the acousto-optic modulator and lock-in amp are not used in this case.

The probe beam is directed into a microscope, consisting of two micro-objectives and a microscope head that can be removed from the beam path during the measurement. A removable mirror positioned before the detector allows the system to detect the probe beam that is either transmitted or reflected from the sample. The pump pulse with $\lambda = 400$ nm is focused onto the sample to an area of $\sim 20 \times 20$ μm^2 for normal incidence and $\sim 20 \times 30$ μm^2 for 45 degree incidence. The probe beam with $\lambda = 800$ nm is focused on the sample surface to a diameter ~ 5 μm , overlapping spatially with the pump spot. The power of the pump and probe beams

was kept below 20 and 0.5 mW, respectively, to avoid overheating and photo-oxidation of the InSe layers.^[85]

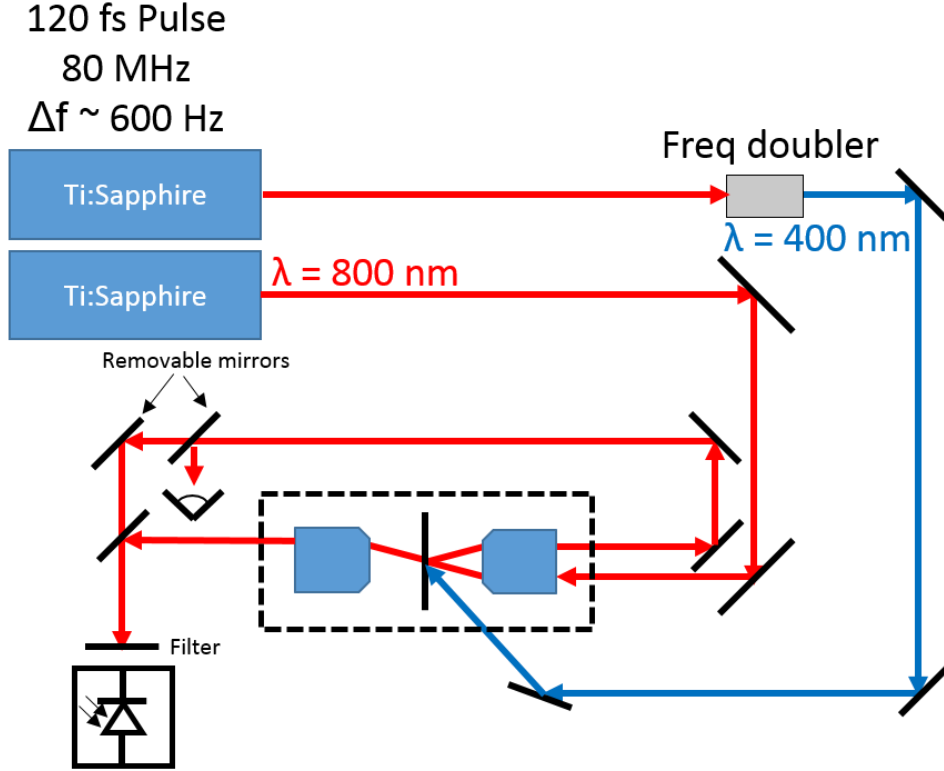


Figure 4-6. Schematic of the ASOPS system.

4.2.3 Picosecond acoustic imaging

A commercial imaging system (See NETA patent^[120]) based on the ASOPS picosecond acoustic principles was used at Le Mans University (see Figure 4-7). This system operates with a reduced pump and probe laser spot size ($d \sim 1 \mu\text{m}$) and the sample is placed upon a motorized xy stage with sub-micron precision.

Here the pump wavelength is $\lambda = 515 \text{ nm}$ with a pulse length of 198 fs and the probe wavelength is $\lambda = 532 \text{ nm}$ with a pulse length of 130 fs. The lasers are pulsed at a frequency of $\sim 42 \text{ MHz}$ with a difference in pulsing frequency of $\Delta f \sim 500 \text{ Hz}$. The power for both the pump and probe beams was kept below 0.5 mW to avoid overheating and photo-oxidation of the InSe layers.

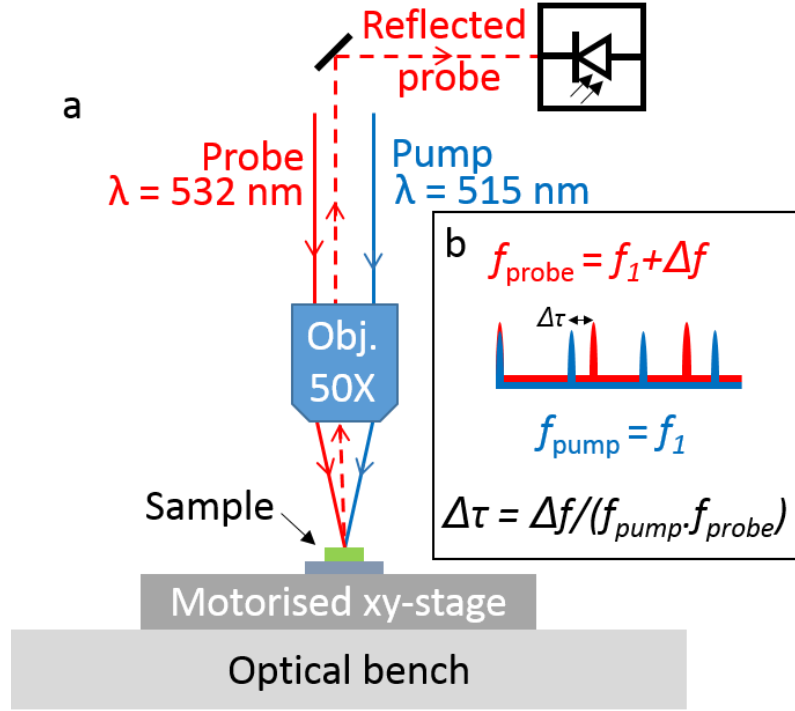


Figure 4-7. (a) Schematic of the picosecond acoustic imaging system. (b) Visualization of the time delay between two mismatched laser pulses allowing for temporal scans in ASOPS.

4.3 Atomic force microscopy

Atomic Force Microscopy was utilized to measure the topography of InSe and hBN flakes. A fine tip of radius, $R \leq 10 \text{ nm}$, upon a cantilever is brought almost into contact with a desirable structure (*i.e.* an InSe flake) close enough to interact with the sample^[121]. Upon the back of the cantilever, a mirror is positioned from which a laser beam is deflected into a photodetector. The cantilever-tip system is driven to oscillate at its resonant frequency via a piezo electric component. The cantilever behaves like an oscillating spring with an inherent force constant and resonant frequency. The tip is brought within an operating distance from the sample, which is typically in the range $10 - 0.1 \text{ nm}$. At such distances, the atomic forces of the sample are sufficient to deflect the tip/cantilever and alter the resonant frequency of the system. A schematic of the system is shown in Figure 4-8.

To probe the topography of the sample, the xy range is incrementally scanned in line segments. Throughout this process, alterations in atomic forces between the tip and the sample are detected through deflections in the laser, which are picked up by a position sensitive photodetector. The current is fed back to the system via a feedback

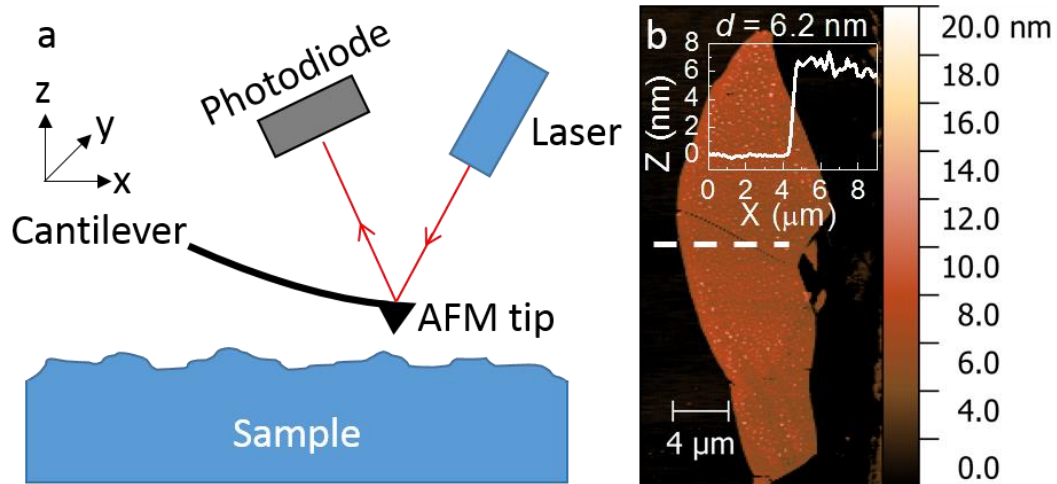


Figure 4-8. (a) Schematic of an AFM tip scanning a surface. (b) Example of an InSe flake on sapphire measured by AFM. Inset – AFM z-profile along the white dashed line shown in the main panel.

loop and the system can recalibrate the tip height in order to maintain a constant tip-sample distance. For AFM measurements, a Tap300AL-G tip was used with a cantilever resonant frequency of $\sim 300 \text{ kHz}$, force constant of $\sim 40 \text{ N/m}$ and tip radius of $\sim 10 \text{ nm}$ ^[122]. AFM measurements were conducted on an Asylum Research MFP-3D system.

4.4 Electrical measurements

Current-Voltage (I - V), photocurrent (PC) and photovoltaic (PV) spectroscopy measurements were conducted by myself at the University of Nottingham. Figure 4-9 shows a diagram of the set up used to measure InSe-capped graphene layers. Here, two gold (Au) contacts (source-drain) were placed either side of an InSe flake on a square pad of graphene (g) on a SiO_2/Si substrate. Silver (Ag) paste was placed on the Si substrate to form the back gate. Further device fabrication details are discussed later and methods for the transfer of InSe flakes are discussed in Chapter 5.

For I - V measurements, a Keithley 2400 sourcemeter was used to simultaneously apply a gate voltage (V_G) and monitor any subsequent leakage current (I_G) through the back gate (this is a sign of electronic breakdown in the device). V_G was typically ramped incrementally through the range $\pm 50 \text{ V}$. A Keithley 2400 sourcemeter was used to apply a voltage (V_{SD}) of 1 mV across the source and drain terminals, and to measure the corresponding current (I_{SD}). This allows for measurement of the resistance (R_{SD}) of InSe-capped graphene as a function of V_G .

Varying the Fermi level (E_F) through the Dirac point of graphene leads to a maximum in R_{SD} versus V_G . The Dirac point of graphene is also discussed in Chapter 2.1.3. When the Fermi level is increased through the conduction band or decreased through the valence band, the conductivity, σ increases with increasing the carrier density of electrons or holes, respectively. This is induced by positive or negative gate voltages, respectively^[123].

I - V measurements were taken under vacuum as this was noted to extend the longevity of the devices. Also, I - V curves were acquired in the dark and under illumination with an unfocused laser source ($\lambda = 405\text{nm}$). This enabled PC measurements. A voltage, V_{SD} , of 1 mV was applied while the photoinduced current, I_{SD} , across the source-drain was measured. A focused laser beam ($\lambda = 405\text{ nm}$, $P = 20\text{ }\mu\text{W}$ and spot diameter $d \sim 1\text{ }\mu\text{m}$) was mapped across the surface of the device in the xy plane at increments of $1\text{ }\mu\text{m}$. PV measurements were conducted in the same way as PC measurements. However, no V_G or V_{SD} was applied. These measurements are presented and discussed in Chapter 8.

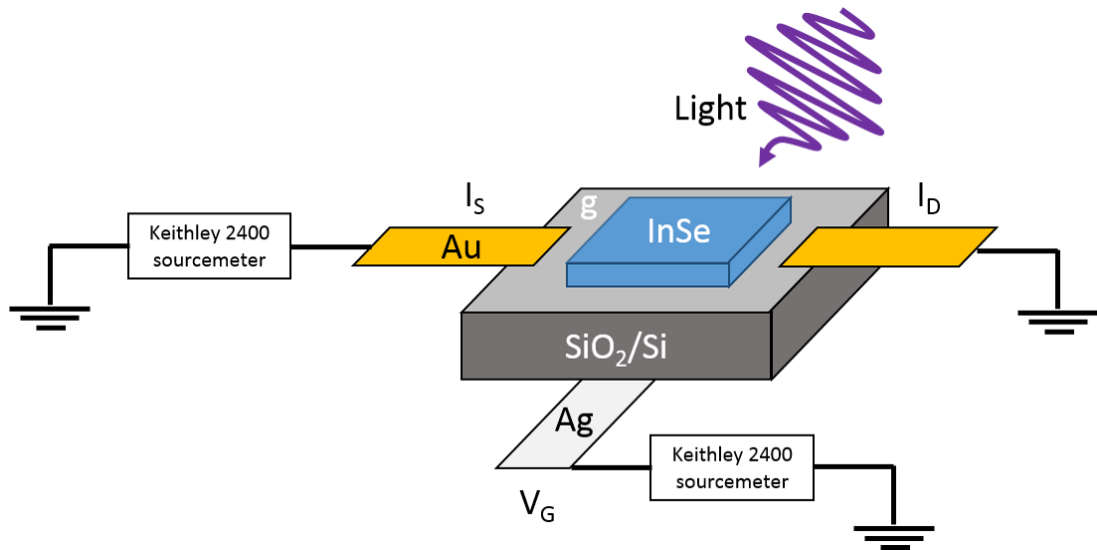


Figure 4-9. Schematic of InSe-capped graphene (g) on a SiO₂/Si substrate, showing the setup used for electrical measurements and the source, drain and gate terminals. The top (Au) contacts provide the source and drain while the base contact (Ag) provides the back gate.

4.5 Device fabrication and metal deposition

Here we discuss the main techniques used for the fabrication of different structures that employ chemical vapour deposition (CVD) grown graphene, gold (Au) contacts and aluminium (Al) transducers.

4.5.1 Graphene patterning

Commercially produced graphene on SiO₂/Si substrates was purchased from Graphenea^[124] with SiO₂ thickness of ~ 300 nm. Individual square pads of graphene (100 µm x 100 µm) were patterned by electron beam lithography (EBL). Two layers of polymethyl methacrylate (PMMA) were spin coated at 4000 rpm for 30 s on the surface of graphene before baking on a hot plate at a temperature of 180 °C for 10 minutes. The first PMMA layer (8% anisole) was allowed to cool to room temperature before application of the second PMMA layer (2% anisole). The bi-layer PMMA acts as a high resolution positive resist for EBL patterning of the square pads. Exposure to the electron beam ‘draws’ the desired pattern in the PMMA by breaking polymer chains. These shorter chains in the desired areas were then dissolved through submersion in a 70:30 solution of isopropanol (IPA):de-ionized water for ~1 min. The areas of the desired graphene pads remained under the unexposed PMMA and the remaining graphene under exposed PMMA. The latter was removed by etching the surface in oxygen plasma. Finally, to remove the PMMA from the graphene pads, the sample was immersed in acetone at a temperature of 60 °C for ~ 1-2 hours before a rinse with isopropanol. Remaining solvent is then dried in pressurized nitrogen gas.

4.5.2 Metal contacts

Once the pads were fabricated, metal (Au and Titanium (Ti)) contacts were applied to the graphene. Here the process of producing a PMMA bi-layer was repeated, as described in the previous section. EBL was then used to ‘draw’ the profile of desirable contacts about the edges of a graphene pad. The exposed PMMA was again dissolved through submersion in a 70:30 solution of IPA:de-ionized water for ~1 min. The remaining unexposed PMMA acts as a stencil for evaporated Au to be shaped into contacts for the graphene pads.

Metal deposition of a Au/Ti bilayer was performed by thermal evaporation in vacuum. Metals are heated sufficiently so that atoms enter a gaseous state (vapour)

and deposit onto a target substrate. First, an initial ~ 10 nm wetting layer of Ti was deposited onto the exposed graphene before a secondary ~ 100 nm layer of Au was deposited. Metals were evaporated onto the surface at a steady rate of ~ 0.3 nms $^{-1}$. Once the sample was cooled to room temperature, excess Au/Ti was removed along with the unexposed PMMA underneath through a lift off procedure. The sample was left in acetone at a temperature of 60 °C for ~ 1 -2 hours before rinsing with IPA, leaving behind the desired contacts on graphene pads. An example of a graphene sample with Au-contacts is shown in Figure 4-10. Large graphene pads ($100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$) with numerous (10) available contacts in a radial pattern were chosen to produce large samples for different experiments. In particular, flakes of InSe and hBN were exfoliated and transferred onto graphene by methods described in Chapter 5.

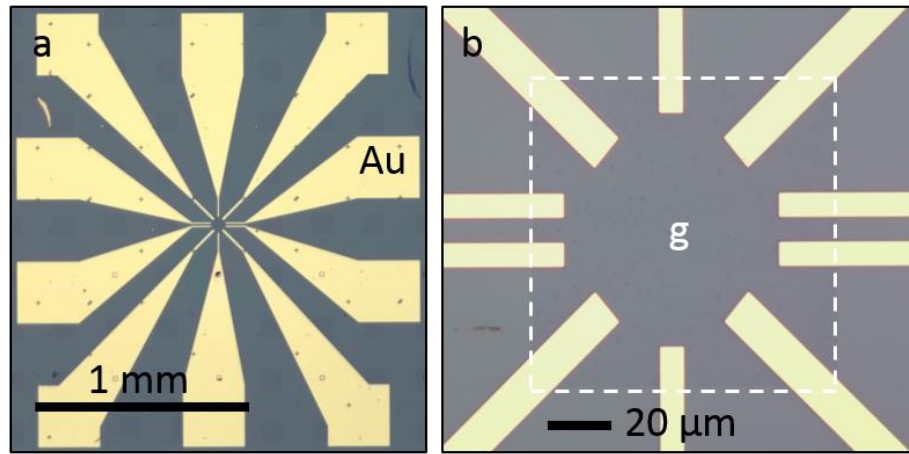


Figure 4-10. Example device showing Au contacts on a graphene pad fabricated by EBL and thermal evaporation of metals. (a) Entire device structure. (b) Optical zoom of the central graphene (g) pad. The white dashed line identifies the graphene layer.

4.5.3 Al transducers

Metal deposition of Al layers onto InSe was conducted by electron beam physical vapour deposition in vacuum. This technique was deemed to produce more uniform layers with greater thickness accuracy than thermal evaporation. Here a target anode (a crucible of Al) was bombarded by an electron beam. The electron beam energy was sufficient to convert target metal atoms into a gaseous state (vapour). The metal atoms precipitate onto the target substrate (*e.g.* InSe) resulting in a uniform film. Al films ~ 35 nm-thick were deposited at a steady rate of ~ 0.05 nms $^{-1}$. Al coated InSe samples are presented and discussed in Chapter 7.

Chapter 5

5 Mechanical exfoliation and dry transfer of van der Waals crystals

The following chapter describes the fabrication processes used in the creation of thin vdW nanolayers and heterostructures. Uniform, thin flakes of InSe or hBN ($d \leq 100\text{nm}$) were exfoliated from bulk crystals and transferred to sapphire, SiO₂ and graphene/SiO₂ substrates by a dry transfer stamping technique. Bulk InSe crystals were grown by Dr. Zakhar Kudrynskyi and Prof. Zakhar Kovalyuk at the Institute for Problems of Materials Science of the National Academy of Sciences of Ukraine, Chernivtsi. Bulk hBN was provided by Prof. Takashi Taniguchi and Prof. Kenji Watanabe at the National Institute for Materials Science of Japan, Tsukuba, Ibaraki. The techniques used here build upon the initial work done by Dr. Garry Mudd at the University of Nottingham and are based on the transfer techniques of Castellanos-Gomez *et al.*^[125]

All vdW nanolayers and heterostructures were prepared by myself at the University of Nottingham except for a single flake of InSe on sapphire which was prepared by Dr. Ryan Beardsley (see Chapter 5, flake labelled R). Flakes fabricated by myself with these techniques were used in a number of studies and resulted in papers published in *Scientific Reports* **6**, 26970 (2016); *Physical Review Letters*, **119**, 157701 (2017); *Physical Review B*, **98.7**, 075408 (2018); *Advanced Functional Materials*, **29**, 1805491 (2019) and *ACS Nano* **13**, 11530 (2019).

5.1 Exfoliation of atomically thin uniform flakes

Exfoliation techniques discussed here are largely based on the techniques used for mechanical exfoliation and isolation of monolayers of graphene from bulk graphite^[1]. Although monolayers of InSe and hBN were not observed through this body of work, monolayers of InSe have been achieved through similar techniques by our colleagues at the University of Manchester^[29]. Also, monolayer hBN can be grown by chemical vapour deposition (CVD) techniques^[9,90]. The techniques discussed here routinely produced uniform thin flakes (down to $d \sim 5\text{ nm}$) with a minimum lateral area of $\sim 10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$. This lateral area size was desirable for different reasons:

a) device fabrication; b) picosecond acoustic measurements with laser spot diameter of $\sim 5 \mu\text{m}$; c) imaging of the samples by picosecond acoustics, μPL and μRaman (see Chapter 4).

The material used here for both exfoliation and transfer of flakes is a Gel Pak DGL/17-X4 polymer film. This is a solid silicone-based film laminate similar to polydimethylsiloxane (PDMS). The film has a thickness of $\sim 0.43 \text{ mm}$ and has sufficient retention strength for exfoliation of thin layers. This ‘elastomer’ allows for a light adhesion to a flake and is commonly used in device storage and transportation^[126].

