Synthesis and application of two dimensional non-layered nanomaterials derived from liquid gallium

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

Nitu Syed

M.Sc. (Electrical and Electronic Engineering), Bangladesh University of Engineering and Technology
B. Sc. (Electrical and Electronic Engineering), Bangladesh University of Engineering and Technology

School of Engineering
College of Science, Engineering and Health
RMIT University

August 2019
Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

I acknowledge the support I have received for my research through the provision of an Australian Government Research Training Program Scholarship.

Nitu Syed

15/08/2019
Acknowledgements

First and foremost, I would like to thank the almighty Allah to be the most gracious and merciful all through my life. I gratefully acknowledge the funding provided by RMIT University for awarding me with Vice-Chancellor's PhD Scholarship (VCPS) and School of Engineering for the top up scholarship. I would like to appreciate the support provided by Australian Research Council (ARC) and Centre for future low-energy electronics technologies (FLEET) for giving me the opportunity to participate in several valuable educational programs.

I would like to convey my heartiest appreciation and sincere thanks to my honourable supervisors Dr. Torben Daeneke and Professor Chris McConville for providing me with the opportunity to undertake this exciting work. I am very thankful to Dr. Torben Daeneke for his invaluable inputs to my work, continuous guidance and encouragement throughout this PhD research. I would like to thank my another supervisor Dr. Dorna Esrafilzadeh (University of New South Wales) for her support and suggestions.

I am indebted to Professor Kourosh Kalantar-Zadeh to whom I would like to express my heartfelt gratitude for not only being a great supervisor during my first two years of PhD but also for playing the role of a great mentor in this tough journey. His constant scientific inputs as well as advice have gotten me to where I am today. My deep appreciation also goes out to Dr. Jian Zhen Ou and Dr. Ali Zavabeti for their scientific advice and many insightful discussions.

None of this research could have been conducted without the access to the world-class equipment and the expert staff of the RMIT Microscopy and Microanalysis Facility (RMMF), the Micro Nano Research Facility (MNRF) and RMIT chemistry laboratories. I have been privileged for the opportunity to work here. My sincere thanks to the
approachable and supportive technical staff Dr. Zeyad Nasa, Dr. Chenglong Xu, Paul Jones and Dr. Edwin Mayes. This PhD would not have been possible without the collaboration and support of my co-authors and friends at RMIT University. I would particularly like to thank Md Mohiuddin, Azmira Jannat, Robi Datta, Nripen Dhar, Farjana Haque, Bao Yue Zhang, Naresh Pillai and Kibret Messalea. Thanks are due to all my friends, relatives, students and colleagues who always loved, inspired and supported me. I am grateful to my workplace Independent University, Bangladesh (#IUB) for granting my study leave and supporting me to pursue higher education.

Last but not least, there are no words to convey my deepest gratitude to my family. I would like to express my deepest love and affection to my father Md Shahiduzzaman and my mother Begum Noorjahan with respect, for being the most supportive parents in the world. Their prayers for me are always the biggest strength of mine. Especially I can’t thank you enough Mom for encouraging me throughout this experience. I would like to acknowledge my younger sister Nabila Sayed for taking care of my family while I am away from home. My beloved daughter Samarah, has always kept me in sheer happiness. Lastly, my beloved husband, Tanjib Rubaiyat, has been an endless torrent of encouragement, humour, patience, tolerance and love. Thank you for supporting me in every step throughout this tough journey and he deserves this Ph.D. just as much as I do.
I dedicate this PhD thesis to

my parents, my husband Tanjib Rubaiyat and my baby Samarah

for their constant support and unconditional love.
Table of Contents

Declaration .......................................................................................................................... ii

Acknowledgements .......................................................................................................... iii

Abstract ............................................................................................................................. x

Publications ....................................................................................................................... xiii
  First-authored publications .......................................................................................... xiii
  Co-authored publications ............................................................................................ xiii

List of Figures .................................................................................................................... xvi

List of Tables ..................................................................................................................... xxiv

Abbreviations .................................................................................................................... xxv

Chapter 1 .............................................................................................................................. 1

Motivations and objectives ............................................................................................... 1
  1.1 Motivations ............................................................................................................... 1
  1.2 Objectives ................................................................................................................ 5
    1.2.1 Sonication assisted synthesis of gallium oxide suspensions featuring trap state absorption: test of photochemistry .............................................................. 5
    1.2.2 Printing two-dimensional gallium phosphate out of liquid metal .................... 6
    1.2.3 Synthesis of centimetre-scale ultra-thin 2D gallium nitride nanosheets from liquid metal derived oxide layer ................................................................. 7
  1.3 Organisation of thesis .............................................................................................. 8
  1.4 References ................................................................................................................ 10

Chapter 2 .......................................................................................................................... 15

Literature review .............................................................................................................. 15
2.1 Introduction .................................................................................................................. 15
2.2 Two-dimensional (2D) materials ............................................................................ 16
2.3 Gallium and gallium compounds ............................................................................. 19
  2.3.1 Gallium .......................................................................................................... 19
  2.3.2 Gallium compounds ....................................................................................... 21
    2.3.2.1 Gallium oxide (Ga₂O₃) ........................................................................... 21
    2.3.2.2 Gallium mono-chalcogenides (GaX) .................................................... 22
    2.3.2.3 Gallium nitride (GaN) .......................................................................... 23
    2.3.2.4 Gallium phosphate (GaPO₄) ................................................................... 25
2.4 Potential of liquid metals ......................................................................................... 26
  2.4.1 Fundamental properties of bulk liquid metals .............................................. 26
  2.4.2 Surface properties of liquid metal ................................................................. 27
  2.4.3 Applications of liquid metal .......................................................................... 30
  2.4.4 Liquid metal surface as a reaction medium for synthesizing 2D materials... 31
    2.4.4.1 Liquid based exfoliation of 2D nanostructures from liquid metal interface................................................................................................................... 31
    2.4.4.2 Synthesis of large-area 2D nanosheets using liquid metal reaction media 32
2.5 Summary .................................................................................................................... 34
2.6 References ............................................................................................................... 35

Chapter 3 ......................................................................................................................... 44

Sonication assisted synthesis of gallium oxide suspensions featuring trap state absorption: test of photochemistry ................................................................................ 44

3.1 Introduction ............................................................................................................. 44
3.2 Experimental section .............................................................................................. 46
  3.2.1 Sonication assisted synthesis of Ga₂O₃ nanoflakes ........................................ 46
    3.2.1.1 Exfoliation of 2D GaOOH nanoflakes .................................................. 46
    3.2.1.2 Annealing for the conversion of 2D GaOOH to α-Ga₂O₃ ...................... 47
  3.2.2 Measurement and instrumentations ............................................................... 47
3.3 Results and discussions .......................................................................................... 48
  3.3.1 Characterizations of 2D GaOOH and Ga₂O₃ nanoflakes ............................... 48
  3.3.2 Photocatalytic dye degradation performance of 2D Ga₂O₃ nanoflakes....... 57
Chapter 4

Printing two-dimensional gallium phosphate out of liquid metal

4.1 Introduction

4.2 Experimental section

4.2.1 Two-step liquid metal based synthesis of large-area 2D GaPO4 nanosheets

4.2.1.1 Van der Waals printing process of 2D Ga2O3 sheets

4.2.1.2 Transformation of 2D Ga2O3 to 2D GaPO4 sheets by phosphatization

4.2.2 Exfoliation of free-standing 2D GaPO4 sheets

4.2.3 Piezoresponse force microscopy (PFM) measurements

4.2.4 Peak-force quantitative nano-mechanical (PFQNM) mapping

4.2.5 Density functional theory calculations

4.2.6 Measurement and instrumentation

4.3 Results and discussions

4.3.1 Synthesis of large-area 2D GaPO4 nanosheets

4.3.2 Characterizations of 2D GaPO4 nanosheets

4.3.3 Thermal stability of the synthesized 2D GaPO4

4.3.4 Out-of-plane piezoelectric properties of 2D GaPO4 synthesized on SiO2 substrate

4.3.5 DFT simulation results of the piezoelectric performance of GaPO4

4.3.6 Piezoelectric and elastic properties of free-standing GaPO4

4.4 Conclusions

4.5 References

Chapter 5

Synthesis of centimetre-scale ultra-thin 2D gallium nitride (GaN) nanosheets from liquid metal derived oxide layer

5.1 Introduction

5.2 Experimental section
5.2.1 Synthesis of extra ordinary large 2D GaN nanosheets .......................... 109
5.2.1.1 Squeeze-printing process of the 2D Ga$_2$O$_3$ sheet .............................. 109
5.2.1.2 Transformation of 2D Ga$_2$O$_3$ to 2D GaN sheets via ammonolysis process ................................................................. 111
5.2.2 Mechanical cleaning procedure ............................................................ 113
5.2.3 Synthesis of 2D GaN nanoplatelets ...................................................... 114
5.2.4 Two-step liquid metal based synthesis of 2D InN sheets ...................... 114
5.2.5 Fabrication of the Hall device ............................................................... 115
5.2.6 Hybrid density functional theory (DFT) calculations ............................ 115
5.2.7 Instrumentation and characterizations .................................................. 116
5.3 Results and discussions ......................................................................... 117
5.3.1 Characterizations of 2D GaN nanosheet .............................................. 117
5.3.2 Characterizations of 2D GaN nanoplatelets .......................................... 126
5.3.3 Characterizations of 2D InN nanoplatelets ............................................ 127
5.4 Conclusions ............................................................................................ 129
5.5 References ............................................................................................. 129

Chapter 6 .................................................................................................... 134

Conclusions .................................................................................................. 134

6.1 Concluding Remarks .............................................................................. 134
6.1.1 Synthesis of 2D Ga$_2$O$_3$ featuring trap state absorption ..................... 134
6.1.2 Synthesis of large area 2D GaPO$_4$ ...................................................... 135
6.1.3 Synthesis of centimetre-scale 2D GaN ............................................... 137
6.2 Future Work .......................................................................................... 138
6.2.1 Two-dimensional metal oxide and hydroxide nanoflakes of other material 138
6.2.2 Synthesis of large-area nanosheets of new 2D metal compounds utilizing other molten metals ......................................................... 138
6.2.3 Functional applications of the large area 2D metal compounds .......... 139
Abstract

The field of two dimensional (2D) materials has received considerable attention and experienced substantial development over the past two decades. Various families of 2D materials have been explored to date leading to ample success in wide range of applications. However, despite many significant advances the synthesis of large area, ultra-thin 2D materials remains a great technological challenge, limiting their commercial application. Additionally, the field of 2D materials is mostly focused on stratified materials with layered crystal structures due to the prevailing synthesis techniques. This leaves many non-layered materials unexplored, which could be suitable candidates in their 2D morphologies for future applications. Recent progress in the field of liquid metal chemistry can offers new avenues of investigation and a range of unexploited possibilities in the domain of 2D materials. Liquid gallium and gallium based alloys feature low melting points that are close to room temperature and undergo Cabrera-Mott oxidation process in air, creating atomically thin 2D metal oxides on the surface. In addition, the developed surface oxides demonstrate minimal adhesion to the parent metal which allows to delaminate these naturally occurring 2D materials with relative ease. Alloying can be used to expand the number of accessible 2D materials, unfolding new opportunities for the synthesis of many previously inaccessible 2D materials. Therefore, this PhD thesis aims to develop 2D metal oxide and further metal compounds that are derived from liquid metal gallium through the harvesting of its interfacial oxide skin. The isolated metal oxides will be then subjected to further chemical conversion to create desired metal compounds in 2D morphology. The synthesized 2D materials will be explored for potential applications in catalysis and different functional devices.

The first objective of this thesis was to exfoliate 2D gallium oxide nanoflakes from gallium droplets immersed in aqueous solution. Gallium is a near room temperature liquid
metal with extraordinary properties that partly originate from the self-limiting oxide layer formed on its surface. Taking advantage of the surface gallium oxide, this work has introduced a novel technique to synthesize porous gallium oxide (Ga$_2$O$_3$) nanoflakes at high yield by harvesting the native oxide skin of gallium. The synthesis process followed a facile two-step method comprising liquid gallium metal sonication in DI water and subsequent annealing. In order to explore the functionalities of the product, the obtained $\alpha$-Ga$_2$O$_3$ nanoflakes were used as a photocatalytic material to decompose organic model dyes. Excellent photocatalytic activity was observed under solar light irradiation. To elucidate the origin of these enhanced catalytic properties, the electronic band structure of the synthesized $\alpha$-Ga$_2$O$_3$ was carefully assessed. It was found that the excellent photocatalytic performance is associated with the presence of trap states which are located at $\sim$1.65 eV below the conduction band minimum.

To broaden the versatility of 2D materials for different future “wafer-scale” applications, scalable and low cost synthetic routes must be developed to deposit large-area 2D gallium compounds utilizing liquid gallium as a precursor. In the second part of this thesis, large-area 2D nanosheets piezoelectric material gallium phosphate (GaPO$_4$) was synthesized providing new opportunities for piezosensors and energy harvesting. GaPO$_4$ is an archetypal piezoelectric material which does not naturally crystallize in a stratified structure and hence cannot be exfoliated using conventional methods. Until now, no 2D piezoelectric material has been manufactured in large sheets, making it impossible to integrate these materials into silicon chips or use them in large-scale surface manufacturing. This work reports a low temperature liquid metal based two-dimensional printing and synthesis strategy to achieve this goal. The synthesis process was consist of surface-printing of the interfacial oxide layer of liquid gallium, followed by a vapour phase reaction. The method offers access to large-area, wide band-gap two-dimensional GaPO$_4$
nаносheets of unit-cell thickness, while featuring lateral dimensions reaching centimetres. The unit-cell thick nanosheets presented a large effective out-of-plane piezoelectric coefficient of $7.5\pm0.8$ pm V$^{-1}$. The printing process developed here was also suitable for the synthesis of free-standing GaPO$_4$ nanosheets. The low temperature synthesis method is compatible with a variety of electronic device fabrication procedures, providing a route for the development of future two-dimensional piezoelectric materials.

Following the successful exfoliation of non-layered GaPO$_4$, liquid gallium was further used as a platform to exfoliate centimetre-scale 2D gallium nitride (GaN) nanosheets. Gallium nitride is a semiconductor of great technological importance with excellent electronic and optical properties. The synthesis relied on the ammonolysis of liquid metal derived 2D oxide sheets that were squeeze transferred onto desired substrates. Wurtzite GaN nanosheets featured typical thicknesses of 1.3 nm, an optical band-gap of 3.5 eV and a carrier mobility of 21.5 cm$^2$ V$^{-1}$s$^{-1}$. In order to assess the versatility of the synthesis method, an adapted synthesis process utilizing liquid indium instead of liquid gallium was explored to synthesize 2D indium nitride (InN) featuring a thickness of 2.0 nm. The method provides a scalable approach for the integration of 2D morphologies of industrially important semiconductors into emerging electronics and optical devices.

Overall, the author of this PhD thesis believes that the outcomes presented herein will contribute to the advancement of nanotechnology through the development of scalable and low cost synthesis paths and will work as a platform for many future investigations into the synthesis and applications of 2D materials.
Publications

First-authored publications

Sonication-assisted synthesis of gallium oxide suspensions featuring trap state absorption: test of photochemistry

Printing two-dimensional gallium phosphate out of liquid metal
N Syed, A Zavabeti, J Ou, Md Mohiuddin, N Pillai, B J Carey, B Y Zhang, R S Datta, A Jannat, F Haque, K Messalea, C Xu, C F McConville, T Daeneke, K Kalantar-Zadeh

Wafer-sized ultra-thin gallium and indium nitride nanosheets through the ammonolysis of liquid metal derived oxides

Co-authored publications

A liquid metal reaction environment for the room-temperature synthesis of atomically thin metal oxides

Highly Active Two-Dimensional $\alpha$-MoO$_3$$_3$ for Electrocatalytic Hydrogen Evolution Reaction
Degenerately Hydrogen Doped Molybdenum Oxide Nanodisks for Ultrasensitive Plasmonic Biosensing

Two dimensional PbMoO₄: A photocatalytic material derived from a naturally non-layered crystal

Liquid phase acoustic wave exfoliation of layered MoS₂: critical impact of electric field in efficiency

Exploring electric field assisted van der Waals weakening of stratified crystals

Bi₂O₃ monolayers from elemental liquid bismuth

Exfoliation Behavior of van der Waals Strings: Case Study of Bi₂S₃
2D SnO/In₂O₃ van der Waals Heterostructure Photodetector Based on Printed Oxide Skin of Liquid Metals
Manal MYA Alsaif, Sruthi Kuriakose, Sumeet Walia, Nitu Syed, Azmira Jannat, Bao Yue Zhang, Farjana Haque, Naresh Pillai, Torben Daeneke, Jian Zhen Ou, Ali Zavabeti
*Advanced Materials Interfaces*, 6, 1900007 (2019)

Ordered intracrystalline pores in planar molybdenum oxide for enhanced alkaline hydrogen evolution
F Haque, A Zavabeti, BY Zhang, RS Datta, Y Yin, Z Yi, Y Wang, N Mahmood, N Pillai, N. Sved, H Khan, A Jannat, N Wang, N Medhekar, K Kalantar-zadeh, J Z Ou

Liquid metals for tuning gas sensitive layers.

Self-Limiting Galvanic Growth of MnO₂ Monolayers on a Liquid Metal—Applied to Photocatalysis.

Liquid metal core–shell structures functionalised via mechanical agitation: the example of Field's metal
List of Figures

Figure 2.1. (a) A sheet of graphene. (b) Weakly bonded graphene layers found in graphite. ................................................................................................................................. 18

Figure 2.2. Layered 2D materials family. Blue cells represent monolayers of 2D materials showing stability under ambient conditions; green denotes probability of stability of 2D materials in air; pink denotes 2D unstable materials in air, but may be stable under inert atmosphere. Grey cells show 3D compounds easily exfoliated down to monolayers.................................................................................. 18

Figure 2.3. (a) Crystal structure of α-Ga, (b) crystal structure of α-Ga showing only short bonds \( d < 2.5 \text{ Å} \), (c) crystal structure of α-Ga showing only the long bonds......................................................................................................................... 20

Figure 2.4. Unit cell of β-Ga2O3. It possesses two inequivalent Ga sites: Ga(I), Ga(II) and three inequivalent O-sites: O(I), O(II) and O(III). The Ga(I) sites have tetrahedral coordination, and the Ga (II) sites have octahedral coordination 21

Figure 2.5. Structure of monolayer gallium chalcogenides GaX (X = S, Se, Te) showing the top and side views. .................................................................................................................. 23

Figure 2.6. The crystal structure of GaN exhibits a unit cell (dotted box) with cell parameters of 5.19 Å along the long axis and 3.19 Å along both of the short axes.......................................................................................................................... 24

Figure 2.7. Ball and-stick representation of the synthesised GaPO4 crystal: (a) Unit cell of GaPO4 along z axis, (b) side view showing an out-of-plane structure exhibiting unit cell parameter \( c = 11.05 \text{ Å} \)................................................................................................................. 25

Figure 2.8. A cross-sectional diagram of a liquid metal droplet, with possible crystal structures of thin layer Ga2O3 as indicated. ........................................................................................................... 28

Figure 2.9. Schematic of the surface oxide skin of gallium featuring the electron density profile plotted for the interface ........................................................................................................................................ 29
Figure 2.10. (a) Schematic representation of the van der Waals exfoliation technique. The pristine liquid metal droplet is first exposed to an oxygen containing environment. Touching the liquid metal with a suitable substrate allows transferring the interfacial oxide layer. Optical images are shown on the right-hand side. (b) Schematic representation of the gas injection method (left), with photographs of the bubble bursting through the liquid metal (middle) and an optical image of the resulting sheets drop-casted onto a Si/SiO₂ wafer. ....... 33

Figure 3.1. Step-by-step schematic of the synthesis process converting gallium metal into gallium oxide nanoparticles during sonication. (a) A bulk gallium droplet with surface oxide, kept in DI water. (b) The bulk gallium metal splits into smaller liquid metal entities with cracks on their surface oxide skin during sonication. (c) Delamination of small oxide nanoparticles from the cracked surface oxide layer. (d) Oxide nanoparticles separated from the bulk gallium metal after completed reaction and centrifugation. .......................................................... 49

Figure 3.2. (a) Bulk gallium droplets in DI water. (b) Suspension of hydrated oxide nanoparticles prepared after 60 min of sonication prior to centrifugation. (c) Gallium oxide suspension after centrifugation, annealing and re-suspension. ..................................................................................................... 50

Figure 3.3. XRD data of (a) as synthesized nanoflakes indexed to GaOOH and (b) annealed material indexed to α-Ga₂O₃. .................................................................................................... 51

Figure 3.4. (a) SEM image of the GaOOH (b) High-magnification SEM image of the GaOOH nanoblocks. (c) The TEM image of the GaOOH, presenting plate-like structures. (d) HRTEM of GaOOH, displaying the lattice fringes. The top right inset shows the SAED pattern of GaOOH, which indicates the observed interplanar spacing is 0.25 nm that corresponds to the d-spacing of (021) plane for orthorhombic GaOOH. ................................................................................................. 52

Figure 3.5. (a) SEM image of α-Ga₂O₃. (b) High-magnification SEM images of Ga₂O₃ nanoflakes. (c) TEM image of α- Ga₂O₃ indicating the flake like porous (A) and nonporous (B) populations as indicated. The insets show lattice fringes
Figure 3.6. AFM image of α-Ga₂O₃ nanostructures. Inset: height profile along the white line. ................................................................. 54

Figure 3.7. XPS of synthesized Ga₂O₃ (a) Ga 3d and (b) O 2s. Peak at the binding energy of 20.68 eV signifies the valence state Ga³⁺ in Ga₂O₃. No metallic gallium (Ga⁰) is observed in the Ga 3d region. Peak observed at a binding energy of 531.1 eV corresponds to O 1s state of Ga₂O₃. ............................................... 55

Figure 3.8. (a) UV-vis absorbance spectrum of α-Ga₂O₃ exhibiting a broad absorption feature between 280-400 nm. (b) Tauc-plot of the UV-vis data where plot a and hv represents the optical absorption coefficient and photon energy respectively. (c) PESA spectrum of α-Ga₂O₃. (d) VB XPS analysis is showing the presence of trap states. ............................................................................. 57

Figure 3.9. (a) UV-vis absorption spectrum of Congo Red (CR) in the presence of the Ga₂O₃ catalyst after indicated length of simulated solar light irradiation. (b) Photodegradation of CR under solar light irradiation. (c) UV-vis absorption spectrum of Rhodamin B (RhB) in the presence of the Ga₂O₃ catalyst. (d) Photodegradation of RhB under solar light irradiation. ................................. 59

Figure 3.10. (a) Degradation kinetics of Congo red dye under solar light irradiation where the slope is found to be 0.0161 min⁻¹. (b) Degradation kinetics of RhB with a slope of 0.014min⁻¹. ................................................................. 60

Figure 3.11. (a) Degradation of Congo red in the presence of photocatalyst but in the absence of solar irradiation. (b) Degradation of Congo red under solar light irradiation without any photocatalyst. ............................................................ 61

Figure 3.12. (a) Energy level diagram of Ga₂O₃ representing the possible photocatalytic mechanism with the estimated valance band maximum (VBM) and CBM. The
DOS was determined by VB XPS. HOMO and LUMO values for CR and RhB are also demonstrated. (b) Room temperature PL spectrum

**Figure 3.13.** Room temperature PL spectra of $\alpha$-Ga$_2$O$_3$ in air obtained at the excitation wavelength of 532 nm.

**Figure 4.1.** Gallium droplets with different diameters (a) before the formation of Ga$_2$O$_3$ oxide skin and (b) with surface oxide skin.

**Figure 4.2.** AFM images (a, c) 2D Ga$_2$O$_3$ sheets imaged before and after (b, d) conversion into 2D GaPO$_4$.

**Figure 4.3.** Scanning electron microscopy of the micro-cavities and free-standing 2D nanosheets. (a) The schematic for the cross section of the SiO$_2$/Si wafer with micro cavities. SEM images of (b) array of micro cavities, (c) an uncovered square hole, (d) fully and partially covered cavities by GaPO$_4$ nanosheet, (e) cavity covered with Ga$_2$O$_3$ flake before phosphatization process which is showing an even bulged surface area, (f) hole covered with GaPO$_4$ nanosheet showing a wrinkled surface.

**Figure 4.4.** AFM topography (a) an uncovered square cavity and its depth profile along the red line, (b) AFM image of a cavity covered with GaPO$_4$ nanosheet and its height profile along the red line.

**Figure 4.5.** (a) Schematic illustration showing the PFM set up. (b) Topography of a PPLN substrate, (c) PFM phase, and; (d) PFM amplitude of a standard PPLN sample as reference with a PR drive amplitude of 10 V at 17kHz.

