Towards high-efficiency atomically thin solar cells: Understanding the nature of excitons in van der Waals heterostructures - Final Report

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Preface

1 Introduction

The Aim of my stay at Massachusetts Institute of Technology in Cambridge (MA) was to obtain a deeper understanding of the exitonic processes in van der Waals heterostructures. This was motivated by my previous research results at Technische Universität Wien. I started my PhD studies at the Photonics Institute in Vienna working with graphene. Graphene is a novel material that was found to have distinct properties, making it a perfect playground for fundamental physics studies and a new base for applications. Theoretical predictions in the late 40ties [1] suggested that graphene has a linear dispersion relation. This is the reason for an extremely high charge carrier mobility in graphene monolayers. Until ten years ago and since the start of the integration of circuits, basing on the development of the first semiconductor transistor, the density of transistors integrated in a single processor had doubled every two years. This lead to the same increase in performance of workstations and desktop computers. But, due to limits arising form fundamental physic principles, this pace could not be followed during the last decade. A new strategy was used, namely parallelization instead of scaling, to avoid the upcoming bottleneck. Nevertheless the performance rise rate dropped and the so called Moore's gap opened. This made it clear that at some point only a fundamental change, specifically a change of the used material, would help to further increase the performance of integrated circuits and processors.

A lot of effort was put into finding a suitable material. Not only a lot of different semiconductors were examined but also novel materials like nano wires and carbon nano tubes were studied. None of these met the requirements that would have made it a promising candidate for the replacement of silicon. Although, graphene was thought to be not mechanically stable on any surface, in 2004 an experiment made by a group of researchers lead by Geim and Novoselov [2] proved everyone wrong. They were to produce an atomically thin layer of graphene. What is probably more important is that by building a field effect transistor they also demonstrated in the very same article that graphene indeed has the property everyone was looking for. The experimentally shown linear dispersion relation leading to the extremely high charge carrier mobility had a huge impact into solid state physics research. In 2010 Geim and Novoselov were awarded with the Nobel Prize in physics. This drew even more attention to this new kind of material. A waste number of groups all around the world started working on projects exploring the properties of this extraordinary material. Due to the expected potential acquiring funding for research was, and still

is, easy especially compared to well established research fields.

Graphene proved to be the expected playground for fundamental condensed matter physics research. This material helped to shine light on many physical effects that were not demonstrated experimentally before. One feature of the dispersion relation, the band gap, showed to be a game stopper in terms of graphene's application for digital transistors in integrated circuits. Graphene has no band gap. Therefore, a field effect transistor made out of graphene conducts carriers in any biassing scheme. This means that it can never be turned off completely, making it useless for digital electronics. A lot of effort was put in opening a band gap. Some groups tried to tackle this problem by etching graphene into thin nano ribbons and they indeed were able to open a gap [3]. But this gap, measuring only a few hundred meV, was far to small for building decent field effect transistors that work at room temperature. Other groups tried to bias bilayer graphene to induce a gap [4] but also this resulted in minuscular gaps. This kept the search for the material that could replace silicon alive.

In 2010 Heinz an coworkers published a work on a material that, like graphene, is atomically thin [5]. This material, namely MoS_2, was found to have a direct band gap in it's monolayer form. Although the calculated mobility of charge carriers in this material was expected to be lower than the one in graphene the probability that it would outperform silicon was quite high. This attracted a lot of interest and many people started working on MoS_2. Exfoliated MoS_2 was found to have a strong fermi level pinning and to be naturally n-doped. This prevents the design of ambipolar transistor circuits and therefore hinders the application of MoS_2 in digital circuits. Luckily it was clear very soon that MoS_2 is only one member of a huge family of atomically thin materials. Transition metal dichalcogenides (TMDs) are materials formed out of one transition metal atom and two chalcogen atoms. Among all possible combinations more than 40 form atomically thin layers [6]. The predicted properties span from superconductors to semiconductors, semimetals and insulators. WSe_2 was the first TMDs being found to be ambipolar. Nowadays intensive research is being done to understand and optimize these materials so that they can play a major role in future electronic circuit designs.

At the end of my MSc studies I built a field effect transistor made out of graphene. During my MSc thesis I fabricated and characterized a graphene made photo detector embedded in a dielectric mirror cavity [7]. Working at the Photonics Institute of Technische Universität Wien, my focus is on optics and optoelectronics. Therefore my interest in atomically thin materials is not due to their unique electrical properties but to the optical properties that differ a lot from those of classical semiconductors. At the beginning of my PhD studies I started to fabricate MoS_2 based transistors. I noticed that the contact area has a major impact on the electrical properties of these devices. Shortly after this I noticed the strong dependency of their resistivity on the illumination power. This effect was reported earlier but incorrectly attributed to the material itself. My measurements showed that it strongly depends on the defect states of the substrate and on the interface between the atomically thin layer and the substrate [8]. After this work I was able to build a heterostructure

formed by two atomically thin layers. Using a dry transfer technique a WSe_2 layer was placed on-top of a MoS_2 layer. This device formed a planar p-n junction and was used to efficiently convert optical into electrical energy [9].

The efficiency of energy conversion measured in my experiments was below the expected values. As, by fabricating and characterizing multi layer heterostructures, the efficiency could not be increased it soon became clear that a deeper understanding of the fundamental optical processes in these materials has to be acquired prior to further optimization steps. Optical processes in transition metal dichalcogenides are dominated by exitonic states [10]. To analyze the interlayer excitons that may play a profound role in the heterostructures under investigation, the wavelength range of interest is below 1.2eV. A modification of our experimental setup in Vienna to match this specifications wasn't an option due to costs above 60.000€ . Therefore I planed to visit Massachusetts Institute of Technology and preform the required experiments in the group of Pablo Jarillo-Herrero. Thanks to the Marshall Plan Scholarship I was able to visit Pablos lab for half a year.

2 Fabrication of the excitonic devices

To better understand the excitonic processes in stacks made out of transition-metal dichalcogenides I developed the structure depicted in FIGURE 1.

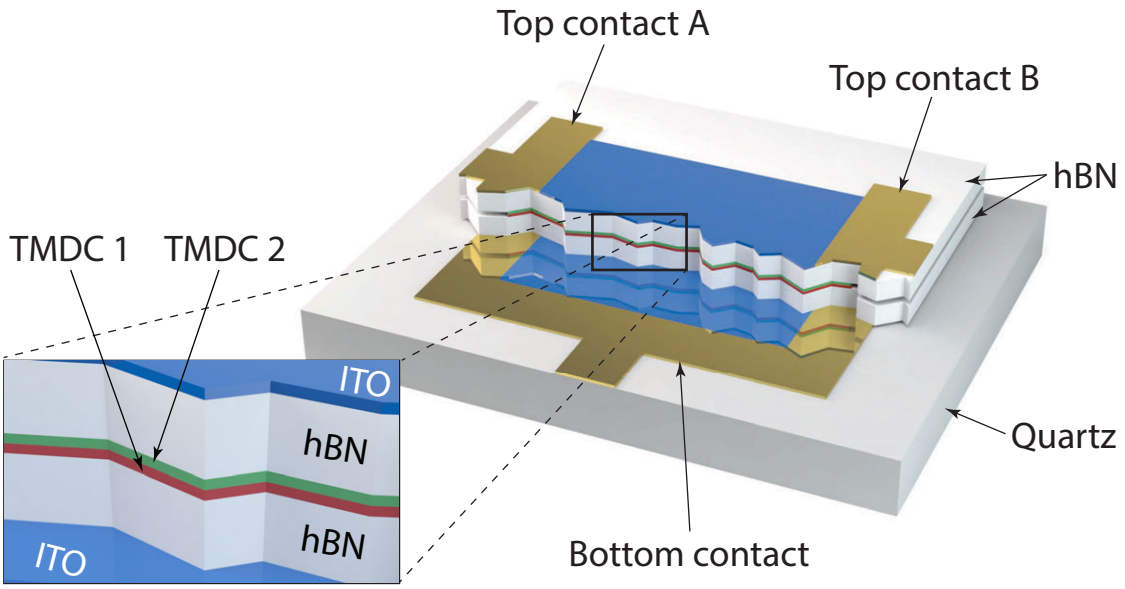

FIGURE 1: Device designed to enable optical measurements of a stack of two atomically thin layers in a transversal electric field.