Figure 5-1 shows how bulk flakes can be mechanically exfoliated into suitable nanolayers for physical studies. Figure 5-1a shows 2 similar structures. A small square of Gel Pak ($\sim 2 \text{ cm} \times 2 \text{ cm}$) is attached to a square glass slide ($\sim 3 \text{ cm} \times 3 \text{ cm}$) with a

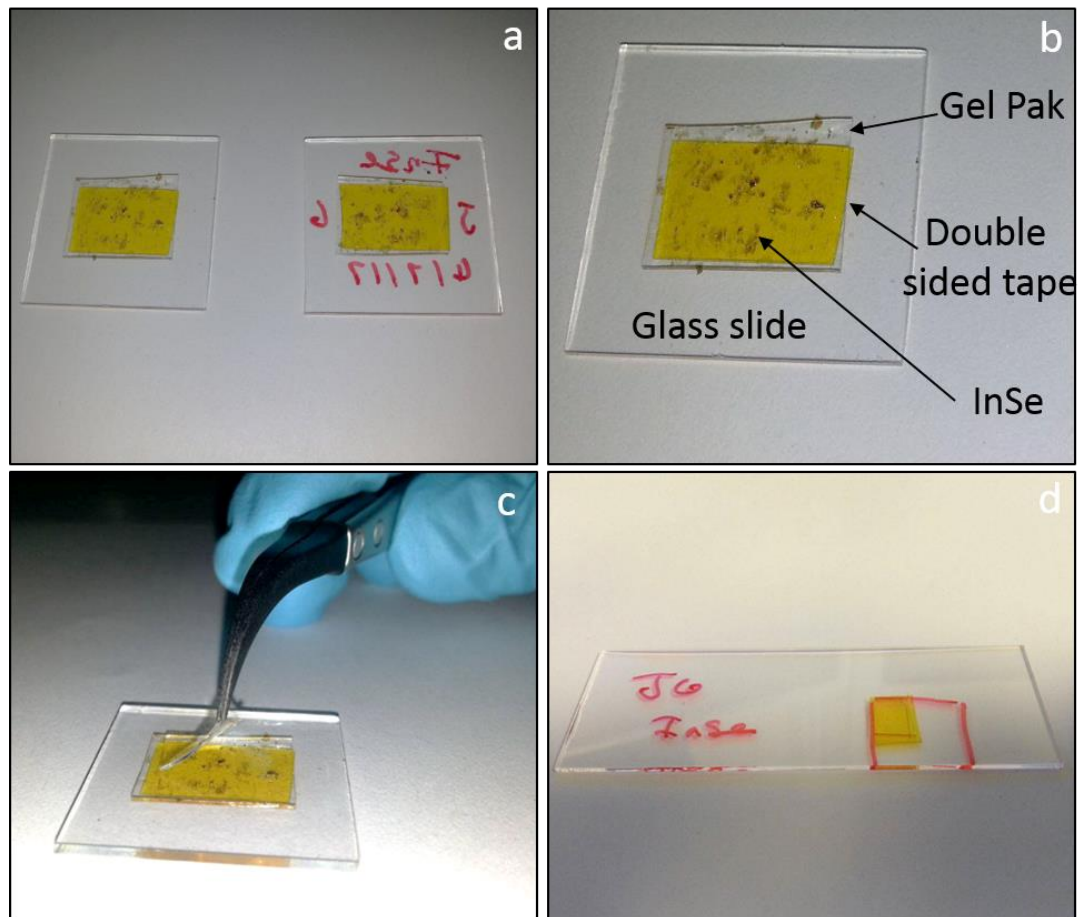


Figure 5-1. (a) Two similar structures consisting of Gel Pak polymer attached to square glass slides for the exfoliation of uniform thin vdWs nanolayers. (b) Wide coverage of InSe flakes exfoliated from bulk. (c) Additional piece of Gel Pak being slowly peeled away from the surface. (d) InSe flakes on Gel Pak polymer attached to a rectangular glass slide ready to be stamped on a substrate. The red square is the approximate stamping region of the system.

double sided tape. First, bulk flakes are deposited onto one of the two Gel Pak surfaces. Then the two Gel Pak surfaces are brought into contact and gently pulled apart. This process is repeated until the Gel Pak surface is evenly covered with flakes (see Figure 5-1b). Once an even coverage is achieved, an additional square of Gel Pak (~1 cm x 1 cm) is placed in contact with one of the 2 surfaces now evenly covered by InSe flakes. Once in contact, the system is left for ~1 hr, so that the polymers can achieve an optimal contact. Figure 5-1c shows a small square of Gel Pak being gently peeled away with tweezers. The polymer is carefully pulled by the corner and is pulled across rather than directly upwards as this assures a slower separation between the polymers in an attempt to maintain nanolayer quality. Stress to the polymer can result in the tearing or folding of flakes.

Finally the Gel Pak is carefully fixed to a rectangular glass slide with double sided tape (see Figure 5-1d). This allows for the optical evaluation of the exfoliated flakes. If desirable flakes are found, the glass slide is placed in the stamping apparatus for dry transfer. The optical contrast between the exfoliated nanolayers and the substrate can be used to select suitably uniform flakes^[127]. If the flake is not uniformly thick, then the contrast would vary as the layer thickness changes.

5.2 Dry transfer of thin flakes on a substrate

Once suitable flakes are identified, they can then be stamped onto a desired substrate. The glass slide with the desirable flake is clamped to the stamping arm of the stamping system. Figure 5-2 shows a schematic of the system used to dry transfer flakes of InSe or hBN. The main features of the system are as follows: A stamping arm with a manually operated micrometer stage stack capable of xyz translation with dual-goniometers for surface alignment correction; a motorised stage capable of 360-degree rotation and xy translation; a microscope display with up to a x50 objective aligned perpendicular to the two horizontal planes brought into contact under stamping (the substrate and the flake to be stamped). The focal point of the microscope can be varied to check that the flake and substrate are suitably aligned up until the point of contact.

It is usual for some drift to occur (of the order of a few μm) in the xy plane as the stamping arm is lowered. The motorized stage and the stamping arm may be used to account for misalignments. It is sometimes desirable to place multiple selected

flakes onto a single substrate. This is possible through careful cutting of the Gel Pak with a scalpel blade after locating a desired flake. By incrementally trimming the edges of the polymer and checking the distance from the polymer edge to the desired flake by microscope, it is possible to create polymer squares as small as $\sim 1 \text{ mm}^2$ around the desired flake. This allows for the transfer of multiple flakes to a substrate without risk of damaging flakes stamped prior with consecutive transfers. This has a secondary benefit, the Gel Pak may trap debris or air pockets when adhering to the tape below. A raised area of the polymer due to trapped debris/air may not allow for successful flake transfer as the mechanical contact between surfaces is compromised. Goniometers may, but not always, correct for this. Trimming the polymer down prior to stamping was noted to reduce this effect.

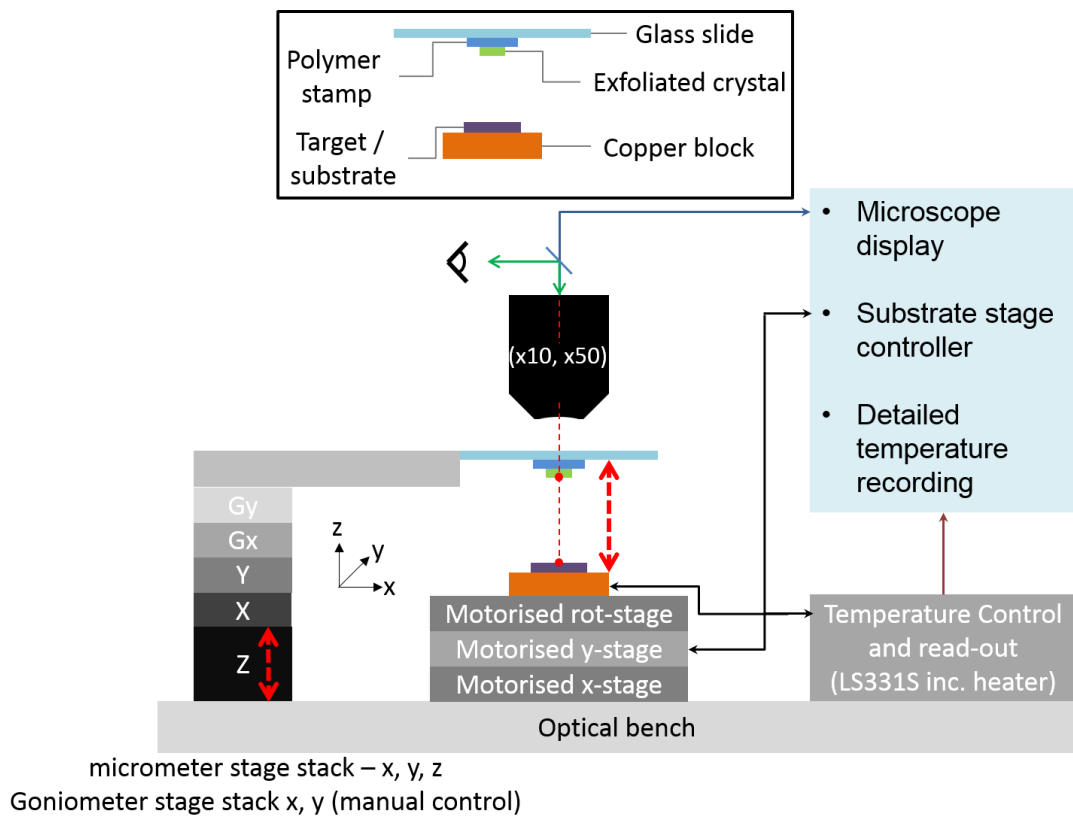


Figure 5-2. Schematic of the stamping system used for the deterministic transfer of flakes onto a substrate. The system sits on an optical bench and features a motorized stage (bottom) capable of xy translation and 360-degree rotation; a stamping arm (left) with xyz translation, dual goniometers and a microscope display.

The target substrate is attached to a copper plate, which can be used to apply heat to the sample. It has been shown for other vdW materials^[128] (e.g. hBN, graphene) that thermal heat can improve the heterostructure interface formed by dry transfer

methods. Temperature controlled exfoliation studies have shown that in the case of graphene, larger monolayers can be achieved through increased temperature^[15]. Novel uses of temperature and appropriate polymers can selectively control whether nanolayers and heterostructures are either stamped to a substrate, or picked up from the substrate^[128,129].

The interfaces of the material to be deposited and the target substrate are brought into contact through lowering of the stamping arm. The point of contact can be detected by the optical contrast change from the polymer contacting the substrate, as illustrated in Ref. [125].

The viscoelastic property of the polymer allows us to vary the adhesion between the polymer and the flake through mechanical manipulation of the viscoelastic polymer. The adhesive strength varies with the peeling rate, causing a ‘kinetic switching’ between adhesion and release of flakes as they are deposited on the substrate^[130,131]. At fast peeling rates the polymer is relatively adhesive compared to the substrate, while at sufficiently slow peeling rates ($\sim 1 \text{ mm s}^{-1}$ or slower in the case of PDMS), the polymer/flake adhesion strength becomes less than that of the substrate/flake adhesion strength and flakes are successfully deposited through preferential adhesion.

Figure 5-3 shows an example of a hBN/InSe heterostructure fabricated using the methods described above. Here a uniform flake of InSe has been stamped onto a SiO_2

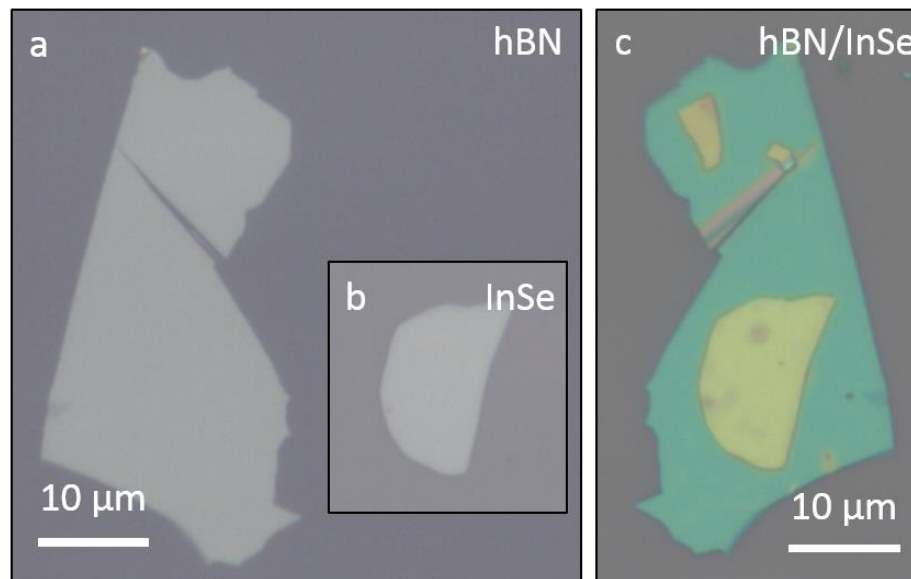


Figure 5-3. (a) Flake of hBN exfoliated onto Gel Pak polymer. (b) Flake of InSe stamped on a SiO_2 substrate by a dry transfer technique. (c) hBN/InSe heterostructure fabricated from the successful stamping of hBN on an InSe flake. Real colour images taken by optical microscope.

substrate and a flake of hBN has been selected as an encapsulation layer. hBN is commonly used as an encapsulating layer for many vdW materials (e.g. GaSe, InSe^[132]) as it is known to preserve the crystal quality and prevent oxidation effects. hBN has also been used as a dielectric gating layer in FETs fabricated from InSe and graphene^[29]. In Chapter 7, the strength of the elastic coupling between InSe and hBN at the vdW interface is investigated using picosecond acoustic techniques.

Figure 5-4 shows an example of a graphene Hall bar partially capped by InSe. Here the translational and rotational capabilities of the stage and stamping arm are needed to assure that the flake of InSe covers half of the Hall bar while avoiding the relatively thick ($d = 100$ nm) gold (Au) contacts. This device has been designed in such a way that the InSe-capped and uncapped graphene sections are connected in series with the same electrical current, I , flowing through both of them (see Figure 5-4b and c). The electrical properties of the two graphene channels can be compared in a simultaneous measurement. Recent low temperature ($T \sim 2$ K) transport measurements at the University of Nottingham on such systems have shown that through transfer of photoexcited carriers across the InSe/graphene vdW interface, the electronic properties of the graphene can be controlled. The Fermi energy of graphene can be tuned across the Dirac point so that the graphene layer can exhibit p or n -type conductivity^[34] through photoexcitation of carriers in the InSe layer. Also, the Hall resistance of graphene can be modified by gate modulated carrier injection into graphene from InSe so that the Fermi level remains pinned between the $n = 0$ and $n = 1$ Landau levels as their degeneracy increases with increasing magnetic field, B .

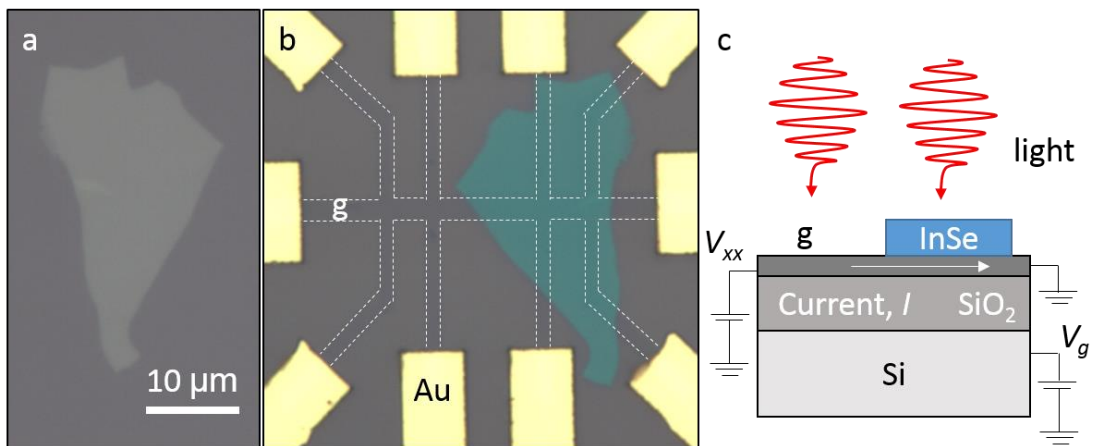


Figure 5-4. (a) Flake of InSe exfoliated onto Gel Pak polymer. (b) Flake of InSe stamped onto a prefabricated graphene (labelled g) Hall bar on a SiO₂ substrate by dry transfer methods. (c) Schematic of the device shown in (b). The white arrow shows the direction of the current, I .

This ‘pinning’ of the Fermi level in InSe-capped graphene leads to an extended giant quantum Hall plateau^[35].

In Chapter 8, the strength of coupling between InSe and graphene at the vdW interface is investigated using picosecond acoustic imaging techniques in an attempt to link charge transfer phenomena and the strength of nanomechanical coupling at the InSe/graphene vdW interface.

5.3 Summary

It is shown that through mechanical exfoliation and dry transfer, it is possible to create multilayer heterostructures and devices from individually exfoliated vdW flakes on a range of substrates. The quality of such samples may be assessed through the observation of physical phenomena dependent on the sample and interface quality. In the case of InSe/graphene Hall bars, there is evidence of charge transfer at the InSe/graphene vdW interface^[29]. This ‘modulation doping’ of the graphene, controllable by electric and magnetic fields has resulted in the observation of a giant quantum Hall plateau and doping tuneable graphene^[34,35]. In InSe based vdW heterostructures measured by a picosecond acoustic technique, there is evidence of ideal elastic interfaces when coherent acoustic phonons are generated in the structure up to frequencies of 100 GHz^[133]. This phenomenon is further discussed in Chapters 7 and 8.

Chapter 6

6 Nanomechanical probing of the layer/substrate interface of an exfoliated InSe sheet on sapphire

The following chapter describes the picosecond ultrasonics experiments in mechanically exfoliated flakes of InSe on sapphire substrates. Coherent acoustic phonons are generated in the InSe layer by the picosecond acoustic techniques described in Chapter 4.2.1 and Chapter 4.2.2. The thickness of InSe flakes was measured by atomic force microscopy (AFM). Flakes were prepared and transferred on sapphire by the methods described throughout Chapter 5. The measurements in the following chapter were the first performed during the work of the thesis, the conclusions of which are developed further in Chapters 7 and 8.

AFM measurements were conducted by myself and Dr. Ryan Beardsley. The picosecond acoustic studies were conducted by myself, Dr. Ryan Beardsley and Prof. Andrey Akimov. The results of this chapter were published in *Scientific Reports* **6**, 26970, (2016).

6.1 Introduction

Experiments with coherent phonons were made possible by the availability of lasers for the generation of ultrashort light pulses. This has led to a new field of research, picosecond (ps) ultrasonics, which has extended traditional acoustics and ultrasonics to higher frequencies and shorter wavelengths^[26,115], thus stimulating and advancing topical research areas in condensed matter physics, including the following.

(i) Phonon transport. Of particular interest is phonon transport through the interface between two nanostructures or between one system and its environment^[27,134-139]. Acoustic mismatch theory, which describes phonon transport through an elastically perfect interface with strong bonds, does not always apply. Thus different approaches are often required to understand and control phonon transport in real systems.

(ii) Phonon interactions. Interactions of coherent phonons with thermal phonons^[140], electrons^[141-145], plasmons^[117,146,147], and magnons^[148-154] are intensively studied in metallic^[155] and semiconductor^[156,157] nanoparticles, multilayered

heterostructures^[143-145,158,159], and patterned surfaces^[117,146,147,150,160]. These interactions underpin a wide range of phenomena, such as piezoelectricity, light scattering, phonon-assisted tunnelling, etc., and the design and successful development of devices for electronics^[161] and optoelectronics^[162].

(iii) Phonon nanoscopy. Coherent phonons with THz frequency can probe interfaces and nanoobjects buried below a surface with atomic depth resolution (e.g., $\ll 1\text{nm}$). Since its first use to probe and control the quality of microchip contacts^[163], nanoscopy has been used to image interfaces^[164,165], chemical reactions^[166], and biological cells^[167]. Also, acoustic, optic and acousto-optic parameters of inhomogeneous materials can be probed with a nanometer spatial depth resolution^[168].

Of critical importance in the studies highlighted in (i)–(iii) is the generation and detection of quantized coherent phonons in various nanoobjects (e.g., in single nanoparticles^[139,155,156,169,170] and quantum wires^[171]). In this case, the phonon spectrum consists of well-defined resonances each with a linewidth Δf that is smaller than the resonance frequency f , and finesse defined by the quality factor $Q=f/\Delta f$. A number of recent works have focused on two-dimensional (2D) nanometer-thick layers where phonons are quantized in the direction perpendicular to the 2D plane. Examples include submicrometer free-standing membranes based on Si^[172], GaAs^[173] and GaN^[174], and phonon nanocavities^[175].

Among 2D systems, van der Waals (vdW) crystals have emerged as a new class of materials for several potential applications. In a vdW crystal, the atoms in each layer are bound by strong covalent bonds, whereas the planes are held together by weak vdW interactions. Thus several physical properties of these materials, including elastic properties (e.g., sound velocity) are strongly anisotropic. The extended family of vdW crystals includes graphene, transition metal dichalcogenides (e.g., MoS₂, WS₂, etc.), metal chalcogenides (e.g., InSe, GaSe, etc.), hexagonal boron nitride (hBN), and many others^[2,176]. For this new class of materials, picosecond acoustics could help to address several important open questions. The interface between two vdW layers or between a vdW layer and its supporting substrate may or may not be elastically perfect, thus influencing thermal and charge transport. For example, the control of phonon transport across a vdW interface could provide a strategy to probe and tune thermal conductivity for specific applications in electronics and thermoelectrics^[2,176-179]. The interaction of coherent phonons with charge carriers

could enable new routes for the generation of microwave frequencies as it is done in nanoelectromechanical (NEMS) systems in the MHz-GHz frequency range^[180], in piezoelectric heterostructures for the sub-THz range^[181], and traditional semiconductor devices such as Schottky diodes^[141,182] and tunneling devices^[142]. Also, due to strong elastic anisotropy and phonon quantization, 2D vdW layers could provide an ideal system for phonon nanoscopy and nondestructive sensitive imaging of molecules and cells coupled to the nanolayers by vdW forces. Although these research areas are still in their infancy, recent experimental works have demonstrated the possibility of generating coherent phonons in vdW nanolayers, including graphene^[136], WSe₂^[183], WTe₂^[184] and MoS₂^[185].

The picosecond acoustic technique described in Chapter 4 was used to observe the coherent elastic vibrations of the fundamental thickness mode of InSe nanolayers on a sapphire substrate and to measure the values of f and Q for the nanomechanical acoustic phonon resonances. The comparison of the experimental results with a simple theoretical analysis enables us to assess the mechanical adhesion of InSe on the substrate. In this chapter it is demonstrated that InSe layers with a thickness between 50 and 120 nm can behave effectively as a free standing membrane with frequency in the range of tens of gigahertz.

6.2 InSe crystals on sapphire

Data for the 5 InSe flakes measured and discussed in this chapter are shown in Table 6-1. The thickness of the flakes, as measured by AFM, and the corresponding frequency of the resonances, as measured by picosecond acoustics, are shown for the different samples. The theoretical frequencies for free standing flakes and elastically ideal interfaces, where acoustic mismatch is valid, are shown on the right of Table 6-1. The calculations are discussed further in Chapter 3.4 (See Eqs. (38) and (40)). These data are discussed further in the following sections of this chapter. Optical images of flakes 2-5 are shown in Figure 6-1. The optical contrast indicates that the thicknesses are uniform across large areas of the flakes. AFM data for these flakes are shown in Figure 6-2. The AFM images and z-profiles show uniform thicknesses d , with fluctuations of up to ± 5 nm. Flake 2H (Figure 6-1c and Figure 6-2c) shows a relatively large variation of d about the flake edge. This could be due to the flake being deformed or damaged by the stamping process. Picosecond acoustic measurements were taken

Flake	Thickness, d , AFM (nm)	Frequency, f , (GHz)			
		Measured	Calculated		
			$n = 1$ (free)	$n = 1$ (ideal)	$n = 2$ (ideal)
1 (R)	114 ± 2	11.6 ± 0.4	11.0	5.5	16.4
2 (1A)	100 ± 4	13.3 ± 0.1	12.5	6.3	18.9
3 (1C1)	94 ± 5	13.4 ± 0.3	13.3	6.6	19.9
4 (2H)	57 ± 4	26.2 ± 1.1	21.9	11.0	32.9
5 (2A)	54 ± 3	23.1 ± 0.6	23.1	11.6	34.7

Table 6-1. The measured thicknesses and resonant frequencies of 5 InSe flakes exfoliated on a sapphire substrate. The expected resonant frequencies for free standing and elastically ideal interfaces are calculated from the measured thickness.

