HORIZON EUROPE PROGRAMME
HORIZON-CL4-2023-DIGITAL-EMERGING-01-33

GA No. 101135196

Developing New 2D Materials and Heterostructures for Printed Digital Devices

2D-PRINTABLE - Deliverable report

D5.1. – Electrical characterization of LPE derived novel materials

Funded by the European Union

No.	DXXX	
Related WP	WP 5	
Deliverable Title	Electrical characterization of LPE derived novel materials	
Deliverable Date	01.10.24	
Deliverable Type	REPORT	
Dissemination level	Public (PU)	
Author(s)	Georg Duesberg (UniBw M) Kangho Lee (UniBw M)	2024-09-09
Checked by	Georg Duesberg (UniBw M)	2024-09-09
Reviewed by	Jonathan Coleman (TCD) - Project Coordinator	01.10.2024
Approved by	Jonathan Coleman (TCD) - Project Coordinator	01.10.2024
Status	Draft v1.7	2024-09-24

Document History

Version	Date	Editing done by	Remarks
V1.0	2024-09-09	Kangho Lee (UniBw M)	
V1.1	2024-09-17	Georg Duesberg (UniBw M)	
V1.7	2024-09-24	Georg Duesberg (UniBw M)	
V2.0	2024-09-24	Jonathan Coleman (TCD)	
FINAL			

Project Scientific Abstract

The 2D-PRINTABLE project aims to integrate sustainable large-scale liquid exfoliation techniques with theoretical modelling to efficiently produce a wide range of new 2D materials (2DMs), including conducting, semiconducting, and insulating nanosheets. The focus includes developing the printing and liquid phase deposition methods required to fabricate networks and multicomponent heterostructures, featuring layer-by-layer assembly of nanometer-thick 2DMs into ordered multilayers. The goal is to optimize these printed networks and heterostructures for digital systems, unlocking new properties and functionalities. The project also seeks to demonstrate various printed digital devices, including proof-of-principle, first-time demonstration of all-printed, all-nanosheet, heterostack light-emitting diodes (LEDs). In conclusion, 2D-PRINTABLE will prove 2D materials to be an indispensable material class in the field of printed electronics, capable of producing far-beyond-state-of-the-art devices that can act as a platform for the next generation of printed digital applications.

Public summary

Prior to evaluation of excellent electronic properties of macroscale printed devices, individual nanosheets must be assessed first because it tends to be limited by quality of the inter-nanosheet junctions. Therefore, it is necessary to configure electrical measurement for fundamental characterization. Herein, we produce individual nanosheet field-effect transistors in 5-terminal contact electrodes after a nanosheet transfer onto high-k dielectric substrates from various EE-TMD or LPE-TMD dispersions. A process for the consecutive EBL has been developed. We defined multiple contact electrodes on individual TMD nanosheets on a range of various materials. That way, it was possible to perform 4-point probe measurements allowing precise determination of the conductance of individual nanosheet while removing parasitic components or minimizing their contribution at the contact interfaces. Particularly in the case of EE-$PtSe_2$ nanosheets, this type of measurements has been carried out for the first time.

This type of assessment of novel TMD materials will eventually suggest an index indicating the maximum achievable mobility for subsequent printed devices, therefore it will be also compared with and benchmarked against theoretical prediction and THz time domain spectroscopy results. Not only for single nanosheets, but the same measurement scheme will be applied to networks, film, and multicomponent heterostructures.

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Abbreviations & Definitions

Abbreviation	Explanation
2D	Two Dimension(al)
LPE	Liquid Phase Exfoliation
LED	Light-Emitting Diode
EE	Electrochemical Exfoliation
TMD	Transition-Metal Dichalcogenide
EBL	Electron-Beam Lithography
PR	Photoresist
ER	Electron-Beam Resist

1 Introduction

WP5 will fully characterize the electrical properties of individual flakes, networks, and films, and heterostructures. Individual single nanosheet among them is a prerequisite prior to the other forms because it serves the basis for follow-up research. Individual objects, for example single nanosheets, flake-level homo- and hetero-structures, need to be structured with electrical electrodes for electrical characterization.

Single 2D TMD/graphene nanosheets have been provide by TCD and UKa. In D5.1, various TMD nanosheets were dispersed by drop-casting method onto pre-patterned substrate and then interfaced with electrodes in a typical field-effect transistor structure via combined lithographic techniques. As a result, the process flow for device fabrication of the individual nanosheets from EE-TMD dispersions has been successfully established and strove for evaluation in electrical properties of pristine nanosheets, including only lately assessable materials, such as $PtSe_2$, and the EE method. Structured single TMD nanosheets were measured in the 5-terminal device structure to extract parameters. However, the first attempts were stranded at the relatively low conductivity of individual nanosheets. We are currently working on a plan to break through this issue and also an alternative in parallel.