By sandwiching the heterostructure in between two layers of boron nitride and by using transparent top and bottom gates this structure allows the measurement of optical properties under transversal electric fields. Before traveling to Cambridge I fabricated such devices in the cleanroom at Zentrum für Mikro und Nanostrukturen

of the Technische Universität Wien in Vienna. The stacks of atomically thin layers were fabricated by using a pick up technique consisting of the following steps:

- Preparation of a thin PPC film
- Preparation of a PDMS layer
- Preparation of the microscope slides with PDMS and PPC
- Exfoliation of materials on some sacrificial substrate wafer dices
- Picking up of upper hexagonal boron nitride (hBN) flakes
- Picking up of upper TMD flake
- Picking up of lower TMD flake
- Picking up of lower hBN flake
- Releasing of stack onto the target substrate

The thin PPC films were prepared by dissolving PPC in chloroform (about 5% PPC granulate). Thereafter, about 0.2 ml of this solution were dropped onto a microscope slide. A second microscope slide was then placed on-top of the first one, and with some little bit of pressure removed in a sliding motion. Crucial for this process is the cleanliness of both used microscope slides. The so coated slides were then dried on a hotplate at 80°C.

The PDMS layer was made by mixing PDMS base with the appropriate curing agent (20:1) in a small beaker. This mixture was then put in a centrifuge for removing the captured air bubbles. Then, it was poured onto a photoresist coated silicon wafer on a hotplate. There it was cured for 4 hours at 48°C.

Once both, the thin PPC film and the PDMS layer, were ready a small quadratic part was cut out of the PDMS layer and placed on a clean microscope slide. After this step, using a razor blade, the PPC film was released from the microscope slide it was fabricated on, and transferred on-top of the PDMS quadrate. The so obtained microscope slide forms the basis for the pick up technique.

On silicon wafer dices covered by 280nm silicon dioxide the needed materials were exfoliated. Therefore the bulk piece of the respective material was placed onto a scotch tape and, using a second tape, peeled off again. This was repeated until appropriately thin flakes could be found on the tape. In a last step the so obtained tape, coated with thin layers, was placed on the wafer dices. Some pressure was applied and subsequently the tape was removed. Some thin flakes end up sticking on the silicon wafer dice (due to van der Waals forces). Then using an optical microscope the flakes were preselected. Those flakes that were identified as promising monolayer candidates were then analyzed using photoluminiscence, raman, and atomic force microscopy measurements. Only clean monolayer flakes were used for

To finally form the stack the microscope slide with PPC on PDMS was used to pick up one hBN flake with a thickness of about 20nm. To do so the oxidized silicon wafer

dice with the preselected hBN flake was placed on a heater. After heating up to 68°C the microscope slide was lowered onto the silicon wafer dice so that the PPC made contact with the hBN flake. Thereafter the heater was turned off and after cooling down the PPC the hBN flake was embedded into it. Lifting up the microscope slide then made the hBN detached from the substrate. In subsequent steps all the needed flakes are picked up in exactly the same manner. Once the stack was complete it was positioned on the target substrate and heated up to 102°C. This made the PPC melt and stick on the silicon dioxide. Finally the PPC layer is dissolved in a beaker with chloroform heated to 68°C.

Indium tinn oxide was used as top and bottom gate material. This to ensure the transparency of both electrodes. The bottom gate was structured using standard optical lithography and sputtering of indium tin oxide. It was contacted by a titanium (4nm) gold (80nm) metal layer. After releasing the stack on top of it the upper gate was fabricated in the same way.

FIGURE 2 and FIGURE 3 show microscope images of two of the fabricated devices (#HS1 and #HS6).

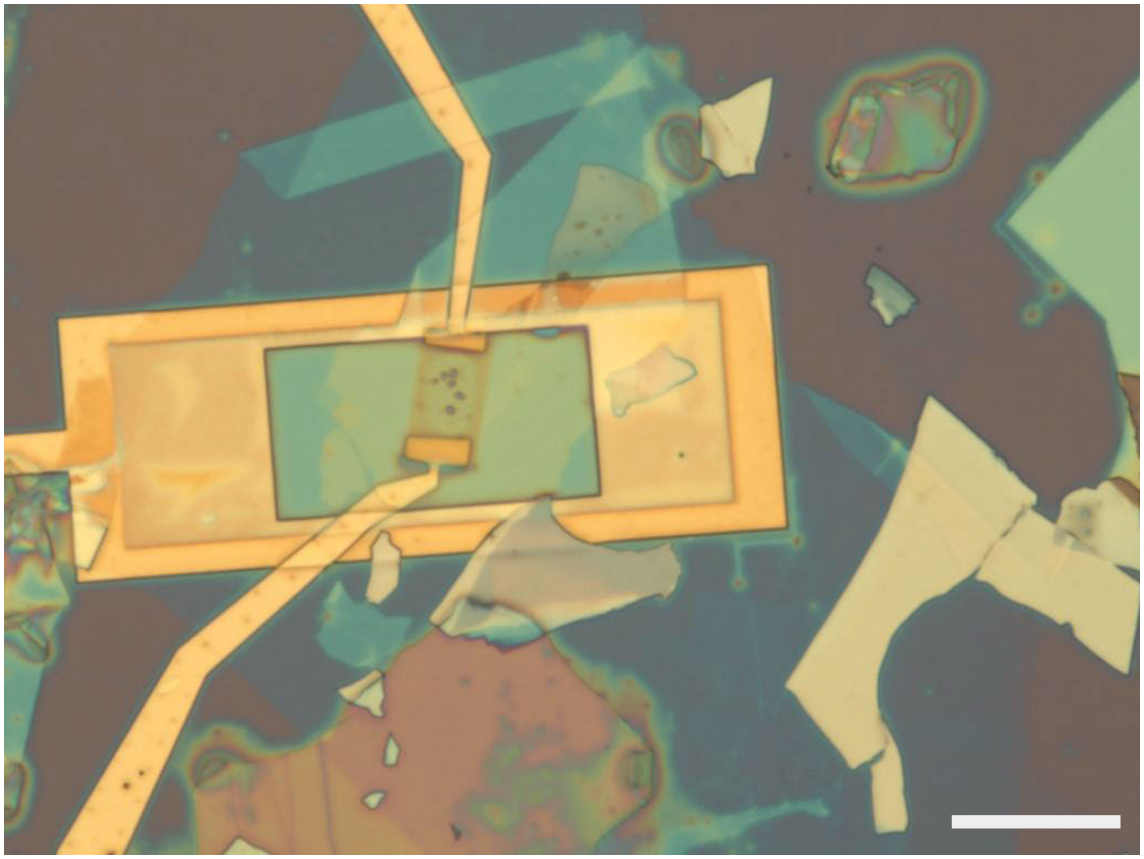

FIGURE 2: Microscope image of device #HS1 fabricated in the cleanroom of Zentrum für Mikro und Nanostrukturen at Technische Universität Wien. The scale bar is 20μm long.