**Figure 4.6.** Crystal structure and printing process of 2D GaPO$_4$ nanosheets. Ball and-stick representation of the synthesized GaPO$_4$ crystal: (a) top view and (b) side view showing an out-of-plane structure exhibiting unit cell parameter $c = 11.05$ Å. (c) Schematic illustration of the van der Waals 2D printing technique of Ga$_2$O$_3$ nanosheet. (d) Schematic setup for the chemical vapour phase reaction system used for synthesising GaPO$_4$ nanosheets.
Figure 4.7. Morphology and TEM characterizations of the printed 2D GaPO4 film. (a) AFM topography of a GaPO4 nanosheet and height profile along the magenta line. (b) TEM micrograph of the GaPO4 film. (c) The SAED pattern of the TEM micrograph. (d) Optical images of synthesized GaPO4 showing homogeneous nanosheets featuring lateral dimensions spanning several millimetres. ............................................................ 85

Figure 4.8. Material characterizations and electronic band properties of 2D GaPO4. (a) XRD and (b) Raman spectra of the synthesized GaPO4 (thick nanosheets). XPS results of (c) Ga 3d and (d) phosphorous 2p regions of the synthesized GaPO4. (e) Enlarged view of EELS for the estimation of the fundamental band-gap and the extended EELS spectrum (inset). (f) XPS valence band analysis of GaPO4 ............................................................................................................. 88

Figure 4.9. Thermal stability characterizations of the synthesized 2D GaPO4. XPS results of (a) Ga 3d and (b) phosphorus 2p regions of the synthesized GaPO4 annealed at 600 °C. (c) Raman spectrum of GaPO4 nanosheet on SiO2 substrate annealed at 600 °C. XPS results of (d) Ga 3d and (e) phosphorus 2p regions of the synthesized GaPO4 annealed at 700 °C.......................................................... 90

Figure 4.10. Characterizations of out-of-plane piezoelectricity of 2D GaPO4 .......... 92

Figure 4.11. Topography and corresponding phase images at different AC voltages during PFM measurements for the GaPO4 flake with unit cell thickness. ............... 93

Figure 4.12. Characterizations of out-of-plane piezoelectricity of 2D GaPO4 nanosheets with different thicknesses......................................................................................... 94

Figure 4.14. Piezoelectric properties of free-standing GaPO4 nanosheet ............ 99

Figure 4.15. Vertical piezoresponse of free-standing GaPO4 nanosheet .............. 99

Figure 4.16. Piezoelectric and elastic properties of free-standing GaPO4 nanosheet. ... 101
Figure 5.1. (a) Schematic illustration of the van der Waals 2D squeeze printing technique of large Ga$_2$O$_3$ nanosheets................................................................. 110

Figure 5.2. (a) Synthesized Ga$_2$O$_3$ on SiO$_2$ (220nm)/Si wafer after mechanical cleaning as mentioned above, shows homogeneous sheet featuring lateral dimensions spanning several centimetres. ................................................................. 111

Figure 5.3. 2D Ga$_2$O$_3$ synthesized on different substrates: (a) glass, (b) quartz and (c) fluorine-doped tin oxide (FTO)................................................................. 111

Figure 5.4. Schematic setup for the chemical vapour phase reaction system used for synthesizing GaN nanosheets using a horizontal tube furnace................. 113

Figure 5.5. XPS spectra of (a) O 1s, (b) N 1s and (c) Ga 2p regions of 2D nanosheets synthesized at 700 °C. The binding energy of N 1s region significantly differs from N 1s levels in GaN. The XPS of O 1s region also shows an intense oxide peak that does not correspond to occasional oxygen defects but rather to the formation of a different material.(d) (a) XRD pattern of as synthesized GaN nanoplatelets obtained from ammonolysis reaction conducted at 700 °C... 113

Figure 5.6. An intermediate bromination step to transform In$_2$O$_3$ to InBr$_3$. ................. 115

Figure 5.7. Synthesis process of the centimeter scale 2D GaN nanosheet. (a) Schematic illustration of the squeeze printing technique to exfoliate oxide skin of gallium metal onto the substrate. The pristine liquid metal droplet is squeezed between two suitable substrates which allow transferring the Ga$_2$O$_3$ layer. Optical image of exfoliated Ga$_2$O$_3$ on SiO$_2$ (300nm)/Si is presented on the right-hand side. (b) Synthesis process of the 2D GaN nanosheet from 2D Ga$_2$O$_3$ using ammonolysis. The crystal structure of GaN exhibits a unit cell (dotted box) with cell parameters of 5.19 Å along the long axis and 3.19 Å along both of the short axes. Optical image of the synthesized GaN on SiO$_2$ (300nm)/Si is exhibited on the right side................................................................. 119
Figure 5.8. Morphology and TEM characterizations of the 2D GaN film. (a) AFM topography of the nanosheet with height profile along the black line. The top inset corresponds to the high-resolution AFM topography of the sheet. The FFT pattern of the (001) plane is displayed in the lower inset. (b) TEM micrograph of the GaN film. The insets represent the lattice fringes (top inset) and the FFT pattern (lower inset).

Figure 5.9. Material characterizations and electronic band structure properties of 2D GaN. (a-b) XPS results of the 2D GaN for the regions of interest, (a) Ga 2p and (b) N 1s. The characteristic doublets for Ga 2p region, 2p1/2 and 2p3/2, are positioned at ~1144.8 and ~1118.1 eV, respectively. The main broad N 1s peak centered at ~397.6 eV corresponds to the expected binding energy for nitrogen region present in GaN. (c) XPS valence band spectrum affirming an energy difference of ~2.7 eV between the valence band maximum (VB_{max}) and Fermi level (E_F). The spectrum was decomposed into three peaks responsible for different bonds. (d) Tauc plot used for ascertaining the electronic band-gap for GaN with simplified electronic band diagram (top left).

Figure 5.10. (a-c) AFM topography, valence band spectrum and Tauc plot for 2D GaN nanosheet synthesized at 900 °C. (d-f) AFM image, valence band spectrum and Tauc analysis for 2D GaN nanosheet grown at 950 °C. (g-h) AFM topography and corresponding height profile of GaN nanosheets synthesized at 1000 °C showing substantial morphological degradation.

Figure 5.11. (a) Undoped GaN (110) slab, (b) oxygen doped GaN (110) slab, (c) Calculated electronic DOS of undoped and O-doped 2D GaN.

Figure 5.12. (a) SEM image of the six-terminal Hall device. (b) Hall resistance (R_{xy}) of the 2D GaN film as a function of applied magnetic field (B). An optical image of the fabricated Hall device is shown in the lower right inset.

Figure 5.13. Characterizations of 2D GaN nanoplatelets. (a) AFM topography of a GaN nanoplatelets and height profile along the magenta line (inset). (b) TEM image of the GaN nanoplatelets. (c) XRD spectrum of the synthesized 2D GaN.
nanoflakes. All of the peaks match well with the previous reports. (d) The GaN nanoplatelets featured an optical band-gap of 3.2 eV which demonstrates a good agreement with previous reports of GaN nanoparticles and films. (e-f) XPS results of Ga 2p and N 1s regions of the GaN nanoplatelets. 

**Figure 5.14.** (a) Optical images of synthesized InN showing homogeneous nanosheets featuring lateral dimensions exceeding centimetres. (b) AFM image of 2D InN sheet and height profile along the magenta line. The insets are showing the high resolution AFM analysis for the 2D InN sheet. A repeated crystal with a lattice constant of 5.5 Å is determined which is in consistent with wurtzite InN. (c-d) XPS was employed to obtain the chemical bonding states of the synthesized 2D InN.
List of Tables

Table 3.1. Comparison of photocatalytic performance of a selection of previously reported gallium oxide and this work. ........................................................... 62

Table 4.1. Comparison of \( d_{33} \) between some previously reported 2D films and this work. ................................................................. 97

Table 4.2. Comparison of \( d_{33} \) between some previously reported bulk materials and this work. ................................................................. 97
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer Emmett Teller</td>
</tr>
<tr>
<td>CR</td>
<td>Congo Red</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DMT</td>
<td>Derjaguin Mueller Toporov</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>PF-QNM</td>
<td>Peak force quantitative nanomechanical mapping</td>
</tr>
<tr>
<td>PESA</td>
<td>Photoelectron spectroscopy in air</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PF-TUNA</td>
<td>Peak force tunnelling atomic force microscopy</td>
</tr>
<tr>
<td>RhB</td>
<td>Rhodamine B</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>UV Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>

xxv
Chapter 1

Motivations and objectives

1.1 Motivations

Two-dimensional (2D) materials are a class of nanomaterials that are typically comprised of one to few-atom-thick layers in one dimension, with the other two dimensions extending beyond the nanometric range. 2D materials have been investigated intensely for the past two decades as researchers are aiming to explore materials that can complement or replace silicon in the electronic industries. Most 2D materials possess significantly distinct physical, chemical and electronic properties when compared with their bulk counterparts, leading to unique effects due to quantum confinements and introducing tunability through thickness control, rendering them to be very promising for various applications. The unique qualities offered by 2D materials include their lateral strength and high crystallinity along the planes, high surface area to volume ratios, transparency, compatibility with surface fabrication processes, etc. The field of 2D material has expanded greatly since 2004, when the archetypal 2D material, graphene, was successfully synthesized from graphite by Novoselov et. al. In the following years the research community has exhibited tremendous enthusiasm for exploring graphene and graphene like 2D materials, including the transition metal dichalcogenides (TMDs), metal oxides, graphitic carbon nitride (g-C₃N₄), hexagonal boron nitride (h-BN) and many more. These 2D materials have shown huge potential in a wide range of applications such as nano-electronic devices, catalysis, energy storage, sensing and biomedicine.
Despite the continuing emergence of remarkable and outstanding advances in the research field of 2D materials, there are still many constraints associated with the use of 2D materials. So far, the discovery of new 2D nanostructures is mainly restricted to intrinsically layered 2D crystals with weak out-of-plane van der Waals bonds\textsuperscript{10,11}, and the number of investigated nonlayered 2D materials remains rather limited, narrowing the choice of available 2D materials. However, different types of nonlayered nanomaterial with 2D morphology are believed to possess fascinating properties that may complement the conventional layered 2D compounds. For instance, the surfaces of 2D nonlayered materials naturally consist of passivated (i.e. hydroxylated etc) dangling bonds, which is distinct from layered materials that feature naturally saturated basal planes. This leads to 2D nonlayered materials to feature highly chemically active interfaces.\textsuperscript{12} This unique property can enhance their capability for a range of applications in nanoscale electronics, catalysis, sensing and optoelectronics.\textsuperscript{13-15} However, insufficient anisotropic driving force for inducing the required two-dimensional growth\textsuperscript{12,16} and the existence of strong out-of-plane chemical bonds have made it difficult to synthesize ultra-thin 2D nanosheets of nonlayered crystal structures. Hence, one of the momentous tasks for upcoming research is to synthesize and explore new nonlayered 2D materials for future applications.

In addition, there are still a number of technological problems associated with the commercial application of 2D nanostructures. For example, synthesizing homogeneous, ultra-thin 2D nanosheets covering large-areas is still a great challenge for the 2D research community. So far, various methods have been proposed to isolate and synthesize different 2D materials from bulk parent crystals. The simplest one is the mechanical exfoliation of 2D nanosheets from layered crystals utilizing adhesive tape.\textsuperscript{17} This process allows to obtain highly crystalline flakes, but with a low yield. Additionally, the flakes usually have lateral sizes of just a few tens of micrometres, which is not adequate for the commercial implementation. Until
now, very few scalable methods have been developed for the large-area production of ultra-thin 2D nanosheets. Consequently, reducing the material thickness to few atoms and also achieving homogeneous wafer-scale 2D nanosheet deposition are still the greatest impediment in this area of research. Apart from this, the cost associated with many of the current 2D fabrication technologies is still prohibitively high. Therefore, researchers should explore new synthesis strategies for obtaining various 2D nanostructures to overcome the limitations of the current conventional methods.

Recent progress in the field of liquid metal chemistry can open up new frontiers and possibilities in 2D materials research. Liquid metals, a class of metals and alloys that are liquid at or near room temperature, have recently fascinated the scientific community due to their simultaneous metallic and liquid natures. Liquid metals offer unique characteristics emerging from the combination of their conductive and soft nature. In the past, the most familiar liquid metal used to be mercury, however, gallium and gallium-based alloys are recently gaining attention as promising alternative to mercury, overcoming its limitations associated with high toxicity. Gallium belongs to the family of low-melting-point post transition metals with unique properties such as the low melting point (~29.6 °C), low toxicity, excellent electrical and thermal conductivities and negligible vapour pressure. Moreover, gallium and its alloys have shown great promise in realizing multifunctional devices including stretchable, reconfigurable and flexible circuits, actuators, and self-healing superconductors.

Like many post-transition metals, a self-limiting interfacial oxide layer grows on the surface of gallium and gallium based alloys on exposure to an oxygen containing environments. The oxide layer functions as a mechanical shell that protects the underlying parent metal from further oxidation. The oxidation of the gallium interface under ambient conditions follows Cabrera-Mott kinetics, leading to the formation of self-limiting nanometer thick oxide layer. Synchrotron based studies of the liquid gallium interface has revealed a
significant electron density loss at the liquid core and oxide interface resulting in a minimum interaction between the liquid metal and the surface oxide. In addition, bulk liquid gallium is monatomic which is by default non-polar. The absence of a solid crystal structure in liquid gallium limits the possibility of interaction with the crystalline lattice of the naturally grown surface oxide. Hence, when gallium is in its liquid state, adhesion of the surface oxide to the parent metal is minimal, allowing to transfer the oxide skin using van der Waals transfer techniques. The high surface tension of liquid gallium further ensures a flat growth platform for this oxide layer. Thus the oxide layers atop of liquid metals are considered as one of planar and homogeneous 2D films that develop naturally and hence can provide ample opportunities in the field of two-dimensional research.\(^1\) Due to the liquid nature of the metal and the absence of covalent bonds across the liquid metal- metal oxide interface, this 2D oxide skin shows limited adhesion to its parent metal, allowing it to be delaminated with ease. As such liquid metal offers an ideal reaction environment for developing 2D nanomaterials that were previously unattainable.

Recently a highly scalable method to produce large-area 2D metal oxide nanosheets using liquid metal as a reaction medium has been demonstrated.\(^1\) The technique shows that the naturally grown oxide layers on the surface of liquid metals or alloys can be isolated as 2D nanosheets onto desired substrates using a van der Waals transfer process. This synthesis method effectively produced large-area 2D oxide nanosheets of various nonlayered crystals from liquid metal. Carey et al. also reported an approach to delaminate and transform the surface oxide skin of gallium into 2D metal chalcogenide compounds.\(^2\)

Although significant achievements have been attained on the understanding and applications of liquid metals in recent years, these interfacial oxide layers have been somewhat overlooked by the broader research community. There are still more opportunities for interfacial scientists to investigate the unexplored interplay between the liquid metal and its oxide. In addition,
several challenges are associated with the delamination of these surface oxides and novel chemical processes should be developed to transform these oxides into different 2D metal compounds. In particular, there is a broad spectrum of gallium compounds ranging from insulators to semiconductors which have not yet been investigated as two-dimensional structures (refer to discussion in section 2.3.2). Hence, new synthesis routes must be developed for advancing the existing liquid metal synthesis processes, with the target of combining atomic-level thickness with wafer sized scalability. Finally, further investigations are essential for the incorporation of the as-synthesized new 2D gallium compounds into different functional devices as electronic, optoelectronic and piezotronic materials which may enable future commercial applications.

1.2 Objectives

The aim of this thesis is to synthesize various nonlayered 2D metal compounds utilizing liquid gallium as a precursor and by harvesting its interfacial oxide skin. Scalable and optimized synthesis strategies will be developed in order to gain access to homogenous and ultra large-area 2D nanosheets of different gallium compounds which were previously inaccessible. Afterwards, the as-synthesized 2D materials will be investigated and explored for different applications.

1.2.1 Sonication assisted synthesis of gallium oxide suspensions featuring trap state absorption: test of photochemistry

Gallium oxide is a wide band-gap material with great possibilities for a range of applications such as optoelectronics, electronic devices, solar cells, gas sensing and more recently, in photocatalysis. The synthesis technique that is used has a profound impact on the morphology, phase, and band structure of the resulting Ga$_2$O$_3$. Until now, many
different wet chemical synthesis methods have been developed for synthesizing Ga$_2$O$_3$.\textsuperscript{40-48} However, such synthesis techniques are associated with several limitations such as process costs, complexity, poor scalability, long duration and the use of toxic precursors and solvents. Herein, the possibility of using the self-limiting surface oxide layer of liquid gallium as a precursor for obtaining 2D Ga$_2$O$_3$ nanoparticles is investigated. The process can open the door for new possibilities in different electronic, optical and photocatalytic applications.

In the first study presented in this PhD thesis, the author will develop a facile and low cost synthesis route to obtain 2D gallium oxide and gallium hydroxide nanoflakes from gallium metal immersed in a liquid environment. This project aims to efficiently harvest the oxide skin of liquid gallium droplets in DI water using a sonication assisted synthesis methodology, which is capable of the efficient and high yield production of 2D nanoflakes. Later the morphological, structural, and optical properties of the synthesized nanoparticles will be carefully investigated. Finally, in order to explore the functionalities of the synthesized product, the obtained nanoflakes will be used as a photocatalytic material to decompose different organic model dyes. The electronic band structures will be investigated to explore the photocatalytic activity under solar light irradiation.

1.2.2 Printing two-dimensional gallium phosphate out of liquid metal

In the second part of this thesis, the author explores a scalable and low temperature liquid metal-based synthesis technique to obtain ultra-thin 2D GaPO$_4$ nanosheets with lateral dimension exceeding several millimetres. Gallium phosphate (GaPO$_4$), is a promising piezoelectric material which is iso-structural with $\alpha$-quartz.$^{49,50}$ It is considered superior to quartz due to a significantly greater thermal stability, and a higher piezoelectric coefficient.$^{50}$ Despite its intriguing properties, GaPO$_4$ has been overlooked as a 2D piezoelectric material.
To date, various hydrothermal synthesis methods have been utilized to generate the bulk crystals of GaPO₄. However, GaPO₄ cannot be synthesized into 2D sheets using conventional methods as it does not grow naturally as stratified crystal. Hence, developing a feasible synthesis route to access large-area 2D nanosheets of GaPO₄ can open new opportunities for piezo-sensors and energy harvesting.

The proposed synthesis method used during this PhD project, will adopt a previously reported van der Waals printing technique to isolate the self-limiting oxide skin from liquid gallium. The surface oxide on liquid metals typically feature weak adherence to the parent metal and can thus be easily transferred to any desired substrate. Following this, the author aims to transform these 2D gallium oxides into ultra-thin 2D sheets of GaPO₄ utilizing a low temperature chemical vapour phosphatization process. In this work, synthesis of very large-area (i.e. many mm²), continuous nanosheets of GaPO₄ will be the prime focus. To date, no 2D piezoelectric material has been manufactured in the form of ultra large-sheets, making it difficult to integrate these piezoelectric materials into silicon chips or apply them in large-scale surface manufacturing. In addition to this, the out-of-plane piezoelectric behaviour of the large-area 2D GaPO₄ sheets will also be investigated so that the as-synthesized nanosheets can open up new possibilities for future 2D piezotronic industries.

1.2.3 Synthesis of centimetre-scale ultra-thin 2D gallium nitride nanosheets from liquid metal derived oxide layer

The wide band-gap semiconductor material gallium nitride (GaN) has been coveted for its promising applications as blue and UV light emitting diodes and high temperature/high power electronic devices. Conventional methods based on elemental epitaxial or chemical vapor deposition techniques for synthesizing thin films of GaN are commonly applied. However, when attempting to synthesize atomically thins samples, these synthesis methods fall short and do not produce 2D GaN films with lateral dimensions exceeding a few hundred
nanometers, rendering the sheets to be very challenging to integrate into silicon chips or to be applied in large-area surface manufacturing. GaN in 2D morphology has been predicted to be an interesting target for synthesis due to its enhanced excitonic effects, superior electronic transport properties and quantum confinement effects, enabling further control on its light-emitting properties. Therefore, a considerable demand exists for the deposition of ultra-large-area 2D GaN in order to access the capabilities that have been predicted through computational studies.

In the final stage of this PhD thesis, the candidate aims to introduce an efficient exfoliation technique to deposit ultra-thin, centimeter sized 2D GaN using atomically thin Ga$_2$O$_3$ nanosheet derived from liquid metal gallium. In order to obtain centimetre-scale 2D Ga$_2$O$_3$ nanosheet, slightly modified van der Waals printing process has been adopted to isolate the surface oxide from liquid gallium droplet. The resulting Ga$_2$O$_3$ nanosheet will be transformed into 2D GaN using an ammonolysis reaction. Further to this, the large-area 2D GaN nanosheets will be investigated to explore their electrical properties. It is projected that this deposition method can be extended to obtain other metal nitrides and indium nitride is synthesized as a further example.

1.3 Organisation of thesis

The primary objectives of this Ph.D. research are (a) to harvest the surface oxide of liquid gallium and (b) to explore facile and low-cost synthesis routes for depositing different nonlayered 2D gallium compounds. There is an emphasis on the synthesis of ultra large-area nanosheets with a thickness of only a few atoms offering substantial commercial potential for future ‘wafer-scale’ processes.
In Chapter 2, an in-depth review of recent literature in relevant areas is presented. The aim is to highlight the areas which require further development of fundamental concepts and present the research gaps that will become the focus of this thesis.

Chapter 3 presents the synthesis and growth route of two-dimensional gallium hydroxides and gallium oxide nanoflakes from the surface of the liquid gallium immersed in water. These 2D gallium oxide nanoflakes will be thoroughly characterized along with the electronic band structure featuring trap states. Furthermore, the application of the as-synthesized material will be investigated for photocatalytic degradation of different organic dyes under visible light irradiation.

The synthesis process of unit-cell thick 2D nanosheets of GaPO₄ is addressed in Chapter 4. A low temperature liquid metal based two-dimensional printing and synthesis strategy is demonstrated to access large-area, wide band-gap 2D GaPO₄ nanosheets. Free standing membranes of 2D GaPO₄ have been developed for further investigation. The out-of-plane piezoelectricity of unit cell thick GaPO₄ sheet is explored experimentally and theoretically so that the synthesized nanosheets could be evaluated as a candidate for future nanoelectromechanical systems.

In Chapter 5, the exfoliation of centimeter-scale 2D GaN is presented. The deposition method follows a facile two-step method to synthesize GaN nanosheets from bulk liquid gallium via a van der Waals printing technique and subsequent ammonolysis reaction. The room temperature carrier mobility and carrier density have been determined using Hall-effect measurements to explore the electrical properties of the as-synthesized 2D GaN nanosheets.

The overall conclusions of Chapters 3, 4 and 5 are summarized in Chapter 6 where the potential for further refinement of the work presented will also be outlined to inform possible future research.
1.4 References


Chapter 2

Literature review

2.1 Introduction

Ultra-thin two-dimensional (2D) materials hold promise owing to their potential to enable highly efficient electronic and optical nano-devices. Many synthetic approaches have been suggested for the development of 2D materials; yet, the synthesis of large-area, ultra-thin 2D materials still persists as a substantial technological challenge. Recent progress in the field of liquid metal chemistry can open new avenues for a range of previously unexplored possibilities in the domain of 2D materials. The unique property of some liquid metals to support the growth of self-limiting surface oxide skins on exposure to air has resulted in the development of various new 2D materials which were previously inaccessible.\(^1\)\(^2\) In particular, liquid gallium and gallium based alloys have attracted significant attention for their remarkable properties which can create more opportunities for the advancement of existing synthesis processes.\(^3\) However, the isolation of the surface oxide form liquid metals and processes for transforming these 2D oxide skins into other 2D compounds are still in their infancy. Therefore, this PhD thesis aims to develop 2D metal oxides and metal compounds that are synthetically derived from liquid gallium through harvesting its atomically thin interfacial oxide. The focus during the development of the synthesis strategies is not only to achieve few atom thick 2D nanosheets, but also depositing large-area 2D nanosheets at projected low cost. In addition, the fundamental properties of the as-synthesized 2D metal compounds and their potential applications in different functional devices will be thoroughly investigated.
methods are likely transferable to other gallium-based alloys as well as for the development of various 2D materials based on other low melting point metals. In this chapter, a brief epitome of the relevant topics will be presented focusing on the work which will be addressed in this PhD thesis.