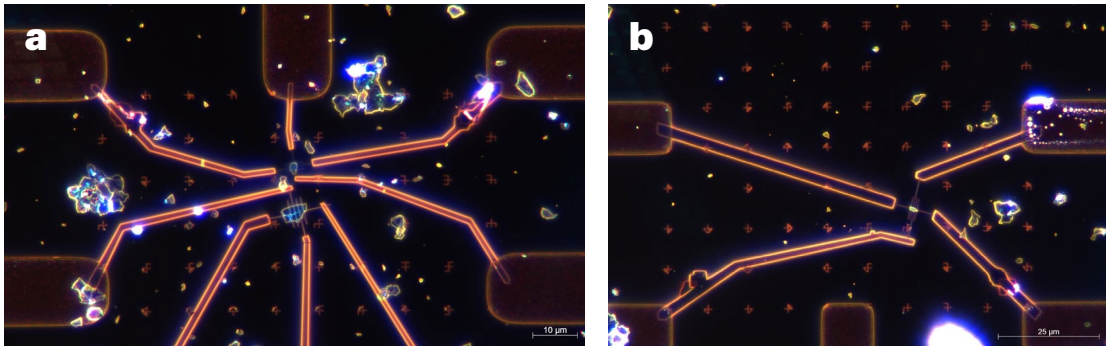

Figure 1. Representative structured individual (a) MoS_2 and (b) $PtSe_2$ nanosheets in dark-field microscopy.

Not only for the field-effect charge carrier mobility, but also THz time domain spectroscopy can derive carrier mobility. This pump-probe technique measures the dispersive AC-mobility of photo-excited charge carriers at THz frequencies, including photoconductivity of TMD nanosheets.

2 Methods

2.1 Background

For in-depth electrical characterizations, 5-terminal device structure, which consists of 4 electrical electrodes with a global back gate electrode, is suggested. However, limitation of the typical lateral length of dispersed nanosheets requires advanced lithographic technique more than conventional photolithography and UniBw M uses electron beam lithography (EBL) to define multiple electrodes onto single TMD nanosheets, as depicted in Appendix B – Lithographic Process Flow.
Additional coordinate system is required to structure these microscale nanosheets and it is prerequisite to nanosheet deposition onto substrates. Therefore, pre-patterned substrates should be prepared before the drop-casting of TMD dispersions. While SiO_2 dielectric layer has been used for many years due to excellent reliability in the semiconductor industry, high-k dielectric materials, such as Si_3N_4, Al_2O_3 (in preparation), and HfO_2 (in plan), are chosen to acquire improved device performance as discussed beforehand. After selective metallization of coordinate and contact pad patterns on Si_3N_4/Si substrates through consecutive photo- and e-beam lithographic processes, pre-patterned substrates were delivered from UniBw M to TCD for TMD nanosheet deposition.
Four different types of single TMD nanosheets were transferred using by drop-casting method from WS_2, $MoSe_2$, $PtSe_2$, and MoS_2 dispersions that were produced by TCD. Afterwards, samples were returned from TCD to UniBw M to finalize structuring process and then electrical electrodes were defined through EBL.
Last but not least, a setup for THz time-domain spectroscopy has been realized at UniBw M as part of WP4 to extract carrier mobilities. This technique will enable us to benchmark our results by contactless measurements and therefore allow us to investigate the impact of contacting and intersheet contacts. The setup was successfully tested in initial measurements using LPE-graphene films provided by UKa, from which intrasheet mobilities were derived.

2.2 Procedures

2.2.1 Pre-patterned substrates

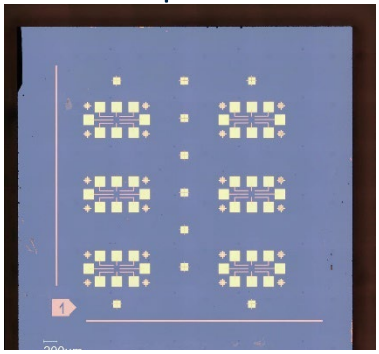

Figure 2. Pre-patterning after consecutive photo- and e-beam lithographic processes for following nanosheet deposition.

First, align markers and lead lines were patterned with Ti/Au=5/25 nm layers on a 93 nm of Si_3N_4 dielectric layer of substates by using a maskless lithography system. They define a 100 by 100 μm^2 of writefield for following EBL work. Second, coordinate patterns were defined in the middle of writefield by EBL and metallized with a relatively thiner layer (Ti/Au=5/10 nm). Third, electrical contact pads were prepared through a maskless lithography system after a metallization of thicker layers (Ti/Au=15/85 nm) in consideration of following wire-bonding, as shown in Figure 2. Last, pre-prepattend substrates were shipped to TCD (Figure 11(a-m)).