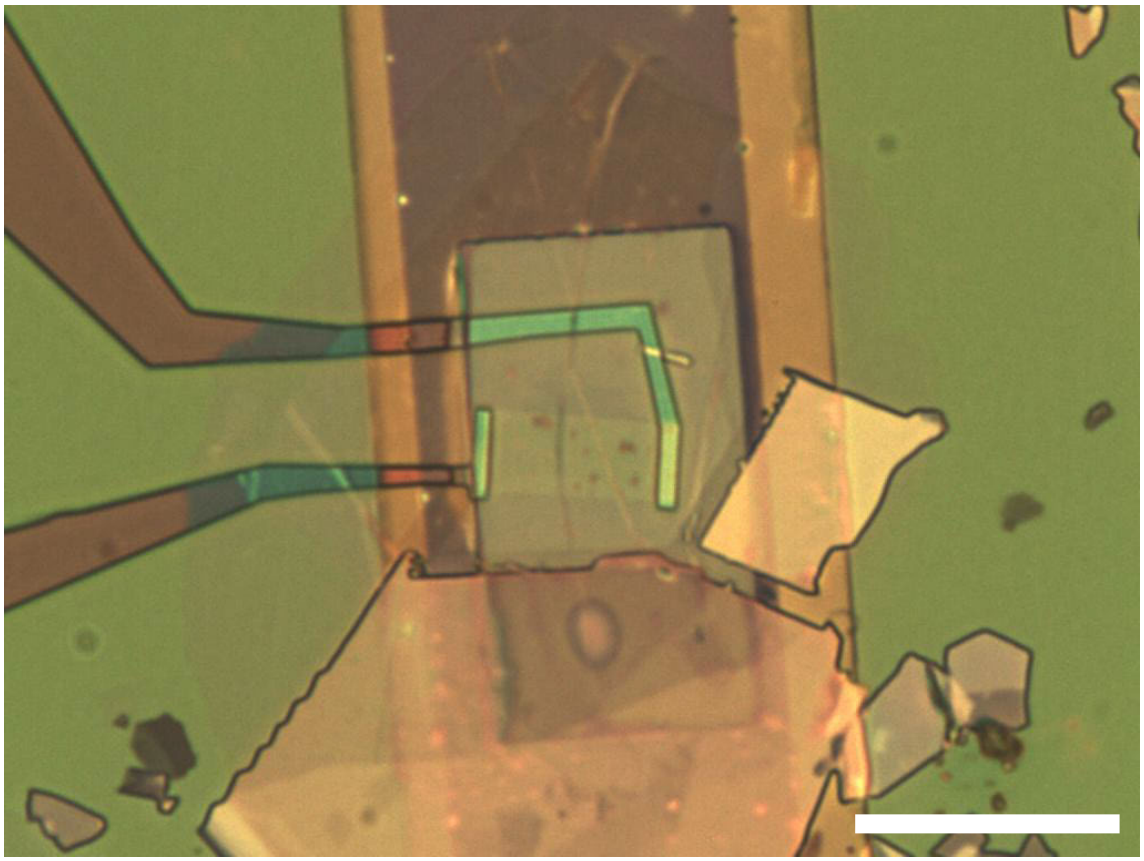

FIGURE 3: Micorscope image of device #HS6 fabricated in the cleanroom of Zentrum für Mikro und Nanostrukturen at Technische Universität Wien. The scale bar is 20μm long.

3 Characterization of the excitonic devices

After fabricating the heterostructures, some few weeks before my stay in Cambridge started, first measurements were preformed in Vienna. I found that some features are visible in the accessible measurement range (1.3eV - 2eV). The first measurements (presented in FIGURE 4) were promising and lead to the assumption that the interlayer exciton can be found at unexpectedly high energies of about 1.5eV. Consecutive measurements on the same device (see FIGURE 5) showed slightly different results. Further measurements on different samples (e.g. those for device #HS6 presented in FIGURE 6 and FIGURE 7) lead to the conclusion that the lower energy peaks should rather be attributed to localized excitons. These could stem from impurities (e.g. adsorbates from the environment or polymer residues from the processing) or crystal defects (e.g. missing selenium atoms in the TMD layers). After my arrival in Cambridge I tried remeasured the same devices, having a look at the lower energy side (below 1.2eV) but other than expected no features could be found. The interlayer excitonic peak that was expected in this energy range is missing. I suspect that the reason for this is either the spatial separation of the two TMD layers (due to the residues at the interface mentioned above) or because of a wrong orientation of the atomically thin crystals to each other. Recent publications suggest that this could strongly impact the coupling efficiency and therefore the formation of the interlayer excitons that I wanted to investigate in a first place.

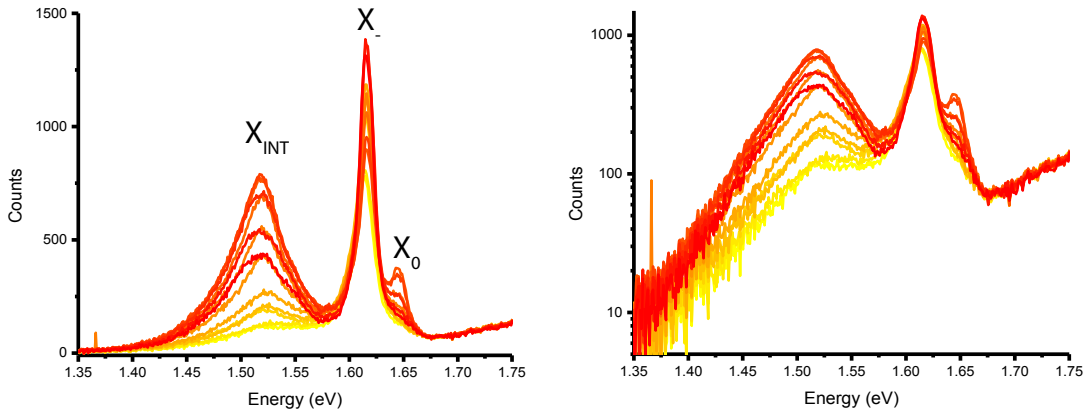

FIGURE 4: Photoluminiscence measurement of the device #HS1. Both plots show the same data, the right one in logarithmic scale for hi-lighting the width of the lowest peek. The peaks that were first attributed to the neutral (X_0), charged (X_-) and interlayer (X_{INT}) excitons are indicated.

4 Fabrication of single material devices

As mentioned above the characterization results did not lead to the hoped understanding of the excitonic processes in TMD heterostructures. Due to the wide spread

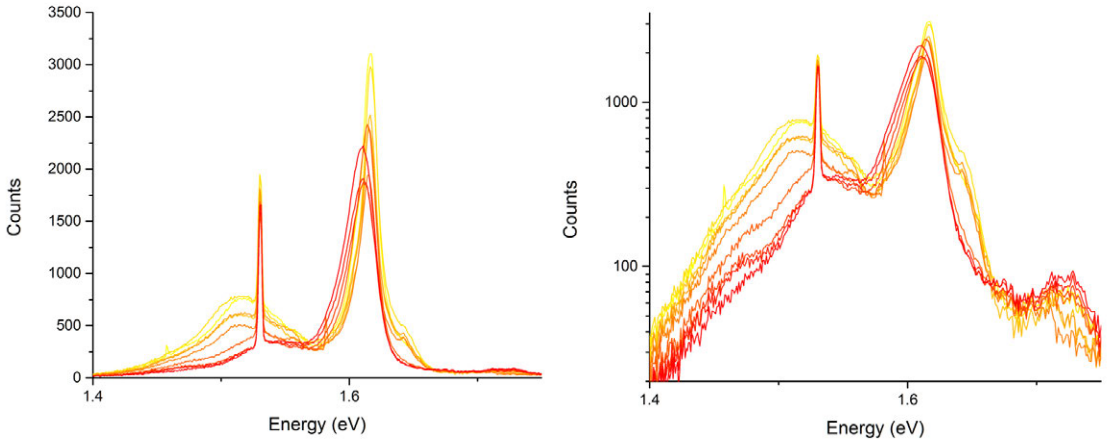

FIGURE 5: Photoluminescence measurement of the device #HS1. The measurement is done in exactly the same way as the measurement above with the only difference of measuring at some other place of the heterostructure. The sharp peak at 1.54eV can probably be attributed to some light generated by the pump laser.

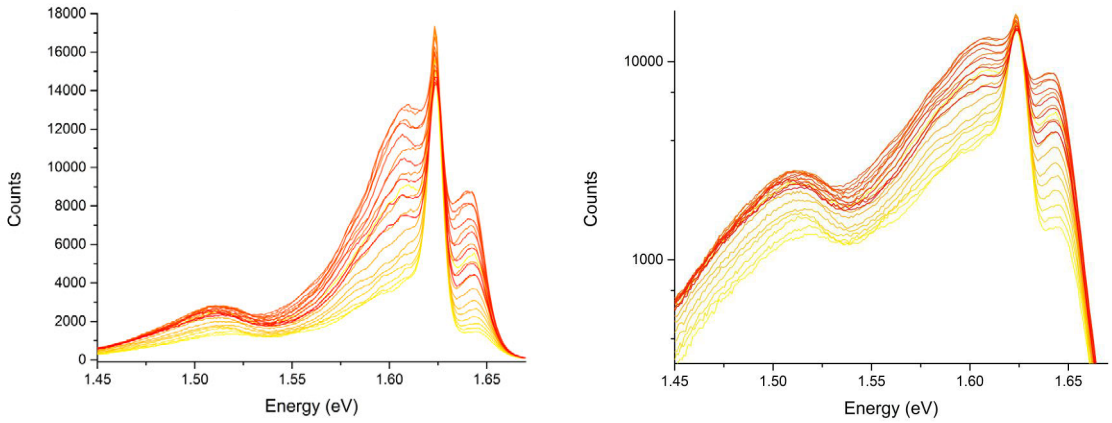

FIGURE 6: Photoluminiscence measurement of the device #HS6. Although the device is nominally the asme as #HS1 the spectral features differ a lot. Neutral, charged and interlayer excitons could be identified but the large energetic shift compared to the first measurements makes the interpretation questionable. The lowest peak should probably rather be attributed to localized excitons.