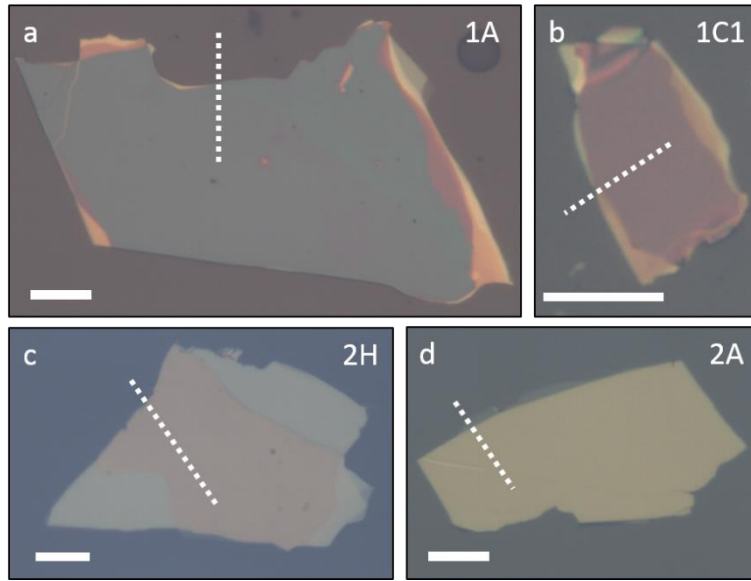


Figure 6-1. Optical images of 4 InSe flakes exfoliated onto a sapphire substrate. (a) corresponds to flake 1A, a 100 nm thick flake; (b) corresponds to flake 1C1, a 94 nm thick flake; (c) corresponds to flake 2H, a 57 nm thick flake; (d) corresponds to flake 2A, a 54 nm thick flake. Scale bar = 10 μm for all flakes. Dashed line – AFM profile locations for Figure 6-2.

about the centre of the flakes and not at the edge. Thus the thickness at this flake edge was not considered in the analysis of the data.

The AFM images in Figure 6-2 show some areas where bubbles have formed on the InSe surface, most notably these can be seen in flake 1A (Figure 6-2a) and flake 2A (Figure 6-2d). The AFM measurements on these flakes were completed after the

picosecond acoustic studies so as not to risk damaging the samples. The optical images from Figure 6-1 were taken immediately after stamping the flakes on sapphire, prior to the picosecond acoustic measurements. For these flakes no bubbles were observed. The formation of bubbles over time could be due to flake oxidation or from prolonged exposure of the flakes to the pump and probe beams.

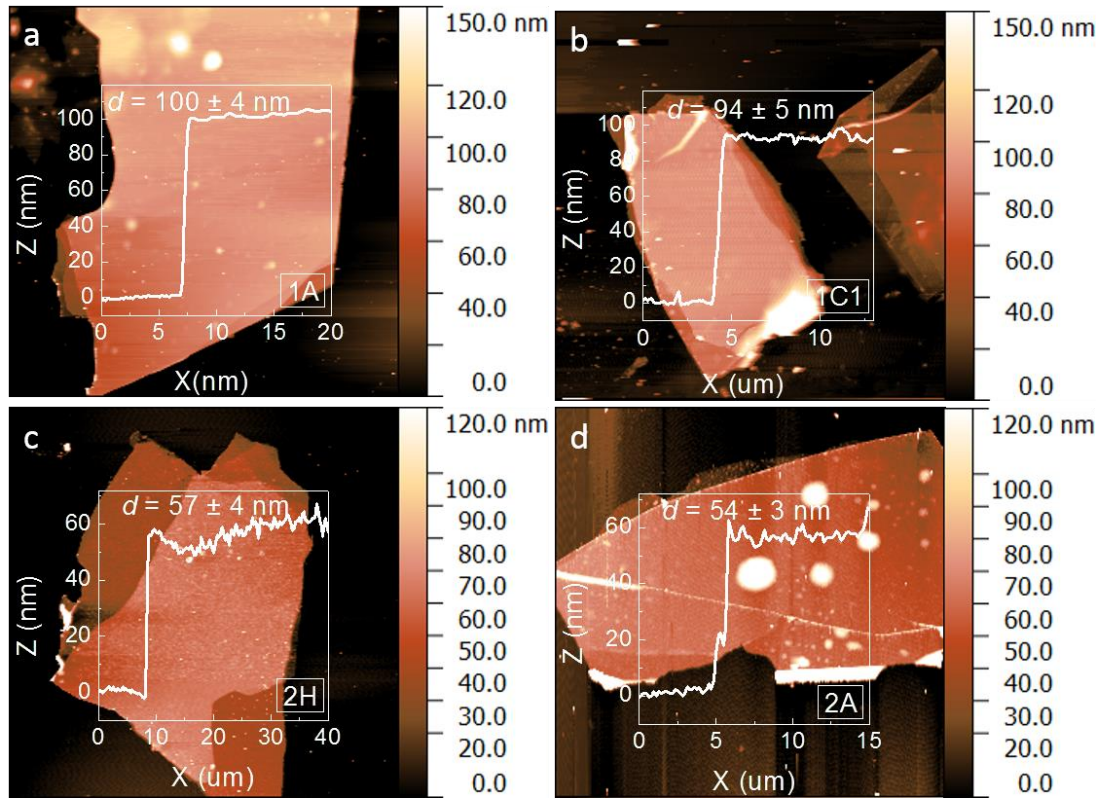


Figure 6-2. (a)-(d) AFM data for flakes 2-5. AFM profile locations seen in Figure 6-1.

6.3 Coherent acoustic spectra of InSe layers

Typical coherent acoustic phonon spectra are shown for 4 flakes of InSe on a sapphire substrate in Figure 6-3. The spectra exhibit strong peaks at frequencies coinciding with the fundamental mode ($n = 1$) of a freestanding flake, as seen in Table 6-1. As flakes become thinner, the signal tends to be weaker and harder to detect. Common in many spectra is the presence of a small peak around ~ 10 GHz. This is an artefact from the process of fitting and subtracting a background signal from the temporal scan (insets in Figure 6-3), where slight curvature remains across the modified signal. For the fitting process, each sample requires a slightly different routine as the profile of the decaying temporal scans exhibit varying degrees of exponential decay. First the region of data where clear oscillations are present is

isolated (typically ~ 0.3 - 0.4 ns) and the data is fitted by either a moving average approximation or exponential decay curve. This is then subtracted from the temporal scans which gives temporal oscillations free of the decaying background signal which are suitable for Fourier transform. The absolute value of the Fourier transform reveals the amplitude spectral density which shows the magnitude of signal components in units of frequency that constitute the temporal signal. Signals were measured across uniform regions on samples to check for consistency. Measured values of frequency for flakes (Flakes 1–5) with different thickness d are shown in Table 6-1. It can be seen that the measured frequency of the oscillations tends to increase with decreasing d . For flakes with $d < 50$ nm no oscillations were detected.

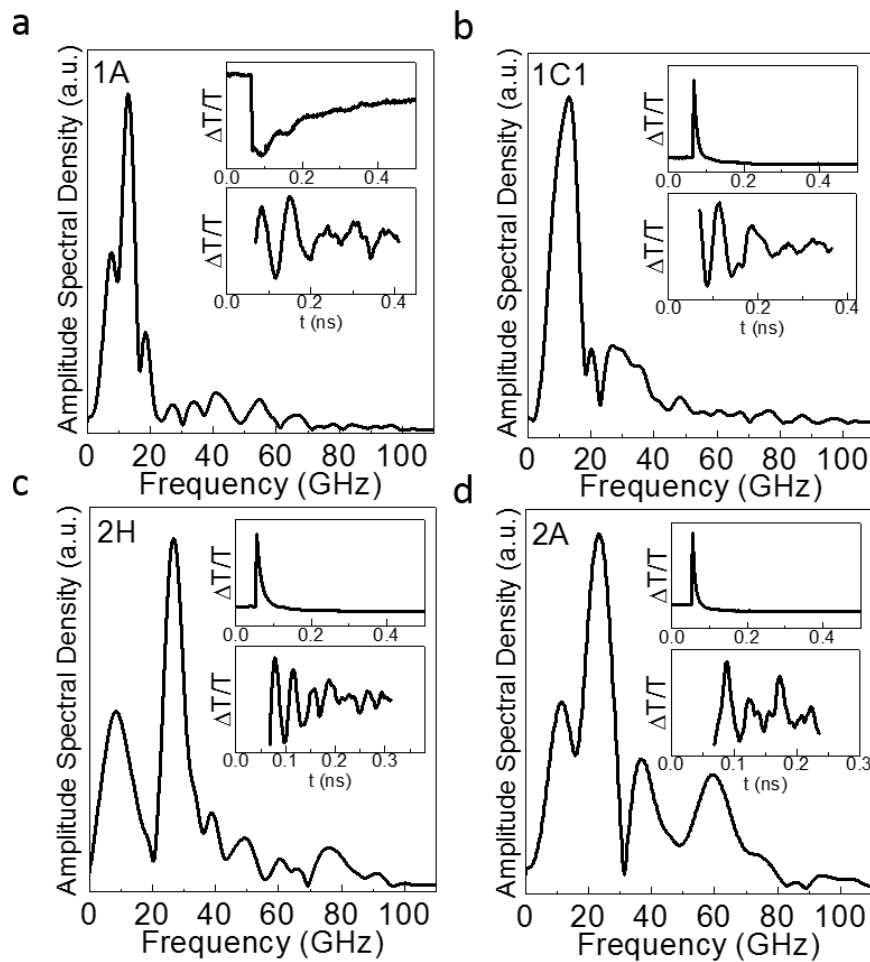


Figure 6-3. Example spectra of 4 InSe flakes on a sapphire substrate. a) corresponds to a 100nm thick flake; b) corresponds to a 94nm thick flake; c) corresponds to a 57nm thick flake and d) corresponds to a 54nm thick flake. Inset: temporal scan (top) and oscillations once the background has been subtracted from the original data.

6.4 The InSe/Sapphire interface: discussion of free and non-free standing layers

Over the last decade oscillatory signals have been observed in picosecond acoustic pump-probe experiments with thin films on substrates^[186-189] and free standing membranes^[172]. These oscillations are attributed to the nanomechanical vibrations of the film in the direction perpendicular to the plane of the layer. Such vibrations correspond to the excitation of coherent longitudinal acoustic (LA) phonons with frequencies governed by the value of the layer thickness and boundary conditions of the nanolayer at the interfaces. As discussed in Chapter 3, in the free standing layers (i.e. membranes), the surfaces are free and the displacements at both surfaces possess anti-nodes. The frequencies of these nanomechanical resonances are:

$$f = \frac{ns_{LA}}{2d}, \quad (59)$$

where s_{LA} is the longitudinal sound velocity in the direction perpendicular to the layer plane, d is the layer thickness and n is an integer. The mode with $n = 1$ corresponds to the modulation of the layer thickness and is known as the fundamental breathing mode. The distribution of strain and displacement modes in such a layer are harmonic functions with wavelength equal to the half wavelength of the corresponding acoustic wave in the bulk. The quality factor of the mechanical resonances is $Q = f/\Delta f$, where Δf is the linewidth of resonances. This is determined by the scattering of phonons and the inhomogeneity of the film thicknesses.

For layers supported by a substrate with an ideal interface, the spectrum depends on the acoustic mismatch. This is described by the difference in the acoustic impedances, $Z_i = \rho_i s_{i,LA}$ where the subscript i defines the layer and ρ_i is its density. As discussed in Chapter 3. When the layer has lower impedance than the substrate, the frequencies of the nanomechanical resonances are:

$$f = \frac{(2n-1)s_{LA}}{4d}, \quad (60)$$

where $n = 1, 2, \dots$. When the layer impedance is higher than that of the substrate, the equation for the resonance frequencies is the same as for the free standing membrane, described in Eq. (59). The Q -factor of the resonances for supported nanolayers is governed by the reflection R of phonons at the interface:

$$R = \frac{|Z_l - Z_s|}{|Z_l + Z_s|}, \quad (61)$$

where the indexes l and s correspond to the layer and substrate, respectively. It is important to note that Eq. (61) is valid only for the case of perfect elastic contact between the layer and the substrate, i.e. an elastically perfect interface. If this condition is not met, other sophisticated theoretical approaches such as the spring model described in Chapter 3^[27] should be used. This will be discussed further in Chapter 7. For comparison of the experimental results with Eqs. (57)-(61), we use the parameters for the InSe layer and sapphire substrate shown in Table 6-2.

	s_i^{LA} (km/s)	ρ_i (g/cm ³)	Z_i^{LA} (MPa·s/m)
InSe	2.5 ^[190]	5.5	14
sapphire	11	4	44

Table 6-2. Acoustic parameters of InSe and sapphire used in this work.

As shown in Table 6-2, the acoustic impedance of the sapphire substrate is significantly higher than that of the InSe layer and so, in the case of an elastically perfect interface, the fundamental thickness mode ($n = 1$) should be calculated using Eq. (60). However, Flake 1, for instance, with $d = 114$ nm, gives a value of $f_1 = 5.5$ GHz, which is a factor of two smaller than the measured value of 11.6 GHz. Eq. (60) for the next resonance, $n = 2$, gives $f_2 = 16.5$ GHz, which is a factor of 1.4 larger than the measured value.

The only way to recover the measured value by calculation is to use Eq. (60), which corresponds to the case of a free standing InSe layer: the calculated value is $f_1 = 11.0$ GHz, which is in good agreement with the measured value. This agreement leads us to conclude that the interface between the InSe and the substrate should not be considered as a perfect elastic interface. Also, we estimate the reflectivity of acoustic phonons as $r = \exp(-\pi/Q)$ ^[186], where $Q = f/\Delta f$. From the values of Q measured in various positions on the InSe nanolayer, we obtain $r = 0.64$ – 0.91 . Similar conclusions can be applied to other flakes, see Table 6-1. An excellent agreement between the measured and calculated values of f as for free-standing layers is obtained for Flakes 3 and 5. In contrast, small differences are noticed for flakes 1, 2 and 4. However, a more sophisticated theoretical analysis^[27,28] of the nanomechanical vibrations in the nanolayers shows that f depends on the elastic coupling parameter at the interface, thus resulting in values of f that may differ from those corresponding to the extreme cases of weak and ideal elastic coupling, as described by Eq. (59) and Eq.

(60), respectively. Figure 6-4 illustrates a comparison between experimental data and expected theoretical values for free standing InSe flakes of various thicknesses.

The most likely reason for the imperfectness of the interface is surface roughness of the substrate rather than that of the InSe layer, which tends to form abrupt and atomically smooth interfaces with other layered compounds^[101]. AFM measurements show the roughness of the substrate to be ~ 10 nm, which is higher than the thickness deviations in the InSe flake. To achieve an elastically perfect interface between the substrate and the exfoliated layer, the surfaces should be flat and clean down to the atomic level. The roughness of the substrate surface in our sample is far beyond this level. Thus it is unlikely that mechanical exfoliation of InSe on a rough substrate can provide an ideal elastic contact between the two materials.

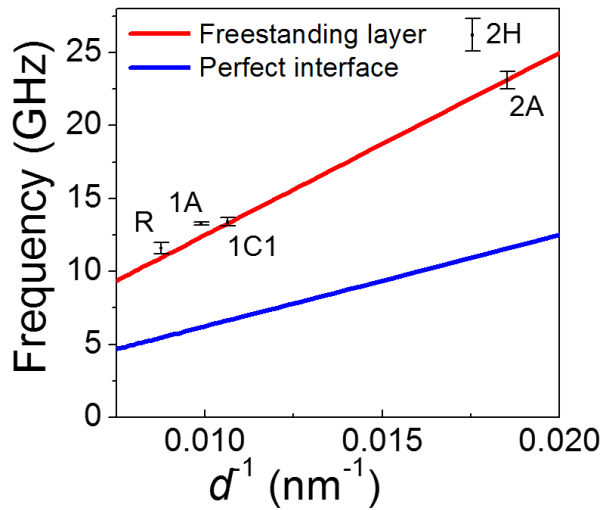


Figure 6-4. Peak phonon spectra frequencies plotted against the inverse thickness, d^{-1} , for the 5 InSe flakes measured by picosecond acoustics. Plotted alongside the data are the expected phonon frequencies for free standing InSe flakes (red), as calculated by Eq. (57), and ideal InSe-sapphire interfaces (blue), as calculated by Eq. (60).

6.5 Summary

It is shown that an elastically imperfect interface tends to form between a sapphire substrate and an exfoliated van der Waals InSe crystal with thicknesses down to about 50 nm. With respect to the properties of interfaces between thinner flakes and/or other substrates, additional experiments have been performed in Chapters 7 and 8. Nanomechanical probing of an interface using coherent phonons is successfully demonstrated.

The findings suggest applications where the elastic properties of such an interface may be exploited. For example, layered structures with elastically imperfect interfaces may still possess efficient carrier transport and thus provide a high efficiency or figure of merit, ZT , in thermoelectric nanodevices^[19,20,191]. The figure of merit is defined as

$$ZT = \frac{\sigma S^2 T}{\kappa}, \quad (62)$$

where S is the Seebeck coefficient, T is the temperature and σ and κ are the electrical and thermal conductivities, respectively. The figure of merit is a unitless measure of performance based on interconnected thermoelectric physical parameters. High electrical conductivity, Seebeck coefficient and low thermal conductivity are necessary in order to maximize the figure of merit and efficiency of thermoelectric materials^[20]. A value of ~ 1 is considered a benchmark for efficient thermoelectric performance^[19]. The anisotropic nature of materials such as InSe would impact the figure of merit depending whether measurements are in or out of plane. The value of ZT monolayer InSe has been theoretically estimated at around 0.2 – 0.35 in the zigzag direction and 0.1 – 0.4 in the armchair direction, at 300 K^[192].

Alternatively, if the 2D nanolayer requires efficient thermal coupling to a substrate heat sink, the deposition of a soft nanometer transition layer (e.g. a polymer) on the substrate surface and annealing after the exfoliation may be included in the device fabrication procedure. The present work also indicates that nanomechanical probing of interfaces between 2D semiconductor layers and a substrate, or other nanolayers, could be successfully used for the study of elastic interface properties and hence the development of methods to control these interface properties.

Chapter 7

7 Coherent acoustic phonons in van der Waals nanolayers and heterostructures

The following chapter describes the detailed studies of nanomechanical resonances in vdW heterostructures based on InSe and hBN on a sapphire substrate. The chapter expands the scope of Chapter 6 by focussing on studies of the interface between two vdW crystals, as well as the substrate/heterostructure interface. Coherent acoustic phonons are generated and detected in the InSe layer by the picosecond acoustic technique described in Chapter 4. The theoretical acoustic spectra of the various samples documented herein are determined by the spring model described in Chapter 3.5.2. The thickness of InSe flakes was measured by atomic force microscopy (AFM). Flakes were prepared and transferred by the methods described in Chapter 5.

AFM measurements were conducted by myself while picosecond acoustic techniques were conducted by myself and Prof. Andrey Akimov. The results of this chapter were published in *Physical Review B*, **98**, 075408, (2018).

7.1 Introduction

During the last decade, techniques for the generation and detection of coherent acoustic phonons with frequencies from tens of gigahertz (GHz) to several terahertz (THz) have enabled novel approaches to the investigation of a wide range of materials and nanostructures. For the realization of novel hybrid systems fabricated from various vdW layers, it is important to understand the properties of the interface between the semiconductor nanosheet and the substrate or a neighbouring vdW layer. Most of the studies performed on van der Waals heterostructures to date have been directed towards the measurement of the electron transport through the heterostructure or of the charge transfer at an interface^[176]. However, the phonon transport through an interface plays an equally important role^[17,18] as it defines the cooling rate and so governs the thermal properties of a multi-layer structure. In particular, the balance of electron and phonon transport between nanolayers determines the efficiency, or figure of merit, ZT , to produce thermoelectric power in thermoelectric devices^[19,20,191]. This

is expected to be enhanced in metal chalcogenide thin layers due to the singularity in the density of states and the large number of conducting modes near the band edge^[193].

The microscopic origin of the phonon transport and thermal conductance through the interface of a nanodevice lies in the strength of the elastic bonds between atoms at the surfaces of two contacting materials. The interlayer phonon modes in 2 dimensional (2D) nanolayers have been studied using Raman scattering^[23]. However, the bonds may not be perfect across the whole area of the nanolayer; in this case, an effective way to study them is to monitor the nanomechanical vibrations of the nanostructure^[27,135,194,195]. 2D nanolayers possess nanomechanical (i.e. phonon) resonances in the gigahertz (GHz) and terahertz (THz) frequency ranges (see Chapter 3). The frequency f and quality factor Q of these resonances depend on the elastic properties of the nanolayer/nanolayer or nanolayer/substrate interface, depending on the particular structure, and thus provide information about the elastic bonds at the interface.

Here, we use coherent phonons with frequencies from 10 to 100 GHz, generated and detected using ultrafast optical (pump-probe) methods, for the nondestructive investigation of nanomechanical oscillations in InSe nanolayers and InSe/hBN heterostructures. These studies enable us to probe the vdW bonding between the layers and their adhesion to the substrate. The GHz and sub-THz nanomechanical oscillations have frequency, amplitude, and spectral width that depend on the stiffness of the interfacial bonds at the interface. In particular, we find that the interface between InSe and hBN can be described by acoustic mismatch over a wide frequency range $f \leq 100$ GHz, as attested by use of the spring model described in Chapter 3.

7.2 InSe based heterostructures and InSe nanolayers on sapphire

Data for the samples measured and discussed in this chapter are shown in

. The thickness of the flakes, as measured by AFM, and the corresponding interface coupling strengths, as measured by picosecond acoustics, are shown for the different samples. All samples are on a sapphire substrate. Samples based on thin (<70 nm) InSe layers contain an Al transducer deposited on top of InSe or hBN/InSe. These data are discussed further in the following sections of this chapter. The coupling parameters G_S and G_H for each sample are presented on the right.

Sample	InSe thickness (nm)	hBN thickness (nm)	Al thickness (nm)	G_{S1} (GHz)	G_{S2} (GHz)	G_H (GHz)
InSe	114 ± 2			4		
	100 ± 4			20		
	94 ± 5			70		
InSe/hBN	50 ± 6	81 ± 4		10		1000
hBN/InSe	44 ± 4	70 ± 5				1000
InSe(T)/InSe(B) T = Top, B = Base	77 ± 4 (T) 50 ± 3 (B)			26		1000
Al/InSe	41 ± 2		33 ± 5	8	1000	
Al/InSe	12.0 ± 2.0		38 ± 4	13	90	
	6.5 ± 0.6		38 ± 4	13		
	5.4 ± 0.8		38 ± 4	26		
Al/hBN/InSe	10 ± 3	14 ± 3	35 ± 2	10		1000

Table 7-1. Measured thicknesses and coupling parameters G_S and G_H for the samples discussed in this chapter.

These parameters are extracted from our ‘spring’ model (as discussed in Chapter 3) and describe the strength of coupling at the interfaces of a vdW flake and the underlying substrate (G_S) or the strength of coupling between 2 adjacent vdW nanolayers in a heterostructure (G_H). The coupling parameters can be expressed as:

$$G_H = \eta_H \frac{Z_1 + Z_2}{2\pi Z_1 Z_2}, \quad (63)$$

and

$$G_S = \eta_S \frac{Z_S + Z_2}{2\pi Z_S Z_2}, \quad (64)$$

where Z_1 , Z_2 , and Z_S are the acoustic impedances of the outer, inner nanolayers, and substrate, respectively, and η_H and η_S are the strength of the effective ‘springs’ at the heterostructure and substrate interfaces, respectively. These parameters characterize the spring constant per unit area and have units Nm^{-3} . The parameters G_S and G_H have the dimension of frequency. If the values of G_S and G_H are large compared to the

resonant phonon frequencies f , then the interface is assumed to be ideal and described by acoustic mismatch (AM). Conversely, if the value of G_S and G_H are relatively small compared to the frequency range of the experiment, then a broken interface is assumed. In some cases, more than one value of G_S was needed to describe the spectra.

