Ultra low temperature photoluminescence imaging of nano objects under high magnetic field

INTRODUCTION

An important part of modern science is the investigation of smaller and smaller structures with properties determined by a nano-sized group of atoms or molecules. Examples are semiconductor quantum dots, organic nanostructures and carbon-based systems like nanotubes and graphene. These systems represent at the same time fascinating physical properties and a large industrial application potential. To unravel their electrical, optical and magnetic properties it is crucial to measure the response of individual nanostructures, because in ensemble measurements only the average value of an observable parameter is detected, and essential information is lost about the behaviour of individual objects. For instance, temporal information about dynamical processes might be lost by ensemble averaging, as well as spectroscopic information when the averaging occurs over objects that are not precisely identical. The development of local characterisation techniques is therefore of the utmost importance. High magnetic fields are an important tool in the study of nano-objects, as the magnetic length (4 nm at 40 T) is comparable to typical dimensions of nano-objects, leading e.g. to significant changes in their energy spectrum, allowing insightful magneto-spectroscopy experiments. In recent years significant progress has been made in the development of scanning probe techniques or other single-object or local-spectroscopy methods, and some of them have been implemented in commercially available superconducting magnets (<12 T). Currently, there is an urgent need to develop local probe and single-object measurements in the highest (non-destructive) magnetic fields available (90T), to benefit from the powerful combination of nanoscience and high fields.

In this research project we will develop optical techniques, notably spectrally resolved micro-photoluminescence (μPL) spatial mapping, combined with the high pulsed magnetic fields facility at LNCMI-Toulouse, to investigate the physics of emerging nano-materials; (i) monolayer and few layer transition metal dichalcogenides such as MoS$_2$, WS$_2$ and WSe$_2$, and (ii) single core/shell and core/multi-shell nano wires (e.g. GaAs/AlAs). This requires the development of a μPL setup capable providing spectroscopically resolved images of the sample at low temperatures which can then be used to select individual nano objects for a μPL investigation in pulsed magnetic fields up to 90T. We will then combine μPL with ultra fast optical techniques e.g. pump-probe and time resolved μPL to probe the carrier dynamics.

Layered transition metal-dichalcogenides

Layered compounds involving transition metals from group VI and chalcogens (the so-called dichalcogenides) are promising candidates for exploring atomically thin structures. The basic building block consists of a monolayer of a transition metal with a chalcogen monolayer above and below. All the dichalcogenides have a strong intra layer chalcogen-metal covalent bond while, the layers are weakly held together by van der Waals forces. Nevertheless, the inter layer coupling plays a significant role in determining the band structure. Bulk crystals are semiconductors with an indirect
gap in the near infrared spectral range. In contrast, single layer transition metal dichalcogenides such as molybdenum disulfide (MoS₂), tungsten disulfide (WS₂) or tungsten diselenide (WSe₂) are two dimensional (2D) semiconductors with a direct gap in the visible spectral range at the K and K’ points of the Brillouin zone [Mak10, Splendiani10, Eda11, Albe02, Gutierrez13, Zhao13, Wang12, Cao12, Mak13]. Moreover, electronic levels have quadruple degeneracy (twice for the valley, and twice for the spin degrees of freedom). The carriers at the K and K’ points behave as massive Dirac fermions and the population of each valley can be controlled by the circular polarization of exciting light. Hence, the dichalcogenides have potential applications in “valleytronics”. However, for “valleytronics” applications, an understanding of the carrier dynamics, notably the inter valley scattering processes is crucial.

The optical response of a single layer of these materials is dominated by excitonic effects; the optical spectrum is characterized by the presence of two low-energy exciton peaks (A and B excitons) that arise from vertical transitions from a spin-orbit-split valence band to a doubly degenerate conduction band at the K point of the Brillouin zone [Frey98, Klein01, Ramasubramaniam12]. The physics of excitons in 2D semiconductors is known to be extremely rich once additional carriers are introduced into the system; the optical spectra consist of emission from both neutral (X) and charged excitons (X±). It has been shown that a gate can be used to tune the carrier density and hence the exciton charge state in single layer molybdenum disulfide and molybdenum diselenide [Mak13,Ross13]. Very recently, we have shown that in doped WS₂ tuning the excitation power alone allows us to select the exciton charge state [Mitioglu13]. While in standard semiconductors the dissociation energy of the charged exciton is relatively small (a few meV), in exfoliated dichalcogenides this energy is approximately an order of magnitude larger. Hence, the ability to control the exciton charge state in semiconductor structures which emit light at room temperature and in the visible range is expected to open many possibilities for optoelectronics applications.