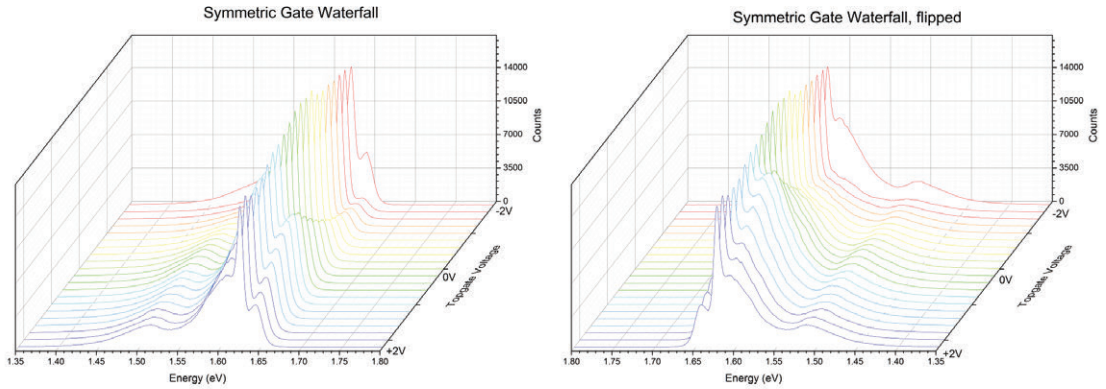

FIGURE 7: Photoluminiscence measurement of device #HS6. To better visualize the measurement results presented above the gate voltage dependent spectra are plotted in a waterfall diagram.

of measured data, I decided to fabricate some simpler devices that consist of a single TMD layer encapsulated in-between two layers of hBN. FIGURE 8 shows such a device. This device was fabricated with the same methods used for the heterostructure devices described above.

5 Characterization of the single material devices

As also the TMD heterostructure devices the simpler, single material, devices were fabricated in Vienna. Also a first optical characterization was preformed in Vienna. The shift of the neutral and charged exciton peaks to lower energies with increasing temperature could be described by the Varshni equation and does not differ from the behavior of conventional semiconductors. Also further measurements and more devices could not help to clarify the origin of the broad lower energy peak. As it vanishes for quite low temperatures it can probably be attributed to localized excitons with small localization energies (about 10meV). These results further indicated that prior to optimizing the heterostructure presented above, the fabrication processes have to be improved.

6 Silicon photonics project

Due to the unexpected results obtained in the spectral characterization of the heterostructure samples, namely the missing presence of the interlayer exciton feature, and my short stay of only half a year, Pablo suggested that I rather join the silicon photonics project. His group, after their publication in nature nanotechnology [11], continued to work on split gated devices made out of TMDs. Just a few months before my arrival in Cambridge they were able to find one member of the TMD family, namely $MoTe_2$, that has a band gap compatible with silicon based

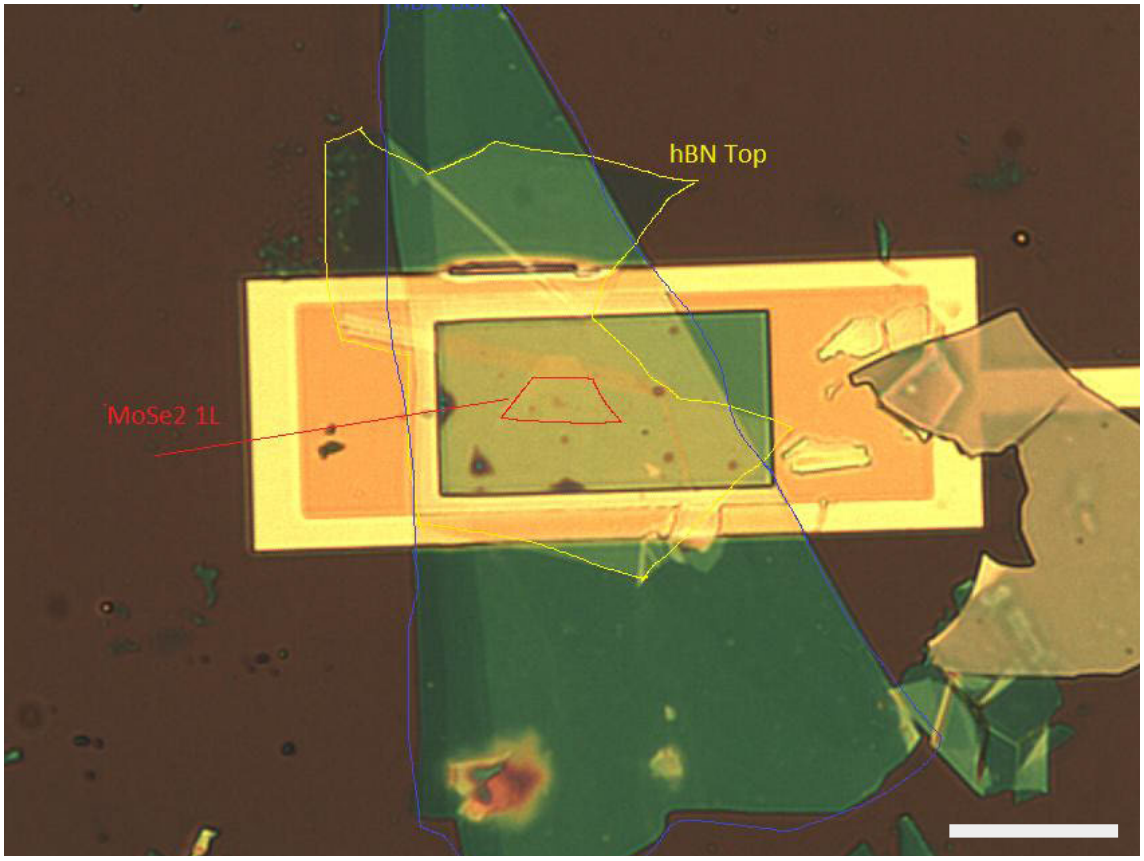

FIGURE 8: Single material device (#SL4) fabricated in the cleanroom of Zentrum für Mikro und Nanostrukturen at Technische Universität Wien. The scale bar is 20μm long. The individual layers are outlined.

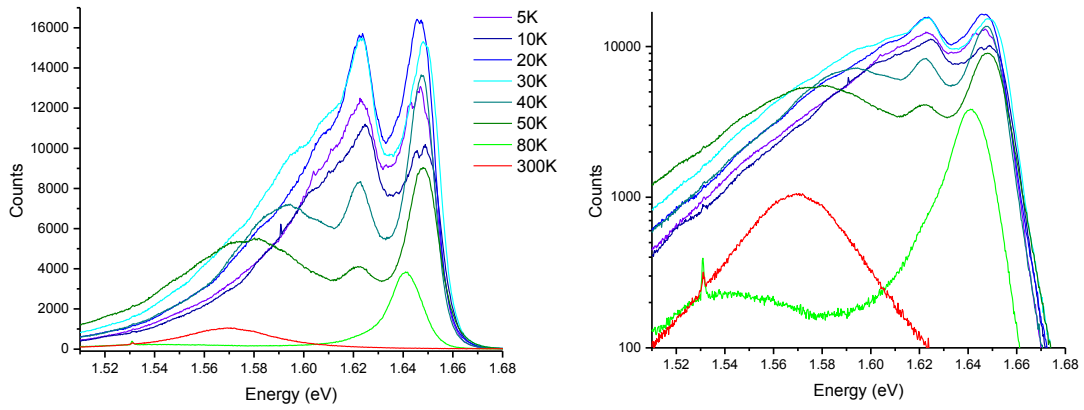

FIGURE 9: Temperature dependent Photoluminescence spectrum of the single material device #SL4.

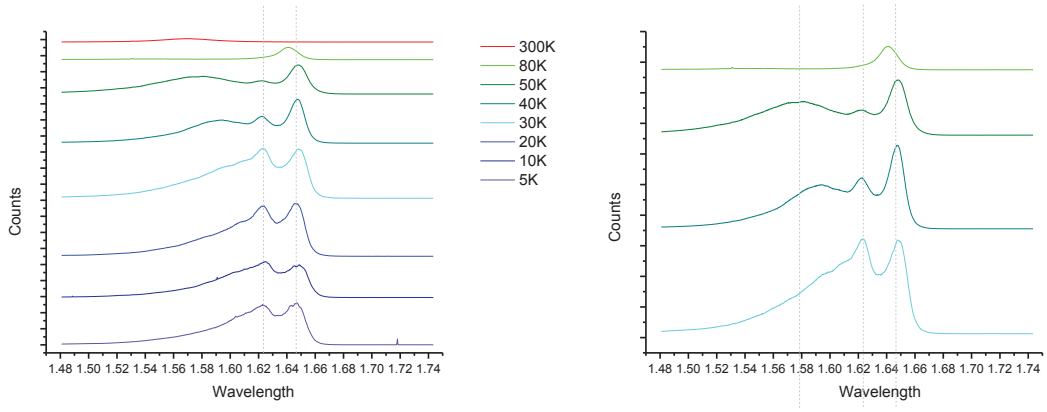

FIGURE 10: Photoluminescence measurement of the single material device #SL4 displayed as a waterfall diagram.

devices. As the excitonic emission lines can be found at 1140nm for monolayers and 1180nm for bilayers at room temperature. As this is just below the band gap of silicon, $MoTe_2$ based devices can be used for efficiently emitting light into a silicon waveguide and detecting light guided in such a waveguide. The key point of silicon photonics is the substitution of the communication technology used inside and in-between silicon integrated circuits. Instead of communicating by using electric signals, optical signals are used. Therefore one main energy dissipation source in integrated circuits, the impedance of the electric connects in and in-between the chips, would strongly be reduced. Furthermore, the data transmission rates inside and in-between could be increased, reducing the number of needed communication lines. By using TMD based emitters and detectors the processes used would have one big advantage: CMOS compatibility. This means that all the used processes could be done in standard semiconductor cleanrooms.