A reminder of the various pump probe configurations used in this chapter are shown in Figure 7-1 alongside a reminder of the background subtraction of the temporal data prior to Fourier transform to produce the amplitude spectral density. The fitting process is the same as that described in Chapter 6.3. Theoretical spectra are calculated using the spring model described in Chapter 3.5. Here, resonances and their profiles (amplitude and width) are determined entirely by the layer thicknesses, the elastic properties of the layers and the subsequent acoustic mismatch, and the strength of coupling at the interfaces. Resonant peaks in the theoretical spectra can be shifted and broadened by varying the strength of the coupling parameters, G_S and G_H . For example, resonant phonons in an InSe layer that is weakly coupled at its interfaces will not readily decay due to poor transmission and a narrow resonant peak is expected. Conversely, strong coupling at the interface will lead to the resonant phonons decaying more readily and a broad peak is expected.

Optical images of the InSe/hBN, hBN/InSe and InSe/InSe heterostructures are shown in Figure 7-2. Optical images of the Al coated nanolayers are shown in Figure

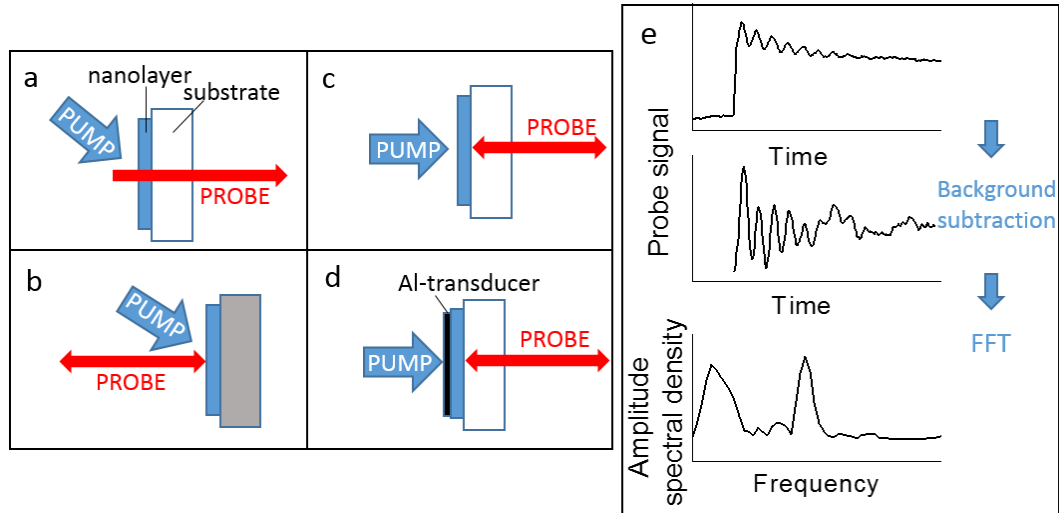


Figure 7-1. (a)-(d) Schemes for pump-probe experiments in transmission (a) and reflection (b), (c), (d) geometries. The stress in the nanolayers is excited directly (a-c) or through an Al-transducer (d). (e) (top panel) temporal signal; (middle panel) temporal signal after subtraction of a slow decaying background; (bottom panel) phonon spectrum obtained by fast Fourier transform (FFT) of the temporal signal after subtraction of the background.

7-3. The optical contrast indicates that the thicknesses are uniform across large areas of the flakes. AFM data are shown in Figure 7-4. These are described further in Chapter 4.

The AFM images and z-profiles show uniform thicknesses d , with fluctuations of up to ± 6 nm in the case of bulk InSe and hBN. Thinner flakes of InSe show smaller

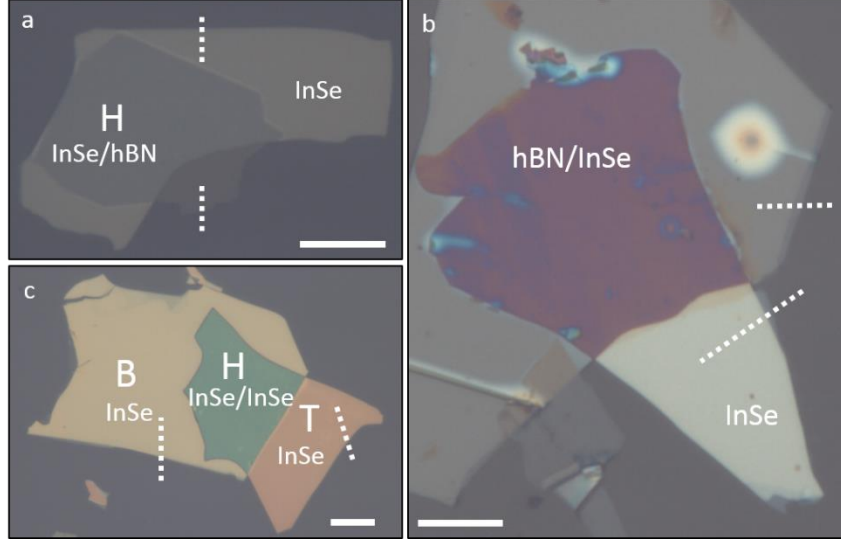


Figure 7-2. Optical images of 3 InSe and InSe-hBN heterostructures on a sapphire substrate. (a) InSe/hBN heterostructure. InSe thickness = 50 nm. hBN thickness = 81 nm. (b) hBN/InSe heterostructure. hBN thickness = 70 nm. InSe thickness = 44 nm. (c) InSe/InSe homojunction. InSe (T) thickness = 77 nm. InSe (B) thickness = 50 nm. Scale bar = 10 μ m for all flakes. Dashed line – AFM profile locations for Figure 7-4.

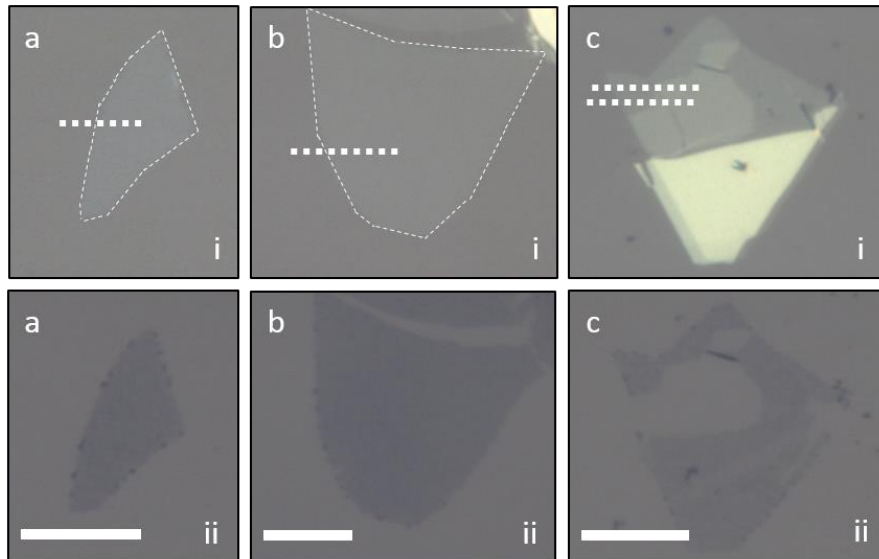


Figure 7-3. Optical images of 2 thin InSe flakes (ai-bi) and an hBN/InSe heterostructure (ci) on a sapphire substrate. (aii-cii) Optical images after Al deposition. Al thickness = 35 nm. (a) InSe thickness = 5.4 nm (b) InSe thickness = 6.5 nm (c) hBN thickness = 77 nm. InSe thickness = 50nm. Scale bar = 10 μ m for all flakes. Dashed line – AFM profile locations for Figure 7-4.

thickness fluctuations of up to ± 3 nm. The AFM images in Figure 7-4 show some areas where bubbles have formed on the InSe surface, most notably these can be seen in Figure 7-4c and e. The AFM measurements on these flakes were completed after the picosecond acoustic studies so as not to risk damaging the samples. The optical images from Figure 7-2 and Figure 7-3 were taken immediately after stamping the heterostructures on sapphire, prior to the picosecond acoustic measurements. For these heterostructures, generally no bubbles were observed optically, except for the case of Figure 7-2b, where an uneven surface is present about the edges of the heterostructure boundary and is identified by colour variation in the optical contrast. Our measurements avoided these areas. As in the cases seen in Chapter 6, the formation of

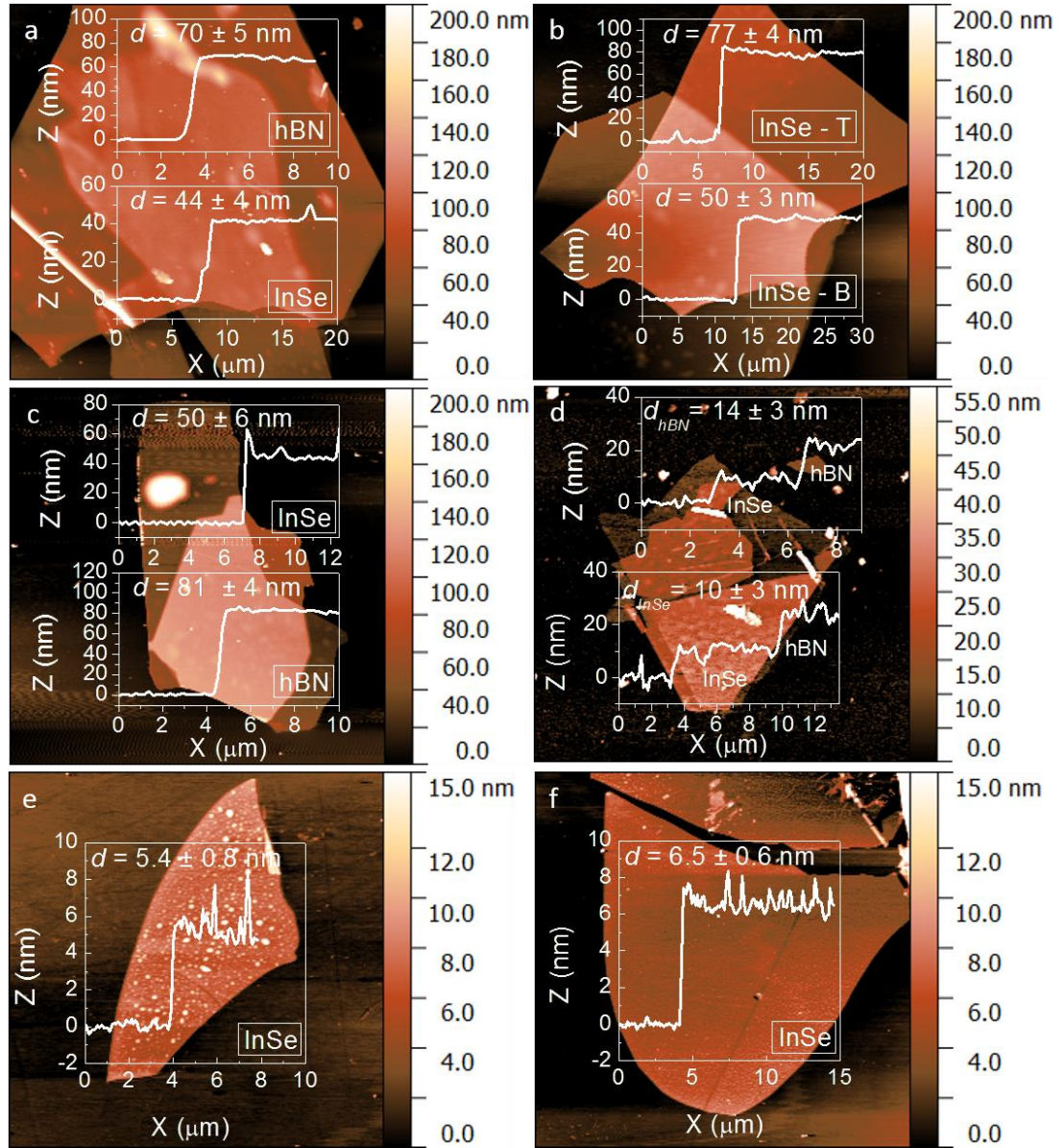


Figure 7-4. (a)-(f) AFM data for the samples seen in Figure 7-3 and Figure 7-2.

bubbles over time could be due to flake oxidation or from prolonged exposure of the flakes to the pump and probe beams.

Figure 7-1 shows the 4 different pump-probe alignments used on samples in this chapter. Bulk flakes and heterostructures were measured in the transmission and reflection geometries shown in Figure 7-1a and c, respectively. Thin flakes and heterostructures were measured in the geometry shown in Figure 7-1d where a thin transducer layer of Al was used to generate and detect nanomechanical resonances. Figure 7-1c shows an example of how reflection could be measured for a sample on a non-transparent substrate such as SiO₂. Figure 7-1e shows how the resonant frequencies are extracted from the temporal scans through removal of the background signal and use of fast Fourier transform (FFT).

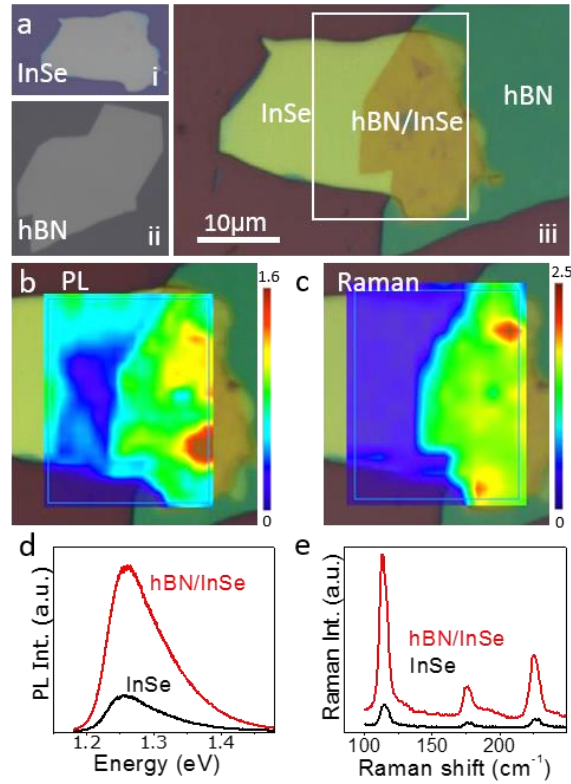


Figure 7-5. (a) Optical images of InSe and hBN layers before [(i) and (ii)] and after (iii) their stacking to form an InSe/hBN heterostructure on a SiO₂ substrate. The rectangle in part iii is mapped by μPL and μRaman in part [(b) and (c)]. [(b) and (c)] Maps of the μPL (b) and μRaman (c) intensities for the sample shown in part (a-iii). Each map is overlaid on the optical image of the sample and shows the InSe and hBN/InSe areas. [(d) and (e)] Representative μPL (d) and μRaman (e) spectra for InSe before (black) and after (red) the stamping of the hBN layer

7.3 Photoluminescence and Raman spectra on InSe nanolayers and heterostructures

Figure 7-5 shows the optical images for an InSe/hBN heterostructure and the individual InSe and hBN layers prior to stamping of hBN on InSe. Room temperature ($T = 300$ K) μ -photoluminescence (μ PL) and μ -Raman maps, and representative spectra are shown in Figure 7-5b–e. By comparing the spectra acquired in areas with and without the hBN layer, we find that the encapsulation of InSe by hBN does not modify the energy of the Raman modes and/or of the PL emission of pristine InSe. However, it induces a significant increase of both Raman and PL signals. This behaviour, which is not observed when the hBN layer lies below the InSe layer, is indicative of an increased absorption of light by the InSe layer due a smaller reflection of the laser light at the interface between air and hBN (refractive index $n_{\text{hBN}} = 1.8^{[196]}$), compared to air ($n_{\text{air}} = 1$) and InSe ($n_{\text{InSe}} = 2.7^{[103]}$).

7.4 Coherent acoustic spectra of InSe nanolayers

Experiments on relatively thick ($a \sim 100$ nm) InSe layers were carried out using the schemes described in Chapter 4.2.1 and Chapter 4.2.2. A simple schematic is shown in Figure 7-1a. Figure 7-6 shows the measured coherent phonon spectra for three separate InSe layers with approximately the same thickness $a \sim 100$ nm on a sapphire substrate. The background free temporal evolutions are also shown in the insets of Figure 7-6. It can be seen that all spectra consist of a distinct spectral line between 10 and 20 GHz. Despite the layers having similar thicknesses, the lines are centred at different frequencies and the spectral width is twice larger for the lowest curve. Blue and red vertical bars indicate the phonon frequencies calculated from AM and weak elastic coupling of the layers with the substrate, respectively.

The values of G_S obtained from the comparison of the measured and calculated spectra are shown in the same graph. The resonance at the top of Figure 7-6 indicates a regime of weak coupling of InSe to the substrate; the one at the bottom has a broad spectral line centered at a frequency equal to that expected from AM; the middle spectrum shows instead two lines that cannot be described by a single coupling parameter G_S : the spectral lines centered at 13.4 and 18.0 GHz are reproduced by the spring model with $G_S = 1$ and 20 GHz, respectively. Thus, from this study, we conclude that InSe layers on sapphire can exhibit different mechanical properties and

elastic coupling to the substrate. This result extends the results presented in Chapter 6 where we have shown the behaviour of InSe flakes on a sapphire substrate to be like free-standing layers. Here, we show through numerous systematic studies that the coupling strength may vary from that of acoustic mismatch to free-standing layers.

Experiments with thinner InSe layers were performed using the scheme shown in Figure 7-1d using an Al transducer. The deposition of the Al film by electron beam evaporation on InSe produced a uniform high-quality thin (33 nm) film. Thus we expect strong elastic coupling for the Al/InSe interface. Figure 7-7 shows the measured and calculated phonon spectra for an InSe layer with thickness $a = 41$ nm on sapphire.

Four lines can be seen in the measured spectrum of the 41-nm-thick InSe layer (Figure 7-7). The assumption of AM with the substrate ($G_S = 1000$ GHz) reproduces

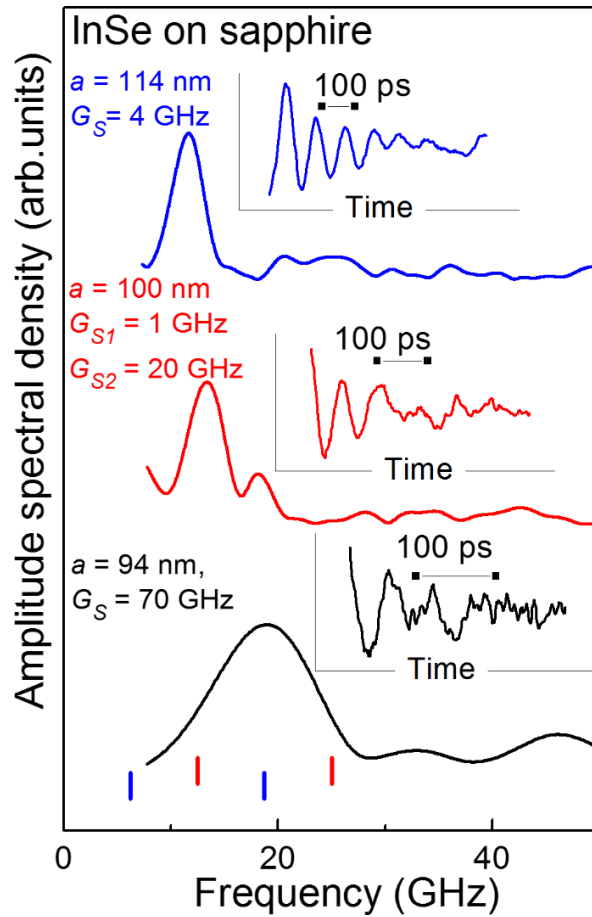


Figure 7-6. Phonon spectra for different InSe nanolayers on a sapphire substrate. The insets show the temporal evolution of the pump probe signals after background subtraction. Vertical bars indicate the calculated phonon frequencies for an InSe nanolayer (thickness $a = 100$ nm) coupled to the sapphire substrate in the limit of strong (blue bars, $G_S = 1000$ GHz) and weak (red bars, $G_S \sim 0$ Hz) elastic coupling. The values of G_S are deduced from the best fits of the spring model to the data.

the three high frequency spectral lines. The low frequency line centered at $f = 26$ GHz agrees with the calculated spectrum by assuming a lower G_S -value ($G_S = 8$ GHz).

Figure 7-8 shows the measured spectra for three InSe layers with thicknesses from $a = 5.4$ nm to $a = 12$ nm. We can compare the measured resonances with the calculated ones only for $f > 40$ GHz. The low frequency resonances with $f \sim 20$ GHz (see shaded square in Figure 7-8) have a very low quality factor $Q < 1$. For these resonance modes, we may conclude only that $G_S > 10$ GHz and that the phonon resonance frequency has weak dependence on G_S . The red vertical arrows in Figure 7-8 and the values above them show the measured resonance frequencies and the corresponding G_S values obtained from the comparison with the calculated spectra.

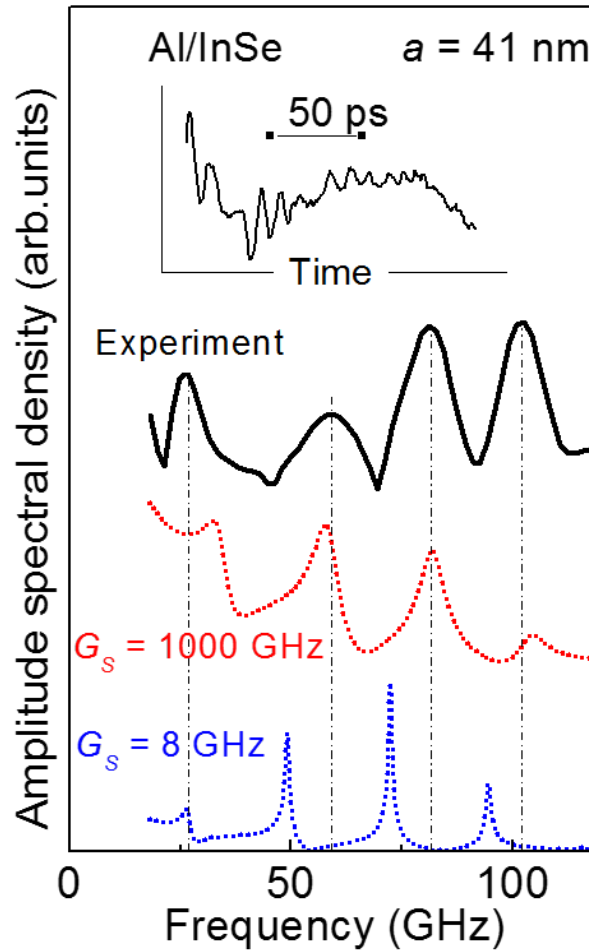


Figure 7-7. Measured (solid lines) and calculated (dotted lines) phonon spectra for InSe nanolayers with thickness $a = 41$ nm on a sapphire substrate. Red and blue curves correspond to acoustic matching and weak coupling of the InSe nanolayer to the sapphire substrate, respectively. Phonons are excited via a 33-nm-thick Al transducer. Vertical dashed-dotted lines indicate the central frequencies of the measured phonon resonances. The inset shows the background free temporal evolution of the measured signal.