Figure 1.1: (a) Optical microscope image and (b) AFM image of the WS₂. (c) AFM height profile along the path indicated by the green line (d) Raman spectra measured at T=300K on the single layer area of the flake (red line) and bulk WS₂ (black dashed line). The inset shows the strain induced shift of Raman spectra taken at two different positions on the single layer area of the flake.
We have already acquired considerable experience in characterizing exfoliated transition metal-dichalcogenides. For example, flakes of WS$_2$ placed on a silicon substrate. The position of the PL emission and its intensity changes significantly as a function of the position reflecting the change in the number of layers as we move across the flake. These results seem to indicate that there is not an abrupt transition between the properties of mono layer and few layer WS$_2$. Few layer WS$_2$ can also give bright PL and the only reliable method to identify mono-layer WS$_2$ is to measure precisely the separation of the WS$_2$ Raman peaks. Typical micro Raman spectra, together with optical and AFM images, of mono-layer WS$_2$ are presented in Fig.1.1. The different spectra where acquired at different positions on the WS$_2$ flake seen in the insert. The bulk crystal shows two Raman peaks at 355 cm$^{-1}$ and 421 cm$^{-1}$ corresponding to the well known active Raman modes. However, for the single layer these two peaks shift towards each other by 2 cm$^{-1}$ providing irrefutable evidence for the monolayer nature of this area of the flake. Understanding how the electronics properties of WS$_2$ evolve as we go from bulk to monolayer is a fundamental question which we will necessarily address in this project.

The application of a high magnetic field quantizes the orbital motion of the massive Dirac fermions at the K and K’ points. However, the lack of inversion symmetry in monolayer dichalcogenides leads to markedly different reaction of the two valleys to the magnetic field. In a simple two band model, the Landau level energy spectrum is given by $E_n = \pm \sqrt{\Delta^2 + (\hbar v)^2}$, where $\Delta = m^* v_F^2$ is half of the “mass gap” of the Dirac fermions and $v_F$ is the Fermi velocity. The characteristic magnetic energy $\varepsilon = \sqrt{\hbar v_F/\ell_B}$ where $\ell_B = \sqrt{\hbar/eB}$ is the magnetic length. Due to the large direct gap of the monolayer dichalcogenides (~1.6-2eV) we have $\Delta^2 \gg \varepsilon^2$ and a Taylor expansion gives $E_n \approx \pm (\Delta + n\hbar v_F^2 eB/\Delta)$ so that the Landau levels evolve linearly with magnetic field corresponding to particles with a relatively heavy effective mass $m^* = \Delta/v_F^2 \approx 0.5m_e$. For $n > 0$ the Landau levels occur in pairs in each valley (one in each band). The $n = 0$ Landau level is particular with a single Landau level per valley. For both spin orientations, the $n = 0$ Landau level is fixed to the top of the valence band for the K valley and to the bottom of the conduction band for the K’ valley. This is a direct result of the particular winding properties of the Berry phase and is also necessary to ensure the correct zero field microscopic chiral selection rules in the $B \to 0$ limit. The selection rules for dipole allowed transitions are $\Delta n = \pm 1$ so that circularly polarised light can be used to select the valley in either excitation or detection (see Figure 1.2). Furthermore, the large spin orbit splitting of the valence band, which is of the order of a few hundred meV, means that circularly polarised light effectively selects both the spin and valley degrees of freedom: The A and B exciton transition are energetically separated (by the spin orbit splitting of the valence band) so that resonant excitation can be used to select only the A exciton efficiently pumping a single valley provided the excitation is circularly polarised. In detection the circular polarisation of the A exciton emission selects both the valley and the spin. Thus, single layer transition metal dichalcogenides form an almost perfect model system to investigate the valley and spin degrees of freedom of massive Dirac fermions with a view to “valley-tronics” applications.
Figure 1.2: Schematic of the calculated Landau levels at the K and K’ points of the Brillouin zone of MoS$_2$. Dipole allowed optical transitions (change in Landau level index Δn=±1) are indicated by the arrows (circular polarization σ± indicated by solid/broken lines). Note the specific behavior of the n=0 Landau level which, depending upon the valley, only occurs in either the valence band (K) or conduction band (K’). Due to the large SO splitting of the valence band circularly polarized light selects both valley and spin. After Rose et al [Rose13].

Nano wires

Semiconductor nanowires (NWs) represent a rapidly expanding field of research largely due to their great technological promise [Hu99, Cui01, Therland06, Lieber07, Lu07]. For example, transistor action has been demonstrated using carbon nanotubes and silicon nanowires [Tans98, Cui03], it has been suggested that indium phosphide nanowires can be used as building blocks in nanoscale electronics [Duan01], and doped radial core-multi-shell NWs have good chances to find industrial applications as high efficiency solar cells [Krogstrup13, Spirkoska11, Fickenscher13, Estrin13, FontcubertaiMorral08]. NWs with two dimensional (2D) carriers localized at the core/shell interface offer new perspectives in quantum electronics [Lieber07]. However, to introduce carriers the control and understanding of the doping mechanisms in NWs is crucial.