The silicon photonics project was a collaboration with Professor Dirk Englunds group. The main task of Pablos group was to built the TMD based emitter/detector. Whereas, the main task of Dirks group was to built the silicon waveguides. Due to my broad background Pablo suggested that I get involved in both tasks.

On the waveguide side we decided to base the work on silicon photonic crystals. Photonic crystals are artificial periodic structures. In our case we planed to use silicon on insulator wafers as substrates. By etching small holes with a diameter of less than 300nm perfect in plane mirror could be created. For the out of plane propagation the numeric index difference acts as a mirror by total internal reflection. By using this technology we can open the door to high density integration of optical interconnects. This because photonic crystals, other than conventional slab waveguides, allow bending radii of less than 1μm.

As stated above Pablos group was working on split gated TMD devices. As $MoTe_2$ was found to be compatible, from a spectral perspective, with light transmission in silicon, it was clear that it would be a great match.

7 Fabrication of photonic crystals

After the simulation of photonic crystal cavities and waveguides (see FIGURE 11)

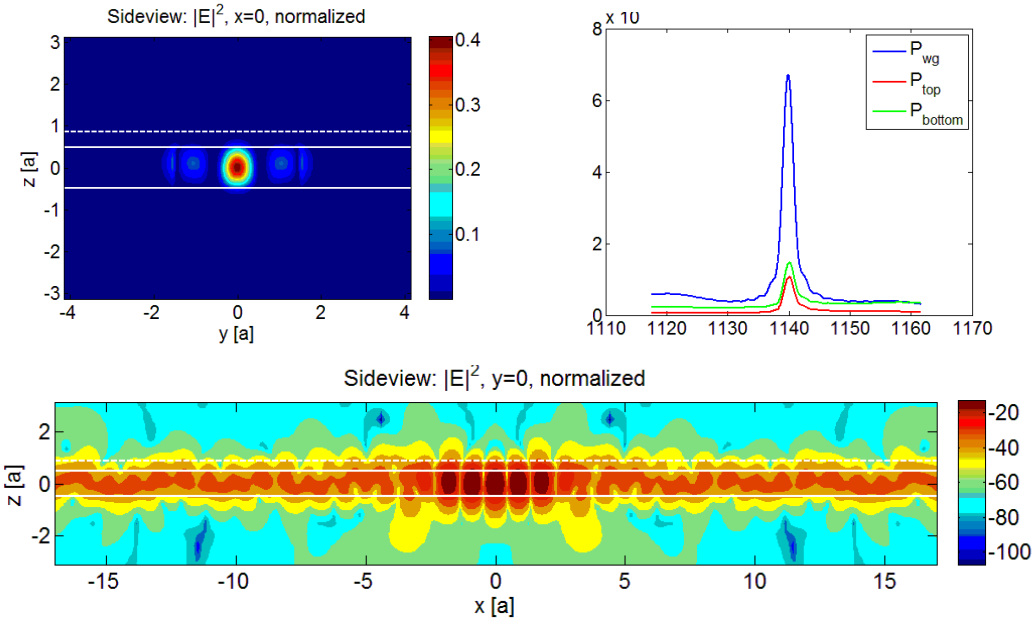

FIGURE 11: Simulation of the electromagnetic field distribution inside the photonic crystal waveguide. The upper right plot shows the resonance of the cavity and the design frequency of the waveguide centered at 1140nm.

first chips were fabricated. Scanning electron microscopy images of the structures showed major problems with the fabrication processes. Due to my processing experience, acquired during my Master and PhD studies at TU Wien, i was able to help to sort out the problems in a few iteration steps. FIGURE 12 shows the first fabrication results. I suggested to take an image of the electron beam lithography resist directly after development and prior to the etching of the structures.

The results indicated that the problems are not due to the electron beam lithography but due to the etching. By modifying the etch parameters (ICP/RF ratio) we were able to get better results (see FIGURE 13).

Finally by introducing a longer conditioning time (longer than 40 minutes) before the actual etching step we were able to obtain perfectly round holes and steep edges (see FIGURE 14).

Additionally the impact of a hBN layer on the performance and spectral features of the photonic crystals was investigated. For this experiment hBN flakes with thicknesses ranging from 50 to 100μm were transferred onto freestanding photonic crystals by the polymer based stacking method described in the section "Fabrication of the excitonic devices". Microscope images of the results are shown in FIGURE 15.

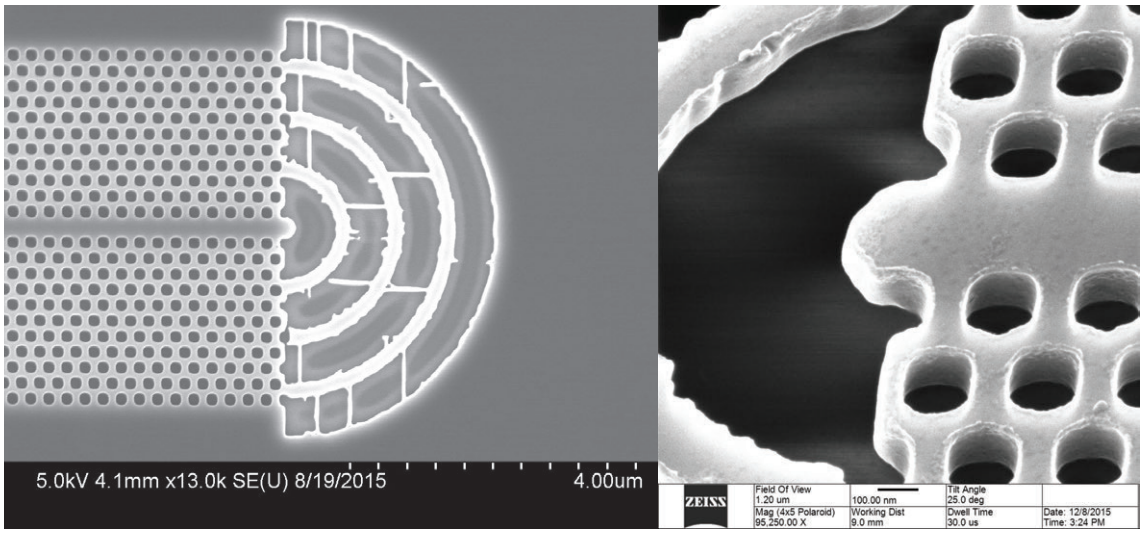

FIGURE 12: Images of the first fabricated photonic crystals. The left image is recorded using a scanning electron microscope, the right and more detailed one using a helium ion microscope.