For $a = 12$ nm, two spectral lines are observed corresponding to $G_S = 10$ and 90 GHz. For thinner layers, one spectral line is detected with values of G_S from 13 GHz ($a = 6.5$ nm) to 26 GHz ($a = 5.4$ nm). From the data and analysis (Figure 7-6, Figure 7-7 and Figure 7-8) of InSe layers with a wide range of thicknesses, from 5 to 100 nm, we conclude that the coupling parameter G_S of an InSe layer to sapphire can have values from ~ 1 GHz to more than 100 GHz, without any direct correlation with the InSe layer thickness. Our results also show that the measured phonon spectrum cannot always be described by a single parameter G_S . We have observed several cases when a good fit in the whole frequency range requires two or more values of G_S .

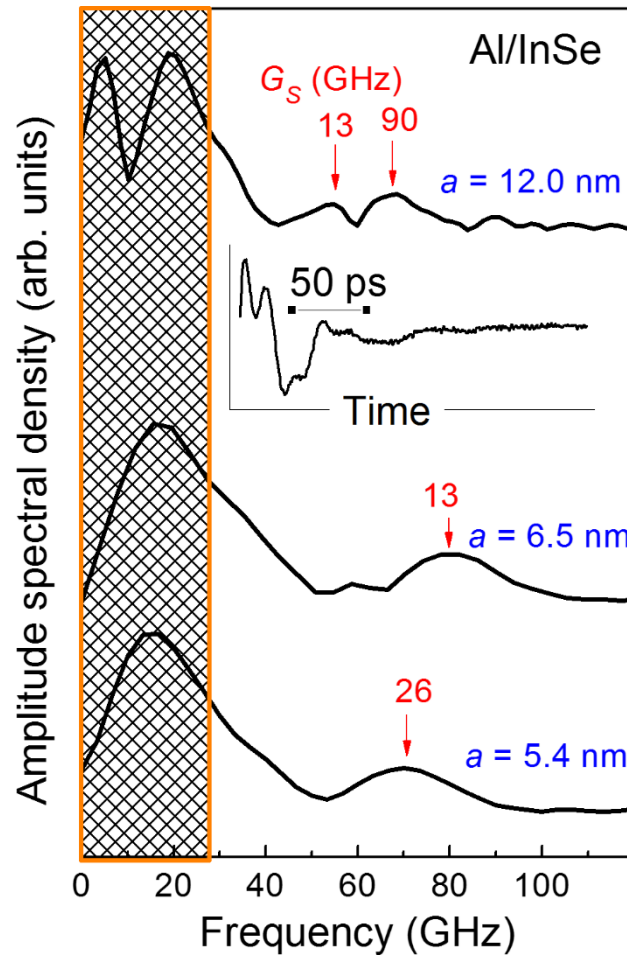


Figure 7-8. Measured phonon spectra for InSe nanolayers with different thickness on a sapphire substrate. Phonons are excited via a 38-nm-thick Al-transducer. Vertical arrows indicate the frequencies of the phonon resonances obtained from the calculated spectra with corresponding values of G_S . The shaded area marks the low-frequency spectrum. The inset shows the temporal evolution of the pump-probe signals after background subtraction for the 6.5-nm-thick layer.

7.5 Coherent acoustic spectra of InSe/hBN and hBN/InSe heterostructures

Figure 7-9 shows the results for an InSe/hBN heterostructure on a sapphire substrate measured using the transmission geometry shown in Figure 7-1a. In this heterostructure, an individual InSe nanolayer ($a = 50$ nm) is stamped onto an hBN layer ($b = 81$ nm) to form a heterojunction. Two resonances at $f = 18$ and 30 GHz are clearly seen in the measured spectrum indicating efficient elastic coupling between the layers. If there was no good elastic contact between the layers, the spectrum would reveal only the nanomechanical resonances excited in the top InSe layer. In fact, the

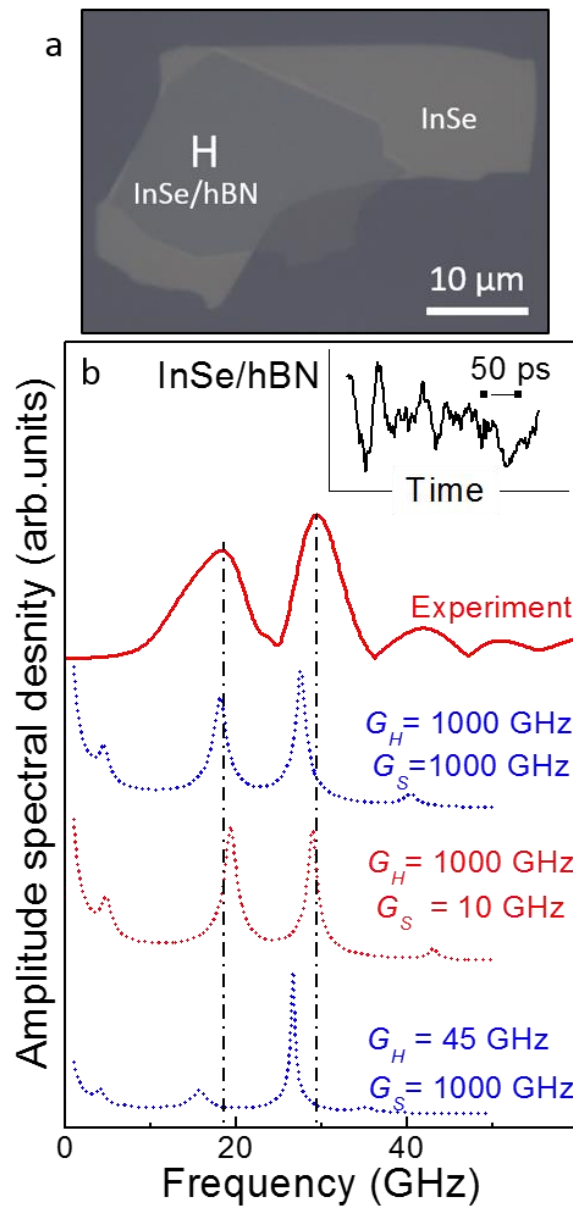


Figure 7-9. (a) Optical image of an InSe/hBN heterostructure. (b) Measured (solid lines) and calculated (dotted lines) phonon spectra for the InSe ($a = 50$ nm)/hBN ($b = 81$ nm) heterojunction.

underlying hBN layer cannot be excited directly as it is transparent at the wavelength of the pump probe ($\lambda = 400$ nm). As for the case of the InSe/InSe homojunction, also in this case the calculated spectrum indicates acoustic mismatch at the InSe/hBN vdW heterointerface [see dotted lines in Figure 7-9b]. The best agreement between our model with the experiment is obtained for $G_H = 1000$ GHz and $G_S = 10$ GHz [Figure 7-9b, red dotted line].

Figure 7-10 shows the results for an hBN/InSe heterostructure on a sapphire substrate also measured using the transmission geometry shown in Figure 7-1a. In this heterostructure, an individual hBN nanolayer ($a = 44$ nm) is stamped onto an InSe

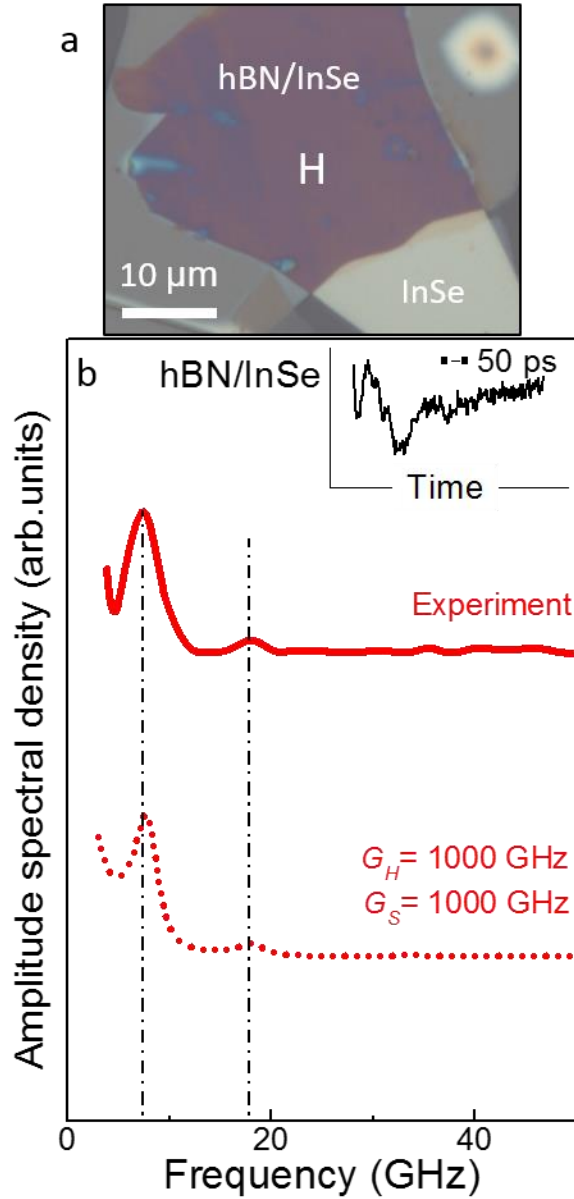


Figure 7-10. (a) Optical image of an hBN/InSe heterostructure. (b) Measured (solid lines) and calculated (dotted lines) phonon spectra for the hBN ($a = 44$ nm)/InSe ($b = 70$ nm) heterojunction.

layer ($b = 70$ nm) to form a heterojunction. Here we see two resonances at $f = 8$ and 18 GHz in the experimental spectra, which again indicates efficient elastic coupling between layers as nanomechanical resonances can only be indirectly excited in the hBN layer through the excitation of InSe. However, for this sample we see that the spectra are better reproduced by the theoretical curves when we assume strong ideal contact at both the heterostructure and substrate interfaces (*i.e.* $G_H = 1000$ GHz and $G_S = 1000$ GHz).

One explanation for the improved coupling may be due to the hBN being mechanically stamped onto InSe. Stamping the heterostructure in this order may improve the adhesion at the InSe/sapphire interface. Also, as the stamping process is random in terms of the alignments of crystals, it could be that an elastically favourable alignment of InSe and sapphire has been achieved by chance.

7.6 Coherent acoustic spectra of a thin hBN/InSe heterostructure

Figure 7-11 shows the results for an hBN/InSe heterostructure on sapphire with thicknesses of the hBN and InSe layers of $a = 14$ nm and $b = 10$ nm, respectively. Coherent phonons were injected into the heterostructure from an Al-film (thickness of 35 nm) evaporated on top of the hBN layer [experimental scheme Figure 7-1d].

From the observation of four distinct spectral lines in the frequency range up to 150 GHz and the comparison with the calculated phonon spectra (dotted lines in Figure 7-11b), we conclude that there is a strong coupling at the heterointerface. The best agreement is obtained assuming $G_H = 1000$ GHz and $G_S = 10$ GHz. If we assume that the coupling at the vdW heterointerface drops to $G_H = 30$ GHz (see the lowest dotted curve in Figure 7-11b), the spectrum would show only two resonances.

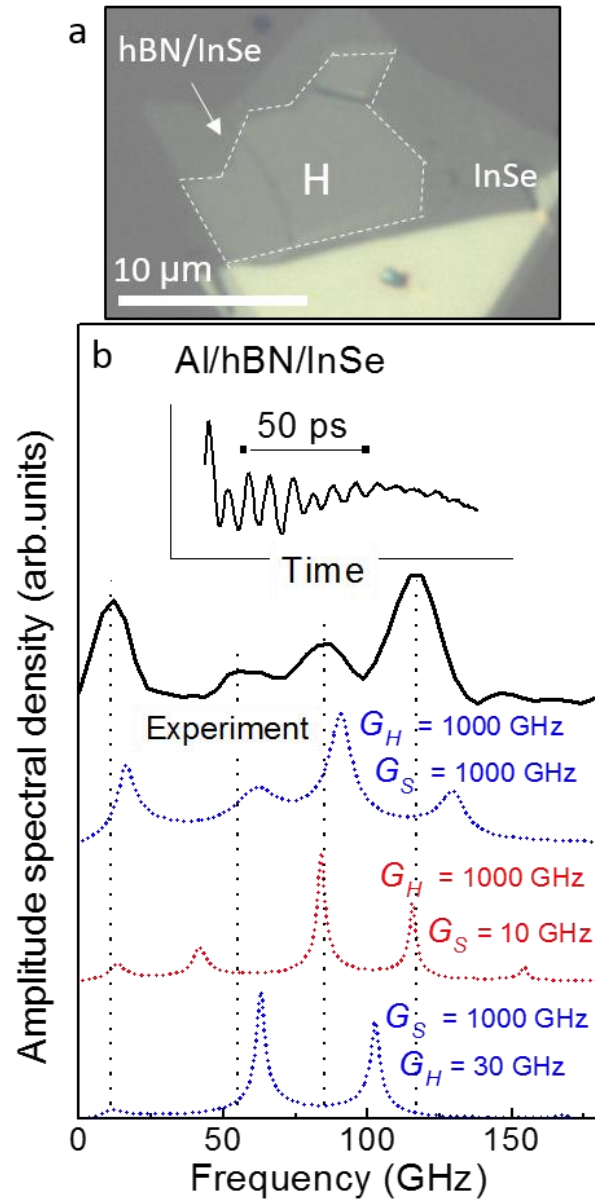


Figure 7-11. (a) Optical image of a thin hBN/InSe heterostructure (b) Measured (solid line) and calculated (dotted line) phonon spectra for an hBN/InSe heterostructure on a sapphire substrate. The inset shows the temporal evolution of the pump-probe signals after background subtraction. The hBN and InSe layers have thickness of $a = 14$ and $b = 10$ nm, respectively.

7.7 Coherent acoustic spectra of an InSe/InSe homojunction

Figure 7-12 shows the results of a vdW homojunction obtained by exfoliation and mechanical contact of two InSe layers of thickness $a = 50$ nm and $b = 77$ nm on a sapphire substrate. The optical image of the heterostructure [see image in Figure 7-12a] shows three distinct areas: the area H of the heterostructure where the layers overlap and two regions where the top (T) and base (B) InSe layers do not overlap, thus they can be probed separately. In the experiments, we used the geometry presented in Figure 7-1c.

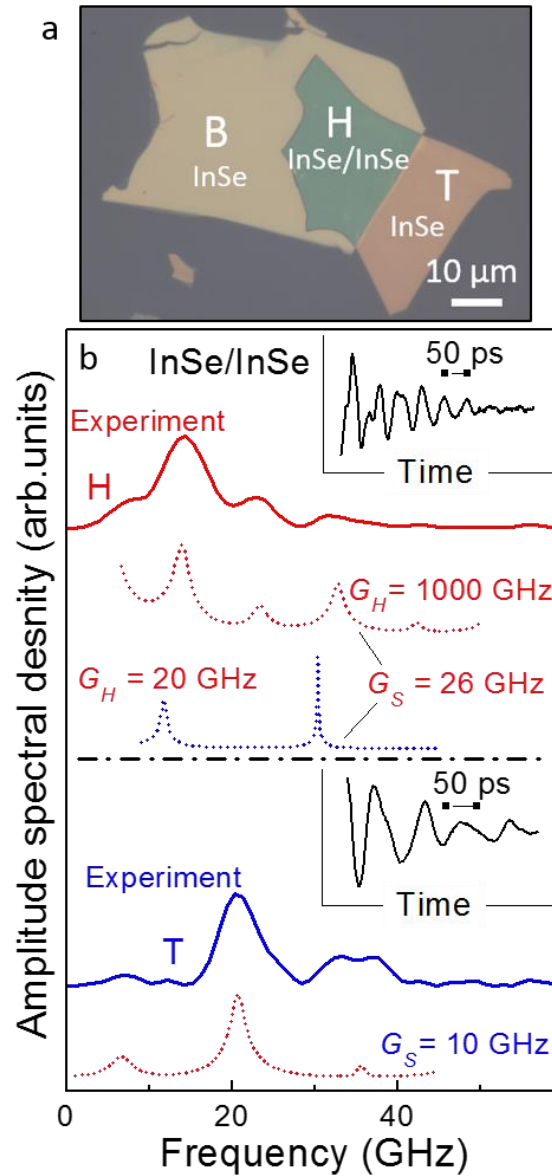


Figure 7-12. (a) Optical image of an InSe/InSe homojunction. B, T, and H correspond to the base, top and overlapping areas of the InSe layers, respectively. (b) Measured (solid lines) and calculated (dotted lines) phonon spectra for the InSe($a = 77$ nm)/InSe($a = 50$ nm) homojunction.

The lower blue solid curve in Figure 7-12b shows the phonon spectrum for the non-overlapping area T. It reveals a peak at $f = 21$ GHz in agreement with that simulated by the spring model with $G_S = 10$ GHz [see lower blue dotted curve in Figure 7-12b]. The red solid curve in Figure 7-12b for the overlapping area H reveals a different spectrum: it consists of several lines at a regular frequency interval of 8.8 GHz. The individual frequencies agree well with those calculated for a single InSe layer with a total thickness equal to the sum of the individual layer thicknesses (e.g., $a + b = 127$ nm) under the assumption of $G_H = 1000$ GHz and $G_S = 26$ GHz. Thus we conclude that the interface between the InSe layers can be considered as elastically “ideal” for transport of coherent phonons with f up to at least 50 GHz.

7.8 Elastic properties of InSe, hBN and their interfaces

In this section, we examine how the frequency and the finesse of the phonon resonances depend on the elastic properties of the nanolayers and vdW heterostructures, and on phonon scattering at interfaces, i.e., the interface between two vdW layers or the interface between a vdW layer and its supporting substrate.

7.8.1 Elastic properties of InSe and hBN

The layered crystal structure of InSe and hBN causes anisotropic elastic properties, e.g., elastic constant tensor c_{ij} and sound velocity s . For our experiments with propagation of coherent phonons in the direction x perpendicular to the vdW layer planes, the sound velocity is calculated as $s = \sqrt{c_{33}/\rho}$ (for values see Table 7-2) using elastic parameters measured in bulk crystals by standard ultrasonics^[190,197] and Brillouin scattering^[198].

To assess whether the use of elastic parameters for bulk crystals is a valid assumption to interpret our findings, we derive elastic parameters from an empirical Lennard Jones potential $U(r)$ for the vdW interaction between the layers^[199]:

$$U(r) = E_B \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right], \quad (65)$$

where r_0 is the distance between the edges of the atomic monolayers and E_B is their binding energy. In hBN, r_0 corresponds to the interlayer period, e.g., $r_0 = c \sim 0.7$ nm. In InSe, each vdW monolayer consists of four covalently ionic

bonded atomic sheets (Se-In-In-Se) of thickness 0.53 nm. The distance between Se-atoms at the boundaries of each vdW layer is $r_0 \sim 0.38 \text{ nm}$ ^[200,201]. The value of E_B for hBN is $E_B = 13 \text{ meV}/\text{\AA}^2$ ^[202]; also, vdW interactions in InSe were found to be as weak as in graphite and other vdW crystals^[201], for which E_B is in the range 13 to 21 meV/ $\text{\AA}^2$ ^[202]. For a small change Δr in the equilibrium separation of the vdW layers, *i.e.*, $\Delta r = r - r_0 \ll r_0$, Eq. (65) can be approximated by a Taylor expansion as

$$U(x) = 36E_B r_0^{-2} (\Delta r)^2, \quad (66)$$

from which we derive the specific stiffness of the vdW coupling:

$$\eta_0 = 72E_B r_0^{-2}. \quad (67)$$

Alternatively, we can estimate the value of η_0 from the elastic constant of the bulk crystals:

$$\eta_0 = c_{33}/c_0. \quad (68)$$

Using Eqs. (67) and (68) for hBN, we derive $\eta_0 = 3.1 \times 10^{19} \text{ N/m}^3$ and $\eta_0 = 3.7 \times 10^{19} \text{ N/m}^3$, respectively. Thus different models give similar stiffnesses for hBN. Also, using Eq. (68) and the values for c_{33} and r_0 for InSe (see Table 7-2), we derive $\eta_0 = 4.5 \times 10^{19} \text{ N/m}^3$. From this value of η_0 and Eq. (67), we estimate that $E_B = 15 \text{ meV}/\text{\AA}^2$ for InSe, within the range of values of E_B reported for other vdW crystals^[12].

We use the same “spring” model approach to describe the elastic coupling between two materials (described in Chapter 3.5, Eq. (52)) and calculate the maximum coupling parameter G_0 between two vdW layers of the same material. Using the estimated values of η_0 , we obtain $G_0 \sim 1.0$ and 1.5 THz for InSe and hBN, respectively. These values are smaller than the zone edge phonon frequencies for propagation perpendicular to the layers, *i.e.*, $f = 1.2$ and 2.4 THz for InSe^[203] and hBN^[197], respectively, but much higher than the maximum phonon frequency $f \sim 100 \text{ GHz}$ measured in our experiments. Thus we conclude that our use of the continuous approximation with bulk elastic parameters and sound velocity of InSe and hBN is valid in our analysis of the phonon spectra.

	InSe	hBN	Al	sapphire
Density (kg/m ³)	5500	2180	2700	4000
LA sound velocity (km/s) along c-axis	2.50 ^[190]	3.44 ^[197]	6.42	11.00
Acoustic impedance, (MPa s/m)	14	7.5	17	44
Elastic constant, C_{33} (GPa)	36	26		
vdW interlayer period (nm)	0.8	0.7		
Spring stiffness of vdW bond (10 ¹⁹ N/m)	3.7	3.4		

Table 7-2. Elastic parameters of InSe, hBN, and Al used in the calculations.

7.8.2 Elastic properties of interfaces

In the analysis of phonon transport, the elastic properties of interfaces are as important as the elastic properties of the nanolayers themselves. The interface defines the absolute value of the reflection $|R|$ and phase shift ϕ of the specular phonon reflection at the interface. The value of ϕ varies from 0 to π depending on the elastic coupling. This phase shift governs the interference of coherent phonons and hence defines the frequency f_n of the phonon resonances.

We use a phenomenological spring model to describe the interface between two materials (see Chapter 3). In this model, the interface is described as a weightless spring with a frequency independent specific stiffness η . As shown in the various results of this chapter, the value of f_n measured in several layers and heterostructures agrees well with acoustic mismatch ($G_i \gg f_n$), thus indicating a good elastic contact at the interface over a wide frequency range. However, in some cases, we have to assume a weak coupling between a layer and its supporting substrate ($G_S \sim f_n$) and/or different values of G_S . To interpret these results, we examine the morphology of the interfaces.