Significant efforts have been made to obtain high mobility 2D carriers in GaAs heterostructures grown by molecular beam epitaxy (MBE). Remote or modulation doping, which spatially separates the carriers from the dopant atoms, was a crucial step in the discovery of the fractional quantum Hall effect. The direct application of the modulation doping techniques to GaAs/AlAs NWs would seem to be a natural evolution. Today high quality GaAs/AlAs nanowires with a large aspect ratio and typical diameters of a few tens of nanometers are routinely grown by MBE using the vapour-liquid-solid (VLS) method [Titova06, Pistol08, Shtrikman09a, Shtrikman09, Spirkoska09, Algra11, Jahn12, Musin12, Assali13]. While core multi shell NWs would seem to be ideally suited for modulation doping, in practice achieving a significant doping remains a challenge. In the VLS method, depending upon the growth plane, dopants can act as donors or acceptors [Hilse10] and the dopant incorporation can be different for axial and lateral (sidewall) growth [Dufouleur10] resulting in an inhomogeneous dopant distribution, or even compensation and negligible doping [Casadei13]. In NWs the use of the AlGaAs ternary alloy for the shell can lead to the segregation of the Ga and Al atoms leading to the formation of the quantum dots [Heiss13, Funk13]. On the other hand both experiment and theory suggest that modulation doping in core-multi-shell NWs can lead to non
uniform charge distribution with an accumulation of charge at the facets or corners of the hexagonal NW which can lead to quantum confinement [Funk13]. We have recently shown that significant doping can be achieved using core/multi-shell NWs [Jadczak14] opening the way for the investigation of the physics of 2D carriers confined at the core/shell interface in NWs.

Magneto-spectroscopy of single GaAs nanowires is a powerful tool to investigate their electronic structure. Our preliminary measurements under low power (nW) excitation at low temperature reveal the striking difference between emission from doped and undoped NWs (see Fig. 1.3). Undoped NWs show several emission lines associated with excitons bound to defect pairs (so called KP series). Such lines were observed before in epitaxial GaAs of very high quality, as reported by Kunzel and Ploog [Kunzel80]. This demonstrates that the optical quality of our GaAs/AlAs core/shell nanowires is comparable to the best GaAs layers grown by molecular beam epitaxy. The emission spectra from doped NWs are considerably richer. In addition to the KP series of lines, emission at higher energy corresponding to the recombination of 2D holes confined at the core/shell interface with electrons in the core of the NW is observed together with the phonon replicas. The anti-crossing observed in the confined emission around B=12T is the signature of a resonant polaron coupling. To observe such a coupling occupancy arguments lead to the conclusion that the Fermi energy of the 2D carriers has to be similar to or greater than the phonon energy (33 and 36meV for the TO and LO phonons) demonstrating the large carrier density present in the core/multi-shell nanowire.
Currently, the quantum electronics group at LNCMI-Toulouse has two permanent researchers, and three PhD students (including one CSC student). In addition to access to the high magnetic field facility (35T at T=25mK in Grenoble and 80T at T=50mK in Toulouse) the group has the following equipment:

(i) An Oxford Instruments Kelvinox top-loading dilution refrigerator (T=8mK) equipped with a 16T superconducting magnet. The fridge can be used for both optical and transport measurements. We are in the process of implementing µPL in the dilution fridge. The sample is placed on x-y piezo (Attocube) translation stages and light is focused onto and collected from the sample using a microscope objective mounted close to the sample. Once working, this system which will be capable of making spectrally resolved spatial maps, at mK temperature and in magnetic field, will be unique in the world. In parallel we are also developing µPL in the pulsed magnetic fields up to 80T.

(ii) An Oxford Instruments HiRes optical cryostat for zero field µPL and µRaman characterization of the sample. The spot size of 1µm diameter is small enough to allow individual NWs to be measured. The cryostat is mounted on motorized x-y translation stages, again to allow us to take spectrally resolved spatial maps (see Figure 1.4). Excitation is provided by a tunable Ti-sapphire laser and a number of other solid state lasers. We have an Acton spectrometer equipped with a CCD camera. We have recently purchased a start of the art femto-second Ti-sapphire laser, OPO and streak camera for time resolved (pump-probe).

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Samples are provided through numerous collaborations with world leading laboratories, e.g. Weizmann Institute of Science (NWs, GaAs 2DEG), Physics Department, University of Nottingham (GaAs 2DEG), Institute of Applied Physics, Republic of Moldova (monolayer and bulk WS₂ and MoS₂), University of Warsaw (epitaxial graphene).

This thesis will be co-directed by Paulina Plochocka (LNCMI-Toulouse). For further information concerning the scientific activities of the group please the 2013 annual report http://www.toulouse.lncmi.cnrs.fr/spip.php?rubrique38&lang=en
Recent Publications of the Quantum Electronics group


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