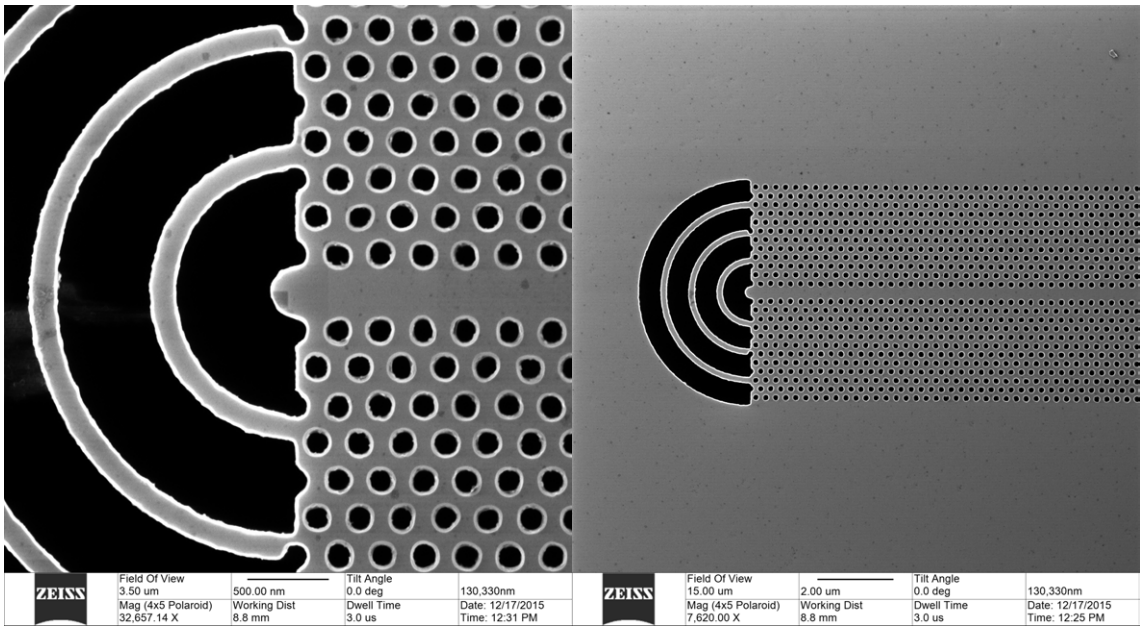

FIGURE 13: Helium ion microscope images of the photonic crystals fabricated using an optimized etching recipe.

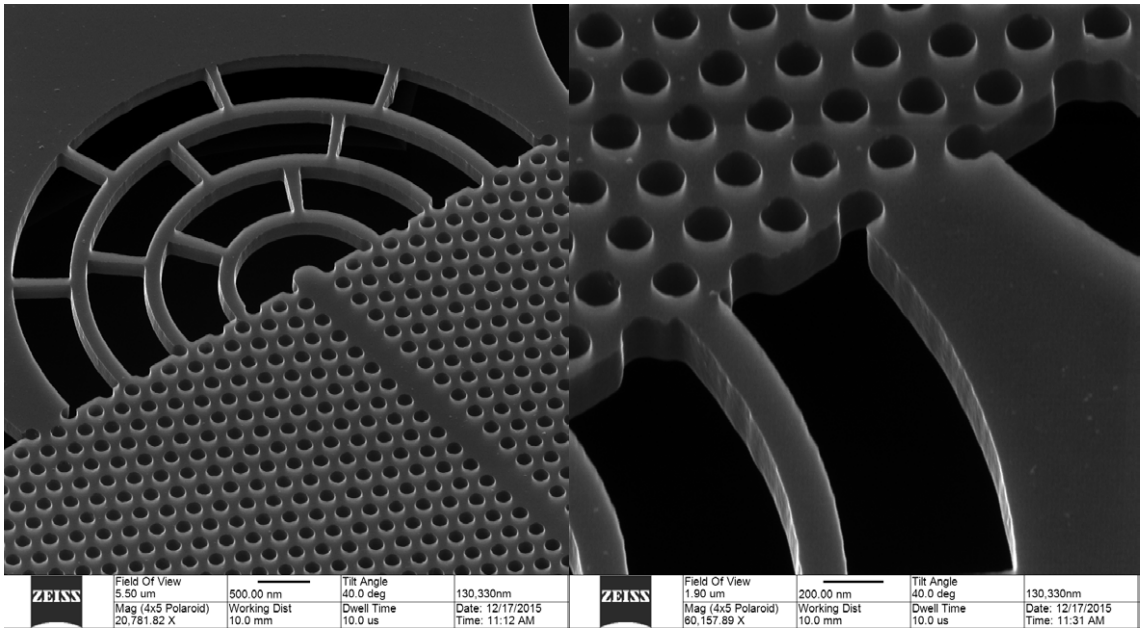

FIGURE 14: Helium ion microscope images of the photonic crystals fabricated after the improvement of the etching process.

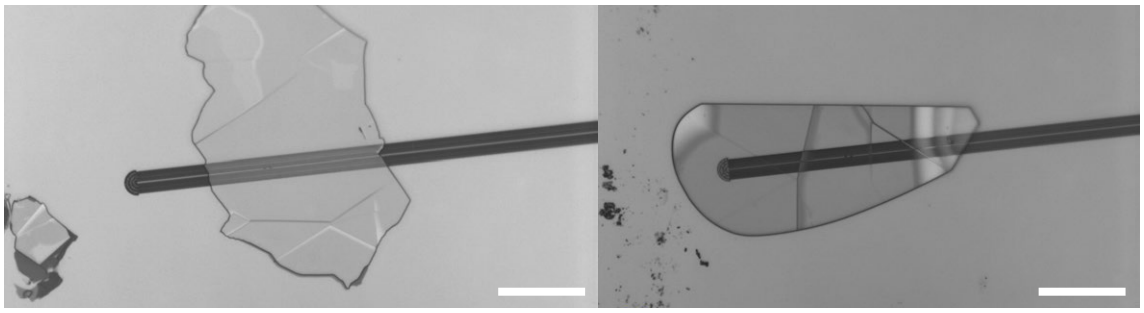

FIGURE 15: Microscope images of the hBN flakes on top of the photonic crystal waveguides and cavities. The scale bar is 20μm long, the left hBN flake is 100nm thick, the right one 400nm.

8 Characterization of photonic crystals

The fabrication of photonic crystals has a big impact on their spectral features. Small changes during the etching and/or electron beam lithography process lead to intolerable deviations in the performance of the final devices. Therefore photonic crystal cavities were fabricated and characterized optically. This was done using a cross-polarization setup. Broadband, linear polarized light with a determined polarization is used to illuminate a cavity. The reflection is filtered with a 90°rotated polarization filter and analyzed using a spectrometer. Rotating the polarization allows to identify the resonant modes of the photonic crystal cavity. Thereby the cavity that has the largest spectral overlap with the TMD emitter/detector can be found. FIGURE 16 shows the measurement results that showing that hBN can introduce a maximum frequency shift of 20nm. This was later simulated and is in agreement with the simulation results.

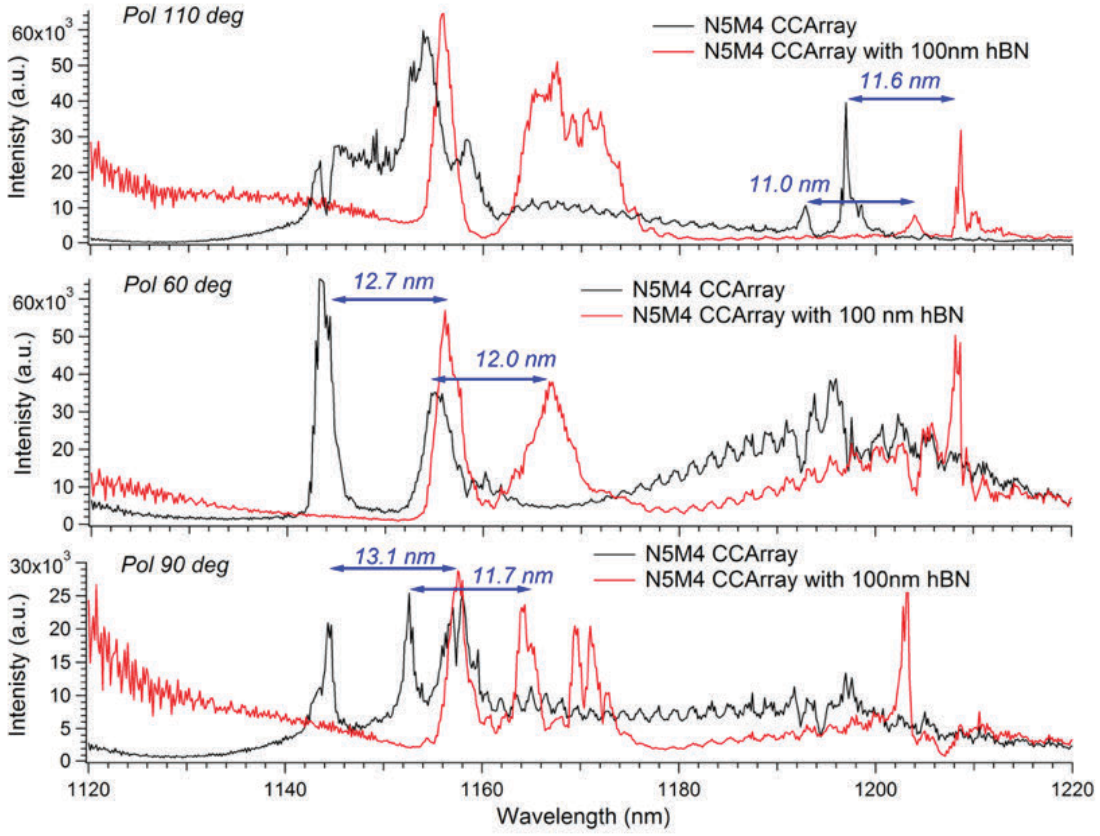

FIGURE 16: Measurement of the resonance frequency shift due to a 100nm thin hBN layer. The results show that the offset due to the hBN is about 12nm.