2.2.2 Drop-casting of TMD nanosheets

In TCD, four different TMD (WS_2, $MoSe_2$, $PtSe_2$, and MoS_2) nanosheets were deposited on aforementioned pre-patterned substrates by using drop-casting method, as shown in Figure 3. Afterwards, samples were sent back to UniBw M for following EBL work (Figure 11(n)).

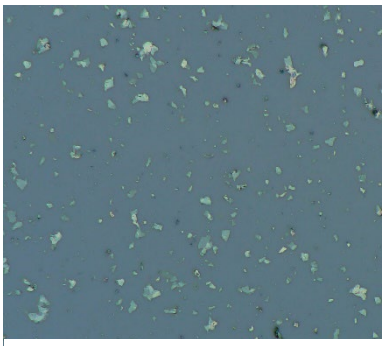

Figure 3. Dispersed WS_2 nanosheets on a substrate by drop-casting method. Optical image: Dr. Tian Carey (TCD).

2.2.3 Structuring individual nanosheets

All deposited nanosheets are randomly found on the substrates (Figure 3) and some of them were carefully selected for further EBL process in consideration of size, location, thickness, and so on. After SEM inspection of delivered samples (Figure 4(a)), electrical electrode structuring of selectively chosen TMD nanosheets were finalized in the 4-point probe configuration, as shown in Figure 4(b). In consideration of extrinsic semiconducting property of TMD nanosheets, different interlayers (Ti or Ni) were applied for metallization to engage intimate interfacial contacts relying on materials. As a result, 7 MoS_2, 6 $PtSe_2$, and 1 $MoSe_2$ nanosheets obtained electrical electrodes for characterisation whereas WS_2 nanosheets were not found on the affordable position (Figure 11(o-r)).

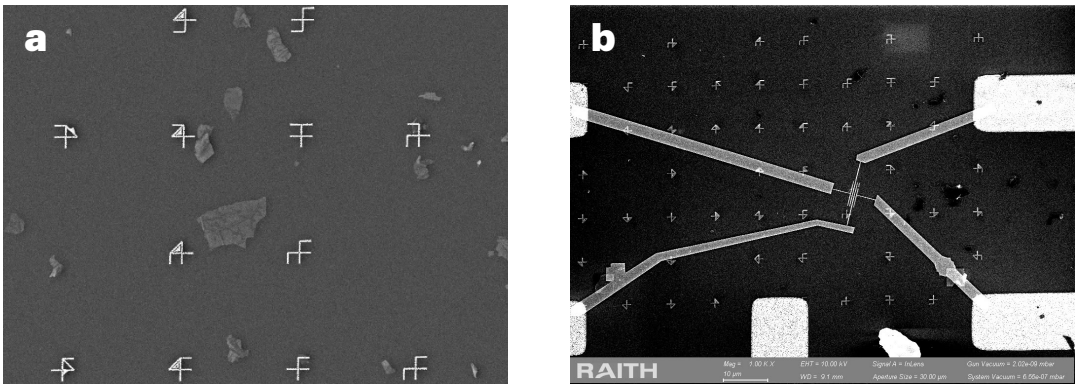

Figure 4. (a) Drop-casted MoS_2 nanosheets on coordinate patterns. (b) A structured $MoSe_2$ nanosheet in the 4-point probe configuration.

Afterwards, all structured samples were sequentially loaded into the probe station to measure, and wire-bonding was additionally carried out after sample mounting onto prototyping boards due to a probing issue (Figure 5(a)).

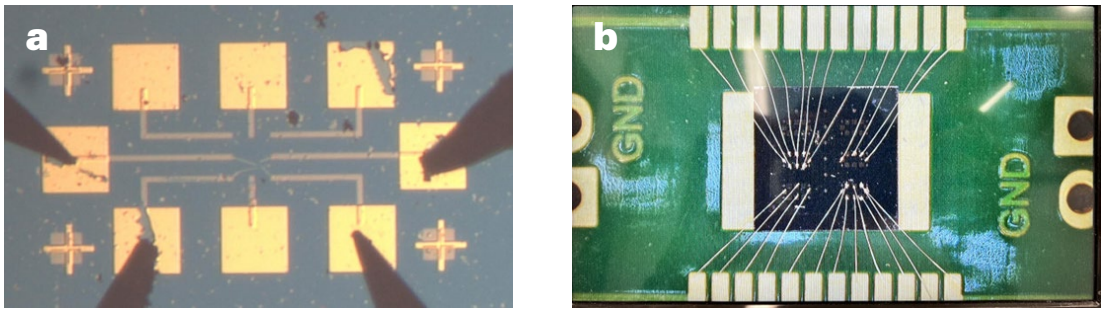

Figure 5. (a) Probing in the probe station. (b) A sample substrate on a prototyping board after wire-bonding.