2.2 Two-dimensional (2D) materials

2D materials are a group of materials with a thickness of a few nanometres or less. Charge carriers in these materials are able to move freely in the 2D plane, while their movement is restricted in the third direction.4 Due to the ultimate tenuity, most of the 2D materials show superior structural, optical and physical properties arising from their atomic thickness, which can be uniquely distinct from their bulk parent materials. In particular, ultra-thin 2D nanosheets offer excellent mechanical flexibility, large surface area to volume ratios and optical transparency, which provide new prospects for next-generation electronic and optical industries.5,6 Single atom thick graphene was one of the first 2D nanomaterial, which was delaminated from graphite by Novoselov et.al. in 2004.7 It has been considered as a model 2D system because of its unprecedented physical, chemical, electrical and optical properties. However, few limitations such as the existence of intrinsic defects, the absence of an electronic band-gap and difficulties in controlling the number of layers during synthesis, have stimulated enormous interest toward the exploration of substitute 2D materials that feature their own diverse and remarkable properties.4,7-9

Layered van der Waals compounds are materials that have strong in-plane covalent or ionic bonds in two directions leading to the formation of stable sheets, but exhibit weak van der Waals bonds between the individual planes.10 The archetypal example is graphite which consists of weakly arranged graphene layers allowing the easy separation of each individual sheet (Figure 2.1).11 Similar structures exist for a plethora of materials. Over the past few years
transition metal dichalcogenides (TMDs) have been a separate prime focus of many researchers, stimulated by the realization of the first MoS$_2$ field-effect transistor$^{12}$ and strong photoluminescence observed in single layer MoS$_2$$^{13}$. TMDs are a group of layered hexagonal crystals where a monolayer consists of a transition metal from groups 4-10 in the periodic table (represented in common notation as “M”) sandwiched between two chalcogen atoms such as sulphur (S), selenium (Se) or tellurium (Te) (represented as “X”), with the stoichiometry of MX$_2$.$^{11}$ Currently over 40 different TMDs have been reported, which consist of different combinations of chalcogen atoms and transition metals.$^{14}$ A wide range of 2D transition metal oxides (i.e. MnO$_2$, MoO$_3$, WO$_3$)$^{15,16}$ and 2D layered hydroxides$^{16,17}$ have also generated a remarkable amount of interest. In addition, layered 2D nanostructures of group III-VIs (i.e. InSe, GaSe, GaS)$^{18}$, group V-VIs (i.e. Bi$_2$Te$_3$ and Sb$_2$Se$_3$)$^{19,20}$, the metal trichalcogenides, and metal trihalides have attracted intense research interest for the last few years (Figure 2.2). These ultra-thin 2D nanostructures have proven to be potential and promising materials for a huge array of applications such as electronics, sensing, catalysis, optoelectronics, energy storage (batteries, supercapacitors and solar cells) and photonics.$^{15,21,22}$ Different other applications have also been manifested in piezoelectronics, biosystems and superconductivity.$^{23-25}$

Until now, different methodologies have been proposed for synthesizing single- or few-layered 2D materials. The synthesis techniques of 2D materials can be classified into two fundamental categories: (1) top-down and (2) bottom-up approaches. In top-down techniques, the exfoliation of 2D nanostructures is achieved by delaminating individual atomic layers from the bulk through micromechanical cleavage$^{12,21,26}$ or laser ablation.$^{27,28}$ Alternatively, different liquid phase exfoliation techniques such as ion intercalation$^{29}$ or ultrasound exfoliation$^{30}$ can be utilized. In contrast, bottom-up techniques build up 2D materials from molecular precursors utilizing thermal and/or chemical reactions such as chemical vapour deposition$^{4,31}$, wet
chemical synthesis\textsuperscript{32}, atomic layer deposition\textsuperscript{33}, or thermolysis\textsuperscript{34}. Several bottom-up methods allow to deposit 2D structures directly onto substrates.

![Graphene and Graphite](image)

**Figure 2.1.** (a) A sheet of graphene. (b) Weakly bonded graphene layers found in graphite. (Reprinted with permission\textsuperscript{35})

<table>
<thead>
<tr>
<th>Graphene family</th>
<th>Graphene</th>
<th>hBN ‘white graphene’</th>
<th>BCN</th>
<th>Fluorographene</th>
<th>Graphene oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D chalcogenides</td>
<td>MoS\textsubscript{2}, WS\textsubscript{2}, MoSe\textsubscript{2}, WSe\textsubscript{2}</td>
<td>Semiconducting dichalcogenides: MoTe\textsubscript{2}, WTe\textsubscript{2}, ZrS\textsubscript{2}, ZrSe\textsubscript{2} and so on</td>
<td>Metallic dichalcogenides: NbSe\textsubscript{2}, NbS\textsubscript{2}, TaS\textsubscript{2}, TiS\textsubscript{2}, NiSe\textsubscript{2} and so on</td>
<td>Layered semiconductors: GaSe, GaTe, InSe, Bi\textsubscript{2}Se\textsubscript{3} and so on</td>
<td></td>
</tr>
<tr>
<td>2D oxides</td>
<td>Micas, BSCCO</td>
<td>MoO\textsubscript{3}, WO\textsubscript{3}</td>
<td>Perovskite-type: LaNb\textsubscript{2}O\textsubscript{6}, (Ca,Sr)\textsubscript{2}Nb\textsubscript{2}O\textsubscript{10}, Bi\textsubscript{2}Ti\textsubscript{3}O\textsubscript{12}, Ca\textsubscript{2}Ta\textsubscript{2}TiO\textsubscript{6} and so on</td>
<td>Hydroxides: Ni(OH)\textsubscript{2}, Eu(OH)\textsubscript{2} and so on</td>
<td>Others</td>
</tr>
</tbody>
</table>

**Figure 2.2.** “Layered 2D materials family. Blue cells represent monolayers of 2D materials showing stability under ambient conditions; green denotes probability of stability of 2D materials in air; pink denotes 2D materials unstable in air, but may be stable under inert atmosphere. Grey cells show 3D compounds easily exfoliated down to monolayers. (Reprinted with permission\textsuperscript{36})”

In comparison to the layered materials, the crystals of non-layered materials are internally connected in three-dimensions with relatively strong bonds between the vertical layers.\textsuperscript{10} The difficulty in achieving bond-cleavage of non-stratified compounds through exfoliation, and the frequent absence of an intrinsic driving force for promoting the anisotropic 2D growth render obtaining ultra-thin 2D structures of non-layered materials a significant challenge. Over the last
few years, a group of non-layered 2D nanomaterials, such as metal oxides (e.g. TiO2, CeO2, In2O3, SnO2, Fe2O3) and metal chalcogenides (e.g. PbS, CuS, CuSe, ZnSe, ZnS, CdSe), have been synthesized. Nearly all of the non-layered 2D materials are achieved through compound specific wet-chemical synthesis approaches. As a result, the number of ultra-thin 2D materials of nonlayered crystals is still very limited owing to the lack of executable synthetic protocols for most materials.

Despite the tremendous achievements and progress in the area of 2D materials, challenges and limitations still exist, providing the motivation to search for new technical approaches and technological applications. From the perspective of material synthesis, the synthesis and development of 2D nanosheets is mainly restricted to intrinsically layered materials, which constitute only a small fraction of the naturally existing materials. Therefore, a significant need persists for the formation of more 2D nanosheets of non-layered materials, to opening up additional scope for a range of applications. However, there are still many challenges associated with the synthesis of desired non-layered 2D nanosheets owing to the limitations of conventional exfoliation techniques. Additionally, it is still a major challenge to deposit few atom thick and laterally large 2D materials, which is a requirement for practical applications. Therefore, developing scalable synthesis routes for the deposition of ultra-thin, large-area 2D materials on variety of substrates could fundamentally enrich the future prospects of 2D industries.

2.3 Gallium and gallium compounds

2.3.1 Gallium

Recently, research interest on gallium has gained renewed momentum. Gallium features the lowest melting point (~29.6 °C) of the post transition metals, exhibiting both covalent and metallic bonding in the solid state. Gallium offers some remarkable properties including low
toxicity, low viscosity in the liquid state, extremely low vapour pressure and exhibits superconductivity at cryogenic temperatures.\textsuperscript{38,39} Gallium persists in its liquid state from near room temperature to 2403 °C, featuring the widest temperature range of the liquid state of all elements. The crystal structure of gallium features covalent dimers of gallium atoms\textsuperscript{40} that are organized in an orthorhombic structure with a short bond length of 2.44 Å within the dimers.\textsuperscript{41} A interatomic distance of 2.71 to 2.79 Å is observed between the gallium dimers (Figure 2.3).\textsuperscript{42} As such, significant structural anisotropy is observed due the existence of the longer Ga-Ga bonds, which facilitates the breakdown of the crystal structure at relatively low temperatures when compared with most other metals.\textsuperscript{2} Over the past few years, research on gallium and gallium based liquid metals has drawn enormous attention leading to numerous significant breakthroughs in microfluidics, 3D printing, flexible and stretchable electronics, reconfigurable devices, optics and reversible electrochemical systems.\textsuperscript{2,38,43,44}

Figure 2.3. “(a) Crystal structure of α-Ga, (b) crystal structure of α-Ga showing only short bonds d < 2.5 Å, (c) crystal structure of α-Ga showing only the long bonds 2.5 Å < d < 3 Å.\textsuperscript{45} (Reprinted with permission.\textsuperscript{2})”

In any oxygen-containing environment, an oxide layer develops on the surface of liquid gallium in a self-limiting reaction.\textsuperscript{38} This atomically thin native oxide skin is very robust and capable to preserve the liquid gallium against deformation.\textsuperscript{38} Previously, this oxide layer was often considered as a nuisance due to its adhesive nature, rendering liquid gallium to be considered as a challenging material for various fluidic applications.\textsuperscript{46} However,
over the past few years the oxide skin of gallium has triggered immense interest, since this interfacial oxide can provide ample opportunities to develop 2D materials (see section 2.4.2).

2.3.2 Gallium compounds

Gallium can form a number of compounds. Some of the well-known layered and non-layered compounds are discussed below:

2.3.2.1 Gallium oxide (Ga₂O₃)

The group III–VI semiconductor gallium (III) oxide (Ga₂O₃) is a promising inorganic compound that crystallizes in five different phases including α, β, γ, δ, and e.⁴⁷ Of these polymorphs, α-Ga₂O₃ and β-Ga₂O₃ are by far the most investigated.⁴⁸,⁴⁹ All of these gallium oxide phases can be prepared under specific conditions.⁵⁰,⁵¹ The first polymorph, α-Ga₂O₃, is rhombohedral with a space group R3c whereas β-Ga₂O₃ features a monoclinic structure and pertains to space group C2/m with lattice parameters \( a = 12.214 \ \text{Å}, \ b = 3.0371 \ \text{Å}, \ c = 5.798 \ \text{Å}, \ \beta = 103.83° \).⁴² The unit cell of monoclinic Ga₂O₃ is illustrated in Figure 2.4.⁵² The polymorphs, δ-Ga₂O₃ and ε-Ga₂O₃ were first synthesized and reported by Roy et al. in 1952.⁵⁰

![Figure 2.4. Unit cell of β-Ga₂O₃. “It possesses two inequivalent Ga sites: Ga(I), Ga(II) and three inequivalent O-sites: O(I), O(II) and O(III). The Ga(I) sites have tetrahedral coordination, and the Ga (II) sites have octahedral coordination. (Reprinted with permission.)”](image-url)
The non-toxic and stable gallium oxides feature wide band-gaps of $E_g \approx 4.2$ - 4.9 eV and relatively low effective electron masses.$^{19,48,53,54}$ Gallium oxide offers great possibilities for a wide range of applications such as optoelectronics,$^{55,56}$ electronic devices,$^{57}$ solar cells,$^{58}$ gas sensing$^{59,60}$ and more recently, in photocatalysis.$^{61,62}$ Until now, different liquid phase methods have been developed for synthesizing $\text{Ga}_2\text{O}_3$, utilizing hydrothermal (with and without surfactant), microwave and other solvothermal approaches.$^{19,47,49,63-68}$ These synthesis pathways have been reported to result in nanorods, nanowires or nanoplates of various dimensions. These synthesis techniques generally require long processing times which can reach several days to ensure acceptable synthesis yields and for the nano plates and sheets there are still challenges associated with the flake size, thicknesses and crystallinity. As such, the large-area and homogeneous deposition of 2D gallium oxide nanosheet has still proven to be a major challenge. In particular, reducing the material thickness to few numbers of unit cells and depositing wafer-scale 2D nanosheet is expected to have a profound impact on this research field.

2.3.2.2 Gallium mono-chalcogenides (GaX)

Gallium mono chalcogenides (GaX) are layered group III-VI semiconductors where X= S, Se, Te. All three materials exhibit the same crystal structure which is composed of layers exhibiting a honeycomb arrangement. Each monolayer consists of two gallium and two chalcogen atoms in the assembling sequence of X–Ga–Ga–X along the c-axis as illustrated in Figure. 2.5.$^{69}$ Two monolayers of GaX form a single GaS unit cell where two adjacent layers are bonded with the van der Waals interaction and the intra-layers are held together by covalent bonds.

GaS and GaSe are indirect-gap semiconductors in their bulk form,$^{70}$ while GaTe is a direct-gap semiconductor.$^{69}$ GaS and GaSe feature wide band-gaps of 3.05 eV and 2.10 eV,
respectively. On the other hand, bulk GaTe features a small direct band-gap of \( \sim 1.60 \) eV. These materials have emerged as novel 2D semiconducting materials which have been explored as promising candidates for different applications in transistors, optoelectronics, gas sensing and nonlinear optics. The successful synthesis of few layer 2D GaX has already been reported using a range of methods such as mechanical exfoliation and chemical vapour phase reaction. Recently a liquid metal approach towards the synthesis of GaS has been reported that is capable of achieving large-area deposition.

![Figure 2.5](image.png)

**Figure 2.5.** Structure of monolayer gallium chalcogenides GaX \((X = S, Se, Te)\) showing the top and side views. (Reprinted with permissions.)

### 2.3.2.3 Gallium nitride (GaN)

Gallium nitride is a group III-V semiconductor of great technological importance with many diverse applications due to its excellent electronic and optical properties. Crystalline GaN adopts the wurtzite structure, featuring covalent bonds in all three dimensions (Figure 2.6). GaN is the material of choice for the fabrication of phosphorescent light emitting diodes, due to its wide direct band-gap (3.4 eV), which facilitates the efficient emission of blue and near UV light.

The high carrier mobility, chemical robustness together with the piezoelectric and pyroelectric properties of GaN have also led to other important applications, including the
design of optoelectronic quantum wells, a variety of field effect transistors, high power devices, 
energy harvesting systems, sensors and photocatalysts. 82-86

**Figure 2.6.** The crystal structure of GaN exhibits a unit cell (dotted box) with cell parameters of 5.19 Å along the long axis and 3.19 Å along both of the short axes. 87

Conventional methods for depositing thin films of GaN are various, and amongst them, processes based on elemental epitaxial or chemical vapor deposition techniques are the most common. 88-92 While elemental epitaxial methods allow the controlled formation of ultra-thin films, they involve considerable costs. Conversely, lower costs CVD methods do not allow thin films with several unit-cell thicknesses to be achieved due to the inherently inhomogeneous nucleation. None of these methods have been reported as being capable of synthesizing few nanometer thick 2D GaN nanosheets, which is still considered as a great technological challenge.

In addition, 2D GaN has been the focus of computational studies which have identified this compound as a potential key to novel 2D devices because of its intriguing excitonic effects, superior electronic transport properties and quantum confinement effects. 93 Consequently, a considerable interest exists for synthesizing large-area 2D GaN in order to access its predicted extraordinary capabilities. Recently Balushi et. al. reported the synthesis of 2D GaN utilizing
a migration-enhanced encapsulation technique. This developed method gives access to ultra-thin 2D GaN, confirming the existence of many of the predicted fascinating characteristics that diverge from bulk GaN. However, the synthesis technique does not produce 2D GaN films with lateral dimensions exceeding a few hundred nanometers, while rendering the 2D nanosheets encapsulated between conductive graphene sheets which prohibits their use in devices. Hence, a more scalable synthesis route must be developed to obtain large-area 2D GaN, in order to access the capabilities that have been anticipated through computational methods for practical devices.

2.3.2.4 Gallium phosphate (GaPO₄)

Gallium phosphate (GaPO₄), is a well-known piezoelectric material that is isostructural with α-quartz. The crystal structure of gallium phosphate (Figure 2.7) exhibits trigonal symmetry with cell parameters of \( a = 4.87 \, \text{Å} \) and \( c = 11.05 \, \text{Å} \) and \( \gamma = 120^\circ \).

![Figure 2.7. Ball and-stick representation of the synthesised GaPO₄ crystal: (a) Unit cell of GaPO₄ along z axis, (b) side view showing an out-of-plane structure exhibiting unit cell parameter \( c = 11.05 \, \text{Å} \).](image)

GaPO₄ is considered superior to quartz for several technical applications due to a significantly higher thermal stability, comparable quality factor (Q) and a higher piezoelectric
Moreover, the α-phase of bulk GaPO₄ is stable up to 930 °C and thus this material can be very promising for high temperature sensors, offering a nearly temperature independent piezo effect. GaPO₄ does not naturally crystallize in a stratified structure and hence eliminates the choice of common exfoliation techniques. To date, various hydrothermal synthesis methods have been investigated to obtain bulk GaPO₄ crystals. A flux method has also been reported to grow GaPO₄ single crystals leading to spontaneous crystallization through slow cooling. However, the majority of these synthesis methods are complex and lead to 3D bulk crystals. The development of 2D piezoelectric materials is expected to lead to significant new technological advances, due to the high flexibility of 2D materials and the inherently high surface area to mass ratio, which may lead to ultra-sensitive sensors and efficient piezoelectric energy harvesters. Current methods are incapable of synthesizing 2D morphologies of conventional piezoelectric materials such as GaPO₄. Hence, the synthesis of large-area 2D GaPO₄ nanosheets will have a profound impact on 2D piezotronics.

2.4 Potential of liquid metals

2.4.1 Fundamental properties of bulk liquid metals

The term liquid metal usually refers to metals and alloys which remain in liquid state at or near room temperature. Liquid metals are intriguing as they possess both metallic and fluidic properties, providing a great combination of conductivity and flexibility. The five elemental metals that are liquid at or close to room temperature are mercury (Hg), francium (Fr), caesium (Cs), gallium (Ga), and rubidium (Rb). Of these, francium is radioactive while both caesium and rubidium are explosively reactive with water and air, rendering these materials to be inappropriate for most applications. Mercury has historically been the most commonly used liquid metal, but the implementation of mercury in commercial applications has been restricted since the 1990’s due to its severe toxicity. These constraints have led to
gallium-based devices being predominantly developed during the past 3 decades. Gallium and alloys based on gallium have several remarkable properties, making them desirable for different applications.\textsuperscript{106}

Gallium has a melting point of \(29.8^\circ\text{C}\) and can stay in its liquid form up to \(2403^\circ\text{C}\). The high boiling point results in liquid gallium featuring essentially no vapor pressure at commonly encountered temperatures.\textsuperscript{106} Liquid gallium has a very low viscosity (only twice that of water) but significantly higher electrical (\(7.1 \times 10^6 \text{ S cm}^{-1}\)) and thermal conductivities. The melting temperature of gallium can be lowered further by adding other metals resulting in different alloys such as \(\text{EGaIn} (75\% \text{ Gallium, 25}\% \text{ Indium})\) with a melting temperature of \(15^\circ\text{C}\). \(\text{Galinstan} (68.5\% \text{ Gallium, 21.5}\% \text{ Indium, 10}\% \text{ Tin})\) is another popular liquid alloy with a reported freezing temperature of \(-19^\circ\text{C}\).\textsuperscript{38} \(\text{Galinstan and EGaIn have a similar bulk conductivity of } \sim3.4 \times 10^6 \text{ S m}^{-1} \text{ (at } 20^\circ\text{C})\text{ which is } \sim50\% \text{ lower than that of pure gallium.}^2\) Overall, due to several unique and interesting properties, liquid metals have drawn enormous interest for diverse applications.\textsuperscript{2}

2.4.2 Surface properties of liquid metal

Most liquid metals react spontaneously with oxygen in ambient air, creating an ultra-thin surface oxide layer in a self-limiting reaction (Figure 2.8).\textsuperscript{1} This native oxide skin is robust and protects the liquid metal from further oxidation. The growth of surface oxides on metals at low to moderate temperatures can usually be described by the Cabrera–Mott oxidation model.\textsuperscript{107} The Cabrera-Mott oxidation model depicts that an initial monolayer of surface oxide develops instantaneously when a metal is exposed to ambient air. This oxide film acts as a diffusion barrier to protect the metal from further corrosion. Some of the metal’s electrons tunnel through the thin oxide layer and induces charges on the oxide interfaces. Electrons tunnelling from the metal core to the free side of the oxide film ionize the surface adsorbed oxygen atoms. This ‘diffusion’ of electrons between the Fermi level of the parent metal and
acceptor levels of chemisorbed oxygen at the oxide surface results in an electric field across
the oxide film, known as the Mott potential. This self-generated electric field significantly
lowers the energy barrier for ion migration through the oxide film, leading to rapid initial
oxidation rates and therefore an increase in the oxide layer thickness. As the oxide grows, the
electron tunnelling process is inhibited. Simultaneously, the thicker oxide layer increases the
distance between the surface adsorbed ionized oxygen species and the electron within the metal
leading to a reduction of the field strength. Hence, the driving force for the oxide growth
diminishes as the oxide is becoming thicker, leading to self-termination of the growth
process.

The Cabrera–Mott oxidation model can also be applied to elucidate the surface
oxidation process of post transition metal based liquid metals. When liquid gallium or
gallium based alloys like galinstan and EGaIn, are exposed to an oxygen containing
environment, an ultra-thin and flat oxide skin readily forms. This oxide film does not grow
significantly with higher oxygen concentrations and temperature. It has been observed that
the surface oxide of galinstan and EGaIn are also predominantly composed of gallium oxide,
regardless of the presence of either indium and tin within the alloy. This finding, together with
other recent work, led to the conclusion that the composition of the surface oxide of alloys is
mainly dominated by the oxide which offers the highest reduction in Gibbs free energy.

![Figure 2.8. A cross-sectional diagram of a liquid metal droplet, with possible crystal structures of thin layer Ga_2O_3 as indicated. (Reproduced with permissions.)](image-url)
Synchrotron based studies of the liquid metal gallium interface have revealed that the electron density profile features a prominent minimum of the electron density distribution at the boundary between the liquid metal and its naturally grown surface oxide (Figure 2.9) which is represented by a simple electron density model proposed by Regan, M. J., et al. Here the oxidation of liquid-gallium surfaces has been explored utilizing surface x-ray scattering techniques. This model reveals that the liquid/oxide and oxide/vacuum interfaces are atomically flat with a significant electron density loss at the liquid core and oxide interface. The finding indicates that the interaction between the liquid metal and the surface oxide is weak. The absence of a solid crystal structure also impedes cumulative atomic interactions of liquid metal over large-areas rendering any weak interactions that may occur to be localised, inhibiting macroscopic attachment. As a result the interfacial 2D oxide skin shows minimal adhesion to the metallic core, enabling a unique route to synthesize and exfoliate different 2D materials.

Figure 2.9. Schematic of the surface oxide of Ga, with the electron density profile plotted for the interface. Top: the projected atomic structure of gallium and gallium oxide layer where the atomic diameters for O\(^{2-}\), Ga\(^{3+}\), covalent (Cv) Ga and metal (Me) Ga is 2.64 Å, 1.24 Å, 2.44 Å and 2.50 Å,
respectively. Bottom: the thin solid line represents the corresponding electron density profile with its different components; the underlying liquid Ga (large dash line) and the Gaussians representing the Ga\textsuperscript{3+} (dash-dotted line) and O\textsuperscript{2-} layers(short-dashed line). (Reproduced with permissions\textsuperscript{109})

2.4.3 Applications of liquid metal

The unique and remarkable properties of liquid metals have made it a cogent material for a range of applications. Though mercury has been traditionally implemented for liquid metal applications, environmental concerns and the inherent toxicity of mercury have led to it being gradually phased out. Over the past decades, liquid gallium and its alloys have exhibited huge potential as a mercury replacement for a wide range of applications\textsuperscript{46,106,112} . Firstly, liquid gallium and its alloys have shown great promise in the development and operation of microfluidic systems because of their flexibility and fluidity\textsuperscript{112} . Liquid metals also provide a promising route for developing self-healing, soft and stretchable wires which can be stretched to utmost strains while upholding metallic conductivity\textsuperscript{106}.

The use of liquid metal for realizing various electrical interconnects has also facilitated the integration of electronic components into microfluidic systems. In addition, the ability to reconfigure liquid metals into desired shapes has enabled a range of reconfigurable and stretchable electronics (e.g., switches, reconfigurable antennas, and reconfigurable circuits). These liquid metal based reconfigurable electronics can be patterned in the desired geometry and offer plasticity which can be exploited to change connections within a circuit at will\textsuperscript{38,106}.

Over the past few years, liquid metals have also offered promising opportunities in 3D printing and inkjet printing\textsuperscript{113} . Liquid metal printing has been used for designing and fabricating different strain gauge devices\textsuperscript{114} , small antennas\textsuperscript{115} , fully 3D printed LEDs\textsuperscript{116} , and various customized circuits\textsuperscript{117} . Another important traditional application employing liquid metal is the development of miniature microfluidic modules including pumps, valves, and electrodes\textsuperscript{112} . Today,
different liquid metal batteries have been investigated as an alternative energy storage device with good cycle performance and increased device lifetime. Liquid metal alloys are also used in numerous sensing devices. One of the most common application of liquid metals in sensing is as liquid electrodes which respond to heavy metal ions and feature self-renewing interfaces.

2.4.4 Liquid metal surface as a reaction medium for synthesizing 2D materials

The self-limiting interfacial oxide layers atop of different liquid metals are considered as one of the highest quality 2D films that develop naturally. Liquid metals like gallium and gallium-based alloys can be an ideal reaction medium for growing 2D crystals on their surface. The interfacial oxide skin can be effectively delaminated because of the weak attractive force between the parent liquid metal and the surface oxide skin. As a result, this 2D oxide layer can open up unique synthesis routes to develop different 2D materials. Hence, synthetic approaches to isolate these surface oxide layers typically involve the growth of oxide layer, succeeded by applying external energy in a form of mechanical exfoliation as discussed below:

2.4.4.1 Liquid based exfoliation of 2D nanostructures from liquid metal interface

Liquid metal droplets submerged in aqueous solution can be utilized as a platform for the exfoliation of various 2D nanostructures. The reaction route based on liquid metal/H₂O interface can be used to produce various 2D nanostructures which were previously inaccessible with conventional methods. Sonication-assisted liquid-phase exfoliation technique can be one of the efficient way to delaminate surface oxide from parent metal in aqueous environment. An attempt was undertaken to explore this method by directly synthesising gallium carbides via sonicating liquid gallium in hydrocarbons. Recently Zavabeti et al. have demonstrated a gas injection synthesis method to produce Ga₂O₃ nanoflakes by injecting air into the liquid galistan immersed in DI water (Figure 2.10 (b)). These liquid based synthesis techniques are suitable for
obtaining high-yield production of the targeted oxide or hydroxide nanosheets. However, these synthesis approaches demand the parent metal to be in liquid form during sonication within the aqueous environment and hence, these exfoliation routes can be applied to limited liquid metals that melt below the boiling point of the selected solvent.