9 Pick and Place of photonic crystals

One alternative idea to the fabrication of TMD devices on top of photonic crystal structures was the transfer of a photonic crystal onto a working TMD emitter/ detector. For this approach suspended photonic crystal structures were fabricated (see FIGURE 17).

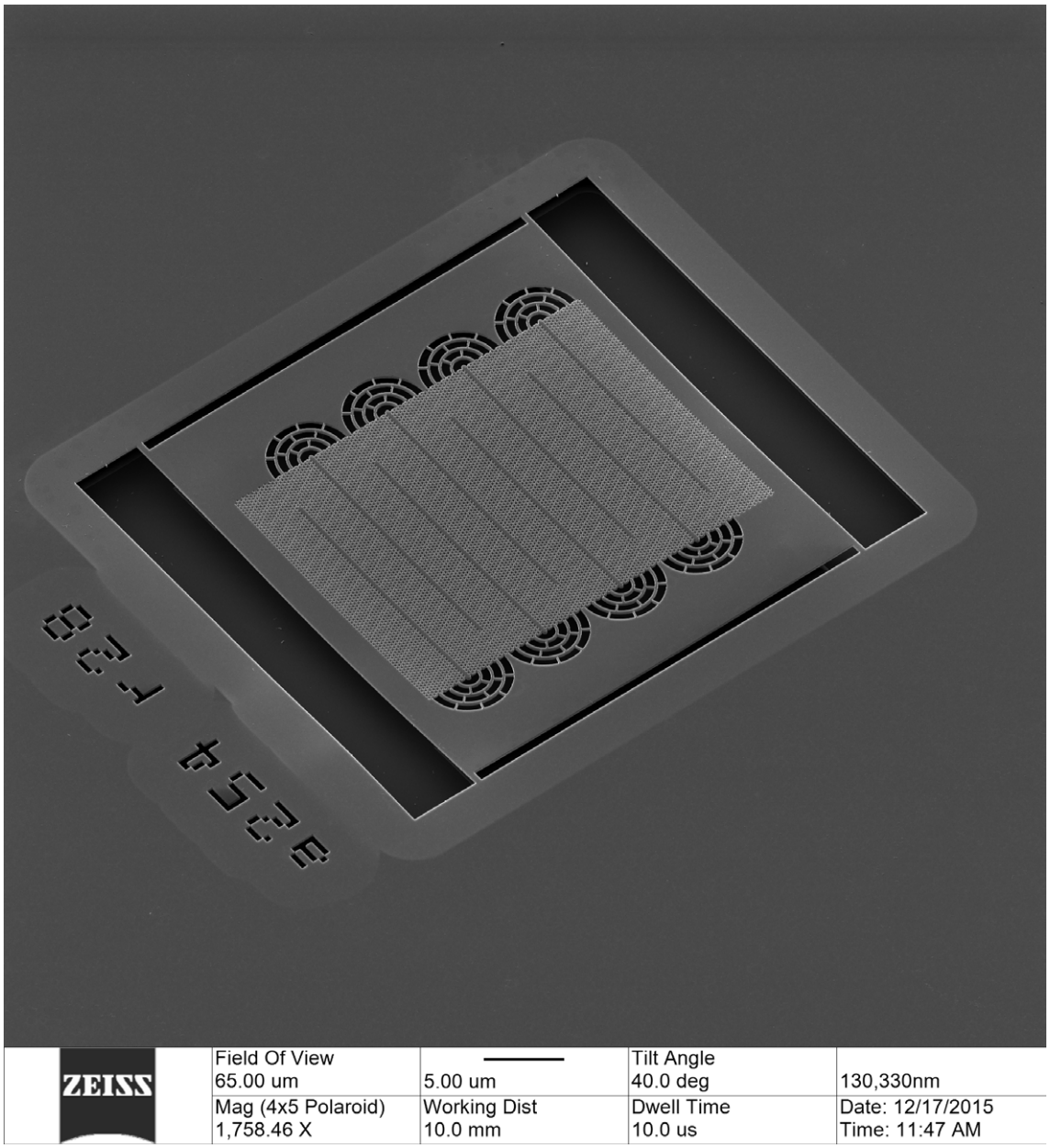

FIGURE 17: Helium ion microscope image of a freestanding photonic crystal structure.

Using a thin tungsten needle (tip diameter < 500nm) these structures were broken out of the host substrates and placed onto the target (see FIGURE 18).

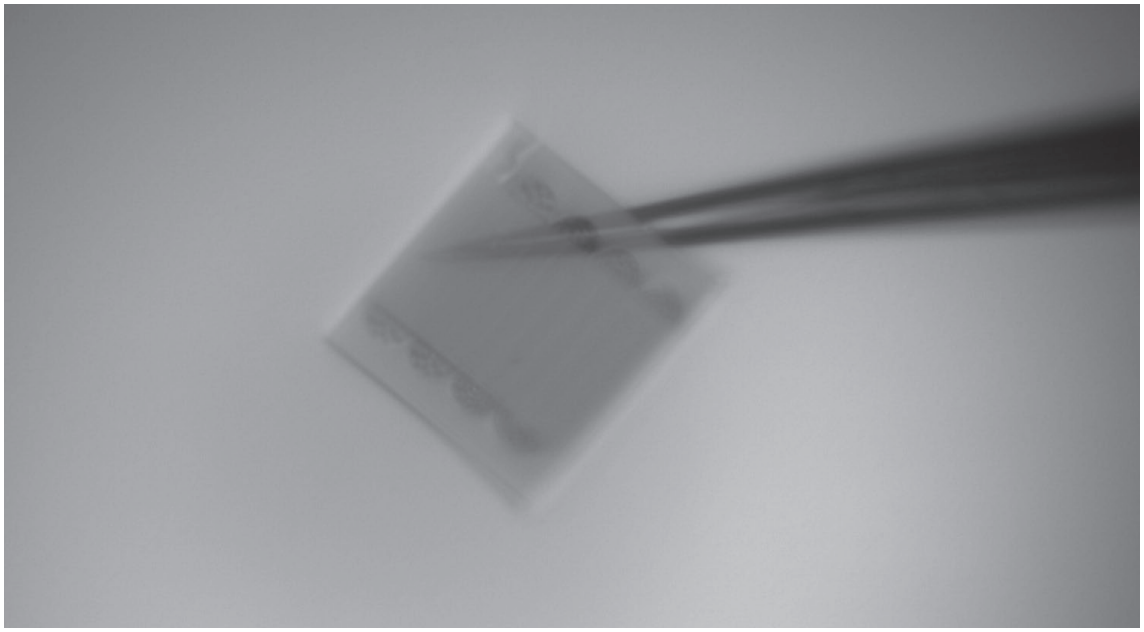

FIGURE 18: Microscope image of a photonic crystal chip picked up with a tungsten needle for transfer on to a TMD emitter/detector.

The results show that, in case of fabrication problems with the method described two sections above, the transfer of characterized photonic crystals to an existing TMD heterostructure device would be a viable path.

10 Fabrication of $MoTe_2$ devices

The fabrication of the $MoTe_2$ devices is done with the methods described in the section "Fabrication of the excitonic devices". To ensure good drain and source contacts, as well as a low absorption of the light that propagates in the waveguide, thin graphene layers were used as electrodes. The TMD layer was encapsulated into two hBN layers. One relatively thin (10nm) in between the photonic crystal waveguide and the TMD layer, and one thick (80nm) in between the TMD layer and the split gates. A microscope image of the final device is shown in FIGURE 19.

The two grating couplers on either side of the waveguide are used to couple the emitted light out of the waveguide for electroluminescence measurements, and to couple light into the waveguide for photoluminescence measurements.

11 Characterization of $MoTe_2$ devices

FIGURE 20 shows the measured photoluminescence spectrum.