2.2.4 Annealing

In the previous study of CVD-grown TMD flakes, it has been demonstrated that an annealing process helps to restore linearity of output characteristics and to reveal inherent conductance and carrier mobility. As we expected the same result, samples were annealed in a few mbar of vacuum pressure for 2 h at 150 °C (SetPoint) by using an RTA oven, for comparisons after the first characterization.

2.3 Data Analysis

All electrical measurements have been carried out through Agilent E5270B Precision IV Analyzer and Keithley 6430 Sub-femtoamp Remote SourceMeter®. To exclude contact resistance between TMD nanosheets and metallic contacts, 4-point probe configuration is indispensable in electrical characterisation.

2.4 THz Time Domain Spectroscopy

Figure 6(a) shows the current measurement configuration of THz spectroscopy. Sample was partly deposited on a quartz substrate and the rest area was used as a reference (Figure 6(b)). The acquired time domain signal is transformed to frequency domain spectrum by the fast Fourier transformation process. The proportion of both electric fields of the specimen and the reference yields photoconductivity. After a fitting of complex spectrum based on the Drude model derives charge carrier density and mobility of sample.

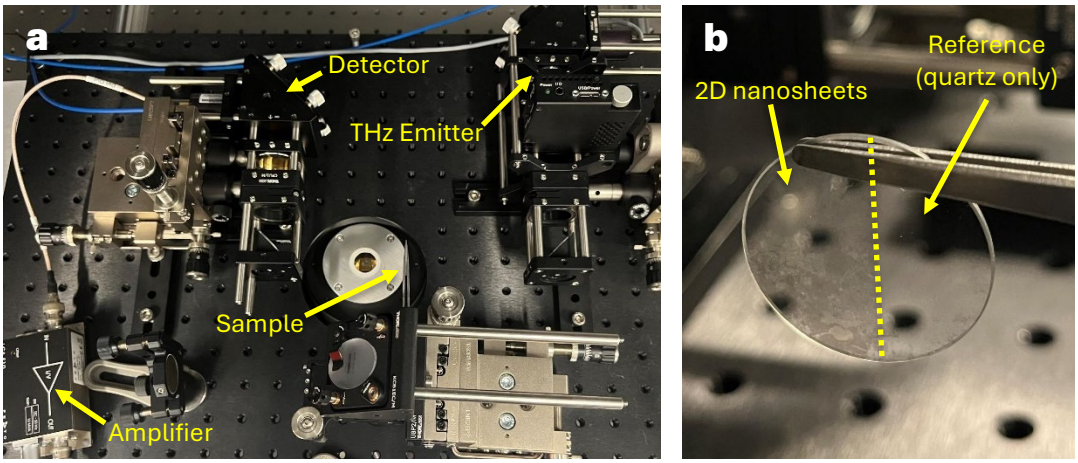

Figure 6. (a) Measurement scheme of THz time domain spectroscopy. (b) EE-graphene is deposited on a quartz substrate.

3 Results & Discussion

3.1 Results

Most TMD materials have a low conductivity in comparison to other semiconducting materials, except a few exceptional cases. Therefore, current source has to be carefully applied in 4-point probe configuration. Notwithstanding induced drain-to-source current was cautiously increased from sub-nA current with care, most TMD nanosheets deteriorated except $PtSe_2$ samples, as shown in Figure 7. A few to tens volt of drain-to-source voltage was expected to measure in the applied current range, but resistance including unexpected parasitic components under the test may be much higher than the experimental design (typically below a few GΩ) because not only nanosheets, but also electrical lead lines and electrodes were damaged after measurement, and it indicates that hundreds volt was applied.