2.4.4.2 Synthesis of large-area 2D nanosheets using liquid metal reaction media

The crucial step in fabricating low dimensional electronic devices is the synthesis of large-area 2D nanosheets on desired substrates. So far, many synthetic routes have been suggested for depositing various 2D materials (as discussed in section 2.2). The simplest one is the mechanical exfoliation of 2D nanosheets from layered crystals utilizing adhesive tape. Unfortunately, reported exfoliated 2D nanosheets have lateral lengths that do not exceed the micrometre range, limiting their application in commercial industries. The recent report of the exfoliation of the surface oxide skin of liquid gallium has offered new avenues for synthesizing laterally large atomically thin 2D materials. Carey et al. have reported a synthesis route to isolate the oxide skin of gallium by rolling the liquid metal over a suitable substrate, which can be described as a process akin to screen printing. Later the surface gallium oxide was transformed into 2D gallium monosulphide (GaS).

Furthermore, recent work by Zavabeti et al. has presented a highly scalable approach to produce extraordinary large-area 2D metal oxide nanosheets harvesting the surface oxide of liquid metal through a process that exploits van der Waals forces during the transfer method. This process demonstrates that the naturally grown interfacial oxide layers on liquid metals can be delaminated and effectively transferred to a flat substrate that is brought into close contact with the molten metal (Figure 2.10 (a)). Zavabeti et. al. also demonstrated that highly reactive elements can be alloyed into the liquid metal at small concentrations. Due to the more favourable Gibbs free energy of formation, the added elements dominate the oxide interface,
expanding the application of liquid metal chemistry towards high melting point metals.\textsuperscript{1} The reported van der Waals transfer method and the screen printing method resulted in large-area 2D metal oxide sheets on a range of suitable substrates, including Si/SiO\textsubscript{2} wafers, quartz, TEM grids and also soft substrates like PDMS opening new possibilities for future flexible electronics.\textsuperscript{125} Many of the exfoliated compounds are also not intrinsically layered, and as such their synthesis in 2D morphology constitutes a significant achievement. In addition, the successful conversion of an exfoliated 2D oxide into a desired 2D chalcogenide reported by Carey et al., clearly demonstrate the versatility and emerging scope of liquid metal synthesis techniques for 2D materials. This can potentially open the opportunity to access a number of previously inaccessible 2D compounds.

![Figure 2.10.](image_url)  
\textbf{Figure 2.10.} (a) Schematic representation of the van der Waals exfoliation technique. The pristine liquid metal droplet is first exposed to an oxygen containing environment. Touching the liquid metal with a suitable substrate allows transferring the interfacial oxide layer. Optical images are shown on the right-hand side. (b) Schematic representation of the gas injection method (left), with photographs of the bubble bursting through the liquid metal (middle) and an optical image of the resulting sheets drop-casted onto a Si/SiO\textsubscript{2} wafer. (Reproduced with permission.\textsuperscript{1})
However, the investigations associated with the isolation surface oxide of liquid metals and transformations of the oxide skin into desirable 2D compounds are still in their early stages. A number of key challenges must be addressed to take the full advantage of the wide variety of layered and non-layered compounds that may be exfoliated from the liquid metal interface. Specifically, there is a wide range of gallium compounds which have been overlooked as potential 2D structures (refer to section 2.3.2). Hence, the unexplored gallium compounds beyond the currently existing selection of 2D materials can open up new opportunities for a wide array of unconventional applications in photonics, electronics, optoelectronics and piezotronics.

2.5 Summary

The domain of 2D materials research has been considered as one of the most active and dynamic research areas in nanoscience due to their interesting properties that are suitable for a number of applications. However, current investigations of 2D materials are predominantly focused on layered crystals and research on 2D non-layered materials is rarely carried out, restricting the development of next-generation electronics. Additionally, there are numerous challenges ahead for synthesizing ultra-thin, large-area 2D nanosheets on desired substrates, limiting industrial applications. Hence, for the wide commercial application of 2D nanomaterials, new synthetic approaches must be explored to empower the scalable deposition of wafer scale 2D nanosheets, while maintaining their ultra-thin features. In the quest to discover new planar materials, atomically thin oxide skins grown on the surface liquid gallium and gallium-based alloys have recently attracted significant interest. However, there are still many challenges ahead for effectively isolating these surface oxides and to transform them into desired 2D materials. In this PhD thesis, the author will address the identified research gaps and develop low-cost and
facile synthesis routes based on liquid metal interfacial oxides. In addition, the as-synthesized 2D gallium compounds will be utilized for different functional applications.

In the following chapter, the author will develop a scalable synthesis approach to obtain 2D gallium oxide and gallium hydroxide nanoflakes from gallium metal immersed in a liquid environment. This project aims to efficiently harvest the oxide skin of liquid gallium using a sonication assisted synthesis route resulting in high yield production of 2D nanoflakes. Chapter 4 will focus on the low temperature liquid metal-based synthesis technique to obtain 2D piezoelectric GaPO₄ nanosheets with few atom thicknesses. Previously reported van der Waals printing technique¹ will be used to isolate the oxide skin from liquid gallium metal which will be transformed into wafer-scale 2D GaPO₄ utilizing a phosphatization technique. Synthesis of centimetre scale 2D GaN utilizing the interfacial oxide skin of liquid gallium will be presented in chapter 5. Chapter 6 represents the final conclusions and offers directions for future research.

2.6 References


Chapter 3

Sonication assisted synthesis of gallium oxide suspensions featuring trap state absorption: test of photochemistry†

3.1 Introduction

With growing global attention concerning environmental remediation, the exploration and implementation of various photocatalysts has attracted significant interest for decomposing various organic pollutants.¹⁻⁵ However, inefficient absorption of the visible solar spectrum, together with rapid deactivation of photocatalysts, limit the practical applications of many such materials.⁶ It has been shown that the semiconductor gallium (III) oxide (Ga₂O₃), despite its relatively wide band-gap, exhibits acceptable photocatalytic performance to decompose different pollutants or organic dyes under UV and visible light irradiation at different phases, stoichiometries and morphologies.⁷⁻¹³ Under optimized conditions, Ga₂O₃ has been shown to have a better photocatalytic performance in comparison to commercial TiO₂ particles, due to its ability to provide photo-generated charge carriers with more suitable redox potentials, leading to higher driving forces for photocatalysis.¹⁴⁻¹⁵ However, there are still serious limitations for the application of Ga₂O₃ as a photocatalyst due to its wide band-gap. Hence, any improvement of the photocatalytic activity of Ga₂O₃ by shifting its photo-response towards the visible range will create a profound positive impact.

Many methods have been investigated to overcome the constraints of photocatalytic activities of Ga$_2$O$_3$ including doping, inducing oxygen deficiency and hybridization. Nevertheless, none of the studies have shown full evidence regarding the changes that occur on the electronic band structure of the modified gallium oxides. A fundamental analysis, establishing a relation between the tuned energy band-gap of Ga$_2$O$_3$ and resulting photocatalytic activity, has rarely been presented. Many different synthetic approaches have been demonstrated for synthesizing Ga$_2$O$_3$ based on hydrothermal (with and without surfactant), microwave and other solvothermal approaches resulting in Ga$_2$O$_3$ of different morphologies, phases and stoichiometries. However, such synthesis techniques generally require long processing time of up to several days for acceptable synthesis yields.

Very recently, liquid metal gallium has drawn attention for synthesizing various gallium compounds based on printing processes. The reported methods generally take advantage of the formation of the self-limiting oxide layer on the surface of liquid gallium at room temperature, utilizing techniques to isolate this layer from the original liquid source. The self-limiting gallium oxide layer grows slowly and may become thicker upon environmental excitations and applied mechanic energy. The existence of the oxide skin on liquid gallium can also provide an opportunity to develop a high yield method for synthesizing Ga$_2$O$_3$ nanostructures. It is hypothesized that vigorous sonication and the application of shear forces should assist in removing the oxide layer. Since this oxide is gradually formed on the surface of the metal, which constitutes a reducing metallic environment underneath, it can potentially feature high densities of oxygen vacancies. It is hypothesized that these oxygen vacancies can aid photocatalysis by reducing the band-gap of Ga$_2$O$_3$ due to the introduction of trap states in the band-gap, allowing the system to operate in the visible region of the solar spectrum.

In this chapter a synthesis process has been investigated utilizing the self-limiting oxide skin of liquid gallium used as a precursor for obtaining the suspensions of Ga$_2$O$_3$ nanoparticles.
A novel two-step synthesis method is demonstrated, leading to gallium oxide nanoflakes and rods, relying on sonicating liquid gallium and annealing the detached native oxide skin. The strong dye degradation performance of the synthesized Ga$_2$O$_3$ nanoparticles has been demonstrated and the electronic band structure of the material is also investigated associated with the enhanced photocatalytic activity. In this chapter, a fundamental analysis of the modified energy band structure is presented that is responsible for the superior photocatalytic performance of Ga$_2$O$_3$ nanostructures.

### 3.2 Experimental section

#### 3.2.1 Sonication assisted synthesis of Ga$_2$O$_3$ nanoflakes

A bath sonication method was adopted to synthesize gallium oxide nanoparticles using gallium metal as the precursor and DI water as both the reaction medium and oxygen source. The synthesis of gallium oxide flakes involves a two-step process as follows:

#### 3.2.1.1 Exfoliation of 2D GaOOH nanoflakes

In the first step, a suspension of hydrated gallium oxide nanoparticles was produced by sonicating bulk liquid gallium in DI water at 50°C. During this step 900 mg of gallium (0.15 ml) were added to 15 ml DI water. The liquid was sealed in a sample vial and sonicated in a bath sonicator for 60 min. The experimental design was influenced by our previous observation indicating that 60 min is sufficient to transform the majority of the bulk metal into solid nanoparticles with only few liquid metal droplets remaining in suspension.$^{28}$ The obtained suspension was then centrifuged for 15 min at 100 RCF (Eppendorf Centrifuge 5702) to remove residual gallium metal and large oxide particles. The supernatant containing hydrated gallium oxide nanoparticles were collected and dried in an electric furnace for around 45 min at 120°C.
3.2.1.2 Annealing for the conversion of 2D GaOOH to α-Ga$_2$O$_3$

In the second step, the dried hydrated gallium oxide nanoparticles were heated in an electric furnace at 450-500°C for 4 h in air using a heating rate of 10 °C/min in the beginning of the procedure (total time 280 min). The gallium oxide flakes were then re-suspended in 6 ml of DI water. Sonication in a bath sonicator for 10 min for the final re-suspension was found to be sufficient to achieve a homogeneous suspension. The reactions that take place during the synthesis of the gallium oxide nanoparticles are:

\[
2 \text{Ga} + 4 \text{H}_2\text{O} \rightarrow 2 \text{GaOOH} + 3 \text{H}_2
\]

\[
2 \text{GaOOH} \xrightarrow{450^\circ \text{C}} \text{Ga}_2\text{O}_3 + \text{H}_2\text{O}
\]

The concentration of a prepared α-Ga$_2$O$_3$ stock solution was measured to be 0.20 mg/ml using thermal gravimetric analysis (TGA). This corresponds to an overall reaction yield of 0.13%. It is noteworthy to highlight that no particular precautions were taken to maximize the yield. Longer sonication times and improved reaction workup procedures will likely increase the yield significantly.

3.2.2 Measurement and instrumentations

To determine the crystallinity and phase purity of the synthesized material, XRD patterns were obtained using a Bruker D4 Endeavour featuring a CuKα X-ray source ($\lambda$=1.54 Å). The nanoparticle morphology, crystal structure and lattice properties were evaluated further by transmission electron microscopy TEM (JEOL 1010) and HRTEM (JEOL 2010F) at acceleration voltages of 100 and 200 kV, respectively. Selected area electron diffraction (SAED) patterns were obtained using the JEOL 2010F microscope. X-ray photoelectron spectroscopy (XPS) was conducted using Thermo Scientific K-Alpha X-ray Spectrophotometer equipped with a monochromatic Al Kα source ($h\nu = 1486$ eV) and a
concentric hemispherical analyser. A pass energy of 100 eV was used to record the core-level and valence band spectra. Absorbance measurements were performed using an Agilent Cary 60 Ultraviolet-Visible Spectrophotometer. Scanning electron microscopy SEM (FEI Scios Dualbeam FIBSEM) was used for exploring the morphological properties. The surface thickness and roughness of the synthesized materials were assessed using a Bruker Dimension Icon atomic force microscopy (AFM). To study the valence band energy levels, PESA (Riken Keiki AC-2) was utilized at a power of 500 nW. The amount of weight variation of the material, as a function of increasing temperature and time, were evaluated by TGA (Perkin Elmer Pyris 1) in an atmosphere of nitrogen gas, providing a measure of the oxide loading in liquid suspension. The photocatalytic performance was evaluated using a Sol3A class AAA solar simulator IEC/JIS/ASTM equipped with a 450W Xenon lamp. The power was adjusted to precisely 1 sun (AM1.5) using a Silicon reference cell accredited by NIST to the ISO-17025 standard. PL spectrum of Ga₂O₃ nanostructures in solvent was collected using a PerkinElmer LS50 luminescence spectrometer with an excitation wavelength of 500 nm. PL measurements of Ga₂O₃ in air were conducted using Horiba Scientific LabRAM HR evolution Raman/PL spectrometer. Solarus (Model 950) Advanced Plasma Cleaning System was used for plasma treatment. The surface properties (surface area, pore size, and pore volume) were measured with the aid of Micromeritics ASAP 2400 instrument.

3.3 Results and discussions
3.3.1 Characterizations of 2D GaOOH and Ga₂O₃ nanoflakes

As discussed in the Experimental section, the synthesis was carried out in a two-step process consisting of liquid gallium sonication in DI water followed by annealing, allowing to obtain gallium oxide nanoparticles. During the sonication step, a gallium metal droplet (Figure 3.1a) splits into micro-to nano-sized spherical or quasi-spherical liquid metal structures (Figure
A self-limiting thin oxide layer grows on the surface of these liquid metal droplets, with the oxide layer becoming thicker during mechanical agitation. The thickening oxide film is expected to crack it into smaller pieces with increasing sonication duration. The cracked oxide layers are gradually detached from the gallium surface (Figure 3.1c) to form suspended oxide nanoflakes. Simultaneously, a new self-limiting oxide layer is established on these gallium metal droplets each time an oxide piece departs their surfaces. The breakdown of the liquid metal into smaller droplets and the detachment of oxide flakes from the surface of the metallic gallium is a repetitive process. Thus, the fraction of these nanoplatelets suspended in DI water increases with longer sonication periods. The size of the droplets becomes smaller with sonication time and their number increases. This process continues until the bulk of the liquid gallium is transformed into nanoflakes. A reaction time of 60 min was found to be sufficient to transform the majority of the liquid bulk into oxide nanoparticles. Near the end of the sonication process, the residual larger particles and any remaining metal are removed from the suspended nanoflakes via centrifugation (Figure 3.1d).

**Figure 3.1.** Step-by-step schematic of the synthesis process converting gallium metal into gallium oxide nanoparticles during sonication. (a) A bulk gallium droplet with surface oxide, kept in DI water. (b) The bulk gallium metal splits into smaller liquid metal entities with cracks on their surface oxide skin during sonication. (c) Delamination of small oxide nanoparticles from the cracked surface oxide layer. (d) Oxide nanoparticles separated from the bulk gallium metal after completed reaction and centrifugation.
Figure 3.2 a-b show the bulk liquid metal droplet in DI water before sonication and the suspension of hydrated oxide nanoparticles after the morphological transformation due to ultrasonic agitation. Figure 3.2c shows the re-suspended final product after centrifugation and annealing. The slight grey coloration of the final product might be due to residual metallic impurities. If present, however, these impurities should be in very small concentration as they were not encountered during extensive scanning electron microscopy (SEM) and transmission electron microscopy (TEM) imaging and were below the detection limit of X-ray photoelectron spectroscopy (XPS) analysis, which will be discussed later on.

X-ray diffraction (XRD) was utilized to characterize the crystal phase and crystallinity of the resulting products. Figure 3.3a shows a typical XRD pattern of the 2D nanoparticles after sonication. The diffraction peak positions in this pattern showed prominent XRD peaks locating at 18.1°, 21.6°, 26.4°, 32.8°, 36.1°, 40.1°, 50.6° and 56.3°. These obtained peaks can be indexed to (020), (110), (120), (130), (111), (140), (221) and (151) crystallographic planes of orthorhombic phase of GaOOH with lattice constants of $a = 4.58$ Å, $b = 9.80$ Å, $c = 2.97$ Å.
The XRD pattern of the 2D nanostructures after annealing was also obtained. The observed new peaks positioned at 24.6°, 33.7°, 36.8°, 41.6°, 50.4°, 55.3°, 63.6° and 65.3° (Figure 3.3b) correspond to (012), (104), (110), (113), (024), (116), (214) and (300) planes of hexagonal \( \alpha \)-Ga\(_2\)O\(_3\). No obvious diffraction peak arising from the corresponding hydroxide was detected, indicating a total transformation of GaOOH into \( \alpha \)-Ga\(_2\)O\(_3\) with lattice constants \( a = b = 4.97\ \text{Å}, \ c = 13.42\ \text{Å} \).\(^{29-30}\)

**Figure 3.3.** XRD data of (a) as synthesized nanoflakes indexed to GaOOH and (b) annealed material indexed to \( \alpha \)-Ga\(_2\)O\(_3\).

SEM and TEM images along with the SAED patterns were obtained for further morphological and structural analysis of the GaOOH and Ga\(_2\)O\(_3\) particles. These obtained data for the intermediate product GaOOH is presented in Figure 3.4a-d. GaOOH nanoparticles were found to display a plate-like non-porous morphology.
Figure 3.4. (a) SEM image of the GaOOH (b) High-magnification SEM image of the GaOOH nanoblocks. (c) The TEM image of the GaOOH, presenting plate-like structures. (d) HRTEM of GaOOH, displaying the lattice fringes. The top right inset shows the SAED pattern of GaOOH, which indicates the observed interplanar spacing is 0.25 nm that corresponds to the d-spacing of (021) plane for orthorhombic GaOOH\cite{1}.

Figure 3.5 a-b depict the SEM images of the final product after annealing, revealing that the sizes of the $\alpha$-Ga$_2$O$_3$ nanoflakes are not uniform and that the nanoflakes consist of two types of structures. The most commonly observed structures are plates of 25-250 nm widths and length of approximately 50-500 nm. These plate-like nanostructures were found to be porous which is clearly visible in the high magnification SEM image (Figure 3.5 b). The presence of a small population of non-porous rod-like structures of Ga$_2$O$_3$ with width around 20-80 nm is also observed in the sample. The morphological structure of $\alpha$-Ga$_2$O$_3$ flakes was characterized further by TEM and HRTEM analysis. Herein the existence of porous plate-like and non-porous rod-like structures of Ga$_2$O$_3$ nanoflakes could be confirmed (Figure 3.5 c-d). The nature of the pores in the larger plates of Ga$_2$O$_3$ was investigated further using HRTEM, which revealed that these plates consist of crisscrossed rods which are placed out of registry,
leading to pore formation (Figure 3.5d). The formation of these porous structures might be caused by dehydration and shrinking during the conversion process from GaOOH to Ga$_2$O$_3$. The bottom two inset images of Figure 3.5c illustrate the SAED pattern and the lattice fringes for the synthesized nano particles. The right inset profile displays well-defined lattice fringes with the $d$-spacing of approximately 0.50 nm between two lattice planes, consistent with the unit cell dimension of hexagonal Ga$_2$O$_3$. The left inset exhibits the SAED image which provides the inter-planar spacing of 0.25 nm that is consistent with the $d$-spacing values of the (110) plane of hexagonal $\alpha$-Ga$_2$O$_3$. 

**Figure 3.5.** (a) SEM image of $\alpha$-Ga$_2$O$_3$. (b) High-magnification SEM images of Ga$_2$O$_3$ nanoflakes. (c) TEM image of $\alpha$-Ga$_2$O$_3$ indicating the flake like porous (A) and nonporous (B) populations as indicated. The insets show lattice fringes (bottom right inset) and SAED pattern (bottom left inset). (d) HRTEM micrograph of porous Ga$_2$O$_3$ flakes.

The surface morphology and thicknesses of the synthesized Ga$_2$O$_3$ nanoflakes were investigated using AFM. The height profiles indicate that the nanostructures have a typical
thickness of approximately 5 to 20 nm (a typical flake of 6 nm thick as presented in Figure 3.6). The pores are not resolved during AFM imaging, since their dimensions are smaller than the radius of the AFM tip, which defines the resolution of the technique. Considering the lengths, widths and thicknesses of the synthesized structures the obtained nanomaterial can be described as either quasi-one dimensional (nano-rods) or quasi-two dimensional (nano-plates or nano-flakes).

![AFM image of α-Ga2O3 nanostructures. Inset: height profile along the white line.](image)

**Figure 3.6.** AFM image of α-Ga2O3 nanostructures. Inset: height profile along the white line.

The chemical bonding states of the synthesized Ga2O3 were confirmed by XPS (Figure 3.7). As shown in Figure 3.7, peaks at binding energy of 20.68 and 532.1 eV can be attributed to the valence state Ga 3d (Ga$^{3+}$) and O 1s in Ga2O3, respectively.$^{28}$ No metallic gallium (Ga$^{0}$) was observed in the Ga 3d region, confirming the efficiency of the oxidation process and the subsequent reaction workup. Furthermore, the characteristic oxygen and gallium peaks of GaOOH located at 530.8 and 19.8 eV, respectively, were not observed, evidencing quantitative dehydration.$^{32}$ The observed binding energies are all consistent with the previous reported values for Ga2O3.$^{28}$
Figure 3.7. XPS of synthesized Ga$_2$O$_3$ (a) Ga 3d and (b) O 2s. Peak at the binding energy of 20.68 eV signifies the valence state Ga$^{3+}$ in Ga$_2$O$_3$. No metallic gallium (Ga$^0$) was observed in the Ga 3d region. Peak observed at a binding energy of 531.1 eV corresponds to O 1s state of Ga$_2$O$_3$.

Optical properties of Ga$_2$O$_3$ samples were explored by UV–vis absorption spectroscopy, which is illustrated in Figure 3.8 a-b. The spectrum of synthesized Ga$_2$O$_3$ shows strong absorption in the UV region (Figure 3.8 a). Light absorption of α-Ga$_2$O$_3$ starts at around 260 nm which is consistent with previous reports. Further inspection reveals a relatively broad but weak absorption peak in the wavelength range between 280-400 nm, which may be caused by the presence of trap states in the band-gap of the synthesized oxide.

The band-gap of α-Ga$_2$O$_3$ has been calculated using a technique proposed and substantiated by Tauc et al. Tauc plot analysis was utilized to determine the band gap using the optical absorption strength with respect to the difference between the photon energy and the band gap as follows:

$$(a h \nu)^{1/n} = A(h \nu - E_g),$$

where $h$ is Planck's constant, $\nu$ is the photon's frequency, $a$ is the absorption coefficient, $E_g$ is the band gap, and $A$ is a proportionality constant. The value of $n$ denotes the nature of the electronic transition, whether direct ($n=1/2$) or indirect ($n=2$). In this work, $(a h \nu)^2$ was used while measuring the band gap of α-Ga$_2$O$_3$ since it is well known to have a direct allowed transition. The transparent behaviour is evident from the absorption curve which approaches to nearly zero at low photon energies; the absorption gets stronger near the bandgap value and
shows a region of linearity along the \((ahv)^2\) plot (Fig. 3.8 b). Extrapolation of this linear region to the X-axis intercept yields the optical bandgap of the material. Thus the direct band-gap of \(\alpha\)-Ga\(_2\)O\(_3\) has been determined as 4.65 eV which is consistent with previous literatures.\(^{7,13-14}\)

Different other components of the electronic band structure of Ga\(_2\)O\(_3\) were obtained using valence band XPS (VB XPS) and photoemission spectroscopy in air (PESA). PESA analysis is usually conducted to determine work function of metals and the ionization potential (IP) of semiconductors. The IP of semiconductors may refer to either the valence band position or to trap states within the band-gap, provided that their density is high enough to result in a detectable signal.\(^{35-36}\) The PESA spectrum of Ga\(_2\)O\(_3\) (Figure 3.8 c) reveals an unusual two-step dependency instead of the commonly observed single emission edge. The ionization potential of the sample was determined to be \(-4.25\) eV, with the second emission edge having energy of approximately \(-5.0\) eV. The unusual shape of the PESA spectrum is indicative of the presence of trap states, leading to the conclusion that the PESA signal originates from inter-band-gap states rather than electrons in the valence band.