The elastic coupling between the exfoliated nanolayers depends on the quality of the surfaces, which can be non-uniform over the area ($5 \times 5 \mu\text{m}^2$) of the probing spot. Figure 7-13 shows the AFM images and x-profiles for an InSe layer on a sapphire substrate. The AFM data show that the roughness of the InSe surface (up to 1 nm) is significantly larger than for the sapphire substrate ($\sim \pm 0.1$ nm). Also, it is larger than that of hBN, which has an abrupt and atomically smooth surface^[204,205]. Thus the most likely reason for the imperfectness of the interface revealed in our experiments is the surface roughness of the InSe layer.

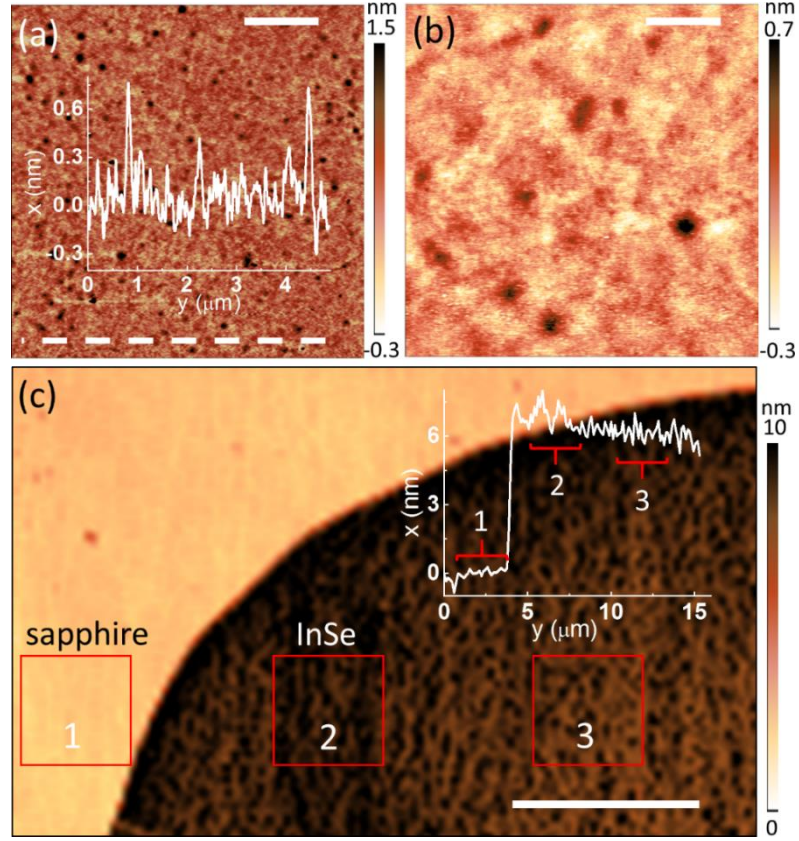


Figure 7-13. (a) AFM image of a 5 μm x 5 μm region of InSe (scale bar = 1 μm). Inset: AFM profile along the white dotted line. (b) AFM image of a 1 μm x 1 μm region of InSe (scale bar = 0.2 μm). (c) AFM image of an InSe nanolayer on a sapphire substrate. (Inset) AFM profile along a line through regions marked by squares 1-2-3. (scale bar = 5 μm).

This also implies inhomogeneities in the coupling parameters η_s and η_H . Two atomically flat vdW layers interact elastically via vdW forces and have a binding energy $E_B \sim 10 \text{ meV}/\text{\AA}^2$, which does not depend strongly on the specific material^[201,202]. The value of E_B gives a stiffness $\eta_0 \sim 10^{19} - 10^{20} \text{ N/m}^3$ and corresponding coupling parameter $G_0 \sim 10^3 \text{ GHz}$. Due to the strong dependence of the vdW potential energy on distance [Eq. (65)], the increase of r by only one layer of atoms due an imperfect interface results in the decrease of η_0 and G_0 by almost two orders of magnitude ($G \sim 10 \text{ GHz}$), leading to changes in the complex phonon reflectivity R [see Chapter 3] and phonon resonance frequency f_n . Thus, for sub-THz phonons, the areas of atomically perfect interface behave as in the case of AM while the increase of the separation between interfaces of just one atomic layer results in the reflection of sub-THz phonons, as for the case of a free surface.

To characterize the coherent phonon resonances, we consider two types of regions. The first type, labelled “AM,” has an atomically flat interface: the distance x

between the layers is uniform with a coupling parameter $G_{AM} \sim 10^3$ GHz. The second type corresponds to a “free surface” (FS): the distance between the layers is $x \geq 2x_0$ with a coupling parameter $G_{FS} \leq f$. It is important to compare the average size of the AM and FS regions, L_{AM} and L_{FS} , respectively, with the phonon wavelength λ . For InSe, the value of $\lambda = s/f$ varies from 250 nm down to 25 nm for f in the range 10–100 GHz. In the assumption that the correlation length is small compared to λ , we may consider L_{AM} and $L_{FS} \ll \lambda$, and then for the phonon resonances observed in our experiments the interface roughness is averaged over λ . In this case, we can characterize the interface using a single coupling parameter:

$$G = G_0 \frac{S_{AM}}{S_{AM} + S_{FS}}, \quad (69)$$

where S_{AM} and S_{FS} are the areas of the AM and FS regions within the probe spot. We refer to this type of interface as “mono.” For $S_{AM} \gg S_{FS}$, we have $G = G_0 \sim 1$ THz and the interface may be considered as elastically perfect and the AM model valid for all acoustic phonons, provided that the phonon dispersion is not important. An alternative case is that of a “broken” interface, i.e., $S_{AM} \ll S_{FS}$ and hence $G \ll G_0$. In general, the interface may have a more complicated morphology. For instance, in the area of the probe spot, there may be areas with different mean values of G . Examples of areas of InSe with different surface roughness and hence different G are shown in Figure 7-13c by squares labelled 2 and 3. Their typical in plane size ($\sim 1 \mu\text{m}$) is larger than λ . The corresponding profiles in Figure 7-13c of these areas demonstrate that the roughness of the surface in area 2 is higher than in area 3, thus leading to $G_3 > G_2$ and a “dual” interface featuring regions of both strong and weak interfacial coupling. The increased roughness will in turn increase the separation between layer interfaces and reduce the strength of the coupling parameter G . In general, we can identify both “mono” and “dual” interfaces for InSe layers on a sapphire substrate. In contrast, we find that the interface between two vdW layers (e.g., the interface in InSe/InSe and InSe/hBN) is elastically perfect within the measured frequency range as shown by the agreement between experimental spectra and theoretical spectra based on AM.

The comparison between the experimental and calculated spectra in Figure 7-9 through Figure 7-12 indicates that the phonon frequency would be very different if the layers were not elastically coupled. Thus we may exclude the case of weak coupling ($G_H \leq f$) at the interface between two vdW layers in all our heterostructures. Also, we

can explain the phonon spectra using the acoustic mismatch model over a wide frequency range up to 120 GHz (Figure 7-11b). At a first glance, it may seem surprising that the interface of InSe/InSe and InSe/hBN heterostructures has a stronger elastic coupling compared to the InSe/sapphire interface since the surface roughness of the InSe layer is the same in both cases. To explain this behavior, we note that there is a difference in acoustic impedances between InSe and sapphire: $Z_{\text{sapphire}} = 3.2Z_{\text{InSe}}$. Thus the value of G_0 for the interface of InSe with sapphire is noticeably smaller than for InSe/InSe and InSe/hBN interfaces [see Eqs. (53) and (54)]. Also, the more rigid sapphire substrate may not be able to adapt to the InSe surface compared to the case of two van der Waals layers.

In summary, we have shown that the frequencies of the phonon resonances are dependent on both the thickness of the layer and elastic coupling at the interface. The latter factor was not considered in earlier works^[183-185] where it was assumed that the nanolayer has either a perfect elastic contact with the substrate^[185] or behaves as a suspended film^[183]. In our work, we show that the elastic properties of vdW interfaces can be probed by sub-THz coherent phonons. None of the other existing measuring techniques can access this information. In particular, some of the available microscopy techniques, such as TEM, examine only static surface properties, whereas others, such as AFM, can only probe surfaces and/or low-frequency elastic properties.

7.8.3 Scattering and decay of coherent phonons

An important characteristic of a phonon resonance is its linewidth $f \sim (2\tau^*)^{-1}$, where τ^* is the phonon decay time. The measured linewidths indicate $\tau^* \leq 50$ ps. Different mechanisms can contribute to τ^* , *e.g.*^[186,206-208],

$$(\tau^*)^{-1} = (\tau_S)^{-1} + (\tau_A)^{-1} + (\tau_I)^{-1} + (\tau_D)^{-1} + (\tau_R)^{-1}, \quad (70)$$

where τ_S is the time of the diffusive scattering at interfaces and free surfaces; τ_A is the anharmonic decay time; τ_I is the effective time related to inhomogeneities in film thickness; τ_D describes the decay of the laterally localized resonance due to acoustic diffraction, and τ_R describes the phonon decay time due to energy emission into the substrate. Only τ_R is included in our previous theoretical analysis and can be expressed as

$$\tau_R = -\frac{2d}{s_{LA}\ln|R|}, \quad (71)$$

where s_{LA} is the sound velocity of the nanolayer, d is the layer thickness and R is the amplitude reflection coefficient R_{ij} for the strain between 2 media, i and j :

$$R_{ij} = \frac{Z_j - Z_i}{Z_j + Z_i}. \quad (72)$$

For AM ($G_S \gg f$) and for an InSe nanolayer layer with $a \sim 100$ nm on a sapphire substrate, we estimate $\tau_R \sim 100$ ps, which is about three times longer than the value $\tau^* \sim 30$ ps derived from the measured phonon spectra (see lower spectrum in Figure 7-6). The calculated value of τ_R increases for weak coupling and correspondingly small values of G_S . Thus the difference between the measured and calculated τ_R is due to other decay mechanisms, which are discussed below.

The value of τ_A is governed by third-order elastic constants, which are not known for the studied vdW layers. We may assume that τ_A is not much different from the values found in other crystalline materials for which $\tau_A > 1$ ns at frequencies below 100 GHz^[209]. This time is significantly longer than the measured time and thus it will be not considered further.

The value of τ_D is governed by the lateral dimension L_G of the local AM and FS resonators characterized by an effective rigidity G at the interfaces in Eq. (69). The value of τ_D can be estimated as the time taken for an acoustic wave to travel a diffraction length L_D , e.g., $\tau_D \approx L_D/s \approx (L_G^2/2)/s$, where L_G is the diameter of the acoustic beam. Since $L_G \gg \lambda$, τ_D is much longer than the measured time. For example, for phonons with $\lambda \sim 100$ nm in an InSe film strongly coupled to sapphire, τ_D becomes equal to the measured time when $L_G \sim \lambda$. Thus the losses due to diffraction are not important only for the local resonators with L_G significantly exceeding the acoustic wavelength ($L_G \gg \lambda$).

The decay time τ_I could be caused by inhomogeneous broadening of the resonance spectral line due to the long-scale (~ 1 μ m in the plane of the nanolayers) thickness variations of the InSe and hBN nanolayers. The AFM profiles of our layers show variations in the thickness of $\pm 10\%$. Thus τ_I can represent a significant contribution to the measured lifetime. For example, the measured lifetime $\tau^* \sim 80$ ps for 13 GHz phonons in an InSe nanolayer weakly coupled to sapphire (upper spectrum in Figure 7-6) could be assigned to $\pm 15\%$ variations in the InSe film thickness.

Finally, the decay time τ_s in Eq. (70) accounts for the losses caused by diffusive scattering at an interface due to their roughness, point defects, monolayer steps and/or boundaries between regions with different G . The AFM image in Figure 7-13 shows variations of the InSe layer thickness over length scales >100 nm.

The analysis leading to conclusions of the decay time τ_s was performed by Prof. V.E.Gusev from Le Mans University using the AFM measured root-mean square roughness σ_{rms} of the surface of InSe. For details, see Ref. [133]. It was concluded that in order to achieve comparable values of τ_s , then $\sigma_{rms} \approx 8$ nm. This value exceeds by an order of magnitude the value $\sigma_{rms} \sim 1$ nm for the InSe surface (see AFM data in Figure 7-13). Thus we may conclude that diffusive scattering of ~ 20 GHz phonons at the interfaces with $\sigma_{rms} \leq 1$ nm is negligible and, therefore, its contribution to τ_s can be ignored.

In summary, from the comparison of the measured and calculated spectra, we find that the measured spectral widths $f_n \geq 10$ GHz exceed those calculated by acoustic mismatch by a factor of 2. In accordance with the estimates presented above, this difference should be mostly attributed to the inhomogeneous broadening of the spectral line.

7.9 Summary

We have used picosecond ultrasonics to measure the coherent acoustic phonon spectra of InSe layers with thicknesses from 5 to ~ 100 nm and their heterostructures. The spectra consist of several well separated lines in the frequency range from ~ 10 to ~ 100 GHz, revealing the existence of nanomechanical resonances in all layers due to phonon quantization in the direction perpendicular to the layer plane. The frequencies of quantized phonons depend not only on the layer thickness, but also on the elastic coupling parameters at the interfaces. The values of the resonance frequencies measured in the present work agree well with those derived from the continuous elastic theory using bulk elastic constants and effective springs with frequency independent stiffnesses. In some cases, the inhomogeneities of the elastic coupling at the interfaces should also be taken into the account to explain the phonon spectrum.

Our data and analysis indicate that the vdW interface of InSe/InSe and InSe/hBN heterostructures can be described by the acoustic mismatch approach and considered as elastically ideal for phonon frequencies up to at least 150 GHz. In

contrast, the elastic coupling of InSe layers to a substrate may not always be ideal and the phonon resonances may not always be described by a single elastic coupling parameter.

The results of this Chapter furthers the conclusions presented in Chapter 6, on the interfaces formed between vdW nanolayers and their underlying substrates. It is shown that vdW nanolayers exhibit varied coupling strengths to an underlying sapphire substrate or adjacent vdW nanolayer. Furthermore, the variable strength of interlayer coupling has been evaluated by using the spring model.

Chapter 8

8 Picosecond acoustic imaging

The following chapter describes the imaging experiments for the interfaces of hBN/InSe/graphene heterostructures on a SiO₂ substrate, InSe layers on sapphire and InSe/InSe homojunctions on a sapphire substrate.

The chapter expands the scope of chapters 6 and 7 by using the picosecond acoustic technique as a means of imaging the strength of elastic coupling at the vdW nanolayer/nanolayer interface as well as at the substrate/nanolayer interface. This allows us to analyse how the strength of elastic coupling varies topographically in vdW heterostructures, as opposed to measuring single points which was done in Chapters 6 and 7. Coherent acoustic phonons are generated, detected and imaged by the picoacoustic technique described in Chapter 4. The thickness of InSe flakes was measured by atomic force microscopy (AFM). Flakes were prepared and transferred to sapphire substrates or pre-fabricated graphene devices by the methods described in Chapter 5.

AFM measurements were performed by myself, while picosecond acoustic techniques were performed by myself, Dr. Elton de Lima Savi, with the help of Prof. Andrey Akimov at Le Mans University. Photocurrent, photoluminescence and Raman measurements were conducted by myself using techniques discussed in Chapter 4. The results of this chapter were accepted for publication in *ACS Nano* **13**, 11530 (2019).

8.1 Introduction

As discussed in previous chapters, in vdW crystals the strong anisotropy of interatomic forces makes possible the use of a simple tape-based fabrication method to realize vdW flakes as thin as one layer^[1,37,83,125,210]. In particular, large area (>10 cm²) layers can now be fabricated by exploiting the adhesion properties of different materials^[211]. Despite considerable progress in the growth of 2D vdW crystals and heterostructures^[212-215], the tape-based fabrication method remains the most common approach to the fabrication of high-quality vdW nanolayers and heterostructures. However, it also presents some drawbacks due to random lateral size and thickness of the layers, and the limited control of the quality of the interface between the layers.

A crucial requirement in the fabrication of 2D structures is their in-plane spatial homogeneity. This can be influenced not only by the uniformity of the individual layers, but also by their adhesion to the substrate and/or another vdW layer. The interface between two materials can be considered ideal when the two contacting surfaces are atomically flat and, correspondingly, the force between the neighbouring layers is homogeneous in the plane. In reality, the interface between two vdW layers or between a vdW layer and its supporting substrate is not elastically perfect. The strength of elastic interaction at the interface depends on the distance between the atoms, which may vary in the layer plane due to defects and surface roughness (see Eq. (65) in Chapter 7). Also, molecular species (adsorbed water, hydrocarbons, etc.) or dust in air between a 2D crystal and a substrate can induce the formation of bubbles with a morphology determined by the vdW attraction of the layer to the substrate and the elastic energy needed to deform it. For example, stiff 2D crystals, such as graphene or monolayer hBN, tend to form small, low-density bubbles and large (up to $100\text{ }\mu\text{m}^2$) areas with an ideal vdW interface^[216].

In general, the high-frequency dynamics (reflection and transmission of phonons up to $\sim 1\text{ THz}$) of elastic properties at the layer interface are difficult to probe. These properties can influence the stability, reliability and performance of electronic devices that require uniform layers and control over the charge and out-of-plane phonon transport across interfaces. For these studies picosecond ultrasonic imaging is ideally suited. Due to the high frequency and corresponding nanometer wavelength of phonons generated by fast laser pulses, high accuracy measurements of thin film thickness (comparable to atomic distances $\sim 0.1\text{ nm}$)^[164,166] and lateral resolution (down to about 100 nm) can be achieved and used to image the elastic properties of different systems. For example, the adhesion of metal contacts in traditional semiconductors^[163], elastic properties of biological systems^[217] and various inhomogeneities in solids^[218].

Here we use picosecond ultrasonic imaging to map spatially the elastic coupling between a vdW layer or heterostructure and its supporting substrate. The difference in acoustic impedances of neighbouring materials gives rise to phonon confinement and resonances, which we measure and model by using elastic equations^[133].

Electrical measurements and maps of photocurrent were directly compared with picosecond acoustic images of a hBN/InSe/graphene device in an attempt to

correlate the strength of elastic coupling and charge transfer at the InSe/graphene interface.

8.2 InSe based heterostructures and homojunctions

This chapter focuses on the measurement of two InSe based samples: an InSe/InSe homojunction on a sapphire substrate and a hBN/InSe heterostructure on a graphene/SiO₂/Si substrate. Data for the samples measured and discussed in this chapter are shown in Table 8-1. The thickness of the flakes, as measured by AFM, is shown for the different samples. Measurements were taken on both heterostructures and single InSe layer regions. Optical and AFM images of the InSe/InSe homojunction and hBN/InSe/graphene heterostructure are shown in Figure 8-1.

Sample	InSe thickness (nm)	InSe thickness (nm)	hBN thickness (nm)
InSe/InSe	50 ± 2 (B)	70 ± 1 (T)	
hBN/InSe	65 ± 4		55 ± 5

Table 8-1. Measured thicknesses for the samples discussed in this chapter. The individual InSe layers of the InSe/InSe homojunction are labelled (B) for the base flake and (T) for the top flake.

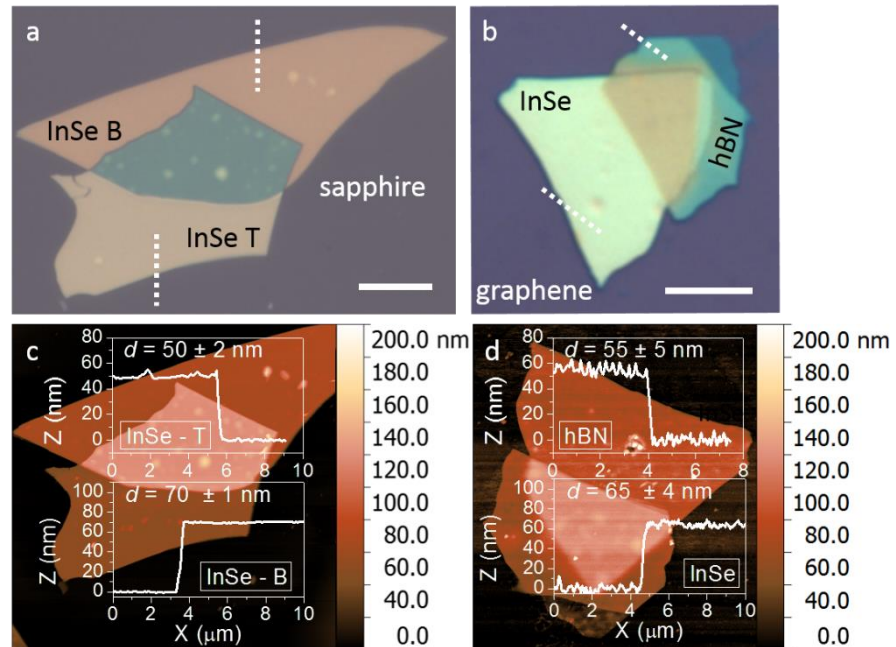


Figure 8-1 . Optical images (a,b) and corresponding AFM data (c,d) of an InSe/InSe homojunction on a sapphire substrate and a hBN/InSe heterostructure on a graphene/SiO₂/Si substrate. (a) InSe/InSe homojunction. InSe (T) thickness = 50 nm. InSe (B) thickness = 70 nm. (b) hBN/InSe heterostructure. hBN thickness = 55 nm. InSe thickness = 65 nm. Dashed line in (a) and (b) – AFM profile (X) locations for (c) and (d), respectively. Scale bar = 10 μ m.

The AFM images and z-profiles show thicknesses d with fluctuations of up to ± 5 nm in InSe and hBN.

The AFM images show some areas where bubbles have formed on the InSe surface, most notably these can be seen in Figure 8-1a and b by small circular marks on the surface. These are of importance to our measurements and are discussed later. The AFM measurements on these flakes were completed after the picosecond acoustic studies so as not to risk damaging the samples. The optical images from Figure 8-1 were taken immediately after stamping the heterostructures, prior to the picosecond acoustic measurements.