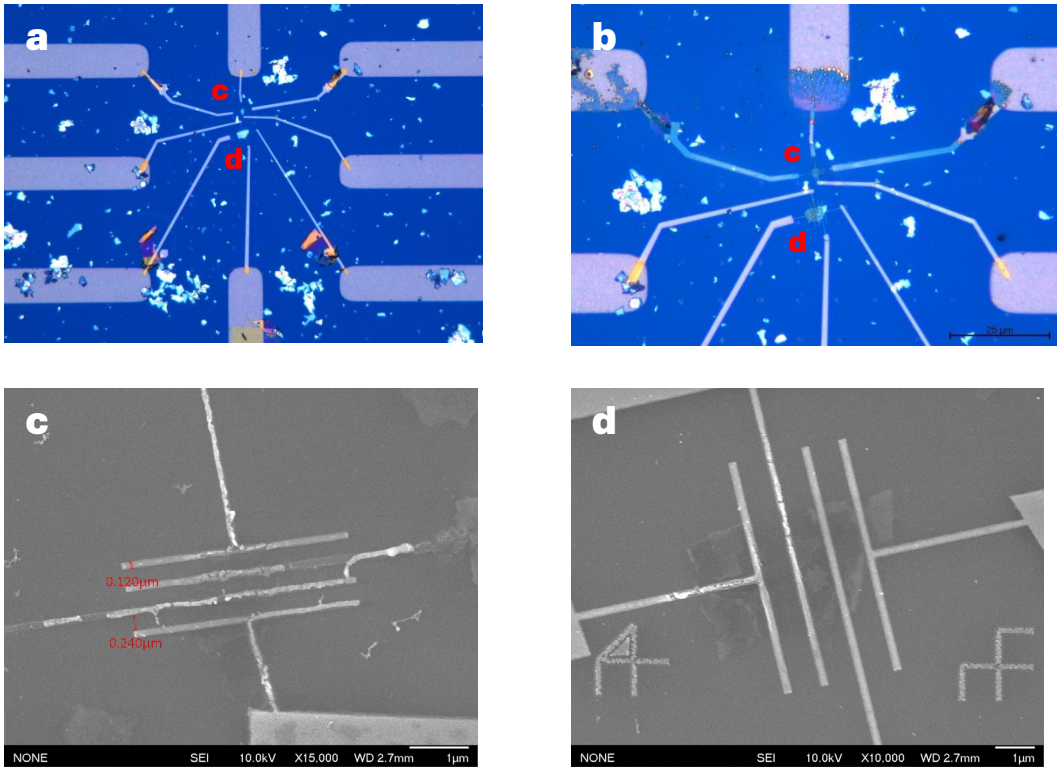

Figure 7. Two structured MoS_2 nanosheets (a) before and (b) after electrical measurements. (c) top and (d) bottom nanosheets were destroyed.

On the other hand, $PtSe_2$ nanosheets have sustained electrical measurements in the same current sweeping range. This distinct difference may consolidate conviction that those TMD nanosheets struggles for too high resistance to inject charge carriers because much higher conductivity of $PtSe_2$ is expected than other TMDs in general. However, some $PtSe_2$ nanosheets showed non-linear output characteristics without any gate dependence. However, $PtSe_2$ only become semiconducting when thinned down to 1 or two layers, such potentially semi-metallic $PtSe_2$ was present.

Only one large and thin $PtSe_2$ nanosheet showed reasonable output characteristic among 6 samples. A minute improvement of gate dependence was observed after a gentle annealing process, but conductance and linearity of output characteristics were noticeably deteriorated, as shown in Figure 8.

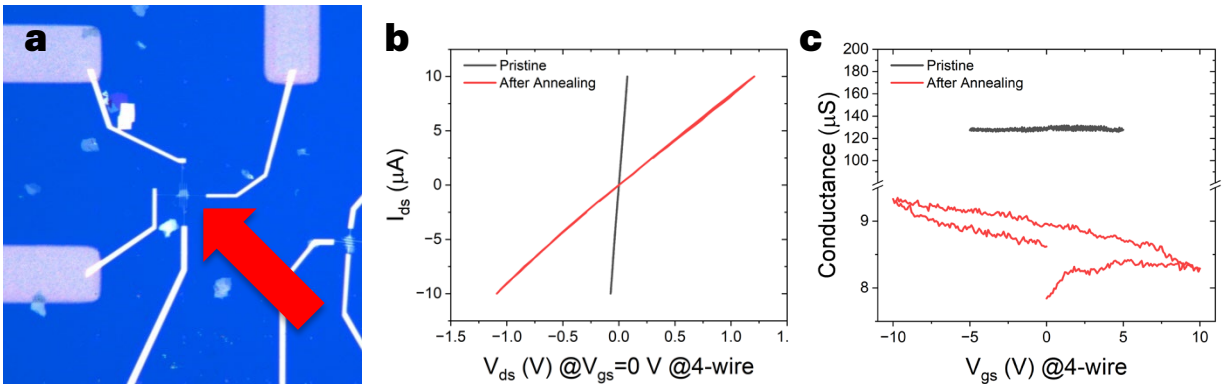

Figure 8. (a) A structured $PtSe_2$ nanosheet. (b) Output and (c) transfer characeteristics before (dark grey) and after (red) an annealing process.

Meanwhile we are developing on a contactless method to measure the mobility of our materials, to avoid any effect during the sample contacting. THz spectroscopy is considerable method as an alternative to determine electrical properties and it can compensate for conventional electrical measurement and support it. It is expected to support and enrich characterisation of nanosheets, networks, and heterostructures in objectives of WP4 and WP5.

The aforementioned THz time domain spectroscopy scheme, as descripted in the chapter of 2.4 THz Time Domain Spectroscopy, was recently completed and its capability has been verified using by LPE-graphene. So far, the averaged absorbance, carrier density, and mobility of deposited LPE-graphene are respectively ~2-6%, 8×10^{12} cm^{-1}, and 380 cm^2/Vs indicating a good agreement with literatures[1,2] in consideration of water absorption/re-emission. This preliminary result confirmed the applicability of following TMD dispersions are also applicable. Accordingly, we are working on a plan to do THz measurement from EE-/LPE-TMD dispersion.