This assertion is confirmed further when the optical band-gap of the material is considered. If the emission edges observed in PESA were associated with the valence band, the conduction band edge would be placed close to or even above the vacuum level, which is obviously not possible. The observations are similar to reports on tin doped indium oxide, where the measured IP corresponds to the top of the dopant-associated trap band and the PESA signal corresponds to the Fermi level of the material.\(^{35}\) VB XPS was employed to investigate the density of states (DOS) of the valence band area of \(\alpha\)-Ga\(_2\)O\(_3\) (Figure 3.8 d). The VB XPS spectrum reveals that the difference between the valence band edge and the Fermi level is approximately 3 eV. It is noted that significant DOS intensity is present between the VB maximum and the Fermi level. This DOS is associated with the aforementioned trap states.
within the energy band-gap. The presence of such trap bands in α-Ga$_2$O$_3$ has been previously reported and associated with oxygen and/or gallium vacancies.$^9, 12, 37$

Figure 3.8. (a) UV-vis absorbance spectrum of α-Ga$_2$O$_3$ exhibiting a broad absorption feature between 280-400 nm. (b) Tauc-plot of the UV-vis data where plot $a$ and $hv$ represents the optical absorption coefficient and photon energy respectively. (c) PESA spectrum of α-Ga$_2$O$_3$. (d) VB XPS analysis is showing the presence of trap states.

3.3.2 Photocatalytic dye degradation performance of 2D Ga$_2$O$_3$ nanoflakes

The photocatalytic performance of Ga$_2$O$_3$ was explored via the decomposition of the organic model compounds Congo red (CR) and Rhodamin B (RhB). Congo red is one of the well-known azo dyes with two azo bonds (-N=N-) chromophore in its molecular structure while Rhodamine B is one of the familiar fluorescent dye used in textile industries. CR and RhB both are very stable with complex chemical structure (Fig. 3.9) containing anionic and cationic
functional groups, respectively. These functional groups are water-soluble and can effectively interact with photocatalysts in presence of hydrophilic surfaces. In addition, both of these dyes were chosen for our experiment due to their UV–visible absorption spectra and use in previous works on evaluating photocatalytic activities.38

The gradual reduction of the characteristic absorbance spectrum for CR dye in the presence of the catalyst under solar light irradiation was monitored to evaluate the photocatalytic degradation performance. The concentration of a prepared resuspended α-Ga₂O₃ stock solution was measured to be 0.20 mg/ml using thermal gravimetric analysis (TGA).39 Prior to solar irradiation, 1.65 ml of the suspended photocatalyst were added to 2 ml of 10 μM CR stock solution, leading to a reaction mixture containing 0.09 mg/ml of Ga₂O₃ and 4.5 μM CR. The solution was then illuminated with simulated AM1.5 1000 W m⁻² solar light, which closely resembles the ambient solar spectrum. Photocatalytic dye degradation was performed for 120 min and the absorbance of the CR solution was measured in regular intervals (20 min) in order to determine the photodegradation rate.

The absorption spectra of the reaction mixture containing CR and suspended α-Ga₂O₃ nanoparticles, before and during photocatalysis, are presented in Figure 3.9 a. It is evident that the characteristic absorption peak of CR centered at 500 nm degrades significantly and almost diminishes within 120 min. The breakdown of the chromophoric configuration of the target dye is confirmed by the steady color change of CR solution from an intense red-pink to almost colorless solution after 120 min of simulated solar light irradiation (inset of Figure 3.9a). Figure 3.9 b illustrates the relative absorbance change (Aₜ/A₀) and dye degradation percentage of CR, where A₀ is the initial absorbance of the dye without any irradiation and Aₜ is the absorbance of the dye at time (t). In the presence of the catalyst and under illumination, it is observed that 70% of CR is eliminated after 60 min (Figure 3.9 b). The reaction kinetics were found to be
well described by a pseudo-first order reaction model.\textsuperscript{40} The photocatalytic activity of the synthesized Ga\textsubscript{2}O\textsubscript{3} was further evaluated by investigating of Rhodamine B (RhB) dye degradation under solar light irradiation, while keeping the identical conditions including the photocatalyst loading and dye concentration that were used for the CR study. RhB shows a prominent absorption band at 554 nm and the absorbance decreased significantly under solar irradiation. The obtained results for RhB dye degradation are presented in Figure 3.9 c-d and the results prove that Ga\textsubscript{2}O\textsubscript{3} nanostructures can also effectively catalyze and degrade RhB dye confirming that Ga\textsubscript{2}O\textsubscript{3} possess a general photocatalytic property. However, the photocatalytic activity of α-Ga\textsubscript{2}O\textsubscript{3} is slightly higher for CR in comparison to RhB. It is seen that nearly 84% of RhB dye is eliminated after 120 min.

Figure 3.9. (a) UV-vis absorption spectrum of Congo Red (CR) in the presence of the Ga\textsubscript{2}O\textsubscript{3} catalyst after indicated length of simulated solar light irradiation. The chemical structure of Congo red is shown
in the top section of the figure. (b) Photodegradation of CR under solar light irradiation. (c) UV-vis absorption spectrum of Rhodamin B (RhB) in the presence of the Ga₂O₃ catalyst. The chemical structure of RhB is shown in the top of the figure. (d) Photodegradation of RhB under solar light irradiation.

To evaluate the nature of the degradation kinetics, \( \ln \left( \frac{A_t}{A_0} \right) \) was plotted against irradiation time and the rate constant \( k \) was obtained as \( 0.0161 \pm 10.7 \times 10^{-4} \text{ min}^{-1} \) and \( 0.014 \pm 7.75 \times 10^{-4} \text{ min}^{-1} \) for CR and RhB dyes, respectively (Figure 3.10 a-b).

**Figure 3.10.** (a) Degradation kinetics of Congo red dye under solar light irradiation where the slope is found to be \( 0.0161 \text{ min}^{-1} \). (b) Degradation kinetics of RhB with a slope of \( 0.014 \text{ min}^{-1} \).

Another two different conditions were considered for the investigation: (a) a blank experiment in the absence of solar light but in the presence of the photocatalyst and (b) a blank experiment in the absence of photocatalyst but in the presence of the solar light. First blank experiment was conducted without illumination revealed a negligible decrease of the dye’s absorbance, which is likely associated with the adsorption of dye molecules to the surface of the catalyst. Overall, the observation of the dark experiment signifies the effective degradation of organic molecules by the catalyst (Figure 3.11a). Another blank experiment was conducted to observe the degradation of CR under solar irradiation without the presence of any photocatalyst (Figure 3.11b). This control experiment confirmed that no degradation of CR
occurred during the experimental timeframe of 120 min, confirming the activity of the photocatalyst.

Figure 3.11. (a) Degradation of Congo red in the presence of photocatalyst but in the absence of solar irradiation. (b) Degradation of Congo red under solar light irradiation without any photocatalyst.

A comparison between the dye degradation performance observed in this work and a selection of previous reports on different phases of gallium oxide is presented in Table 3.1. A meaningful comparison is only possible when considering different light sources used in the respective experimental setup. As can be seen in Table 3.1, most studies utilize high power UV irradiation leading to experimental conditions which are not representative of likely application scenarios. Furthermore, the use of high power UV irradiation leads to exaggerated dye-degradation rates when wide band-gap semiconductors such as Ga$_2$O$_3$ are investigated. Our experimental setup on the other hand utilizes a specially designed solar simulator that provides calibrated light with a spectrum that closely resembles solar radiation as it is naturally observed. Our developed photocatalyst outperforms all previous reports on Ga$_2$O$_3$ despite being tested in a realistic scenario where the near UV photon flux is likely orders of magnitude lower than where high power UV-lamps are used.
Table 3.1. Comparison of photocatalytic performance of a selection of previously reported gallium oxide and this work.

<table>
<thead>
<tr>
<th>Material</th>
<th>Average width/ diameter</th>
<th>Dye concentration (mol/L)</th>
<th>Photocatalyst concentration (mg/L)</th>
<th>Target dye</th>
<th>Illumination source</th>
<th>C/Co after 60 min</th>
<th>Dye degradation after 60 min</th>
<th>Kinetic rate constant, K (min⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Ga₂O₃ nanorods</td>
<td>50 nm</td>
<td>2×10⁻³</td>
<td>1000</td>
<td>RhB</td>
<td>150 W Xenon lamp*</td>
<td>~0.66</td>
<td>34%</td>
<td>~0.015</td>
<td>10</td>
</tr>
<tr>
<td>α-Ga₂O₃ nanorods</td>
<td>(50-100) nm</td>
<td>0.84×10⁻⁵</td>
<td>1000</td>
<td>RhB</td>
<td>UV lamp*</td>
<td>~0.38</td>
<td>62%</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>β-Ga₂O₃ nanobelts</td>
<td>~ (50-90) nm</td>
<td>1×10⁻³</td>
<td>-</td>
<td>RhB</td>
<td>UV lamp*</td>
<td>~0.59</td>
<td>41%</td>
<td>0.0087</td>
<td>12</td>
</tr>
<tr>
<td>β-Ga₂O₃ microspheres</td>
<td>(~1-3) μm</td>
<td>2×10⁻³</td>
<td>1000</td>
<td>RhB</td>
<td>150 W Xenon lamp*</td>
<td>~0.4</td>
<td>60%</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>β-Ga₂O₃ sheet</td>
<td>-</td>
<td>2.15×10⁻³</td>
<td>500</td>
<td>CR</td>
<td>UV lamp*</td>
<td>~0.67</td>
<td>33%</td>
<td>0.005</td>
<td>11</td>
</tr>
<tr>
<td>β-Ga₂O₃ nanorods</td>
<td>(280-400) nm</td>
<td>2×10⁻³</td>
<td>1000</td>
<td>RhB</td>
<td>100W UV lamp*</td>
<td>~0.62</td>
<td>38%</td>
<td>-</td>
<td>82</td>
</tr>
<tr>
<td>Floral β-Ga₂O₃ nanorods</td>
<td>~1μm</td>
<td>2×10⁻³</td>
<td>1000</td>
<td>RhB</td>
<td>150W Xenon lamp*</td>
<td>~0.61</td>
<td>39%</td>
<td>-</td>
<td>82</td>
</tr>
<tr>
<td>α-Ga₂O₃ nanoplates</td>
<td>(25-250) nm</td>
<td>0.45×10⁻⁵</td>
<td>90</td>
<td>CR</td>
<td>AM1.5 1000W m⁻² solar simulator</td>
<td>0.30</td>
<td>70%</td>
<td>0.016</td>
<td>This work</td>
</tr>
<tr>
<td>α-Ga₂O₃ nanoplates</td>
<td>(25-250) nm</td>
<td>0.45×10⁻⁵</td>
<td>90</td>
<td>RhB</td>
<td>AM1.5 1000W m⁻² solar simulator</td>
<td>0.47</td>
<td>53%</td>
<td>0.014</td>
<td>This work</td>
</tr>
</tbody>
</table>

* Energy density per surface area has not been provided

The significant improvement in photocatalytic activity of the synthesized Ga₂O₃ can be attributed to two distinct phenomena: (1) the high porosity of the plates and rods that offer a large surface to volume ratio nanostructure for enhancing photocatalytic activity but more importantly (2) the modified energy band structure of the synthesized Ga₂O₃ due to the presence of trap states. An energy band diagram for the synthesized Ga₂O₃ is proposed in Figure 3.12, based on UV-vis spectroscopy, VB XPS and PESA analysis (Figure 3.8(c-d)). These characterizations revealed that the edge of the aforementioned trap states, which constitutes an extension of the valence band, is located at approximately ~4.25 eV. Considering the VB XPS results that indicate a depth of 3.0 eV of the trap band, the valence band edge is situated at ~7.25 eV (Figure 3.12). Based on the measured direct optical band-gap of 4.65 eV,
we expect the conduction band minimum (CBM) to be situated at −2.60 eV. As discussed before, the broadening of the valance band width is ascribed to the generation of trap states (marked as a grey line). Therefore, the band-gap of Ga$_2$O$_3$ is significantly decreased, leading to the expansion of photocatalytic activity into the visible-light range. Upon solar light irradiation, the excited electrons of Ga$_2$O$_3$ in trap states are promoted to the conduction band. The conduction band position is estimated at highly reducing potentials providing ample driving force for subsequent reactions. Therefore, these photo-generated electrons effectively produce superoxide radicals (O$_2$•⁻) through subsequent reduction reactions. Eventually, these superoxide radicals play a significant role for decomposing the organic dye CR.$^{43}$

In order to fully elucidate possible dye-photocatalyst interactions, we determined the highest occupied molecular orbital (HOMO) and the corresponding lowest unoccupied molecular orbital (LUMO) energies for both investigated dyes. The HOMO level of organic chromophores can be estimated by measuring their ionization potentials using PESA, the corresponding LUMO level can be obtained when the optical gap of the chromophore is considered.$^{44}$ The energy levels of CR dye which have been previously reported as - 5.26 eV and -2.48 eV for HOMO and LUMO, respectively, are shown in Figure 3.12.$^{38}$ Considering the LUMO position of CR, there is a presence of small driving force for electron injection into the conduction band of Ga$_2$O$_3$ (-2.60 eV).$^{45}$ As a result, CR might engage in dye-sensitization of Ga$_2$O$_3$, providing additional charge carriers that may be available for the photocatalytic reaction. The HOMO level of RhB is found -5.32 eV using PESA and the LUMO level can be calculated -2.47 eV using the energy level difference of RhB dye.$^{46}$ Overall, it can be concluded that the enhanced photocatalytic performance is influenced by the reduced band-gap due to presence of trap states, which allow efficient light harvesting while maintaining a conduction band edge that is highly reducing.
The existence of trap states is further investigated by conducting the photoluminescence (PL) analysis of the synthesized Ga$_2$O$_3$ suspension. Figure 3.12 b presents the PL spectrum of the Ga$_2$O$_3$ sample in an aqueous solution excited at 500 nm. A relatively broad emission peak is observed in the range of 625 to 730 nm, which corresponds to the band-gap energy of 2.0 to 1.7 eV. These emissions are consistent with the estimated band-gap values in our study and seem to be originated from the trap states located in their upper valance band area.

![Diagram showing energy levels and PL spectrum](image)

**Figure 3.12.** (a) Energy level diagram of Ga$_2$O$_3$ representing the possible photocatalytic mechanism with the estimated valance band maximum (VBM) and CBM. The DOS was determined by VB XPS. HOMO and LUMO values for CR and RhB are also demonstrated. (b) Room temperature PL spectrum of α-Ga$_2$O$_3$ in solvent.
In order to assess whether the trap states are associated with surface defects or bulk dislocations, PL of the material was obtained before and after etching the surface of Ga$_2$O$_3$ using oxygen plasma. These measurements were carried out in ambient air (drop-casted on SiO$_2$ substrates) and as such the side tails are significantly more stretched around the centre peak in comparison to the in liquid PL measurement. Figure 3.13 shows the change in PL spectrum of Ga$_2$O$_3$ after plasma etching treatment. The Ga$_2$O$_3$ samples were subjected to 3 successive 3 seconds of plasma treatment at 60 W. It is observed that the intensity of the obtained PL peaks has decreased with increasing the etching time. This indicates that trap states, responsible for the reduction of band-gap energy and PL emission, are mostly located on the surface rather than bulk. It is also noticed that in air all PL spectra have significant low-energy tail which are possibly originated from the intra-band transitions between the defect states.

![Figure 3.13. Room temperature PL spectra of α-Ga$_2$O$_3$ in air obtained at the excitation wavelength of 532 nm.](image)

**3.4 Conclusions**

In summary, a new method for synthesizing high surface-to-volume ratio porous plates and rods α-Ga$_2$O$_3$ from liquid metal gallium was demonstrated. A facile two-step method was
introduced to synthesize Ga$_2$O$_3$ nanostructures from bulk liquid metal gallium via sonication and subsequent annealing to produce first gallium oxy-hydroxide and then gallium oxide nanostructures. The morphological, structural and optical properties of the synthesized nanoparticles were thoroughly investigated, leading to the conclusion that the synthesized material was hexagonal $\alpha$-Ga$_2$O$_3$ nanoflakes with high porosity. As an application, the photocatalytic activity of the synthesized oxide nanoparticles was investigated for degrading CR and RhB dyes under solar light irradiation, which exhibited a remarkable performance, reaching dye degradation of 70% in 60 min under a solar sun simulator (outcome of RhB dye is also demonstrated). The mechanism behind the efficient photocatalytic performance of Ga$_2$O$_3$ was investigated and an energy band diagram was established utilizing PESA, valance band XPS and UV–vis analysis. On the basis of the developed energy level diagram, it was concluded that the enhanced photocatalytic performance originated from a narrowed band-gap of 1.65 eV caused by the raised valance band, induced by trap states. As such, a promising scheme is reported for developing effective solar light gallium oxide photocatalysts at high yield following a facile and inexpensive synthesis route enabling future electronic and optical applications.

3.5 References


Chapter 4

Printing two-dimensional gallium phosphate out of liquid metal†

4.1 Introduction

Piezoelectricity is the property of a material that allows the conversion of electrical energy into mechanical force and vice versa.¹ Recently the exploration and implementation of two-dimensional (2D) planes as piezoelectric structures has been a focus of the attention due to the promising properties of these systems.¹⁻³ Mechanical displacements, such as vibration, bending and stretching, are ubiquitously present in the ambient environment and 2D piezoelectric materials may facilitate their sensing and harvesting of their kinetic energy to power miniaturized devices.¹,⁴ The specific qualities offered by 2D materials including their lateral strength and high crystallinity along the planes, large surface area to mass ratios and compatibility with surface fabrication processes, provide the concept of 2D piezotronics with great prospect for future industries. The observation of piezoelectricity in certain 2D materials relies on the loss of centro-symmetry that is seen for the example of doped graphene, hexagonal boron nitride and many odd-layered transition-metal dichalcogenides (TMDs) species.¹,²,⁵,⁶

†The contents of this chapter have been published as Nitu Syed, et al. "Printing two-dimensional gallium phosphate out of liquid metal." Nature Communications 9, 3618 (2018).
Spontaneous piezoelectricity of selected other 2D materials such as: transition metal oxides (e.g. zinc oxide (ZnO))\(^6\); group III-V semiconductors (e.g. aluminium nitride (AlN))\(^6\); and metal monochalcogenides (e.g. germanium monosulfide (GeS) and tin selenide (SnSe)) have also been explored theoretically. The coupling of piezoelectric polarization and semiconductor properties in some 2D semiconductors with a wurtzite or zinc blend structure (e.g. ZnO, GaN and CdS) has resulted in a novel fundamental phenomenon, offering new possibilities in the emerging field of piezotronics.\(^7\) Due to the co-existing piezoelectricity and semiconductor properties, a piezoelectric semiconductor can induce remnant polarization at its surface or at the interface with other materials under mechanical straining. This leads to a redistribution of free charge carriers and alteration of the band structures near the interface, allowing the modulation of electronic transport across the interface due to the existence of strain-induced polarization charges. Electronic devices fabricated by utilizing these interfacial piezoelectric polarization charges as “gate” controlling signal is referred to as the piezotronic effect.\(^7\)

Despite significant progress and unique achievements, many critical obstacles still restrict the field of 2D piezotronics. Firstly, many 2D materials such as 2D TMDs only possess piezoelectricity for structures with an odd number of layers\(^6\) and the strength of the piezoelectric coefficients of some of these 2D materials decreases significantly with increasing sample thickness (number of layers).\(^6,8\) However, this layer dependence of the piezoelectric effect may impose inconsistencies in commercial batch processes. Furthermore, in a large number of 2D systems studied to date, the piezoelectricity is confined within the in-plane piezoelectric polarizations, excluding out-of-plane operation of 2D devices.\(^6,7\) This largely impedes the application of 2D piezoelectric materials in certain nano-electromechanical systems, where out-of-plane piezoelectric constant \((d_{33})\) is one of the important key factors.\(^9\) The separation of flexoelectric and piezoelectric components of \(d_{33}\) is also challenging.\(^10\)
The very recent report on the piezoelectricity of 2D ZnO provides an example of a 2D material with a large out-of-plane piezoelectric coefficient, still with lateral dimensions not exceeding several hundred microns and this does not rely on a surface synthesis processes.\textsuperscript{11} Currently, the exploration of 2D piezoelectric materials is restricted to comparatively low temperatures, and the development of 2D materials which are able to function at elevated temperatures is still not emphasized due to the commonly observed high temperature induced instability of the piezoelectric properties of these materials. Additionally, challenges associated with achieving acceptable levels of sample homogeneity over larger areas, the synthesis of very large-area 2D piezoelectric materials at relatively low temperatures and compatibility with the current silicon processes also remain largely unsolved. These restrictions have triggered an intense quest to explore new large-area 2D piezoelectric materials beyond the currently available selection of 2D materials.

Gallium phosphate is a well-known piezoelectric material that is iso-structural with \(\alpha\)-quartz.\textsuperscript{12,13} It is considered superior to quartz for several technical applications including higher thermal stability up to 930°C.\textsuperscript{13} GaPO\(_4\) does not naturally crystallize in a stratified structure, eliminating the choice of common exfoliation techniques.\textsuperscript{14-16} Moreover, the deposition of high quality, defect free single crystal GaPO\(_4\) is crucial, and so far, no report has addressed the growth of wafer-scale 2D GaPO\(_4\) films.\textsuperscript{17} Hence, the synthesis and deposition of large-area, high quality and homogeneous ultra-thin GaPO\(_4\) nanosheets will have a major impact on 2D piezotronics.

In this work, a promising method has been reported to synthesize extraordinarily large 2D GaPO\(_4\) sheets on suitable substrates using a liquid metal based synthesis process. Recently, liquid elemental gallium and their alloys have drawn significant attention for its use in the printing-deposition of 2D materials.\textsuperscript{18} The reported method takes advantage of the self-limiting atomically thin oxide layer that naturally grows on the surface of liquid gallium which can be
transferred onto a substrate using our devised van der Waals printing technique. The 2D GaPO₄ synthesis process described here relies on harvesting the gallium oxide (Ga₂O₃) skin, followed by a chemical vapour reaction process using phosphoric acid at 350°C. The phosphatization process is conducted at relatively low temperature which is compatible with existing industrial processes. The vertical piezoelectricity for one to several unit cell thick 2D GaPO₄ sheets has been investigated, using a combination of piezoresponse force microscopy (PFM) and density functional theory (DFT) simulations. The experimentally measured vertical piezoelectric coefficient for unit cell thick GaPO₄ is found to be 7.5 ± 0.8 pm V⁻¹, in good agreement with the DFT calculations. The vertical piezoelectric behaviour of 2D GaPO₄ nanosheets with different thicknesses is also demonstrated in this work. Thus, an excellent out-of-plane piezoelectric performance of the synthesized 2D GaPO₄ is demonstrated in this work. Additionally, the developed process is also utilized to fabricate free-standing 2D GaPO₄ membranes over micro-fabricated square holes.

4.2 Experimental section

4.2.1 Two-step liquid metal based synthesis of large-area 2D GaPO₄ nanosheets

The synthesis of 2D GaPO₄ nanosheets involved a two-step process. Ultra-thin Ga₂O₃ sheets were first directly exfoliated onto a substrate from liquid elemental gallium. The isolated film was subsequently phosphatized using a chemical vapour phase reaction between gallium oxide sheet and phosphoric acid.

4.2.1.1 Van der Waals printing process of 2D Ga₂O₃ sheets

2D Ga₂O₃ nanosheets were first printed from liquid gallium following the liquid metal van der Waals exfoliation method reported in our previous work. Gallium melts at 29.76 °C
therefore; the process was conducted on a hotplate at 50 °C. A self-limiting atomically thin gallium oxide skin forms on the metal surface of gallium droplets, when they are exposed to ambient air. The freshly formed gallium oxide skin is exfoliated by touching the liquid metal surface with a suitable substrate (SiO₂ wafer, glass and TEM grids) typically with the aid of tweezers. A gallium droplet was placed on a SiO₂ (300 nm)/Si substrate. After touching the gallium oxide skin, the substrate was separated very carefully. Using this technique atomically thin gallium oxide sheets with large lateral dimensions exceeding several millimetres and reaching centimetres can be exfoliated onto the surface of the substrate. Different gallium droplets with varying diameters of 4 to 20 mm were chosen (Figure 4.1) to harvest Ga₂O₃ nanosheets.