8.3 Picosecond acoustic imaging of single InSe layer and InSe/InSe homojunctions on sapphire

Figure 8-2a shows the optical image of an InSe layer on a sapphire substrate and the specific area ($10 \times 10 \mu\text{m}^2$) scanned by the pump/probe beams with $1 \mu\text{m}$ steps along both x- and y-directions. Figure 8-2b shows a schematic of the two extreme cases where the nanolayer/substrate is perfect or broken. The temporal probe signals measured at three positions and their fast Fourier transforms (FFT) are shown in the insets and main panels of Figure 8-2c. The three spectra in Figure 8-2c illustrate different cases of elastic coupling at the InSe/sapphire interface. The lowest spectrum shows three narrow lines whose frequencies agree with those of a free standing InSe layer, as calculated from $f_n = \frac{s_{LA}n}{2d}$, where $s_{LA} = 2500$ m/s is the sound velocity for longitudinal phonons in InSe along the direction perpendicular to the layer plane^[190], d is the thickness of the layer and $n = 1, 2, \dots$ is the order of the harmonic resonance. The measured frequencies are reproduced with $a = 63$ nm, which is 10% less than the layer thickness measured by AFM. The middle black spectrum in Figure 8-2c has a much lower intensity with resonance frequencies that agree well with those calculated using $f_n = \frac{s_{LA}(2n-1)}{4d}$ for an elastically perfect interface. In this case, phonons can propagate into the substrate, leading to a faster decay of the oscillations and broader spectral lines than for the case of a broken interface/free standing layer. Finally, the upper spectrum in Figure 8-2c corresponds to the mixed case of elastic coupling with perfect and broken interfaces within the probing spot. By measuring the phonon spectra at several positions, we can construct 2D images of the spectral density at specific frequencies. Here, we collate all of the Fourier spectra taken for each position

and compare the relative intensities (arbitrary units) of the amplitude spectral density about a given resonance. For example, Figure 8-2d and e show colour maps of the spectral density at frequencies $f = 20$ GHz [Figure 8-2d] and 27-28 GHz [Figure 8-2e] corresponding to the main spectral lines for broken and perfect interfaces, respectively. Red and white colours correspond to positions with maximum and minimum spectral density (arbitrary units), respectively. It can be seen that there are

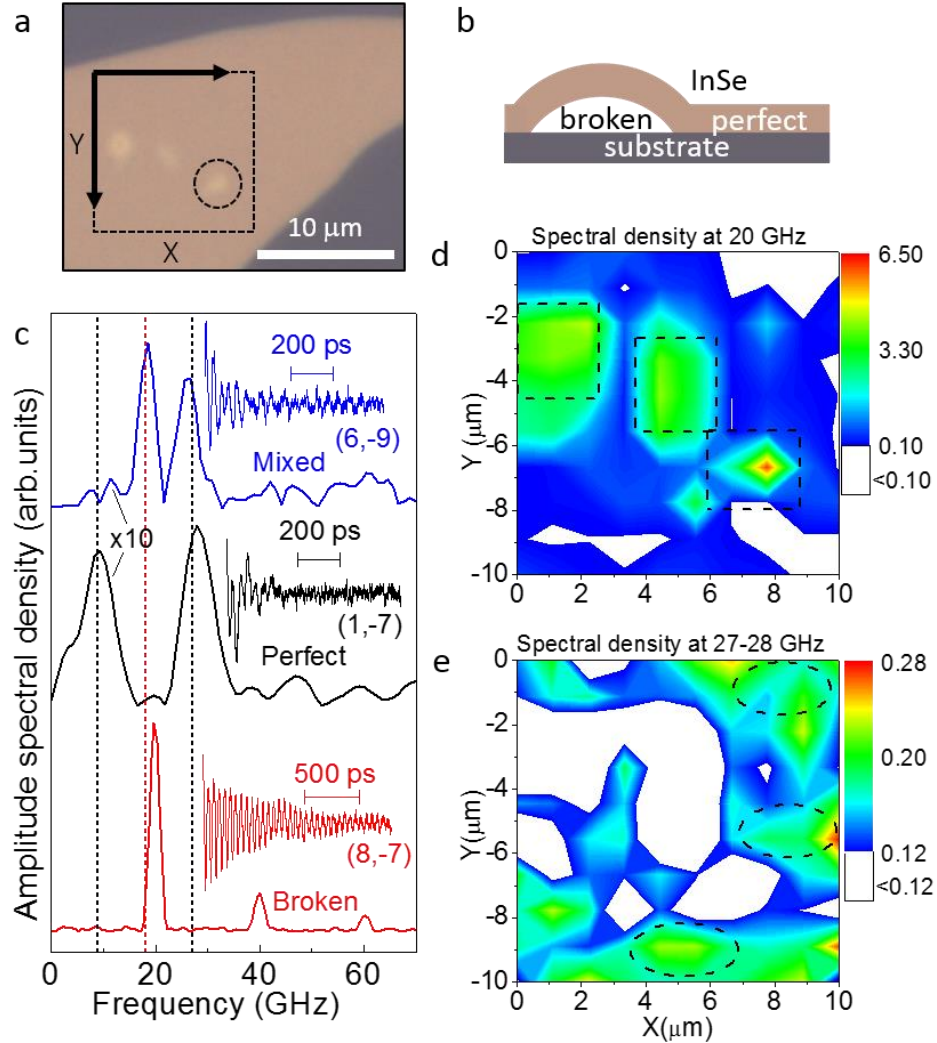


Figure 8-2. (a) Optical image of an InSe flake on a sapphire substrate. The dotted square is the area imaged by picosecond ultrasonics and the circle marks one of the InSe “bubbles”. (b) Schematic of broken and perfect interfaces. (c) Temporal evolutions (insets) and their fast Fourier transforms measured at three different positions with coordinates in microns marked in brackets (d-e). Spectral density images at frequencies of 20 GHz and 27-28 GHz corresponding to the phonon resonances for broken (d) and perfect (e) interfaces. The colour relates to the magnitude of the spectral density for the given frequency. The areas marked by dashed squares and ovals indicate homogeneous regions of broken and perfect interfaces, respectively. Scans taken over 10 x 10 grid with spatial resolution of 1 μm.

extended areas of broken interfaces, as marked by dashed lines. The spectral density of the broken (free standing) interface frequency of 20 GHz is most intense in the green and red regions of Figure 8-2d. These are surrounded by regions corresponding to strong and intermediate elastic coupling. The intensity of the spectral density for perfect and mixed interfaces (27-28 GHz) is most intense in the areas surrounding the broken regions. As seen in Figure 8-2e the spectral density at 27-28 GHz was not detected in the broken regions of Figure 8-2d.

The location of the broken interfaces correlates well with that of InSe bubbles probed by AFM (Figure 8-3a). Indeed, the AFM image reveals a flake with a rough surface and three large bubbles, as also seen in the optical image of Figure 8-2a and b. Each bubble has an irregular base with an average radius r in the range 1.0 to 1.5 μm and height h between 30 nm and 90 nm, corresponding to aspect ratios $h/r = 0.04$ -0.09 and base angles $\alpha = 2^\circ$ - 5° . The Raman spectra acquired on and off the bubbles (Figure 8-3b) reveal distinctive modes peaked at 42 cm^{-1} , 116 cm^{-1} , 179 cm^{-1} , 201 cm^{-1} and 228 cm^{-1} , corresponding to the E , A_1' , E' -TO / E'' , A_2'' -LO, and A_1' vibrational modes of InSe, respectively^[109]. The intensity of all Raman modes tend to be slightly enhanced at the location of the bubbles (see Figure 8-3b and c) whereas the position

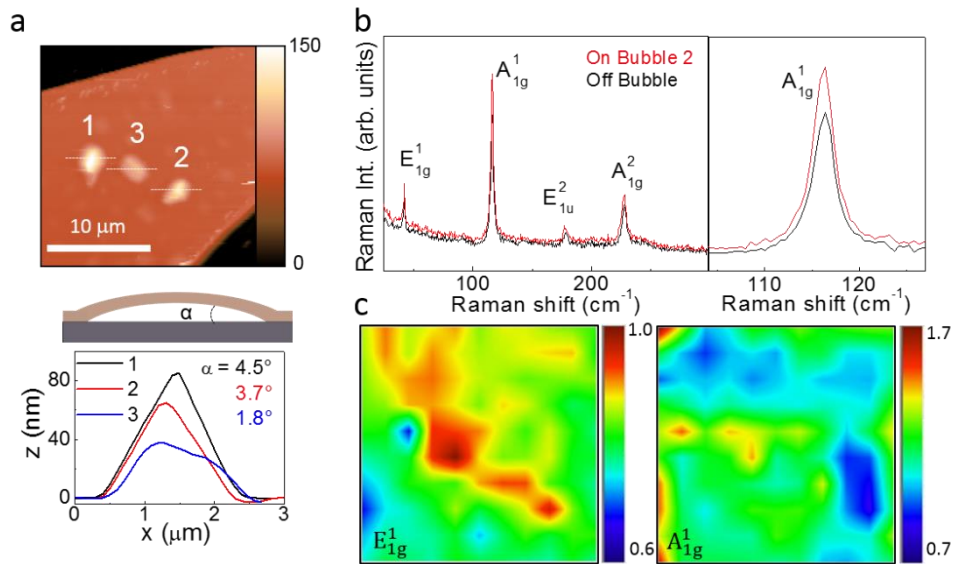


Figure 8-3. (a) AFM image of an InSe layer on a sapphire substrate showing 3 InSe ‘bubbles’ and corresponding z-profiles along the lines shown in part (a). The base angle α is calculated from the ratio between the height and width of the bubble. (b) Micro-Raman spectra on and off bubble 2 shown in part (a) ($\lambda = 532\text{nm}$, $P = 0.3 \text{ mW}$). (c) Raman intensity maps at 40 cm^{-1} (E_{1g}^1) and 114 cm^{-1} (A_{1g}^1). The Raman maps are taken in the area imaged by AFM in part (a).

does not change, indicating negligible strain^[32]. As shown in Figure 8-2b-d, these InSe bubbles behave as free standing layers generating long lived phonons (decay time $\tau \sim 1$ ns) with frequencies of up to 60 GHz. The phonons are long lived due to the broken interface which inhibits the phonon energy being efficiently transferred to the surrounding layers and/or underlying substrate.

The picosecond ultrasonic spectra for an InSe/InSe homojunction on sapphire (see Figure 8-4a) show phonon resonances similar to those of individual InSe layers. In this case, the structure has two interfaces: the interface between the two InSe layers as well as the interface between the bottom InSe layer and the sapphire substrate. Figure 8-4b shows representative temporal signals and their FFTs for three different

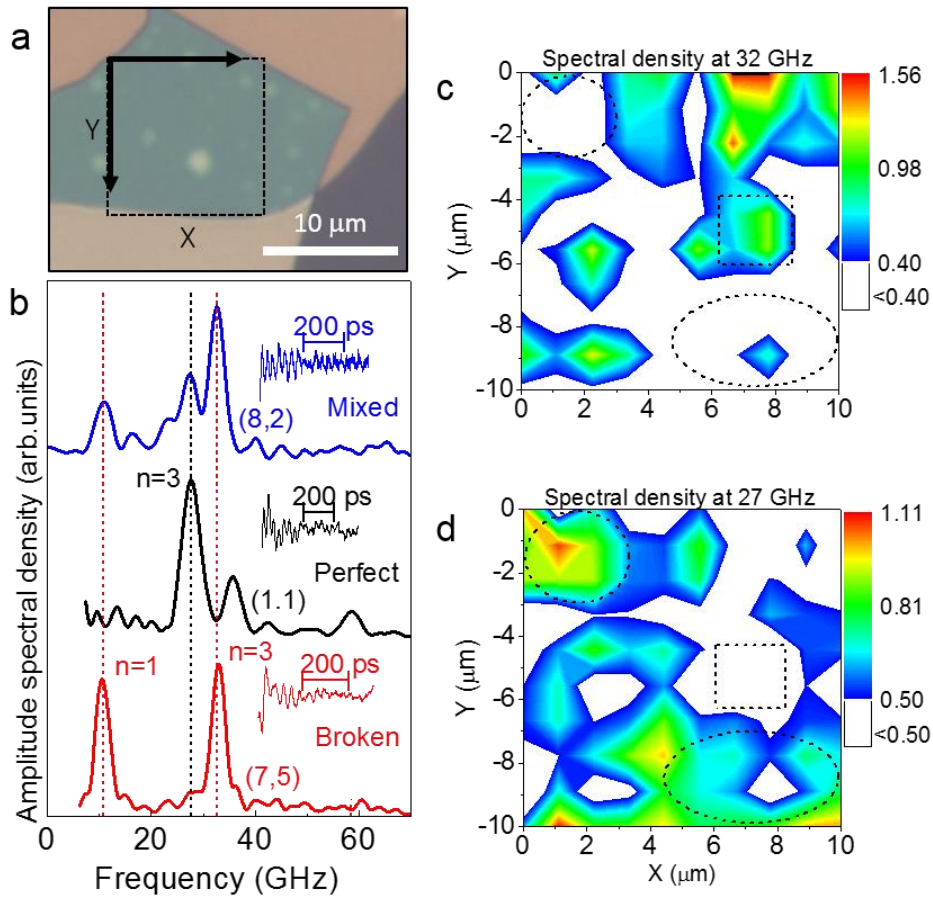


Figure 8-4. (a) Optical image of an InSe/InSe homojunction on a sapphire substrate. The dotted square is the area imaged by picosecond ultrasonics (b) Temporal evolutions (insets) and their fast Fourier transforms measured at three different positions on an InSe/InSe homojunction on a sapphire substrate. Position coordinates inside brackets are in microns. (c-d) Spectral density images at frequencies of 32 GHz and 27 GHz corresponding to the phonon resonances for broken (c) and perfect (d) interfaces. The colour relates to the magnitude of the spectral density for the given frequency. The areas marked by dashed squares and ovals indicate homogeneous regions of broken and perfect interfaces, respectively. Scans taken over 10 x 10 grid with spatial resolution of 1 μm .

locations of the probe spot on the homojunction. None of the spectra corresponds to independent vibrations of the two InSe layers. In contrast, over a wide frequency range, we observe a perfect elastic coupling between the InSe layers, *i.e.* coherent vibrations are generated within a single layer of thickness $a = 115$ nm. This is slightly smaller than the sum of the base and top InSe layer thicknesses, as measured by AFM ($a = 70 + 50 = 120$ nm). As for the case of individual InSe flakes, the coupling of the homostructure to the substrate varies from broken to perfect. Red and black vertical dashed lines in Figure 8-4b correspond to selected coherent phonon resonances for broken and perfect interfaces. From the comparison of the calculated and measured resonance frequencies, we assign the lower and middle spectra in Figure 8-4b to broken and perfect InSe/sapphire interfaces, respectively. The spectra in other locations include a larger number of lines suggesting a mixed nature of the InSe/sapphire interface. The assignment of the different spectra to broken and perfect interfaces is supported by images of the spectral density at specific frequencies: maxima for the spectral density at $f = 32$ GHz (broken interface, Figure 8-4c) correspond to minima at $f = 27$ GHz (perfect interface, Figure 8-4d) and vice versa. We note that similar images (not shown) are produced by mapping the spectral density of other phonon resonances within the same spectrum, implying that the relative intensities of resonant peaks within a spectrum largely remain consistent.

8.4 Picosecond acoustic imaging of hBN/InSe/graphene heterostructures

We now examine the temporal pump-probe traces and corresponding FFT spectra for an hBN/InSe/graphene stack on a SiO₂/Si substrate. Figure 8-5a and b show the optical image and representative temporal pump-probe traces at 4 different positions of the heterostructure: oscillations with a similar period (~ 50 ps) are clearly seen in all traces, but their decay time varies from $\tau = 42$ ps to 86 ps. The corresponding FFT spectra in Figure 8-5b reveal two resonances at $f = 18$ GHz and 32 GHz. These values agree well with the calculated spectra by assuming a perfect elastic coupling at the hBN/InSe interface (thickness 40 nm/40 nm) and a mixed interface between the hBN/InSe and the graphene/SiO₂/Si substrate. The measured resonance frequencies are almost independent on the position, but the intensity of the spectral lines vary strongly from point to point. We note that the graphene layer is not expected to have

any significant effect on the phonon spectrum because of its negligible thickness and its uniform topography on the SiO₂/Si substrate (grown by CVD synthesis by Graphenea in a class 1000 clean room^[124]). Thus the variation in the intensity of the spectral lines and oscillation decay τ are assigned to the non-homogenous coupling between the hBN/InSe heterostructure and the substrate.

The elastic coupling of the heterostructure to the substrate influences the decay time τ of the coherent vibrations and correspondingly the spectral density at a given resonance frequency: weak and fast decaying oscillations correspond to the fast propagation of phonons from InSe to SiO₂/Si at positions where the heterostructure form a perfect contact with the substrate. Figure 8-5c shows a colour map image of the spectral density at $f = 19$ GHz. White colour corresponds to the areas where the

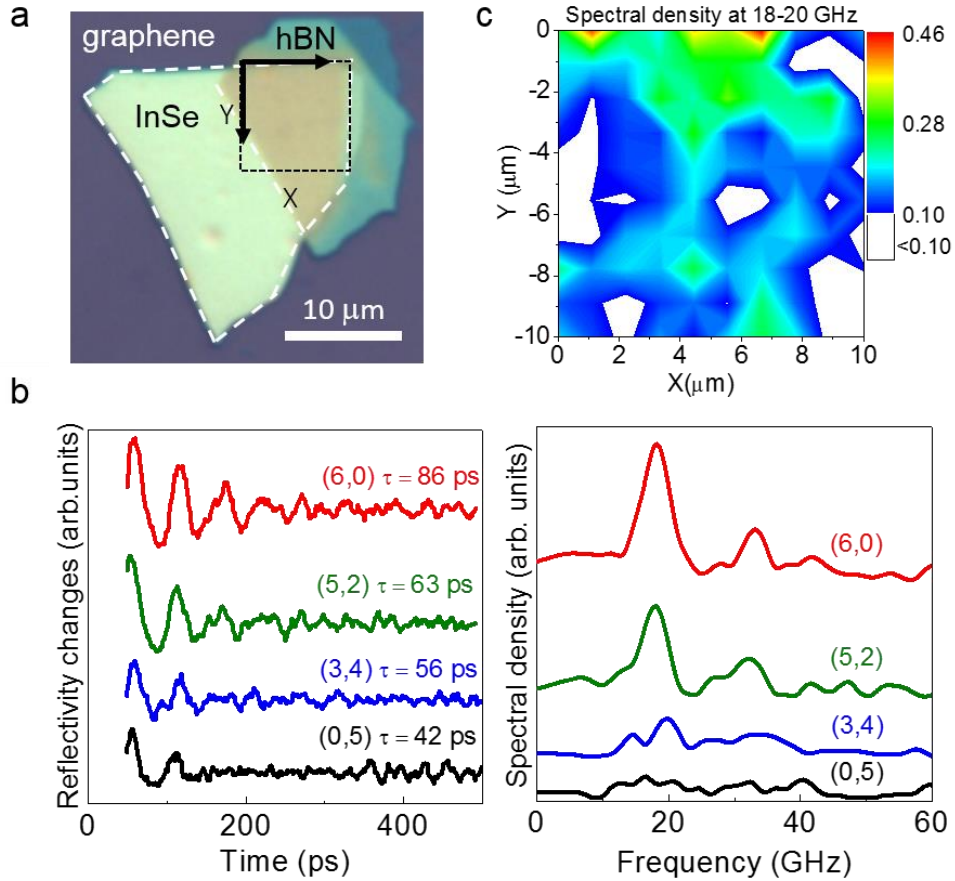


Figure 8-5. (a) Optical image of an hBN/InSe/graphene heterostructure on a SiO₂/Si substrate. The black square indicates the area of the heterostructure imaged by picosecond ultrasonics in parts (b) and (c). (b) Temporal traces of reflectivity and Fast Fourier transforms for different positions of the heterostructure. Coordinates in microns are indicated in brackets. (c) Colour map of the spectral density in the frequency range 18-20 GHz. The colour relates to the magnitude of the spectral density for the given frequency. White areas correspond to the spectral density values below the noise level.

spectral density is below the noise level (determined from the baseline of spectra) and correspondingly the interface is considered to be perfect. In contrary, broken regions show a longer decay time. In this case, the heterostructure behaves as a free standing membrane with a small Q -factor (< 3 , estimated from $r = \exp(-\pi/Q)^{[186]}$), which is significantly smaller than that (~ 10) for InSe layers or heterostructures on sapphire.

8.5 Elastic coupling at the interface of vdW layers: discussion of results

Our data and analysis show that picosecond ultrasonics can map spatially the elastic coupling between a vdW layer or heterostructure and its supporting substrate, revealing extended regions of perfect and broken interfaces. Quantitatively, the strength of this elastic coupling can be described by a stiffness η or a coupling parameter $G_{1,2}$ related to η :

$$G_{1,2} = \eta \frac{Z_1 + Z_2}{2\pi Z_1 Z_2}, \quad (73)$$

where Z_1 and Z_2 are the acoustic impedances of the contacting materials. The $G_{1,2}$ parameter has the dimension of frequency (Hz) and can be compared with the frequency, f of the phonon resonances: the cases $G_{1,2} \gg f$ and $G_{1,2} \ll f$ correspond to perfect and broken interfaces, respectively^[133].

For individual InSe flakes or heterostructure on sapphire (Figure 8-2 and Figure 8-4) there is a significant difference in the acoustic impedances of InSe and sapphire, *i.e.* $Z_{\text{sapphire}} \approx 4Z_{\text{InSe}}$. Thus the frequency of the phonon resonances is strongly dependent on the elastic coupling and reproduced by $f_n = \frac{s(2n-1)}{4a}$ for $G_{1,2} \gg f$ and $f_n = \frac{sn}{2a}$ for $G_{1,2} \ll f$. These cases correspond to values of $\eta \gg 10^{18} \text{ N/m}^3$ and $\eta \ll 10^{18} \text{ N/m}^3$ for $f = 20 \text{ GHz}$, respectively. Typical values for the stiffness between van der Waals layers is in the range $\eta \sim 10^{19}$ - 10^{20} N/m^3 ^[133,202].

The FFT spectra and images in Figure 8-2 show distinct regions with perfect and broken interfaces, and regions where both types of interfaces coexist. Thus the elastic coupling between the vdW layer and its supporting substrate can be highly non-uniform. Due to the strong dependence of the vdW potential energy on distance, small changes in the number of atoms due an imperfect interface or and/or impurities can result in the change of η and G by orders of magnitude, leading to changes in the

phonon reflectivity R at the interface and f . This can be clearly seen for the case in which the InSe layers form bubbles at the interface with the substrate (Figure 8-2 and Figure 8-3). The location of the bubbles in AFM correlate closely with the location of the broken interfaces revealed by picosecond ultrasonics. Interestingly, picosecond ultrasonics also reveal areas with broken interfaces that are either larger than those seen in AFM images or that cannot be seen in AFM, indicating a high sensitivity of phonon resonances to the elastic coupling at the interface.

In contrast to the case of vdW layers on sapphire, for the hBN/InSe/graphene heterostructure on the SiO₂/Si substrate the difference in acoustic impedances is small ($Z_{\text{SiO}_2} \approx Z_{\text{InSe}}$). In this case, the phonon frequencies do not depend strongly on the strength of elastic coupling with the substrate. For example, for a perfect interface, *i.e.* $G_{1,2} \gg f$, no phonon resonances can be generated. Also, if the interface is broken or mixed, the phonon frequencies do not depend strongly on $G_{1,2}$. In this case, the value of the coupling parameter $G_{1,2}$ for a given resonance frequency f is estimated from the measured decay time τ of the oscillations^[133]:

$$G_{1,2} = f \sqrt{\frac{1-R^2}{R^2-R_0^2}}, \quad (74)$$

where $R \approx \exp(-f\tau)^{-1}$ and R_0 is the reflectivity. From the measured values of τ (42 - 86 ps), we derive values of $G_{1,2}$ from 15 GHz to ~ 100 GHz, corresponding to values of η from 10^{18} N/m³ to $\sim 10^{19}$ N/m³.