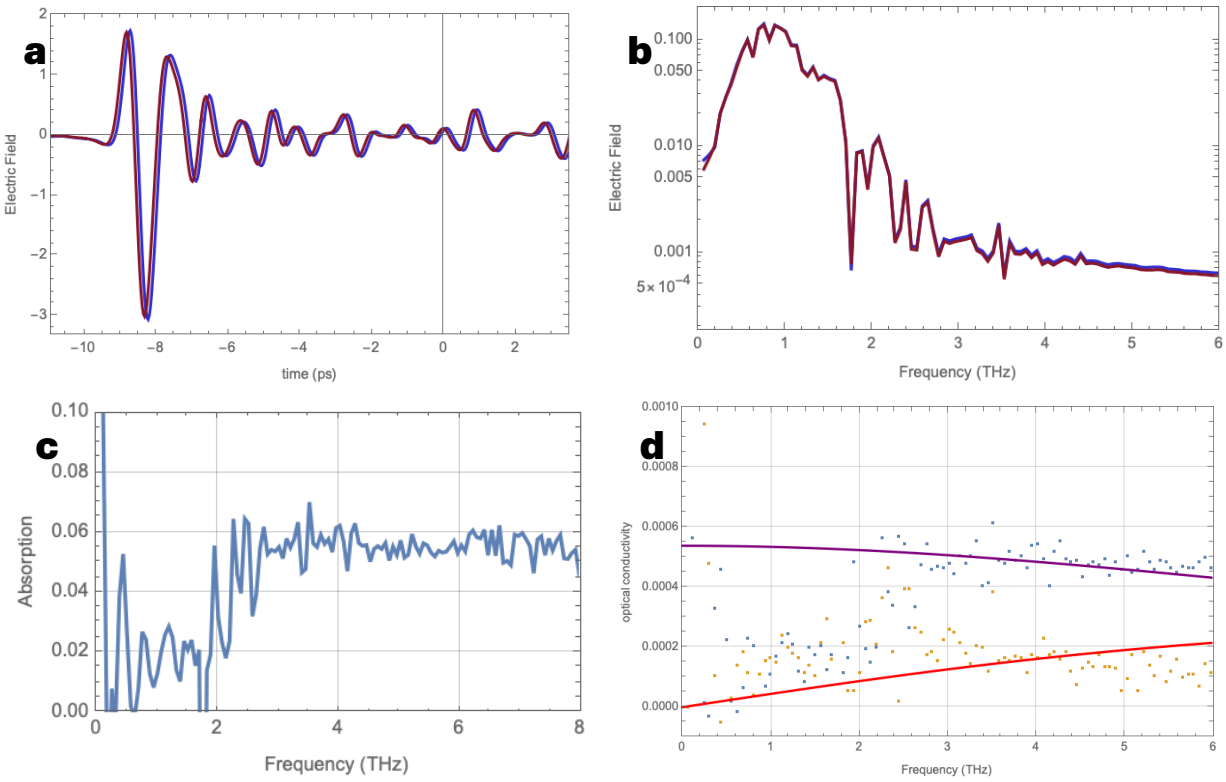

Figure 9. (a) Measured THz time domain signal of LPE-graphene. (b) Fast Fourier transformation of the signal in the frequency domain. (c) Derived absorbance. (d) Complex spectra with fittings for photoconductivity, charge carrier density, and mobility derivations.

3.2 Contribution to project (linked) Objectives

A combined lithographic process flow was established to evaluate electrical performance of TMD-based devices and 5-terminal device structure was successfully fabricated on the individual TMD nanosheets. As a result, a novel EE-$PtSe_2$ FET was realized for the first time.

3.3 Contribution to major project exploitable result

So far, main capabilities to measure of been produced.

4 Conclusion and Recommendation

For electrical characterisation of TMD nanosheets in D5.1, photo- and e-beam lithography processes were consecutively used for device fabrication of individual nanosheets from relevant TMD dispersions. The pre-patterned substrates were exchanged between UniBw M and TCD and TMD nanosheets were dispersed on them. 5-terminal structure was successfully defined onto each nanosheet and tested to evaluate their electrical device performance.

However, relatively small conductivities of most TMD materials prevents full electrical characterisation. Although all samples were carefully tested, most samples were lost at very low current in 4-point probe configuration, unlike relatively higher conductive $PtSe_2$ nanosheets. These results constitute to our knowledge the first successful characterisation of individual nanosheets exfoliated by EE method. It implies that transferred TMD nanosheets have more resistive than our experimental design and it is necessary to figure out the reason why much higher resistance was acquired than inherent resistance of pristine TMD materials. One possible scenario is that unexpected interfacial obstacles surrounding transferred TMD nanosheets. Any residues and contaminants, which can hinder charge injection to nanosheets due to inadvertent energy barrier formation at the interface, e.g. charge traps and Fermi level pinning, during dispersion has been minimized as possible, however it possibly remains on the surface in practice. The same scenario may be considerable to explain inferior contact showing deteriorated linearity in output characteristics and a lack of gate dependence. The second scenario is the contacting process flow induced some damage to the TMD materials, even though similar schemes have been successfully demonstrated by us before. We have fed backed on this result and are working on a plan to refine sample production and to acquire reasonable electrical characteristics.