The dimensions of the 2D oxide sheets varied with the diameter of the droplets. The Ga₂O₃ sheets with lateral dimension of several millimeters were obtained from the gallium droplets with diameter range 1-2 centimeter. However, the experimental limitations for fabricating larger nanosheets mainly depend on the applied force and the approaching angle of the target substrate that is brought into contact with the liquid metal. If the larger liquid-metal droplet is not uniformly touched by the substrate, the transferred area of Ga₂O₃ sheets may lack homogeneity. Conversely, excessive force on the droplet increases the probability of metal inclusions during the transfer of oxide layer. The metal inclusions can be cleaned and removed by following the methods proposed by Jing Liu et al. During the separation of the 2D nanosheets from the gallium metal, the possibility of overlapping and folding of the monolayer along the edges result in increased flake thickness.
4.2.1.2 Transformation of 2D Ga$_2$O$_3$ to 2D GaPO$_4$ sheets by phosphatization

The synthesized ultra-thin gallium oxide sheets were phosphatized by means of a chemical vapour method in a horizontal quartz tube furnace, which utilizes the physical transport of the source vapour to the target (Figure 4.6 d). For the phosphatization technique, phosphoric acid (H$_3$PO$_4$) powder was placed on an alumina boat as source material and heated to 350 °C at a rate of 15 °C/min to induce evaporation. The Ga$_2$O$_3$ samples were placed upside down on another alumina boat located in a comparably low temperature region (around 300 °C) of the tube furnace. Nitrogen gas with a flow rate of 0.6 L/min was used for transporting vapours of H$_3$PO$_4$ towards the Ga$_2$O$_3$ samples. As the H$_3$PO$_4$ vapour reaches the low temperature region, it starts to transform the thin Ga$_2$O$_3$ layer into GaPO$_4$. The optimal duration for the entire process was found to be 75 min after the temperature of the system was saturated to 350 °C. Placing samples in the upside down position ensures that there is no accumulation of phosphoric acid on the synthesized nanosheets. The furnace was allowed to cool naturally to room temperature when the synthesis was completed. Any remaining residue of H$_3$PO$_4$ was finally removed from the synthesized 2D GaPO$_4$ samples by blowing N$_2$ gas. A nitrogen glove-box or desiccator was later used for prolonged storage of the samples.

A strategy towards the targeted synthesis of thicker Ga$_2$O$_3$ sheets can be obtained by multiple subsequent van der Waals exfoliation/printing processes onto the same substrate. The
thickness of the obtained 2D GaPO\(_4\) was found to mainly depend on the original thickness of the exfoliated 2D Ga\(_2\)O\(_3\) sheets. The thickness profiles of two different Ga\(_2\)O\(_3\) oxide nanosheets (0.9 and 2.6 nm thick) are presented in Figure 4.2 a,c, before the phosphatization process. The thickness of the transformed 2D GaPO\(_4\) was consistently ~1.3 times larger than that of the original Ga\(_2\)O\(_3\) nanosheets (Figure 4.2 b,d). The observed change in thickness arises due to the re-crystallization process and the incorporation of phosphate ions into the material.

**Figure 4.2.** AFM images (a, c) 2D Ga\(_2\)O\(_3\) sheets imaged before and after (b, d) conversion into 2D GaPO\(_4\).

### 4.2.2 Exfoliation of free-standing 2D GaPO\(_4\) sheets

Free-standing GaPO\(_4\) sheets were synthesized on SiO\(_2\)/Si wafers with arrays of square micro cavities as shown in the Figure 4.3f. The fabrication of these cavities was conducted by oxidizing a p-doped silicon wafer with a 300-nm thick SiO\(_2\) layer. Square cavities with approximately 2-3 \(\mu\)m length were first patterned and next focused ion beam (dual beam FIB/SEM) was utilized to etch the squares to a depth of 1-2 \(\mu\)m, leaving a series of holes on
the wafer. Finally, 2D GaPO$_4$ sheets over the square cavities were directly synthesized following the liquid metal van der Waals exfoliation techniques and phosphatization process as previously discussed. Scanning electron microscopy (SEM) and AFM images of these free-standing sheets are also presented in Figure.4.3 and Figure.4.4. The wrinkles on the surface of the free-standing and bulged GaPO$_4$ (Figure. 4.3) that are not prominently visible in free-standing Ga$_2$O$_3$, are assumed to be caused by phosphatization process.

**Figure 4.3.** Scanning electron microscopy of the micro-cavities and free-standing 2D nanosheets. (a) The schematic for the cross section of the SiO$_2$/Si wafer with micro cavities. SEM images of (b) array of micro cavities, (c) an uncovered square hole, (d) fully and partially covered cavities by GaPO$_4$ nanosheet, (e) cavity covered with Ga$_2$O$_3$ flake before phosphatization process which is showing an even bulged surface area, (f) hole covered with GaPO$_4$ nanosheet showing a wrinkled surface.
4.2.3 Piezoresponse force microscopy (PFM) measurements

PFM measurements were carried out using a Bruker AFM (Bruker Dimension Icon). NanoScope® 1.8 software was used for data acquisition and analysis. Two types of Pt/Ir coated conductive AFM tip SCM PIT V2 (resonance frequency 75 kHz, spring constant 3N/m, radius ~25 nm) and SCM-PIC-V2 (resonance frequency 10 kHz, spring constant 0.2N/m, radius ~25 nm) were used to obtain the PFM results for the supported and free-standing nanosheets, respectively. The schematic representation of PFM setup is provided in Figure 4.5a. 2D GaPO₄ sheets synthesized on a SiO₂/Si substrate were glued and connected on a conductive tab using silver paste. Inverse piezoelectric measurements were performed in contact mode by applying AC signal (driving excitation) to the conductive AFM tip with a frequency of 15 kHz, chosen to be far away from the cantilever resonance frequency (330 kHz). The forces applied to the supported and free-standing GaPO₄ were approximately 150 and 8nN, respectively. The AC amplitude was swept from 0 to 4 V (0 V DC bias) while the tip was anchored at the piezo-active area chosen from the topography image. The responsive out-of-plane piezoelectric vibration causes the displacement of the cantilever. A lock-in amplifier was utilized to measure the resulting vertical deflection of the cantilever which was reflected in the final output as
amplitude and phase change during PFM imaging. Piezoelectric coefficient, \( d_{33} \) is used to represent the quantitative vertical piezoelectric displacement produced by an out-of-plane electric field. During actual PFM experiments, the piezoresponse coefficient is addressed as an effective piezoelectric constant, \( d_{eff33} \), due to possible factors that affect the PFM measurements such as inhomogeneous electric field and other electrostatic effects.\(^{10,21} \) The out-of-plane piezoresponse amplitude variation was calculated from statistical distribution of the piezoresponse amplitude values of GaPO\(_4\) film and the substrate/background which can be determined by:

\[
\text{Piezoresponse amplitude variation, } V_{PFM} (\text{mV}) = \text{Normal fitting mean (GaPO}_4\text{ nanosheet on the substrate)} - \text{Normal fitting mean (substrate/background)}
\]

\[
\text{Error bar} = \text{Normal fitting standard deviation (GaPO}_4\text{ nanosheet on the substrate)} + \text{Normal fitting standard deviation (substrate/background)}.
\]

Next the \( d_{eff33} \) is determined by the following calculation:

It is assumed that an AC driving voltage was applied with amplitude \( V_{in} (\text{V}) \) to the flake and the resulting piezoresponse displacement is \( A_{PFM} (\text{pm}) \) which is the product of the detected vertical deflection voltage \( V_{PFM} (\text{mV}) \) and deflection sensitivity of the cantilever \( \delta (\text{nm/V}) \).\(^{22,23} \) Therefore, the deflection sensitivity was determined each time a cantilever is mounted or remounted. Finally, \( d_{eff33} \) for an applied AC driving voltage can be determined by

\[
d_{eff33} = \frac{A_{PFM} (\text{pm})}{V_{in} (\text{V})}
\]

\[
A_{PFM} (\text{pm}) = \frac{[V_{PFM} (\text{mV}) \times \delta (\text{nm/V})]}{16}
\]

Here a hardware gain of \( \times 16 \) was used to enhance the piezoresponse amplitude signal during PFM scanning. To assure the reliability and accuracy of our measurements, PFM amplitude
and phase of periodically polled LiNbO₃ (PPLN) was measured by the same PFM instrument and technique as a standard reference (Figure. 4.5b).

**Figure 4.5.** (a) Schematic illustration showing the PFM set up. (b) Topography of a PPLN substrate, (c) PFM phase, and; (d) PFM amplitude of a standard PPLN sample as reference with a PR drive amplitude of 10 V at 17kHz.

### 4.2.4 Peak-force quantitative nano-mechanical (PFQNM) mapping

All measurements were performed using the Peak Force QNM mode with a Dimension Icon AFM from Bruker. AFM tip “ScanAsyst – Air” was purchased from Bruker AFM probes with a force constant of 0.4 N/m, resonant frequency around 70 kHz and nominal tip radius around 2nm.AFM tip “OTESPA-R3” with a force constant of 28 N/m (nominal tip radius around 7 nm) was used to measure the threshold break point of the suspended flake. The deflection sensitivity of the cantilever was measured on a clean sapphire sample for the calibration of the probe. After calibrating the probe, the surface topography and nano-mechanical mapping of the free-standing GaPO₄ flake were collected at a constant peak force with a resolution of 512 pixels. The peak force set point was set to a force of 800 pN.
4.2.5 Density functional theory calculations

DFT calculations are performed to ensure the veracity and the consistency of our experimental measurements. Hybrid DFT calculations were performed using Gaussian basis set ab initio Package CRYSTAL14.24,25 The B3LYP hybrid exchange-correlation functional26 was used to calculate the slab energies. For all atoms a Triple Zeta Valance basis set (TZV), with polarization functions, was used to model the electrons.27

4.2.6 Measurement and instrumentation

The surface thickness and topography images were collected using a Bruker Dimension Icon AFM using “Scanasyst-air” AFM tips. Gwyddion 2.36 software was employed for AFM image processing and analysis. TEM imaging and EELS analysis were obtained by JEOL 2100F TEM/STEM operating with 100 kV acceleration. ImageJ 1.50i and Gatan microscopy suite 1.8.4. softwares were used for TEM image processing. TEM samples are produced by utilizing a TEM grid as a substrate, rather than the SiO2/Si wafer. The TEM samples were prepared by direct deposition of the gallium oxide skin onto TEM grids and subsequent phosphatization. XRD was conducted using Bruker D8 micro-diffractometer equipped with a Vantec 500 detector and 0.5 mm collimator. X-ray was generated using a 40 kV copper source and a current of 40 mA. Raman spectra of the synthesized Ga2O3 and GaPO4 were carried out using a Horiba Scientific LabRAM HR evolution Raman spectrometer equipped with a 532 nm laser source and 1800 mm⁻¹ grating. Two periods of accumulation, each with duration of 240 s, were utilized to scan each of the glass deposited samples. Surface chemical analysis was achieved using a Thermo Scientific K-alpha XPS spectrometer equipped with a monochromatic Al Kα source (hν = 1486 eV) and a concentric hemispherical analyser. The analyser was operated with pass energy of 100 eV to record the core-level spectra (Ga 3d, phosphorous 2p,
O 1s, C 1s, etc.) and 50 eV to record the valance band edge. To remove the possibility of surface charging of the 2D GaPO$_4$ affecting the XPS data, a low energy electron flood gun was used to add electrons of 3-5 eV to the surface. XPS data acquisition and peak fitting analysis was done using the dedicated XPS Avantage software. FTIR spectroscopic measurements were conducted on a Perkin-elmer FTIR spectrometer with a resolution of 4 cm$^{-1}$. FEI Quanta 200 environmental scanning electron microscope ESEM (2002) equipped with an Oxford X-MaxN 20 energy dispersive X-ray spectroscopy (EDXS) detector was employed for exploring the morphology of the free-standing nanosheets and blank cavities. Patterning and etching of square cavities on the SiO$_2$ substrates were performed using a FEI Scios Dual Beam FIB/SEM (focused ion beam/scanning electron microscope) with a gallium beam of 7 nA.

4.3 Results and discussions

4.3.1 Synthesis of large-area 2D GaPO$_4$ nanosheets

The synthesis of ultra-thin GaPO$_4$ is carried out in a two-step process consisting of van der Waals exfoliation followed by a chemical vapour phosphatization step. A schematic illustration of the van der Waals synthesis technique for printing 2D Ga$_2$O$_3$ sheets is depicted in Figure. 4.6c. When a pristine liquid gallium droplet is exposed to ambient atmospheric conditions, a mechanically robust, atomically thin gallium oxide layer grows on its surface in a self-limiting reaction. Synchrotron based studies of the liquid gallium interface have revealed that the electron density profile features a prominent minimum of the electron density distribution at the boundary between the liquid metal and its naturally grown surface oxide.$^{28}$ This finding indicates that there are no covalent bonds between the oxide layer and the parent metal. Furthermore, liquid gallium metal is a monatomic liquid which is by default non-polar, limiting the possibility of interaction further. Hence, interaction between the liquid metal and the surface oxide are expected to be minimal. The absence of a solid crystal structure impedes
cumulative atomic interactions of liquid metal over large-areas rendering any weak interactions that may occur to be localized, inhibiting macroscopic attachment. The absence of covalent bonds between the liquid metal together with the liquid state of the parent metal hence lead to minimal interactions between the oxide and the liquid metal. The van der Waals interactions between the surface oxide and the transfer substrate, on the other hand, comprise of more robust forces between permanent dipoles. The presence of a crystalline lattice within the oxide as well as the substrate ensure that interactions may occur over larger areas, leading to macroscopic attachment.

The high surface tension of liquid gallium further ensures that the vast majority of the liquid metal separates from the oxide during the exfoliation process. Thus minimal metal inclusions are found in the large exfoliated nanosheets which are furthermore consistent with our previous reports for other metals. As such, the interfacial oxide skin can be effectively transferred to a SiO\textsubscript{2}/Si substrate that is brought into the close contact with the liquid gallium surface (Figure. 4.6c). The schematic setup of the chemical vapour phase reaction system to transform the 2D Ga\textsubscript{2}O\textsubscript{3} sheets into 2D GaPO\textsubscript{4} is elucidated in Figure. 4.6d. The phosphatization of Ga\textsubscript{2}O\textsubscript{3} is conducted at a relatively low temperature (300 °C-350 °C) that is compatible with the existing electronic device fabrication processes. The method for growing large-area GaPO\textsubscript{4} sheets is further found to be highly reproducible as the process was repeated in excess of 50 times and always led to uniform, continuous, laterally large atomically thin GaPO\textsubscript{4} films (presented in Figure. 4.7d) with reproducible properties.
Figure 4.6. Crystal structure and printing process of 2D GaPO$_4$ nanosheets. Ball and stick representation of the synthesized GaPO$_4$ crystal: (a) top view and (b) side view showing an out-of-plane structure exhibiting unit cell parameter $c = 11.05$ Å. (c) Schematic illustration of the van der Waals 2D printing technique of Ga$_2$O$_3$ nanosheet. (d) Schematic setup for the chemical vapour phase reaction system used for synthesising GaPO$_4$ nanosheets.

4.3.2 Characterizations of 2D GaPO$_4$ nanosheets

AFM investigation was carried out to determine the surface morphology and thickness of the synthesized 2D films. Due to the limited scan area size of AFM, only a small section of this ultra large GaPO$_4$ sheet is presented in Figure. 4.7a. The typical step-height from the substrate to the GaPO$_4$ nanosheet is found to be approximately 1.1 nm for the majority of the synthesized 2D crystals, which is in excellent agreement with the unit cell dimension of trigonal
GaPO$_4$ in the c-direction ($c = 11.05$ Å). Occasionally some GaPO$_4$ nanosheets of differing thicknesses are also observed during the synthesis process (as discussed in Section 4.2.1.2). Localized inclusions of metallic gallium are only occasionally encountered along the edges of the extraordinarily large sheet. Imaging of an as-grown GaPO$_4$ nanosheet (on SiO$_2$/Si substrate) using optical microscopy (Figure. 4.7d) revealed lateral dimension reaching several millimetres, approaching centimetres. This exfoliation technique is confirmed to reproducibly results in uniform, centimetre-scale GaPO$_4$ nanosheets in repeated tests.

Transmission electron microscopy (TEM) was further used for revealing the structural features and crystal structures of the synthesized nanosheets. The TEM micrograph presented in Figure.4.7b exhibits the translucent sheet-like morphology of the synthesized 2D GaPO$_4$. The crystalline structure of the synthesized GaPO$_4$ is confirmed by the corresponding selected area electron diffraction (SAED) pattern displayed in Figure. 4.7c. The SAED pattern indicates the observed lattice spacing is 0.21 nm corresponding to the $d$-spacing value of (200) plane of trigonal GaPO$_4$. Overall, the TEM results support and substantiate the morphological conclusions drawn from the AFM observations.

**Figure 4.7.** Morphology and TEM characterizations of the printed 2D GaPO$_4$ film. (a) AFM topography of a GaPO$_4$ nanosheet and height profile along the magenta line. (b) TEM micrograph of the GaPO$_4$ film. (c) The SAED pattern of the TEM micrograph. (d) Optical images of synthesized GaPO$_4$ showing homogeneous nanosheets featuring lateral dimensions spanning several millimetres.
X-ray diffraction (XRD) measurement was employed to investigate the crystal structure of the synthesized GaPO$_4$. The XRD pattern of the as-deposited flake (Figure. 4.8a) reveals two dominant peaks at 24.4° and 27.3°, corresponding to the (003) and (102) planes of trigonal α-GaPO$_4$, respectively. Raman spectroscopy is utilized to further validate the composition of the GaPO$_4$ sheets synthesized on a glass substrate (Figure. 4.8b). The Raman peaks at ~420.5 and ~456.6 cm$^{-1}$ can be assigned to vibrations involving internal bending of the PO$_4$ tetrahedra which can be denoted as $A_1$ vibration modes. On the other hand, the 300 cm$^{-1}$ Raman peak that exists in the bulk system, which is considered to be a bending mode along the z axis, is absent in the 2D sample due to geometrical confinement. The Raman peak at 206.2 cm$^{-1}$ can be ascribed to the decoupled bending mode (E-TO5) of the PO$_4$ tetrahedra along the x-y axis. Compared with the bulk GaPO$_4$, this peak is more prominent due to the geometrical confinement along z axis in the 2D sample. Ga$_2$O$_3$ also features peaks at ~198 and ~415 cm$^{-1}$ which are in close proximity to the characteristic Raman modes of GaPO$_4$, however, several Raman features of Ga$_2$O$_3$ (i.e. peaks at ~167, ~320, ~344 and ~475 cm$^{-1}$) are absent in our spectrum, confirming that GaPO$_4$ is successfully synthesized and Ga$_2$O$_3$ is quantitatively converted during the vapour phase reaction. Another interesting observation is that the Raman peak intensity for 456.6 cm$^{-1}$ mode is significantly reduced compared to that of 420.5 cm$^{-1}$ for 2D GaPO$_4$ in comparison to the bulk counterpart. It has been reported that the $A_1$ Raman mode is sensitive to the free charge carrier density in graphene and 2D metal chalcogenides. 2D GaPO$_4$ has a wider band-gap which is likely to include more trap states. The emergence of more polar 2D GaPO$_4$ modifies the interaction between phonon and free charge carriers, generated by the trap states, within the 2D material, leading to phonon self-energy renormalization. Consequently, phonons are weakened; causing the intensity of charge-
sensitive \( A_1 \) Raman mode to be reduced.\(^{38-41} \) Therefore, the observation from Raman spectra suggests that there is an increase in the dipole intensity in 2D GaPO\(_4\).

X-ray photoelectron spectroscopy (XPS) was utilized to obtain the chemical bonding states of the synthesized 2D GaPO\(_4\) material. Figures 4.8c and 4.8d show the spectra of Ga 3\(d\) and phosphorous 2\(p\) regions, respectively for the synthesized GaPO\(_4\) nanosheet. The characteristic main broad peak at 21.4 eV in the Ga 3\(d\) region, is fitted to identify the 3\(d_{3/2}\) and 3\(d_{1/2}\) components at \( \sim21.3 \) and \( \sim21.7 \) eV, respectively, signifying the Ga\(^{3+}\) state in GaPO\(_4\). The characteristic gallium peak for Ga\(_2\)O\(_3\) located at \( \sim20.4 \) eV is not observed, demonstrating quantitative transformation of GaPO\(_4\).\(^{42}\) Additionally, no metallic gallium peak (Ga\(^0\)) was detected in the Ga 3\(d\) region. The peak centred at 25.2 eV incorporates the broad O 2\(s\) feature.\(^{19}\)

The main broad phosphorous 2\(p\) peak centred at \( \sim134.6 \) eV corresponds to the doublets P2\(p_{3/2}\) and P2\(p_{1/2}\), in agreement with the expected phosphorous 2\(p\) region present in GaPO\(_4\). The observed binding energies are all consistent with the previously reported values for GaPO\(_4\).\(^{43-45}\)

All the above-mentioned characterization techniques support the conclusion that all of the deposited 2D GaPO\(_4\) nanosheets show excellent consistency. Figure 4.8e represents the enlarged view of low loss electron energy loss spectroscopy (EELS) spectrum of GaPO\(_4\) for the determination of electronic band-gap. The band-gap value of GaPO\(_4\) is assessed by extrapolating the linear fit of the loss intensity to electron loss energy as illustrated in Figure 4.8e. Therefore, the estimated fundamental band-gap value is approximately 6.9 eV which shows an excellent agreement with previous reports\(^{46-49}\), confirming 2D GaPO\(_4\) to be a wide band-gap material. The inset (Figure 4.8e) shows the extended EELS where the highest intense peak signifies the zero loss peak.\(^{50}\) XPS valence band analysis was conducted to further explore the electronic properties of GaPO\(_4\). The position of valence band maximum (VBM) was determined by linearly fitting the leading edge of the valence band and the baseline of binding
energy where the binding energy scale is with respect to the Fermi level $E_F$. The intersection of these two lines is assigned as the $E_F - E_{VBM}$ value, as shown in Fig.4.8f and the valence band maximum is estimated to lie $3.8 \pm 0.10$ eV below the surface Fermi level.

Figure. 4.8. Material characterizations and electronic band properties of 2D GaPO$_4$. (a) XRD and (b) Raman spectra of the synthesized GaPO$_4$ (thick nanosheets). XPS results of (c) Ga 3d and (d) phosphorous 2p regions of the synthesized GaPO$_4$. (e) Enlarged view of EELS for the estimation of the fundamental band-gap and the extended EELS spectrum (inset). (f) XPS valence band analysis of GaPO$_4$. 
4.3.3 Thermal stability of the synthesized 2D GaPO$_4$

It was observed that the synthesized 2D GaPO$_4$ is stable up to 600 °C. Degradation of the GaPO$_4$ nanosheets was found to begin when the samples are annealed at 700 °C. The thermal stability of the synthesized GaPO$_4$ nanosheets was investigated using XPS of annealed samples. For samples annealed at 600 °C, the characteristic main broad peak for the Ga 3$d$ region is centered at 21.4 eV and the main broad peak in the phosphorus 2$p$ region is centered at a binding energy of 134.7 eV (Figure 4.9a-b), which is consistent with unannealed GaPO$_4$ (Figure. 4.8c), evidencing thermal stability at this temperature. Raman spectrum of GaPO$_4$ nanosheet on SiO$_2$ substrate annealed at 600 °C shows two strong Raman peaks at ~420.8 and ~456.3 cm$^{-1}$ (Figure 4.9c) that are in good agreement with the peak positions of the original GaPO$_4$ nanosheet (Figure. 4.8b), validating the stability of the 2D GaPO$_4$ at temperatures up to 600 °C. When the GaPO$_4$ nanosheet was annealed at 700 °C (Figure 4.9d-e), the XPS results show a significant shift of the Ga 3$d$ peaks to a lower binding energy (20.6 eV) which resembles the spectrum of Ga$_2$O$_3$.\textsuperscript{51} Furthermore, several new P 2$p$ peaks appeared at lower binding energies ranging from 126 to 132 eV, indicating the partial transformation from phosphate to other phosphorous compounds.\textsuperscript{52,53}
Figure 4.9. Thermal stability characterizations of the synthesized 2D GaPO₄. XPS results of (a) Ga 3d and (b) phosphorus 2p regions of the synthesized GaPO₄ annealed at 600 °C. (c) Raman spectrum of GaPO₄ nanosheet on SiO₂ substrate annealed at 600 °C. XPS results of (d) Ga 3d and (e) phosphorus 2p regions of the synthesized GaPO₄ annealed at 700 °C.

4.3.4 Out-of-plane piezoelectric properties of 2D GaPO₄ synthesized on SiO₂ substrate

The non-centrosymmetric nature of single unit cell thick GaPO₄ across the out-of-plane direction is evident from Figure 4.6b, inducing a non-zero vertical piezoelectric response. The fundamental piezoelectric characteristics of the synthesized GaPO₄ thin film are explored by PFM, the most widely and extensively used technique to characterize nanoscale piezoelectric phenomena. During the herein presented PFM measurements, the tip and surface electrostatic interaction is ignored, since the tip-field interaction is significantly reduced by using conductive tips with a high force constant (3 N/m). The vertical piezoelectric response of unit cell thick GaPO₄ nanosheets ($d \approx 1.1$ nm, see Figure 4.10a) is measured by applying an electrical field normal to the surface of the flake through a conductive AFM tip. The thicker
areas at the edges of the sheets can be attributed to folding and restacking of the monolayer along the flake boundaries during the van der Waals exfoliation. Figure 4.10 b-f illustrate the vertical piezoresponse amplitude profiles for this ultra-thin crystal under different drive voltages ranging from 0 to 4 V. The corresponding PFM phase images for different excitation voltages are also presented in Figure. 4.11. No PFM amplitude and phase difference is observed between GaPO$_4$ and the SiO$_2$/Si substrate (a natural reference to the PFM signal) at 0V. However, a nonzero vertical piezoresponse signal is observed at the thick edges of the GaPO$_4$ nanosheet even at 0V, which is probably due to the deviation of the perfect flatness and non-uniform thickness along the boundaries, resulting in a possible non-piezoelectric polarization component.