The main exitonic transition is found to be at 1140nm for a $MoTe_2$ monolayer at

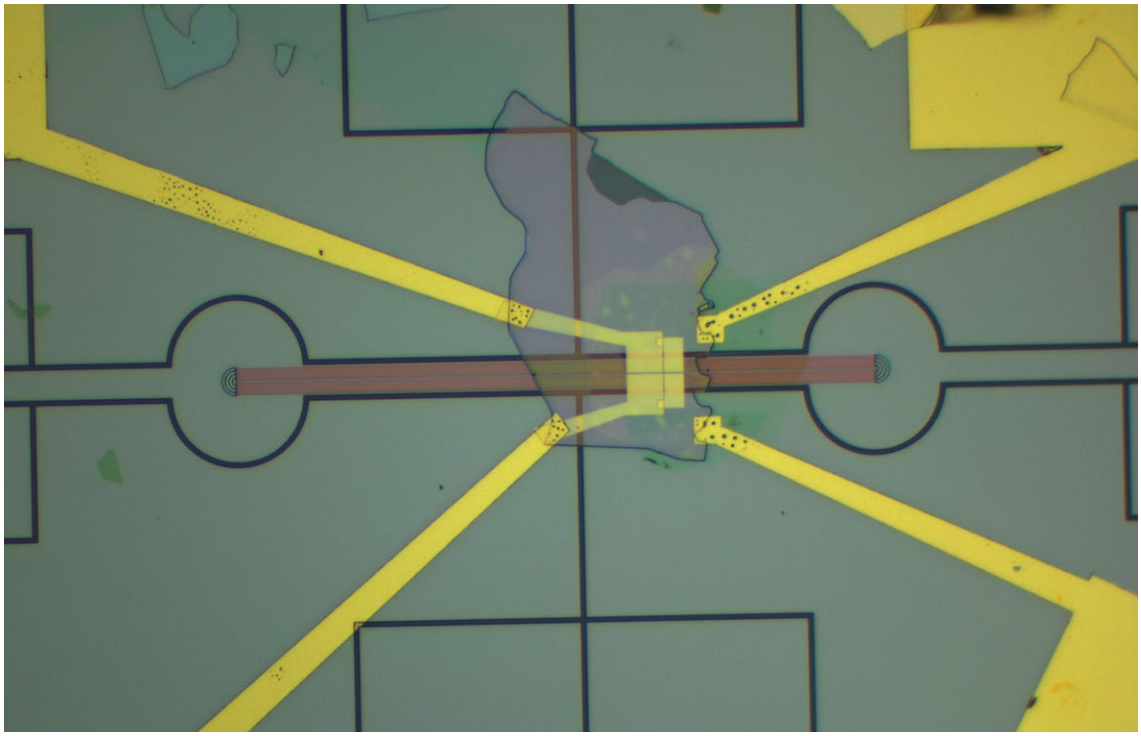

FIGURE 19: Microscope Image of the TMD emitter/detector built on top of a photonic crystal waveguide.

room temperature. FIGURE 21 shows the electroluminsecence spectrum of a $MoTe_2$ bilayer split gate device.

Both measurements were preformed using standard split gate devices. The measurement on the final device are currently in progress and will be completed soon.

12 Summary and Outlook

As described above the experiment regarding the properties of excitons in TMD based heterostructures lead to the conclusion that a cleaner processing has to be achieved. Furthermore, the orientation of the single flakes probably plays a role. With these results in mind we are currently building new devices in the cleanroom of Zentrum für Mikro und Nanotechnologie at Technische Universität Wien. We hope that with this new generation of devices we will be able to carry out new measurements to further understand the coupling of stacked TMD layers. Due to the unexpected measurement results obtained in Cambridge I joined the silicon photonics project. In this project we were able to built a proof of principle device that opens the door to a fully CMOS compatible in chip optical data link. Final measurements are being carried out at the moment and we hope to be able to publish the results in the next few weeks.

At the end of the day both projects could help to make our world's future a more

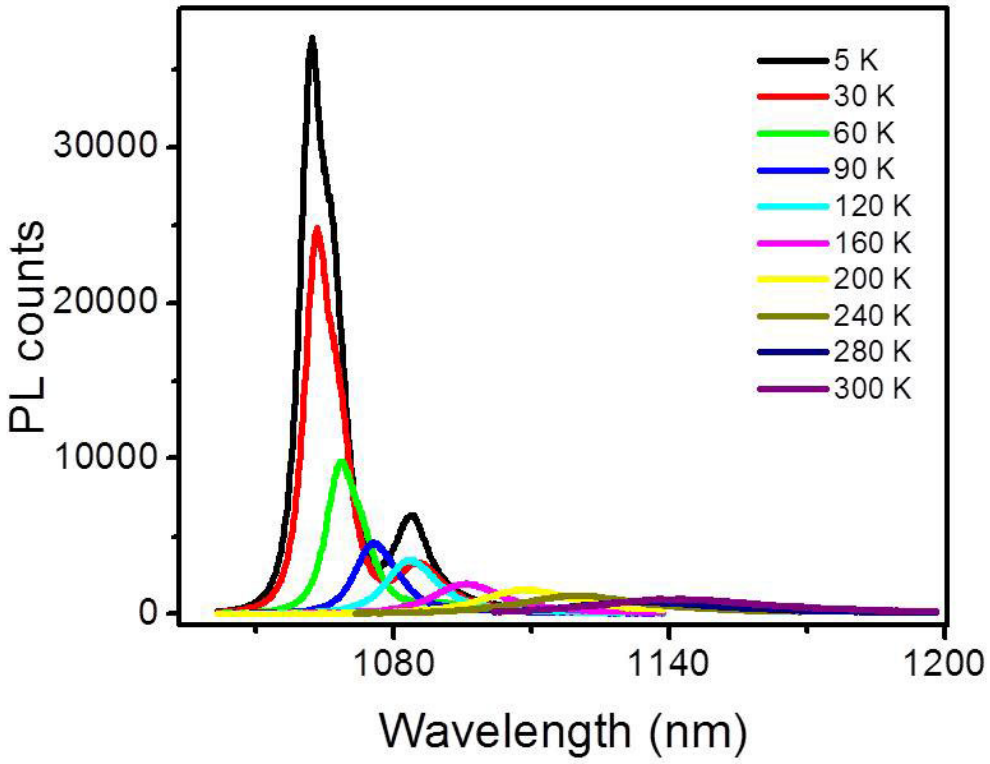

FIGURE 20: Photoluminescence spectrum of a MoTe2 flake at different temperatures.

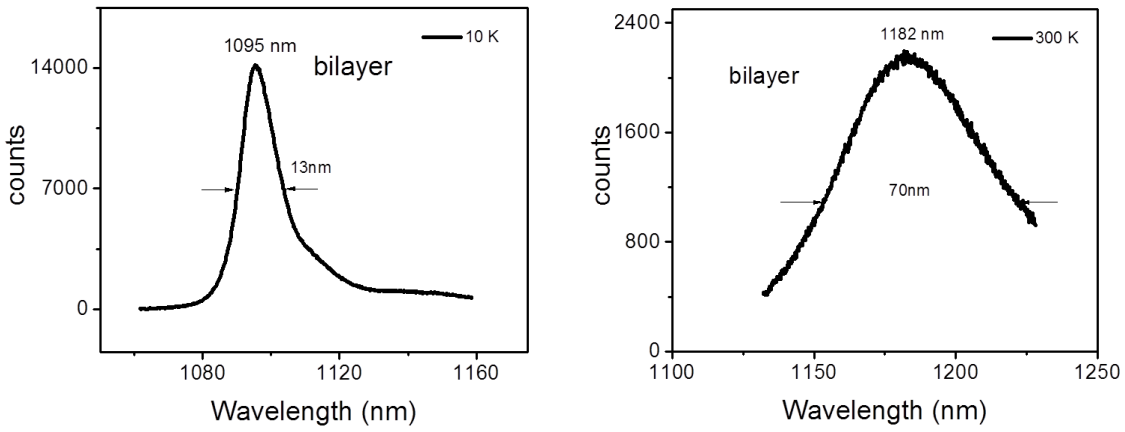

FIGURE 21: Electroluminescence measurement of a MoTe2 split gate device at different temperatures.

sustainable one. The deeper understanding of excitonic processes and inter layer coupling in TMD heterostructures will help to strongly improve a new generation of solar cells. Optical communication in an in between integrated circuits will help to strongly reduce the dissipated power while increasing the performance at the same time.

To conclude I want to point out that my stay at Massachusetts Institute of Technology not only helped me to realize the experiments described above. It also lead to an exchange of experience and knowledge regarding relevant fabrication processes and fundamental physics. I was able to learn a lot and I am confident that this will impact not only my future but also the future of our research group in the Photonics Institute at Technische Universität Wien.

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