At the same time, UniBw M has established a THz measurement setup. The preliminary results promise a lightsome characterisation of following TMD dispersions before structuring. This is a non-contact measurement method to derive electrical properties and hereby we expect to additionally assess the intrinsic mobility of not only single nanosheet, but also networks. The outstanding benefits of this way is non-destructive and contactless nature, independently of the doping type without electrical contacts on the specimen. A major advantage and a potential disadvantage at the same time is indistinguishable sensitivity to both pump-induced charge carriers, e.g. both holes and electron. However, representative parameters are quickly obtainable from the homogeneous nanosheet dispersions, and reduced sample preparation time proposes a fast nanosheet quality evaluation method by screening at the stage of TMD dispersion prior to structuring process. Furthermore, transient analysis of THz spectroscopy is considerable to separately extract each carrier mobility from the added electron and hole mobility. as demonstrated in previous studies[3].

5 Risks and interconnections

5.1 Risks/problems encountered

Risk No.	What is the risk	Probability of risk occurrence[1]	Effect of risk[1]	Solutions to overcome the risk
WP5.1	Device damage during characterisation due to high resistance	2	1	Optimise exfoliation and develop post-transfer cleaning process
WP5.1	Process flow of contacting detrimental to device	2	2	Develop alternative process flow or use contactless method

[1)] Probability risk will occur: 1 = high, 2 = medium, 3 = Low

5.2 Interconnections with other deliverables

Results will affect material choice and methods of later Deliverable of WP.

6 Deviations from Annex 1

If applicable

Report/summarise if/which deviations from the original plan have to be made

7 References

[1] R. R. Nair, P. Blake, a N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, a K. Geim, *Science* **2008**, *320*, 1308.
[2] J. D. Buron, D. M. A. Mackenzie, D. H. Petersen, A. Pesquera, A. Centeno, P. Bøggild, A. Zurutuza, P. U. Jepsen, *Opt. Express* **2015**, *23*, 30721.
[3] H. Hempel, C. J. Hages, R. Eichberger, I. Repins, T. Unold, *Sci. Rep.* **2018**, *8*, 14476.

8 Acknowledgement

The author(s) would like to thank the partners in the project for their valuable comments on previous drafts and for performing the review.

Project partners:

#	Partner short name	Partner Full Name
1	TCD	TCD THE PROVOST, FELLOWS, FOUNDATION SCHOLARS & THE OTHER MEMBERS OF BOARD, OF THE COLLEGE OF THE HOLY & UNDIVIDED TRINITY OF QUEEN ELIZABETH NEAR DUBLIN
2	UNISTRA	UNIVERSITE DE STRASBOURG
3	UKa	UNIVERSITAET KASSEL
4	BED	BEDIMENSIONAL SPA
5	TUD	TECHNISCHE UNIVERSITAET DRESDEN
6	VSCHT	VYSOKA SKOLA CHEMICKO-TECHNOLOGICKA V PRAZE
7	UNR	UNIRESEARCH BV
8	UniBw M	UNIVERSITAET DER BUNDESWEHR MUENCHEN
9	EPFL	ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE

Disclaimer/ Acknowledgment

This project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101135196. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

9 Appendix A - Quality Assurance Review Form

The following questions should be answered by all reviewers (WP Leader, reviewer, Project Coordinator) as part of the Quality Assurance procedure. Questions answered with NO should be motivated. The deliverable author will update the draft based on the comments. When all reviewers have answered all questions with YES, only then can the Deliverable be submitted to the EC.

Question	**WP Leader**	**Reviewer**	**Project Coordinator**
	Georg Duesberg (UniBw M)	Paolo Samori (UNISTRA)	Jonathan Coleman (TCD)
1. *Do you accept this Deliverable as it is?*	Yes	Yes	Yes
2. *Is the Deliverable complete?* - *All required chapters?* - *Use of relevant templates?*	Yes	Yes	Yes
3. *Does the Deliverable correspond to the DoA?* - *All relevant actions preformed and reported?*	Yes	Yes	Yes
4. *Is the Deliverable in line with the 2D-PRINTABLE objectives?* - *WP objectives* - *Task Objectives*	Yes	Yes	Yes
5. *Is the technical quality sufficient?* - *Inputs and assumptions correct/clear?* - *Data, calculations, and motivations correct/clear?* - *Outputs and conclusions correct/clear?*	Yes	Yes	Yes
6. *Is created and potential IP identified and are protection measures in place?*	Yes	Yes	Yes
7. *Is the Risk Procedure followed and reported?*	Yes	Yes	Yes
8. *Is the reporting quality sufficient?* - *Clear language* - *Clear argumentation* - *Consistency* - *Structure*	Yes	Yes	Yes