The piezoresponse displacement is found to increase steadily with higher driving bias. The insets represent the statistical distributions of piezoresponse amplitude variations of the GaPO$_4$ sheet and the substrate. The statistical distributions of the piezoresponse amplitude variations provide the opportunity to characterize the overall effective piezoelectric constant ($d_{eff}^{33}$) for the entire flake area. From the piezoresponse amplitude, we characterize $d_{eff}^{33}$ of GaPO$_4$ sheets quantitatively (details concerning the $d_{eff}^{33}$ calculation are provided in section 4.2.3). The piezoelectric displacement as a function of applied AC voltage is plotted in order to quantify the piezoelectric coefficient of a unit cell thick GaPO$_4$ nanosheet. The piezoresponse displacement shows a linear relationship with the driving voltage (Figure. 4.10 g) providing a value of $d_{eff}^{33}$ of approximately 7.5 ± 0.8 pm V$^{-1}$ from the linear fit, which is approximately two times larger than that of bulk GaPO$_4$ crystal. The improvement in the value of $d_{eff}^{33}$ can be possibly due to a slightly disordered crystal structure exhibited by the 2D GaPO$_4$ films.

From the Raman spectra (Figure. 4.8 b) it was observed that there are significant shifts to lower wavenumbers for both of the ~420.5 and ~456.6 cm$^{-1}$ peaks in 2D GaPO$_4$ with
reference to their bulk values, indicating the weakening of optical phonon vibration modes ($A_1$) of the PO$_4$ tetrahedra along z direction$^{35,36}$. As a result, the PO$_4$ tetrahedra in the 2D GaPO$_4$ crystal structure has relatively low stability and trends to become more disordered along the z direction when external stimuli are applied, due to the crystal’s enhanced asymmetry compared to the bulk counterpart. Therefore, the piezoelectric response resulted in the z direction is expected to augment in the 2D form.

Figure 4.10. Characterizations of out-of-plane piezoelectricity of 2D GaPO$_4$. (a) AFM topography of a unit cell thick GaPO$_4$ nanosheet. (b-f) Vertical piezoresponse amplitude profiles at different AC driving voltages. The insets represent the statistical distribution of the piezoresponse amplitude variations of GaPO$_4$ film (white colour) and the substrate (grey colour). (g) Average piezoresponse amplitude as a function of the applied AC voltage extracted from the statistical distributions of the amplitude variations of GaPO$_4$ and the substrate. Error bars signify the standard deviations which are introduced to indicate
uncertainty of the measurements. (h) Value of $d_{eff}^{33}$ for GaPO$_4$ films with different thicknesses. The bulk value for $d_{33}$ is extracted from reference$^{58}$. Error bars signify the deviations of slope of piezoelectric amplitude for the driving bias voltage (AC) for experimental $d_{eff}^{33}$. DFT simulations of 2D GaPO$_4$ nanosheets of higher thicknesses are not reported due to difficulties with accuracy and energy convergence.

**Figure 4.11.** Topography and corresponding phase images at different AC voltages during PFM measurements for the GaPO$_4$ flake with unit cell thickness. (a-c) The images show that the morphology of the GaPO$_4$ flake is not affected while applying high electric field on its surface. The phase images reveal significant phase variations between the GaPO$_4$ film and substrate.

The vertical piezoresponse was also explored for GaPO$_4$ nanosheets of different thicknesses (Figure. 4.12). The obtained experimental piezoelectric constant is measured to be within the range from 6.9 to 7.2 pm V$^{-1}$ for two to four unit cell thick (~2.2-4.3 nm) GaPO$_4$ sheets (Figure. 4.12a-c, 4.12e-g). However, more gradual thickness dependence behaviour of $d_{eff}^{33}$ is observed for thicker GaPO$_4$ films which are prepared from multiple van der Waals printing process. Two PFM measurements for the thicknesses of 8 and 11 nm films resulted in
the $d_{33}^{\text{eff}}$ values of 6.6 and 6.1 pm V$^{-1}$, respectively, demonstrating a possible decrease towards that of the bulk value reported in previous literature.$^{58}$

**Figure 4.12.** Characterizations of out-of-plane piezoelectricity of 2D GaPO$_4$ nanosheets with different thicknesses. (a-d) Topography and corresponding vertical piezoresponse amplitude profiles for different 2D GaPO$_4$ nanosheets at various AC driving voltages. (e-h) Average piezoresponse amplitude as a function of the applied AC voltage for different GaPO$_4$ nanosheets obtained from the statistical distributions. Error bars denote the standard deviations of the vertical piezoresponse.

### 4.3.5 DFT simulation results of the piezoelectric performance of GaPO$_4$

To facilitate the calculation of unit cell polarization, a periodic $2 \times 1$ supercell of GaPO$_4$ with a (100) plane is cut from the trigonal bulk phase and the top and bottom oxygen atoms in
the slab are stabilized (Figure 4.13). Single- and two-unit cell thick slabs are constructed from the 2×1 supercell. The thickness of the one-unit cell thick slab is ~1.1 nm, corresponding to the experimentally determined sheet thickness, and ~2.2 nm for the two unit cell thick sheet.

Figure 4.13. A periodic 2×1 unit cell of GaPO₄ with a (100) plane cut from the trigonal bulk phase. This shows the top and bottom oxygen atoms in the slab are hydrogen terminated.

To calculate the vertical piezoelectric constant $d_{33}$, an external electric field, $E$ is applied to the slab perpendicular to the surface, and next the strain of the slab in the direction perpendicular to the surface is calculated. The strain under an applied electric field is calculated using equation 4.1:

$$\eta(E) = \frac{(L(E) - L_0)}{L_0}$$

(4.1)

where $\eta$ is the strain, $L(E)$ is the equilibrium length of the slab along the $z$-axis (perpendicular to the surface direction) under the applied $E$ field and $L_0$ is the equilibrium length under zero applied field. The magnitude of the piezoelectric constant can be defined as the variation in the strain $\eta_j$ in terms of the variation in the applied electric field $E_i$ at zero stress ($\tau$) as:
\[ d_{ij} = -\left( \frac{\partial \eta_{ij}}{\partial E_i} \right)_{\tau=0} \]  \hspace{1cm} (4.2)

In the case of \( i=j=3 \) (in the Voigt notation), \( d_{33} \) refers to the strain and the applied \( E \) field in the \( z \)-direction, perpendicular to the surface. The minus sign in equation (4.2) signifies that the piezoelectric constant is negative if the slab undergoes expansion (positive strain) along \( z \) axis as a response to an increasing external field. During the DFT simulation, an electric field of \( 2.6 \times 10^7 \text{ V cm}^{-1} \) is used (corresponds to an applied voltage of \( \sim 2.6 \text{ V} \)) for the unit cell thick slab, while a slight higher field strength of \( 3 \times 10^7 \text{ V cm}^{-1} \) was used for the bilayer slab. The theoretical values of the piezoelectric constant, \( d_{33} \) are calculated to be approximately \( 8.5 \text{ pm V}^{-1} \) and \( 6.7 \text{ pm V}^{-1} \) in magnitude, respectively, for the single and two unit cell thick slabs indicating the slab undergoing positive strain in response to an increasing field, which is consistent with experiments. The experimental value of \( d_{\text{eff}33} \) for the single unit cell thick GaPO\(_4\) sheet is comparable with DFT calculations with a slight mismatch. On the other hand, the experimental value of \( d_{\text{eff}33} \) (\( \sim 6.8 \pm 0.5 \text{ pm V}^{-1} \)) for two unit cell thick GaPO\(_4\) sheet is in good agreement with the DFT computational results. This demonstrates that there is indeed out-of-plane piezoelectric property for the thicker (two unit cell thick) GaPO\(_4\) sheet.

The discrepancy between the real piezoelectric performance and the simulation result is possibly due to the difference between the real 2D sheet and its assumed model (either physical or mathematical). During our DFT simulation the developed unit cell thick GaPO\(_4\) is considered to be a perfectly flat sheet without any defect. Additionally, the DFT calculations are performed considering a completely homogeneous applied electric field normal to the surface of the entire flake area, which is in obvious contrast with the real piezoelectric measurement of the nanosheets.\(^{23}\) Finally, a comparative assessment between the out-of-plane piezoelectric coefficient of 2D GaPO\(_4\) and some other well-established bulk and 2D piezoelectric materials is provided in Tables 4.1 and 4.2. It is noteworthy that the out-of-plane
piezoelectric coefficient of our synthesized 2D GaPO$_4$ outperforms many of the previous reported results$^{5,60,61}$.

**Table 4.1.** Comparison of $d_{33}$ between some previously reported 2D films and this work.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (nm)</th>
<th>Theoretical simulation $d_{33}$ (pm V$^{-1}$)</th>
<th>Experimental effective $d_{33}$ (pm V$^{-1}$)</th>
<th>Temperature stability ($^\circ$C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>~2</td>
<td>-</td>
<td>23.7</td>
<td>&lt; 350</td>
<td>62</td>
</tr>
<tr>
<td>CdS</td>
<td>2-3</td>
<td>-</td>
<td>16.4$^a$</td>
<td>&lt; 600</td>
<td>63</td>
</tr>
<tr>
<td>Graphene on SiO$_2$</td>
<td>0.34</td>
<td>1,400$^b$</td>
<td>-</td>
<td>-</td>
<td>54</td>
</tr>
<tr>
<td>MoSSe</td>
<td>1.4</td>
<td>5.24</td>
<td>-</td>
<td>&lt; 550</td>
<td>60</td>
</tr>
<tr>
<td>MoSeTe</td>
<td>1.4</td>
<td>6.21</td>
<td>-</td>
<td>&lt; 550</td>
<td>60</td>
</tr>
<tr>
<td>MoSTe</td>
<td>1.4</td>
<td>10.57</td>
<td>-</td>
<td>&lt; 550</td>
<td>60</td>
</tr>
<tr>
<td>WSSe</td>
<td>1.4</td>
<td>5.31</td>
<td>-</td>
<td>&lt; 550</td>
<td>60</td>
</tr>
<tr>
<td>WSeTe</td>
<td>1.4</td>
<td>6.71</td>
<td>-</td>
<td>&lt; 550</td>
<td>60</td>
</tr>
<tr>
<td>WSTe</td>
<td>1.4</td>
<td>9.27</td>
<td>-</td>
<td>&lt; 550</td>
<td>60</td>
</tr>
<tr>
<td>Cs$_3$N$_4$</td>
<td>~2</td>
<td>0</td>
<td>1</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>$\alpha$-GaPO$_4$</td>
<td>~1.1</td>
<td>~8.5</td>
<td>7.5±0.8</td>
<td>&lt; 700</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^a$ The effective $d_{33}$ was later multiplied by 2, resulting in a piezoelectric constant of 32.4 pm V$^{-1}$.

$^b$ The number is extremely high and the value is over 5 times the thickness of the graphene unit cell. So such a measurement is practically unlikely.

**Table 4.2.** Comparison of $d_{33}$ between previously reported bulk materials and this work.

<table>
<thead>
<tr>
<th>Bulk Material</th>
<th>Thickness (nm)</th>
<th>Theoretical simulation $d_{33}$ (pm V$^{-1}$)</th>
<th>Experimental effective $d_{33}$ (pm V$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN</td>
<td>~140</td>
<td>-</td>
<td>3.1</td>
<td>2,64</td>
</tr>
<tr>
<td>AlN</td>
<td>~450</td>
<td>-</td>
<td>5.1</td>
<td>2,64</td>
</tr>
<tr>
<td>ZnO nanobelts</td>
<td>~65</td>
<td>-</td>
<td>14-26</td>
<td>22</td>
</tr>
<tr>
<td>$\alpha$-GaPO$_4$ film</td>
<td>1.1</td>
<td>~8.5</td>
<td>7.5±0.8</td>
<td>This work</td>
</tr>
</tbody>
</table>

4.3.6 Piezoelectric and elastic properties of free-standing GaPO$_4$

Free-standing GaPO$_4$ is further used for exploring possible substrate effects, assessing the effect of flexoelectric component and also for obtaining the elastic modulus of the film. The elastic modulus is of particular importance since it allows assessing the suitability of the
developed films for various applications. The surface topography of a free-standing GaPO₄ is depicted in Figure 4.14a. It is evident from the morphological study that the surface of the free-standing GaPO₄ bulges upward with respect to the substrates surface. The substrate areas surrounding the cavity edges are expected to firmly hold the large and continuous 2D gallium oxide sheet. The difference in van der Waals forces over and surrounding the cavities causes the gallium oxide skin to bulge upward when the substrate is lifted off the liquid metal during synthesis. The bulging feature of the free-standing flake may also be enhanced by the air pocket that is trapped inside the cavity. A likely explanation for this effect is the expected volume change caused by the insertion of phosphorous and additional oxygen atoms into the film during the reaction.

Figure 4.14 b-d elucidates the vertical piezoresponse under different excitation voltages for a free-standing GaPO₄. Relatively high piezoresponse deflection signals around the cavity edges are observed (even at 0 V). The possible origin of the non-zero signal near the cavity edges is the emergence of additional strain gradients that arise due to the sharp depth profile of the cavity. Hence, the flat and uniform surface area of free-standing GaPO₄ is considered for further analysis (area A, Figure 4.15) to avoid any contribution of non-zero out-of-plane polarization. No significant amplitude contrast is evident at high voltages between the free-standing GaPO₄ (area A) and the supported film on the substrate (Figure 4.14c-d), indicating a probability of having nearly identical $d^{eff}_{33}$ coefficients for the free-standing and supported films. Detailed calculations of the piezoresponse amplitude variations for the free standing and supported GaPO₄ film is provided in Figure 4.15.
Figure 4.14. Piezoelectric properties of free-standing GaPO₄ nanosheet. (a) AFM topography and (b-d) vertical piezoresponse of free-standing GaPO₄ nanosheet at different AC drive excitation.

Figure 4.15. Vertical piezoresponse of free-standing GaPO₄ nanosheet. (a) Piezoresponse at 0V (background) and (b) 3V, (c) 5V. d-e Statistical distributions of the piezoresponse amplitude variation for the flat and uniform surface area of free standing (area A) GaPO₄ and supported (area B) GaPO₄.
films at different voltages (3V and 5V) and the background (0V). The slope of the piezoresponse amplitude vs AC voltage graphs in both cases are in good agreement.

The nano-mechanical properties of free-standing GaPO₄ have been mapped using peak-force quantitative nano-mechanical (PF-QNM) mapping in order to explore the mechanical strength of the synthesized GaPO₄. This method has been previously applied successfully to other examples of thin films.⁶⁶,⁶⁷ Quantitative results during the PF-QNM scan can be presented as Derjaguin–Mueller–Toporov (DMT) modulus distributions (stiffness distribution). The topographical image of a free-standing GaPO₄ sheet during PF-QNM scan is illustrated in Figure. 4.16a along with the DMT (elastic) modulus map (inset). The DMT modulus distribution (Figure. 4.16 b) reveals that the modulus situates mainly in the range of 12–16.5 GPa. This large elastic modulus demonstrates that the synthesized 2D GaPO₄ sheets are suitable for the manufacture of free-standing membrane based piezoelectric applications. The peak-force quantitative nano-mechanical mapping is next used for estimating the breakdown threshold load for the free-standing GaPO₄ flake by varying the force applied to the tip. The threshold force is found at around 200 nN to break the GaPO₄ membrane (Figure. 4.16 c-e).
Figure 4.16. Piezoelectric and elastic properties of free-standing GaPO$_4$ nanosheet. (a) AFM image of a free-standing GaPO$_4$ flake with DMT modulus map (inset). (b) DMT modulus distributions measured for the flat section (area B of e) of the GaPO$_4$ sheet. The Gaussian mean value of the modulus is found around $15.66 \pm 0.0095$ GPa. (c) AFM image of a suspended GaPO$_4$ nanosheet (before the breakdown occurred) on a cavity with 2 $\mu$m depth. (d) AFM image of the fractured membrane after applying 200 nN load to the tip. (e) Cross sections of the AFM topographic maps of the free standing GaPO$_4$ at two different forces.

4.4 Conclusions

Liquid metals present many potential applications\textsuperscript{68-75} and this work signifies one of the major capabilities for this family of materials, that is their implementation as a reaction media for printing 2D materials which can be used in a variety of applications. The work introduces
a scalable and facile method for synthesising a previously inaccessible, ultra-thin 2D material, GaPO₄, by harvesting the naturally occurring oxide skin of liquid gallium followed by a vapour phase phosphatization process. The unique synthetic approach is simple, cost effective and utilizes relatively low temperatures, providing new avenues for creating extraordinarily large-area, highly uniform 2D GaPO₄ films. Furthermore, these films are compatible with high temperature fabrication procedures used for surface processed chips and high temperature applications up to 600 °C. Here the first experimental evidence of strong out-of-plane piezoelectricity of a unit cell thick GaPO₄ sheet is demonstrated which is further confirmed by the DFT simulations. The observed piezoelectricity for unit cell thick GaPO₄ nanosheet is relatively high, achieving experimental and theoretical $d_{33}$ value of $7.5 \pm 0.8$ pm V⁻¹ and ~8.5 pm V⁻¹, respectively, which holds promise for 2D material based piezotronic sensing and energy harvesting.

The vertical piezoelectric response for free-standing GaPO₄ has also been reported, which is found to be similar to the supported films. The findings highlight that ultra-thin GaPO₄, can be a promising candidate for nano-electromechanical systems requiring high temperature resistant piezoelectric materials. It can further be exploited for creating surface mounted piezo-responsive sensing elements. Overall, this study leads to promising frontiers towards embedding atomically thin piezoelectric building blocks into large-area devices, which may be utilized to harvest the kinetic energy of various mechanical vibrations to power flexible devices.
4.5 References


Wagner, C. D. et al. *NIST Standard Reference Database 20* (ed The National Institute of Standards and Technology (NIST)) (2012 (last updated)).


Chapter 5

Synthesis of centimetre-scale ultra-thin 2D gallium nitride (GaN) nanosheets from liquid metal derived oxide layer †

5.1 Introduction

Since the emergence of graphene, a large variety of two-dimensional (2D) materials have been reported, leading to new paradigms in the design of electronic and optical systems.1-3 Until recently, the discovery of new 2D crystals has been restricted to intrinsically layered crystals that can be exfoliated into 2D nanosheets, significantly limiting the choice of materials that can be considered for the design of devices and functional heterostructures.2,4 However, a considerable need exists for the creation of ultra-thin nanosheets of non-layered materials, to allow accessing new atomically thin systems with novel capabilities that have been predicted through computational methods.4-6 New methods for the deposition of high quality and low cost 2D gallium nitride (GaN) can fundamentally change the future prospects of such industries. As such, in this work the synthesis of extraordinarily large-area ultra-thin GaN has been reported using an ammonolysis strategy on liquid metal derived ultra-thin gallium oxide nanosheets. It is also shown that the method can be expanded to include the fabrication of 2D InN nanosheets.

†The contents of this chapter have been published as N. Syed, et al. Syed, "Wafer-sized ultra-thin gallium and indium nitride nanosheets through the ammonolysis of liquid metal derived oxides." Journal of the American Chemical Society 141,104-108(2019).
Gallium nitride is a semiconductor of great technological importance with many diverse applications due to its excellent electronic and optical properties.\(^7,8\) Crystalline GaN adopts the wurtzite structure, featuring covalent bonds in all three dimensions, and can thus not be mechanically exfoliated.\(^9\) Conventional methods for depositing thin films of GaN are various, and amongst them, processes based on elemental epitaxial or chemical vapor deposition techniques are the most common.\(^10\text{-}14\) While elemental epitaxial methods allow the controlled formation of ultra-thin films, they involve considerable costs. Conversely, lower costs CVD methods do not allow thin films with several unit-cell thicknesses to be achieved due to inherent nucleation. As such, the development of a scalable method for the synthesis of 2D GaN which allows for the deposition of large-area, highly crystalline quality and substrate independent, GaN nanosheets, is necessary in order to reduce the manufacturing cost of 2D GaN and to open the possibility of forming GaN on a range of different substrates. The chapter introduces the synthesis of centimeter scale 2D GaN and InN nanosheets using liquid metal derived oxides which can be deposited directly onto different flat substrates. The content of this chapter was published as an article in Journal of the American Chemical Society.\(^15\)

5.2 Experimental section

5.2.1 Synthesis of extra ordinary large 2D GaN nanosheets

The synthesis of 2D GaN comprises of a two-step process. 2D Ga\(_2\)O\(_3\) sheets were first synthesized from liquid gallium. The exfoliated film was subsequently transformed to GaN using an ammonolysis reaction between gallium oxide sheet and urea.

5.2.1.1 Squeeze-printing process of the 2D Ga\(_2\)O\(_3\) sheet
Gallium melts at 29.76 °C, therefore this entire process was conducted on a hotplate with temperature set at 50 °C. A gallium droplet with radius of ~1-2 mm (liquid gallium droplet was collected using a needle) was placed on a SiO2/Si substrate (Figure 5.1). A second SiO2/Si wafer was firmly pressed onto the droplet, effectively squeezing the droplet into the shape of a thin metal film.16,17 Pressure was applied to the centre of the top substrate with a fingertip to spread the droplet uniformly between the two substrates. If excessive force is used during the squeezing step, the substrates can break or slide laterally, which may damage the synthesized nanosheet. After the squeezing process, the top substrate was lifted and separated vertically, avoiding lateral movements. To quantify the applied force, substrates were placed on a scale and the necessary force for successful transfer was measured, which was ranging from 0.5 to 3 N.18 The strong van der Waals bond between gallium oxides and the substrate enhance the delamination process of the oxide skin formed on the surface of the droplet. The small remaining liquid metal micro-droplets were then removed using a solvent assisted mechanical cleaning protocol (Figure 5.1). High quality Ga2O3 sheets with large lateral dimensions of more than several centimetres (Figure 5.2) could be efficiently exfoliated on both substrates with this squeeze printing method. Substrates featuring high surface roughness were found to be not conducive to the process (Figure 5.3).

Figure 5.1. (a) Schematic illustration of the van der Waals 2D squeeze printing technique of large Ga2O3 nanosheets. The pristine liquid metal droplet is first exposed to an oxygen containing environment. Pressing the liquid metal between two suitable substrates allows transferring the interfacial oxide layer on the both substrates. After separating the substrates, very large and continuous ultra-thin gallium oxide films reaching few centimetres are observed.
Figure 5.2. (a) Synthesized Ga$_2$O$_3$ on SiO$_2$ (220nm)/Si wafer after mechanical cleaning as mentioned above, shows homogeneous sheet featuring lateral dimensions spanning several centimetres. (b) AFM topography of a 2D Ga$_2$O$_3$ layer and height profile along the magenta line (inset). (c-d) XPS analysis of the Ga$_2$O$_3$ sheet after cleaning. (c) Peak observed at a binding energy of 530.1 eV corresponds to O 1s state of Ga$_2$O$_3$. (d) The characteristic main broad peak at 20.2 eV in the Ga 3$d$ region signifies the valence state Ga$^{3+}$ in Ga$_2$O$_3$. The observed binding energies are all consistent with the previously reported values of Ga$_2$O$_3$.$^{19}$

Figure 5.3. 2D Ga$_2$O$_3$ synthesized on different substrates: (a) glass, (b) quartz and (c) fluorine-doped tin oxide (FTO). Both glass and quartz substrates feature a comparatively low surface roughness, enabling the deposition of large-area, homogeneous and continuous 2D Ga$_2$O$_3$ films. On the other hand, the FTO glass substrate has a surface roughness of approximately 15 nm. The increase in roughness significantly affects the synthesis process of the Ga$_2$O$_3$ films, leading to significant loss of uniformity and continuity of the nanosheets.

5.2.1.2 Transformation of 2D Ga$_2$O$_3$ to 2D GaN sheets via ammonolysis process
The synthesized gallium oxide sheets are transformed to gallium nitride via an ammonolysis reaction method following a chemical vapour route (Figure 5.4). The ammonolysis of Ga$_2$O$_3$ sheets was performed in a quartz tube placed in a horizontal tubular furnace. Urea was used as a source material for the ammonolysis process as urea decomposes into NH$_3$ and isocyanic acid (HNCO) as follows:

$$\text{NH}_2\text{-CO-NH}_2 \rightarrow \text{HNCO} \ (\text{g}) + \text{NH}_3 \ (\text{g})$$  \hspace{1cm} (1)

Isocyanic acid formed by reaction (1) is quite stable in the gas phase, but it easily hydrolyzes on the surface of metal oxides, producing ammonia and carbon dioxide.

$$\text{HNCO} \ (\text{g}) + \text{H}_2\text{O} \ (\text{g}) \rightarrow \text{NH}_3 \ (\text{g}) + \text{CO}_2 \ (\text{g})$$

Urea pellets were placed on an alumina boat in the lower temperature region of the tube furnace. The Ga$_2$O$_3$ samples were placed in an upsidedown position on another alumina boat at the center and heated to 800 °C. A heating rate of 10 °C per min resulted in the best results. N$_2$ gas with a flow rate of 50 sccm was used as the carrier gas. The total duration for the entire process was 90 min after the temperature of the system had reached 800 °C. At these temperatures, 2D Ga$_2$O$_3$ samples reacted with the ammonia vapour to grow the 2D GaN films. The synthesized GaN samples were then cooled to room temperature. A nitrogen purged glovebox or vacuum desiccator was used for prolonged storage of the samples.