8.6 Photocurrent and photovoltage imaging of hBN/InSe/graphene heterostructures

Characterization of the hBN/InSe sample by electrical and optical studies was undertaken in an attempt to link the topological variation in the strength of interfacial elastic coupling in the various heterostructure layers with the electrical and optical properties of the heterostructure. Characterization techniques are discussed in detail in Chapter 4. A device schematic and optical images of the device are shown in Figure 8-6a and b. Here a graphene layer is capped with a flake of InSe, which is then partially encapsulated by hBN. Source (S) and drain (D) contacts on the edges of the graphene enable measurements of the resistance of the graphene layer and of the electrical current in the dark and under optical excitation of the InSe layer. Figure 8-6c-e shows photocurrent maps taken on the same sample shown in Figure 8-6b. They reveal that

the device is most active at the edges closest to the source and drain contacts (Figure 8-6b), with the device exhibiting ‘flipped’ positive (red colour) and negative regions (blue colour) of current intensity relative to the background current (green colour). The measured photocurrent arises from the transfer of the photoexcited carriers from the InSe into the graphene. The different sign of the photocurrent can be explained by considering the built-in electric field at the InSe/graphene interface: due to the built-in electric field, the current has opposite polarity at the two graphene electrodes (see Figure 8-6a-inset). The region of the InSe/graphene heterostructure with the largest

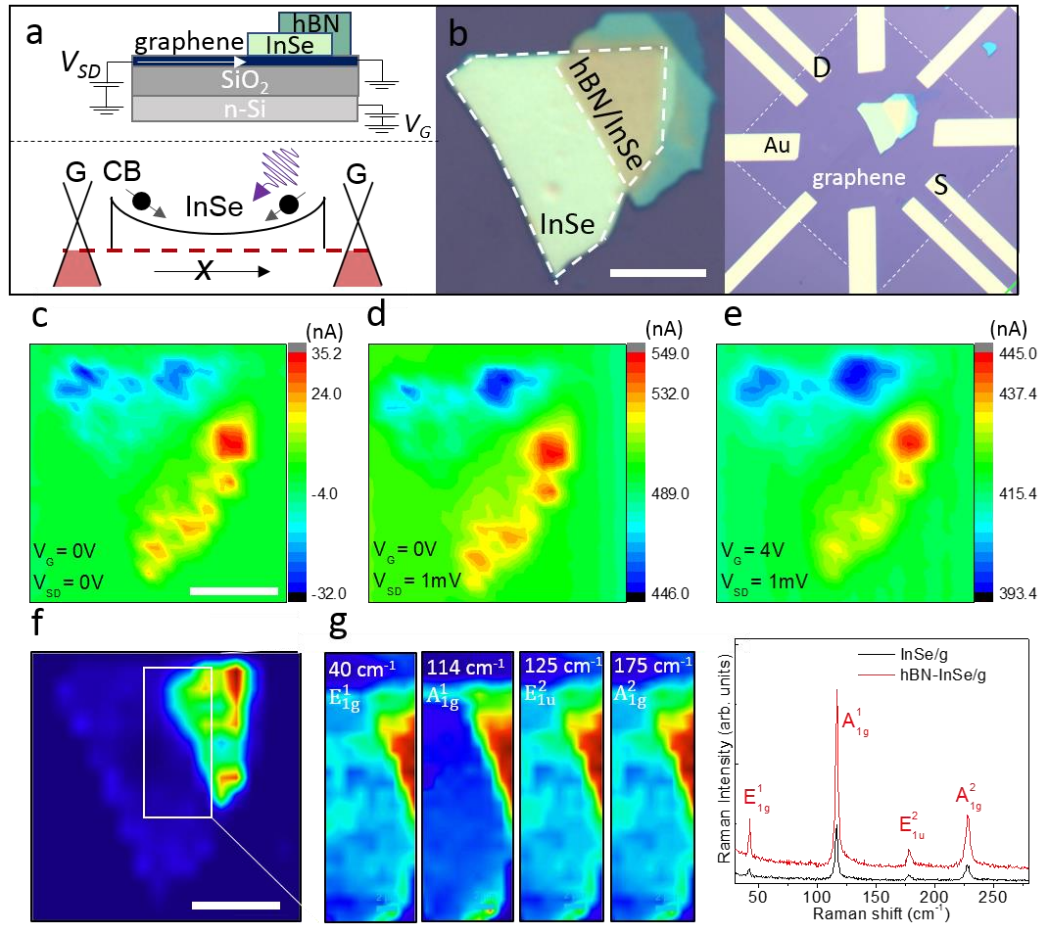


Figure 8-6. (a) Schematic of a graphene/InSe phototransistor partially capped by hBN and band alignment of InSe and graphene. (b) Optical images of the device showing source (S) and drain (D) and of the partially hBN capped InSe on graphene. The dashed line show the InSe flake. Scale bar = 10 μm. (c-e) Map of the current for the region shown in part (b). The map is obtained under light excitation with a focused laser beam ($\lambda = 405\text{nm}$, $P = 20\mu\text{W}$) at (c) $V_G = 0\text{V}$, $V_{SD} = 0\text{V}$, (d) $V_G = 0\text{V}$, $V_{SD} = 1\text{ mV}$ and (e) $V_G = +4\text{ V}$, $V_{SD} = 1\text{ mV}$. Scale bar = 10 μm. (f) Micro-photoluminescence (PL) map at the peak energy of the InSe PL emission ($\lambda = 532\text{nm}$, $P = 0.3\text{ mW}$). The white line indicates the region mapped by Raman in part (g). (g) Micro-Raman maps at 40, 114, 125, 175 cm⁻¹ corresponding to the E_{1g}¹, A_{1g}¹, E_{1u}², A_{1g}² modes. The corresponding Raman spectra at different positions are shown on the right inset.

magnitude of photocurrent is seen in the hBN encapsulated region. This agrees well with the spectra seen in Raman and PL (Figure 8-6f-g), which is indicative of an increased light absorption in the InSe layer due to improved matching of the refractive indices at the hBN/InSe interface relative to the air/InSe interface (see chapter 7). Inhomogeneous regions of current intensity are seen about the edges for different source-drain and gate voltages (Figure 8-6c, d and e). It is noted that other than the increased light absorption effect of the hBN, no correlation was found between the regions of strong PL or Raman (see Figure 8-6f,g), and the intensity of spectral density for resonant frequencies (see Figure 8-8a). This suggests that the PL and Raman response is unaffected by the interfacial coupling strength for the sample in question. It is noted that the InSe layer here is relatively thick (~65 nm) and as such, variations in the coupling strength at the interface will not affect the bulk response of PL and Raman. Perhaps measurements on a sample approaching monolayer thickness would see a correlation between such measurements.

To investigate in further detail the light-induced charge transfer at the InSe/graphene interface, in Figure 8-7 we show the dependence of the resistance (Figure 8-7a), current (Figure 8-7b) and photocurrent (Figure 8-7c) on the gate bias V_G . The Dirac point of the graphene is reached at approximately $V_G = 13\text{V}$ and 10V when measured in the dark and under optical excitation, respectively (Figure 8-7a). This shift is due to charge transfer at the InSe/graphene interface: photo-generated

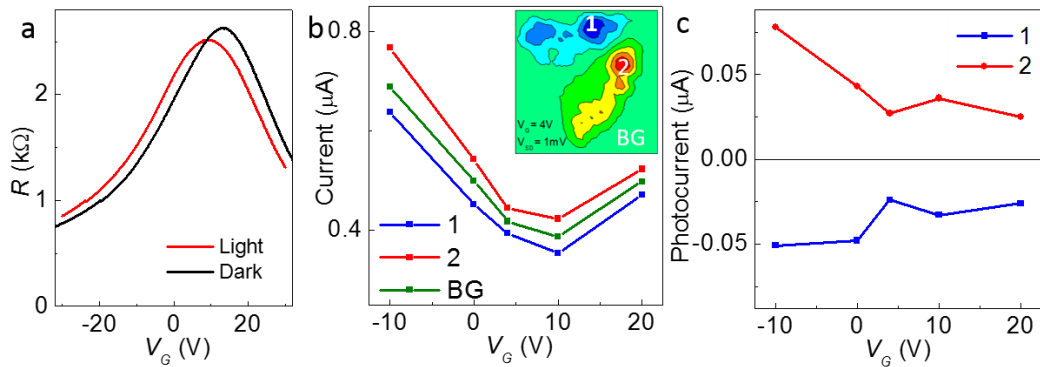


Figure 8-7. (a) Resistance R versus gate bias V_G without (black) and with (red) illumination with unfocussed laser light ($\lambda = 405\text{nm}$, $P = 20\text{ }\mu\text{W}$). (b) Current measured at 'flipped' regions 1 (blue) and 2 (red) for the range $-10\text{V} < V_G < 20\text{V}$ under light illumination with a focussed laser beam ($\lambda = 405\text{nm}$, $P = 20\text{ }\mu\text{W}$). (inset) photocurrent measurement showing relative regions of high (red) and low (blue) current across the whole sample ($V_G = 4\text{V}$, $V_{SD} = 1\text{mV}$). Photocurrent calculated from data in part b) by subtracting the background (BG) from the current at positions 1 and 2.

electrons in the InSe layer are transferred into graphene thus increasing the electron density.

In Figure 8-7b, the current under an incident laser light is shown for 3 positions, the most intense negative point (1), the most intense positive point (2) and a background region on the graphene in the bottom right of the sample (BG). By taking the difference between the measured currents at 1 and 2, and the background current, the photocurrent (*i.e.* the current directly induced by the laser light) is calculated (Figure 8-7c).

A direct comparison of a picosecond acoustic image and a current map on the same hBN/InSe region is shown in Figure 8-8. Both maps show inhomogeneities in the intensity of the spectral density (Figure 8-8a) and current (Figure 8-8b). However, no correlation between the data can be observed. The regions of high spectral density (green and red in Figure 8-8a) do not align with the areas where the magnitude of the current is the lowest or the highest (red and blue in Figure 8-8b).

No correlation between the regions of strong elastic interface coupling and regions of strong photocurrent was seen in the study. One reason for this can be put down to the information obtained by each measurement. Firstly, the picosecond acoustic image shows the elastic coupling strength between the heterostructure and its supporting SiO₂/Si substrate. As seen in Chapter 7, the interfaces between vdW (InSe and hBN) nanolayers in a heterostructure are found to be ideal for frequencies up to ~100 GHz. In contrast, the photo-induced current depends mostly on the

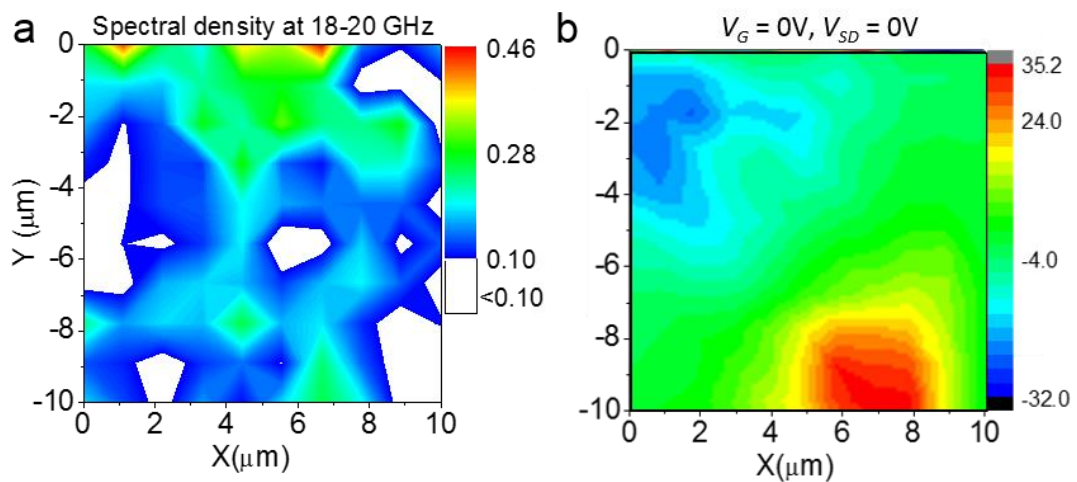


Figure 8-8. (a)) Colour map corresponding to the magnitude of the spectral density in the frequency range 18-20 GHz. White areas correspond to the spectral density values below the noise level. (b) Colour map corresponding to the value of the current for the same hBN/InSe region.

InSe/graphene interface as charge transfer must occur for the current in the graphene layer to be affected. Photo-induced carriers may also diffuse, thus resulting in charge transfer occurring at the InSe/graphene interface at lateral locations different to that of the laser spot. The in plane diffusion length $L_{\perp}$ is of the order ~ 1 mm in n-type InSe^[219]. Comparatively, our picosecond acoustic technique may only measure generated phonons at the location directly under the pump and probe lasers. These factors may explain the lack of correlation between the two measurement techniques.

8.7 Summary

Picosecond ultrasonic imaging reveals a uniform strong elastic coupling between vdW layers over a wide range of frequencies of up to tens of GHz and in-planes areas of $100 \mu\text{m}^2$. It shows extended ($\sim 10 \mu\text{m}^2$) regions of "broken" interfaces corresponding to vdW layers weakly coupled to and underlying vdW layer or substrate and behaving as free standing membranes over a wide range of frequencies of up to 60 GHz with a quality factor $Q \sim 10$. Our attempts to correlate picosecond acoustic images of interfacial coupling strength with those obtained by other characterization techniques did not reveal a link between the strength of coupling and the magnitude of PL, Raman or photocurrent. This suggests that the variations in coupling strength at the interfaces of the samples measured herein are not strong enough to affect the electronic properties of the InSe layers.

In summary, our studies on different samples show that areas of vdW layers mapped by picosecond ultrasonic possess an inhomogeneous elastic coupling at the interface with a sapphire or SiO_2/Si substrate. In contrast, the coupling between the vdW layers can be considered as perfect for frequencies of up to several tens of GHz. The frequency, linewidth and intensity of the phonons generated in the vdW layers are sensitive to the elastic properties of the layers and their elastic coupling to each other and the substrate. The success of picosecond ultrasonic imaging in the characterization of vdW layers and interfaces is extremely important for identifying and sampling areas for specific studies and applications. For instance, miniaturized components for electronics and optoelectronics should possess a good elastic contact with the substrate thus preventing overheating. In contrast, thermoelectric devices requires weak elastic contact resulting in a large temperature difference between the nanolayer and substrate. The choice of the substrate is also essential to optimize the use of the vdW

layers and heterostructures for sensing applications using them as free standing membranes. As shown in our studies, exfoliation and dry transfer of vdW layers on different substrates enable the fabrication of structures with homogeneous elastic properties over areas of $\sim 10 \text{ } \mu\text{m}^2$. Such areas can be selected and used for the fabrication of specific functional devices.

The picosecond acoustic measurements taken prior (see Chapters 6 and 7), lacked the imaging capability seen here, as only single point measurements were possible. This work has furthered the understanding of vdW materials by successfully probing the lateral variations in the interlayer elastic coupling of mechanically formed vdW heterostructures on substrates.

Chapter 9

9 Conclusions and outlook

The primary aim of the PhD project was to assess the strength of interlayer coupling through the use of picosecond acoustics in various vdW heterostructures, combining nanolayers of InSe, hBN and graphene on substrates of Si and sapphire. The key results of the works herein are summarised below.

- (i) The coupling at the vdW interface of InSe/InSe homojunctions and InSe/hBN heterostructures may be seen as elastically ideal for frequencies up to 100 GHz. It is shown that the nanolayer/substrate interface is generally weakly coupled and varies between samples. It is also shown that nanolayers as thin as ~5 nm are weakly coupled to their substrate (sapphire and SiO₂/Si) with no correlation between thickness and coupling strength.
- (ii) Continuous regions of both ideal and broken interfaces are revealed through the use of picosecond acoustics as an imaging technique. Comparisons of photocurrent mapping and picosecond acoustic imaging reveal no apparent links between regions of strong coupling and regions of high photocurrent.

Based on these key results, the findings and consequent future prospects are discussed below.

9.1 Elastic coupling at the nanolayer/substrate interface

The combined studies of this thesis show that elastically imperfect interfaces tend to form between a sapphire substrate and exfoliated van der Waals InSe crystals with thicknesses down to approximately 5 nm. The most likely reason for the imperfectness of the interface is surface roughness of the substrate rather than that of the InSe layer, which tends to form abrupt and atomically smooth interfaces with other

layered compounds^[101]. However, InSe also tends to form bubbles, behaving as a free-standing layer with broken interfaces. To achieve an elastically perfect interface between the substrate and the exfoliated layer, the surfaces should be flat and clean down to the atomic level. It is shown that for InSe flakes with a large range of thicknesses (~ 100 nm to ~ 5 nm) there is not a direct link between the thickness and the coupling to the underlying substrate being found.

We believe that these findings can lay a foundation for further picosecond acoustic studies into the myriad of potential combinations of vdW nanolayers and substrates^[4,5,51]. Similar picosecond acoustic measurements may highlight vdW nanolayer/substrate combinations with ideal elastic coupling suitable for thermoelectric devices. These results were published in *Scientific Reports* **6**, 26970 (2016).

9.2 Elastic coupling in vdW heterostructures

The conclusions of the present work on the elastic properties of vdW interfaces are broader than those of the initial work by Beardsley *et al.*^[24], which reported InSe layers weakly coupled to a substrate. The follow up work is focussed on the elastic properties of the interfaces rather than the layers themselves, as reported in the literature^[183-185]. We show that the elastic coupling at the vdW interface between two nanolayers or between a nanolayer and its substrate may vary and can be described by the spring model through comparisons of experimental and theoretical spectra. In both InSe/InSe and InSe/hBN vdW heterostructures, we observe a strong elastic coupling, well described by the acoustic mismatch model.

The measured spectra of coherent phonons reveal the existence of nanomechanical resonances in all layers of vdW heterostructures, with frequency, amplitude, and spectral width that depend on the strength of elastic coupling between the different layers and/or with the supporting substrate. Our study of the acoustic mismatch between vdW layers in InSe/InSe homojunctions and InSe/hBN heterojunctions reveal elastically ideal interfaces for frequencies up to ~ 100 GHz. In some cases, the inhomogeneities of the elastic coupling at the interfaces should also be taken into the account to explain the phonon spectrum as the phonon resonances may not always be described by a single elastic coupling parameter.

We have shown picosecond acoustic techniques as a viable tool to measure the coherent acoustic phonon spectra and estimate the strength of the elastic coupling of InSe layers with thicknesses from 5 to ~ 100 nm and their heterostructures.

We believe that these findings could lead to further studies into novel multilayer heterostructures with ideal elastic coupling necessary for efficient phonon transport and charge transfer through an interface, as required for efficient heat dissipation. Also of interest is the elastic behaviour of vdW interfaces in thinner layers, approaching the monolayer and also at higher frequencies, approaching THz frequencies. Finally, it may be possible to exploit such techniques to apply strain to vdW materials and modulate the electronic properties^[40] for high-frequency acoustoelectric and acousto-optic devices. For example, 2D InSe has already proved itself to be electronically sensitive to strain^[220]. These results were published in *Physical Review B*, **98**, 075408 (2018).

9.3 Picosecond acoustic imaging

The use of picosecond acoustics as an imaging technique on different samples show that areas of vdW layers possess an inhomogeneous elastic coupling at the interface with sapphire or SiO₂/Si substrates. In agreement with the prior works, it is shown that the elastic coupling between the vdW layers can be considered as perfect for frequencies of up to several tens of GHz.

Picosecond photoacoustic imaging reveals uniform, in-plane regions (up to $\sim 100 \mu\text{m}^2$) of strong elastic coupling between vdW layers over a wide range of frequencies of up to tens of GHz. It also reveals extended ($\sim 10 \mu\text{m}^2$) regions of "broken" interfaces corresponding to vdW layers and heterostructures weakly coupled to the substrate, behaving as free standing membranes over a wide range of frequencies of up to 60 GHz with a quality factor $Q \sim 10$. Our attempts to correlate picosecond acoustic images of interfacial coupling strength with those obtained by photocurrent imaging did not reveal a link between the strength of coupling and the magnitude of the photocurrent.

We believe that these findings will stimulate further studies into picosecond acoustic techniques as a tool for further interfacial characterization of vdW heterostructures. Our technique could prove particularly useful in detecting regions of

broken and ideal interfaces. These results were accepted for publication in *ACS Nano* **13**, 11530 (2019).

9.4 Outlook

This PhD project has led to a greater understanding of the nature of vdW interfaces, yet have also highlighted further questions and avenues for new research.

Means of probing phonon transport across an interface can provide the foundation for designing and exploiting new materials and quantum systems: the strength of coupling between the layers is critical to both charge and phonon transport and thus pivotal to the future development of functional devices, including new device concepts for high-frequency electronics and thermoelectrics. The spectrum of nanomechanical resonances changes significantly when the distance between the layers changes by only one layer of atoms. Thus it could be used to probe interfaces with an unprecedented spatial resolution and over a wide frequency range. To date, the only technique that could offer such spatial resolution is TEM, but this is time-consuming as it requires special sample preparation to expose interfaces to the probing electron beam. Detailed images such as the surface maps taken using the system described in Chapter 4.2.3 (see Chapter 8, Figure 8-2 and Figure 8-4) may be completed in the timescale of ~ 1 hour.

Of particular interest is the possibility of using strain to modulate the electronic properties for high-frequency acousto-electric and acousto-optic devices. In particular, 2D InSe exhibits high mechanical flexibility, can sustain high mechanical strain ($>20\%$) and its electronic properties can change under both uniaxial and biaxial compressive strains^[220]. These properties, which have been only recently predicted by theory^[220], are highly desirable for new “straintronic” devices and sub-THz nano-electro-mechanical and optomechanical devices. In particular, thin layers and heterostructures weakly coupled to the substrate may have high finesse (>10) and be used as sensors for single molecules adsorbed at surfaces and interfaces. Further studies may involve the study of single atomic layers and correspondingly THz phonons. In this case, the approximation of continuous media and acoustic mismatch approach may not be valid. There are no principle limitations to these studies, which will contribute to important advances in the physics of phonons and their exploitation in novel 2D structures.

Identifying regions of both strong and weak elastic contact in multilayer heterostructures through picosecond acoustic imaging could prove essential for further study into miniaturized components in electronics and optoelectronics. For example, a strong elastic contact between layers is highly important for efficient heat transfer, preventing overheating. The successes achieved herein in identifying a range of interfaces in vdW heterostructures could prove useful in identifying combinations of nanolayers suitable for furthering device miniaturization. Furthermore, the phonon transport at interfaces affects the out-of-plane heat transfer and hence the thermal conductivity of a heterostructure^[221]. A degree of control over the phonon transport could enable the tailoring of thermal properties of thin layers^[222] for thermoelectrics and/or thermal insulation with thin coatings.

The vdW heterostructures fabricated in our studies, by mechanical exfoliation and dry transfer techniques, exhibit homogeneous elastic properties over areas of up to $\sim 10 \mu\text{m}^2$ with some behaving as elastically ideal interfaces and others as free standing membranes. Picosecond acoustic imaging enables the non-destructive assessment of these regions in vdW layers and heterostructures which may prove useful for a plethora of potential applications that integrate vdW materials.

Various breakthroughs on 2D materials and heterostructures have been achieved using mechanically exfoliated nanolayers yet further development is necessary. For example, the controlled formation of interfaces is still in its infancy. The fabrication of functional systems requires the precise assembly of diverse materials with precise control of interfacial properties. This will require the development of innovative approaches for making and imaging multi-layered structures for specific applications. Picosecond ultrasonics imaging, together with the fast acquisition rate offered by the ASOPS technique^[223], offers unprecedented opportunities to map and inform the design of novel functional systems and to open unexplored avenues in science and its translation into technologies.

To summarize, picosecond acoustic measurements and imaging techniques provide further means of characterization in vdW structures and devices, highlighting with high interface properties with high spatial resolution.

10 Bibliography

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