10 Appendix B – Lithographic Process Flow

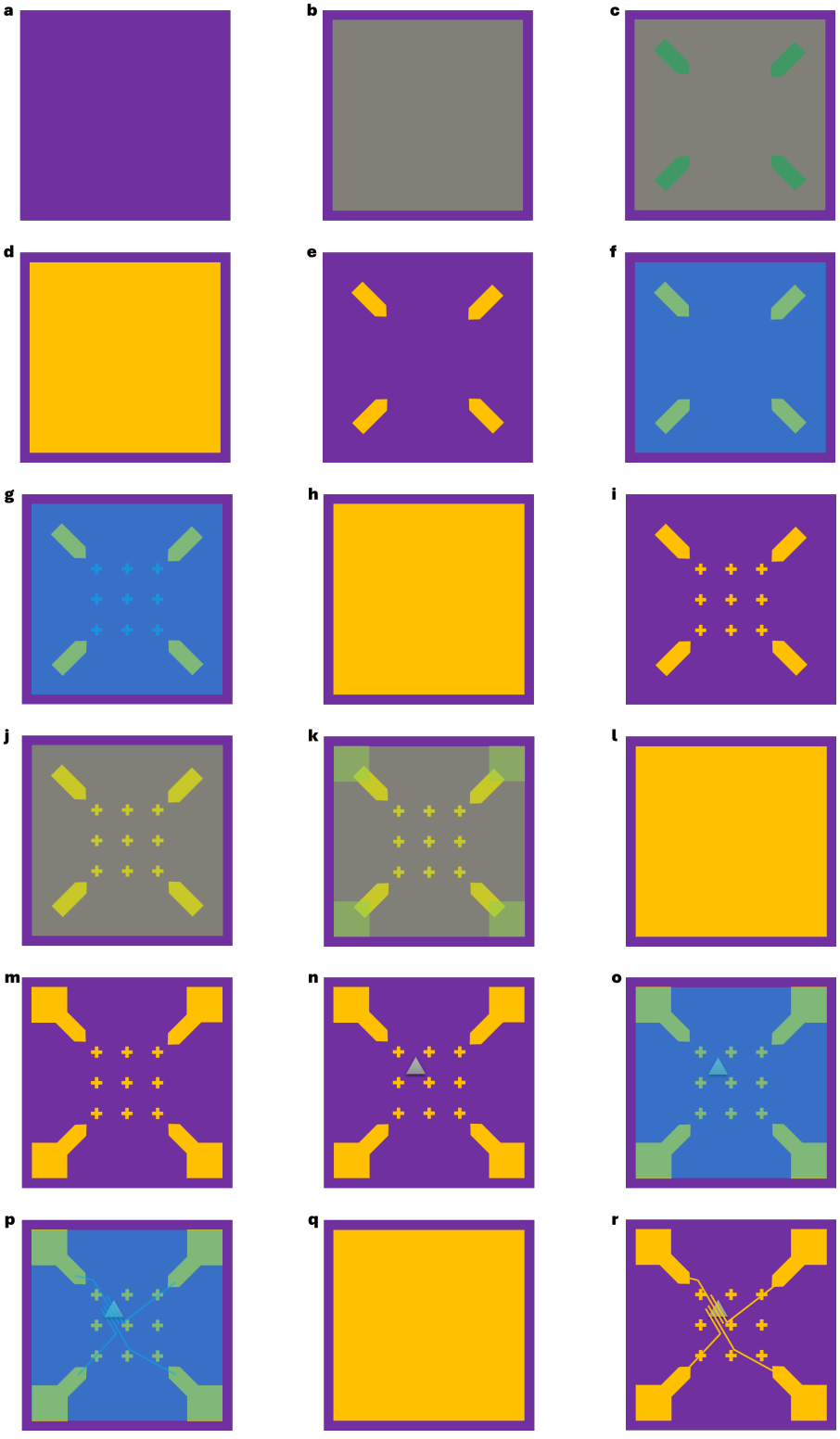

Figure 10. Process flow. Align marker patterning: (a) Substrate, (b) PR spin-coat, (c) photolithography, (d) metal evaporation, and then (e) lift-off. EBL coordinate patterning: (f) ER spin-coat, (g) EBL, (g) metal evaporation, and then (i) lift-off. Contact pad patterning: (j) PR spin-coat, (k) photolithography, (l) metal evaporation, and then (m) lift-off. (n) TMD nanosheet deposition. Contact electrode patterning: (o) ER spin-coat, (g) EBL, (g) metal evaporation, and then (i) lift-off.