Further study shows that reaction temperature has a dramatic effect on the formation of 2D GaN. Synthesis at lower temperatures was found not to be successfully converting Ga$_2$O$_3$ into wurtzite GaN (Figure 5.5). Full transformation of the new wurtzite GaN could be obtained when the reaction temperature was 700°C. Fig. 5.5d shows the XRD patterns of nanoparticles prepared at 700°C dominated by several peaks associated with the formation of $\beta$-Ga$_2$O$_3$ and gallium oxynitride. These represent either unreacted materials, due to slow reaction kinetics, or the formation of new phase of Ga$_2$O$_3$. The XRD results obtained for samples synthesized at 800°C are dominated by the X-ray diffraction peaks of GaN; suggesting that the synthesis is
thermodynamically favoured at higher temperatures and that greater thermal energy is required for the full transformation of Ga$_2$O$_3$ to GaN. Further investigations were carried out at varying reaction temperature in the range of 900–1000 °C to explore the morphological changes and oxygen doping of synthesized wurtzite GaN products (Fig. 5.10).

**Figure 5.4.** Schematic setup for the chemical vapour phase reaction system used for synthesizing GaN nanosheets using a horizontal tube furnace.

**Figure 5.5.** XPS spectra of (a) O 1s, (b) N 1s and (c) Ga 2p regions of 2D nanosheets synthesized at 700 °C. The binding energy of N 1s region significantly differs from N 1s levels in GaN. The XPS of O 1s region also shows an intense oxide peak that does not correspond to occasional oxygen defects but rather to the formation of a different material.(d) XRD pattern of as synthesized GaN nanoplatelets obtained from ammonolysis reaction conducted at 700 °C.

### 5.2.2 Mechanical cleaning procedure

A simple mechanical ethanol washing method was used to remove any liquid metal inclusions left on the Ga$_2$O$_3$ samples as shown in Figure 5.1. During the cleaning procedure ~100 ml of ethanol was heated to boiling point (78.24°C) in a beaker over a hotplate. Following
this, the SiO₂/Si wafer with an exfoliated 2D Ga₂O₃ sheet was submerged in the hot ethanol with the help of tweezers (see Figure 5.1). The metal inclusions can be completely removed by wiping the submerged SiO₂/Si wafer using a wiping tool (cotton bud). The liquid metal particles are easily and efficiently removed by the wiping tool. The gallium oxide flakes were found to be robust and remained attached to the silicon oxide surface during the wiping process due to a very strong van der Waals adhesion between gallium oxide sheets and the substrate. The liquid gallium, on the other hand, was only weakly adhered to the deposited gallium oxide and can easily be removed by wiping the excess liquid metal leaving the 2D Ga₂O₃ sheets clean and damage free.

5.2.3 Synthesis of 2D GaN nanoplatelets

The synthesis process of 2D Ga₂O₃ nanoplatelets was performed in a two-step process comprising of liquid gallium droplet sonication in DI water and subsequent annealing, as reported in our previous work.²¹ Next the 2D Ga₂O₃ nanoflakes was transformed to GaN nanoplatelets by following the ammonolysis reaction as discussed above.

5.2.4 Two-step liquid metal based synthesis of 2D InN sheets

The synthesis of 2D InN comprises of a two-step process. First 2D In₂O₃ sheets were synthesized from liquid indium metal that was melted on a hotplate with temperature set at 200 °C following the squeeze printing method as discussed above. The oxide was then transformed into InBr₃ by treating with HBr fumes (Figure 5.6). The HBr-treated nanosheets were subsequently transformed to InN using the above-mentioned ammonolysis reaction at 630 °C for 90 min. N₂ with a mixture of 1% H₂ gas with a flow rate of ~50 sccm was used as the carrier gas.
Figure 5.6. An intermediate bromination step to transform In$_2$O$_3$ to InBr$_3$. In$_2$O$_3$ nanosheet is exfoliated using the above mentioned squeeze printing method. During the process, 2D In$_2$O$_3$ printed layer is exposed to HBr vapor for ~20 seconds.

5.2.5 Fabrication of the Hall device

Multi terminal Hall devices were fabricated on SiO$_2$ (300 nm)/Si substrates. The GaN nanosheet was synthesized as described above. The electrodes were realised with a maskless photolithography processes on top of the GaN sheet using the Maskless Aligner MLA150 (Heidelberg Instruments). The six metal electrodes Ti/Ag (5/40 nm) for each device were deposited using electron beam evaporation. Finally, the deposited GaN samples were immersed in acetone for the lift off process followed by isopropyl alcohol cleaning to expose the patterned electrodes.

5.2.6 Hybrid density functional theory (DFT) calculations

DFT calculations were performed using Gaussian basis set abinitio package CRYSTAL14.\textsuperscript{22,23} The PBEsol0 hybrid exchange-correlation functional, (which uses the PBE functional revised for solids (PBEsol)\textsuperscript{24} with 25% Hartree-Fock exact exchange) was used to
calculate the slab energies and electronic density of states. For all atoms a Triple Zeta Valance basis set (TZV), with polarization functions, was used to model the electrons.\textsuperscript{25}

### 5.2.7 Instrumentation and characterizations

A Bruker Dimension Icon AFM was used to obtain the surface thickness and topography images using “Scanasyst-air” AFM tips. Gwyddion 2.36 software was utilized for AFM image processing and analysis. The low and high resolution TEM measurements were performed using a JEOL 1010 and a JEOL 2100F with acceleration voltages of 100 and 200 kV, respectively. The Gatan microscopysuite1.8.4. Software Package was used for TEM/HRTEM analysis. Thermally and mechanically robust Si$_3$N$_4$ TEM (Ted Pella, 21587-10) membranes were used to develop the TEM samples that were prepared by directly printing the gallium oxide sheet onto TEM membrane and subsequent ammonolysis. Normal carbon based TEM grids did not sustain the high synthesis temperatures and disintegrated at temperatures above ~400 °C. Therefore, the carbon based TEM grids were substituted with the high temperature resistant TEM grid which was a Si$_3$N$_4$ based material. The Si$_3$N$_4$ TEM grid allows experiments requiring temperatures up to 1000 °C which suits the synthesis process presented in this work. The Si$_3$N$_4$ TEM grids also feature pores which are completely empty and allow analysis of the suspended flakes through the pore without contribution of the TEM grid. XRD was performed using a Bruker D8 micro-diffractometer equipped with a Vantec 500 detector and 0.5 mm collimator. A 40 kV copper source with a current of 40 mA was used for the X-ray generation. XPS analysis was conducted on samples grown on SiO$_2$/Si substrates. Thermo Scientific K-alpha XPS spectrometer equipped with a monochromatic Al Kα source ($h\nu = \sim 1486.6$ eV), and a concentric hemispherical analyzer (CHA) were used to determine the chemical composition of these 2D materials. The analyzer was operated with a pass energy of 100 eV to record the core-level spectra and 50 eV to record the valance band spectra. A low-
energy electron flood gun was utilized to remove any the surface charging effect of the synthesized material. Optical absorption spectroscopy of samples deposited on quartz slides was conducted on an Agilent Cary 60 spectrophotometer in conventional configuration and an Agilent Cary 7000 spectrophotometer equipped with an integrating sphere to account for scattering contribution. Hall measurements were performed using a commercial physical property measurement system (PPMS - Quantum Design, Inc.).

Atomic resolution-AFM characterization: Images were obtained using a Cypher ES Atomic Force Microscopes (Oxford Instrument, Asylum Research, Santa Barbara, CA, USA) at room temperature (25°C) using amplitude modulated-AFM (AM-AFM) in milli-Q water. OMCL-AC55TS (Olympus Corporation, Japan, nominal spring constant (kc) = 55 N/m) were employed in this study. To minimize the imaging force, a set-point ratio (Imaging Amplitude (A)/free amplitude (A0)) of >0.7 – 0.8 was maintained during imaging.26 Each cantilever was calibrated using the thermal spectrum method,27,28 in liquid prior to use, and the lever sensitivity was determined using force spectroscopy. The spring constant is resolved via the inverse optical lever sensitivity (InVOLS) using force curve measurements on the hard surface. The features of all the images presented here rotated as the scan angle was changed and scaled correctly with scan size, meaning that they are not a result of imaging artefacts.

5.3 Results and discussions

5.3.1 Characterizations of 2D GaN nanosheet

The synthesis relies on a two-step process utilizing the printing deposition of 2D Ga2O3, which is then converted into GaN using ammonolysis in a tubular furnace. The Ga2O3 printing process was modified from our previous work,4,19,29 utilizing the squeeze printing method. The technique involves placing a small droplet of the liquid gallium onto a desired substrate, followed by squeezing with a second substrate from the top, spreading the droplet to cover the
entire desired area. The Cabrera-Mott oxidation process in ambient air leads to the formation of a surface oxide on the expanding liquid gallium. The liquid nature of gallium allows the surface oxide to attain uniform contact with the SiO₂ surface, yielding van der Waals attachment. The solid state and the presence of a network of covalent bonds (either crystalline lattice or amorphous network) within the surface oxide as well as the substrate ascertain large area interactions, leading to macroscopic attachment. The high surface tension of liquid gallium further ensures that the liquid gallium returns into spherical shaped micro-droplets during the separation of the two substrates. In this work, a large and continuous ultra-thin gallium oxide film which reached lateral dimensions exceeding several centimeters (Figure 5.2) was obtained. Isolated oxide sheets were then converted into GaN using a high temperature ammonolysis reaction (Figure 5.7). Urea was used as an ammonia precursor, with the reaction occurring at 800 °C. Optical micrographs of the final product (synthesized at 800 °C) revealed that the nanosheet retained its original morphology, while the color contrast had changed, indicating a change in refractive index of the material (Figure 5.7).
Figure 5.7. Synthesis process of the centimeter scale 2D GaN nanosheet. (a) Schematic illustration of the squeeze printing technique to exfoliate oxide skin of gallium metal onto the substrate. The pristine liquid metal droplet is squeezed between two suitable substrates which allow transferring the Ga$_2$O$_3$ layer. Optical image of exfoliated Ga$_2$O$_3$ on SiO$_2$ (300nm)/Si is presented on the right-hand side. (b) Synthesis process of the 2D GaN nanosheet from 2D Ga$_2$O$_3$ using ammonolysis. The crystal structure of GaN exhibits a unit cell (dotted box) with cell parameters of 5.19 Å along the long axis and 3.19 Å along both of the short axes. Optical image of the synthesized GaN on SiO$_2$ (300nm)/Si is exhibited on the right side.

Atomic force microscopy (AFM) was conducted on the deposited Ga$_2$O$_3$ sheets which revealed that the oxide is continuous atomically flat nanosheet with a thickness of ~1.4 nm (Figure 5.2 b), which is slightly thinner than sheets isolated through previously published liquid metal printing techniques. AFM analysis revealed a sheet thickness of nearly ~1.3 nm (Figure 5.8a), which corresponds to three wurtzite GaN unit cells. Atomic resolution AFM imaging (insets) identified a repeated crystal pattern, across the substrate, with a lattice constant of 5.18 Å which corresponds to a wurtzite GaN nanosheet that grew along the (001) direction. The 2D nanosheet was found to be highly crystalline. To gain further insight into the atomic structure of the synthesized nanosheets, high resolution transmission electron microscopy (HRTEM) was conducted. Gallium oxide was directly deposited onto the TEM grid using a previously published van der Waals exfoliation method$^{4,19}$, with the sample being subjected to the ammonolysis process. Laterally large, ultra-thin nanosheets could be found during TEM imaging, with the sheets being highly translucent, indicating the thin nature of the final GaN sample (Figure 5.8 b). Atomic resolution images of the crystal lattice and the associated fast Fourier transform (FFT) analysis also indicates high crystallinity of the synthesized nanosheets with the lattice parameters matching wurtzite GaN which are shown in the insets of Figure 5.8 b. Observation of the (002) plane in the HRTEM images is consistent with a sheet growth along the (001) direction.$^{34,35}$
To assess that a quantitative conversion of Ga$_2$O$_3$ to GaN has occurred, XPS was utilized (Figure 5.9a-b). The characteristic doublets for Ga 2p region, 2$p_{1/2}$ and 2$p_{3/2}$, are positioned at $\approx$1144.8 and $\approx$1117.9 eV, respectively. The main broad N 1s peak centered at $\approx$397.6 eV corresponds to the expected binding energy for nitrogen region present in GaN. The Ga 2p and N 1s peak locations match well with the previous literature obtained for GaN,$^{36}$ and no peaks associated with elemental Ga and Ga$_2$O$_3$ were observed.$^{19}$ Interestingly, the valence band XPS spectrum featured a high density of states in the region between 8-12 eV (Figure 5.9c). This feature indicates a substantial fraction of the nitrogen sites has been substituted by oxygen atoms$^{37}$ while no discernible shifted peaks is observed in the Ga 2p peaks due to the
Ga-O bond. As for the Ga 2p spectrum, the peak position for the Ga-N bond and Ga-O bonds overlap between 1116.9–1118.9 eV.\textsuperscript{38} In addition the concentration of oxygen doping in the synthesized GaN is comparatively diminutive leading to a nearly symmetric peak for Ga 2p region. In ambient air, oxygen can occupy nitrogen sites in the GaN lattice due to the similar bond length of the Ga-N and Ga-O bonds, without causing detectable distortion to the wurtzite lattice, rendering the XRD patterns and HRTEM images indistinguishable.\textsuperscript{37,39}

Due to the ultimately thin nature of the synthesized GaN nanosheets, this surface substitution is expected to have significant effects on the optical and electronic properties. Tauc plots obtained during UV-vis analysis (Figure 5.9d), revealed that the band-gap of the 2D nanosheet is \( \sim 3.5 \) eV, which is considerably lower than that of previously reported graphene encapsulated 2D GaN nanosheets.\textsuperscript{40} This lower band-gap may be expected since oxygen substitution in wurtzite GaN samples is well known to lead to an upward shift of the valence band due to \( \text{O}_2p\text{-N}_2p \) orbital hybridization.\textsuperscript{41} The 2D GaN samples exhibit considerable signs of quantum confinement,\textsuperscript{42,43} since the determined band-gap of the synthesized nanosheets was wider than that of published bulk morphologies of oxygen doped GaN (band-gap between 2.5 and 3 eV), while also being wider than the synthesized 2D GaN nanoplatelets, which featured an increased sheet thickness of around 8 nm and an optical band-gap of \( \sim 3.2 \) eV (Figure 5.13).
Figure 5.9. Material characterizations and electronic band structure properties of 2D GaN. (a-b) XPS results of the 2D GaN for the regions of interest, (a) Ga 2p and (b) N 1s. (c) XPS valence band spectrum affirming an energy difference of ~2.7 eV between the valence band maximum (VB\text{max}) and Fermi level (E_F). The spectrum was decomposed into three peaks responsible for different bonds. (d) Tauc plot used for ascertaining the electronic band-gap for GaN with simplified electronic band diagram (top left).

Higher synthesis temperatures (900 -1000 °C) were explored in order to investigate whether the degree of oxygen substitution may be decreased. The identical ammonolysis reaction as described in section 5.2.1 was followed. When the ammonolysis was conducted at 900°C and 950°C, oxygen contributions to the valence band spectrum associated with Ga_{4s}-O_{2p} peak showed a decrease in intensity, demonstrating a reduction of the degree of oxygen substitution in the GaN crystal structure (Figure 5.10 b, e). However, the complete removal of oxygen could not be achieved. Furthermore, morphological degradation of the GaN nanosheets synthesized at 950 °C was observed during AFM analysis (Figure 5.10d). The valence band spectrum for 2D GaN synthesized at 1000 °C was not explored since the sheet featured significant morphological degradation (Figure 5.10 g-h). These observations indicate
that the 2D GaN nanosheets do contain a degree of residual oxygen that originates from the 2D Ga$_2$O$_3$ sheet. However, surface substitution of N atoms with O in air has been described in GaN, and as such both pathways towards the formations of oxygen defects should be considered. The optical properties (band-gap) of the 2D GaN sheets synthesized at higher temperatures were relatively similar to the properties of samples synthesized at 800°C. This is consistent with the computational analysis for the electronic DOS of 2D GaN nanosheets (Figure 5.11).

![Figure 5.10.](image)

Figure 5.10. (a-c) AFM topography, valence band spectrum and Tauc plot for 2D GaN nanosheet synthesized at 900 °C. (d-f) AFM image, valence band spectrum and Tauc analysis for 2D GaN nanosheet grown at 950 °C. (g-h) AFM topography and corresponding height profile of GaN nanosheets synthesized at 1000 °C showing substantial morphological degradation.

Experimental explorations of the effect of oxygen substitutions in bulk GaN morphologies have revealed that oxygen doping leads to a reduction of the band-gap.

123
Quantum confinement in 2D morphologies on the other hand, has been shown to increase the band-gap.\textsuperscript{44} To assess the effects of these competing processes, electronic DOS of the synthesized GaN nanosheet was calculated using DFT modelling (Figure 5.11), confirming that both processes result in profound modulations of the electronic band structures.

A periodic slab of GaN with a non-polar (110) surface was cut from the wurtzite bulk phase (Figure 5.11a-b). Slab calculations were conducted using a $9\times9\times1$ Monkhorst-Pack k-point mesh. The thickness of the slab was approximately 1.28 nm corresponding to the experimentally estimated monolayer thickness. For the oxygen doped GaN slab, oxygen atoms substitutionally replaced N atoms such the percentage of O doping is 6% corresponding to the experimentally determined doping value. One of the first nearest neighbour gallium (Ga) atom is hydrogen terminated in order to keep the Ga atom 3 coordinated while the corresponding O atom is 2 coordinated as shown in Figure 5.11b.

Figure 5.11c shows the total electronic density of states of the undoped (continuous line) and oxygen doped (dashed line) GaN slab. For each slab the electronic DOS has been shifted so that the Fermi level is set to 0 eV. Analysis of the band structure indicates the undoped GaN slab has a direct band-gap of 3.65eV while the O doped GaN slab has a direct band-gap of 2.85eV, which in good agreement with experimental results. The DFT revealed that oxygen substitution leads to a reduction of the band-gap, while quantum confinement results in a widening of the band-gap.
The room temperature carrier mobility for GaN nanosheets grown at 800 °C was determined using Hall-effect measurements (Figure 5.12). Six terminal Hall-bars were fabricated to determine the carrier mobility and carrier density of the 2D GaN. The Hall carrier mobility measurements of the micro-fabricated devices were performed in a sample-in-vacuum cryostat with a built in superconducting magnet. The devices were kept at 300 K (room temperature), and characterized by using variable magnetic fields (B) from -4T to 4T.

The typical measurement consists of injecting the current (I) between electrodes labelled 1 and 4 as shown in Figure 5.12a and recording the longitudinal resistance $R_{xx}$ between electrodes 2, 3 and Hall resistance $R_{xy}$ between electrodes 3 and 5. The Hall carrier mobility ($\mu$) can be calculated by combining Hall coefficient $R_H = \frac{R_{xy}}{B}$ and longitudinal conductivity $\sigma_{xx} = \frac{L}{(W, R_{xx})}$ and $\mu = R_H \times \sigma_{xx}$

Here $B$ is the magnetic field, $W$ and $L$ are the channel width and length, respectively. The deduced carrier density of the 2D GaN was also calculated and found to be approximately
1.6\times10^{10} \text{ cm}^2 \text{ using } n_{2D} = \frac{1}{e.R_H} \text{ where } e \text{ is the unit charge } 1.6\times10^{-19} \text{ C. The observed carrier mobility was } 21.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \text{ which is comparable to large-area CVD grown MoS}_2. As such, the developed synthesis technique and the isolated 2D GaN should be considered suitable for the development of optoelectronic and electronic 2D devices.

**Figure 5.12.** (a) SEM image of the six-terminal Hall device. (b) Hall resistance ($R_{xy}$) of the 2D GaN film as a function of applied magnetic field ($B$). An optical image of the fabricated Hall device is shown in the lower right inset.

### 5.3.2 Characterizations of 2D GaN nanoplatelets

To confirm that the process results in a phase pure product, a sample of 2D Ga$_2$O$_3$ nanoplatelets\textsuperscript{21} was further utilized as a GaN precursor. The powder XRD of these GaN nanoplatelets closely resembled the XRD pattern of wurtzite GaN with no impurity phases. Detailed results for the 2D GaN nano- platelets are provided in Figure 5.13.
Figure 5.13. Characterizations of 2D GaN nanoplatelets. (a) AFM topography of a GaN nanoplatelet and height profile along the magenta line (inset). (b) TEM image of the GaN nanoplatelets. (c) XRD spectrum of the synthesized 2D GaN nanoflakes. All of the peaks match well with the previous reports.47 (d) The GaN nanoplatelets featured an optical band-gap of 3.2 eV which demonstrates a good agreement with previous reports of GaN nanoparticles and films.48 (e-f) XPS results of Ga 2p and N 1s regions of the GaN nanoplatelets. The main two components 2p_{1/2} and 2p_{3/2} of Ga 2p region are positioned at ~1144.7 and ~1118.2 eV, respectively, which is consistent with previous studies.36 The broad N 1s peak centred at ~397.4 eV is in good agreement with the expected nitrogen peak for GaN.36 All the XPS spectral energies were obtained by calibrating relative to the C1s peak located at 284.8 eV.49

5.3.3 Characterizations of 2D InN nanoplatelets

In order to assess the versatility of the synthesis method, an adapted synthesis process utilizing liquid indium instead of liquid gallium was explored. InN is a group III-V semiconductor with very interesting electronic and optical properties that may find applications
in laser diodes, light emitting diodes and several further optoelectronic devices.\textsuperscript{50} InN is less stable than GaN and undergoes significant decomposition to In and N at elevated temperatures (above 650 °C),\textsuperscript{51,52} while also undergoing morphological transformations following the vapor-solid mechanism. Due to these limitations, direct conversion of 2D In\textsubscript{2}O\textsubscript{3} to 2D InN was found to be not practical, and an intermediate bromination step was utilized that effectively converted In\textsubscript{2}O\textsubscript{3} into the more reactive InBr\textsubscript{3} through the exposure of the 2D In\textsubscript{2}O\textsubscript{3} nanosheet to HBr vapor (Figure 5.6).\textsuperscript{29} Ammonolysis was then successfully carried out utilizing urea as the NH\textsubscript{3} source at a temperature of ~630 °C. XPS analysis of the product confirmed the successful synthesis of InN as shown in Figure 5.14 c-d, with an AFM determined thickness of ~2 nm. High resolution AFM analysis was utilized to confirm the crystallographic properties of the final product over HRTEM imaging, since the necessary bromination step rendered the 2D sheet to be too fragile to sustain sheet integrity during synthesis. A crystal lattice with a constant of 5.5 Å was determined, which is in excellent agreement with the structure of wurtzite InN (Figure 5.14b).\textsuperscript{52,53}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Figure 5.14. (a) Optical images of synthesized InN showing homogeneous nanosheets featuring lateral dimensions exceeding centimetres. (b) AFM image of 2D InN sheet and height profile along the magenta line. The insets are showing the high resolution AFM analysis for the 2D InN sheet. A repeated}
\end{figure}
crystal with a lattice constant of 5.5 Å is determined which is in consistent with wurtzite InN.\textsuperscript{53} (c, d) XPS was employed to obtain the chemical bonding states of the synthesized 2D InN. The characteristic main broad peak at 444.7 eV and 452.2 eV corresponds to In 3d\textsubscript{5/2} and In 3d\textsubscript{3/2} peak respectively in InN. The peak centred at ~396.6 eV corresponds to the N 1s peak of InN. The observed binding energies are all consistent with previously reported work\textsuperscript{54} which further confirms the stoichiometry of the printed InN. (e) Tauc plot for synthesized 2D InN, revealing an effective optical band-gap of ~3.5 eV.

5.4 Conclusions

In conclusion, a liquid metal-based van der Waals printing technique exploiting Cabrera-Mott oxidation processes was reported that allowed depositing centimeter sized 2D gallium and indium oxide sheets. These sheets could then be converted into highly crystalline 2D Wurtzite GaN and InN, using a urea based ammonolysis reaction. The 2D GaN sheet was found to be oxygen doped leading to a narrower than expected band-gap, while featuring a high Hall-effect carrier mobility of 21.5 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}. This work provides a pathway towards integrating 2D morphologies of well-known high performance semiconductors into emerging 2D material based electronic and optoelectronic devices and heterostructures using a liquid metal based techniques.

5.5 References


Chapter 6

Conclusions

6.1 Concluding Remarks

The work demonstrated in this PhD research was devoted to address the research gaps and overcome the current challenges outlined at the beginning of this thesis. The main aims of this research were to utilize liquid gallium chemistry as a potential pathway to synthesize two-dimensional materials by harvesting its naturally grown surface oxide skin. These objectives were completed throughout the production of three published works as the first author and an additional thirteen co-authored papers. This thesis has contributed to the growing body of knowledge regarding the synthesis of large area 2D gallium compounds and has led to the development of 2D gallium-based materials with non-stratified structure through facile and low cost reaction methods. Detailed discussions regarding the outcomes of developed materials and their functional applications are organized as follows:

6.1.1 Synthesis of 2D Ga2O3 featuring trap state absorption

During the first stage of the project, a reaction approach centred on the liquid metal/H2O interface was used to develop a platform for the exfoliation of 2D nanostructures. A scalable, low cost and fast sonication-assisted exfoliation route has been demonstrated for creating suspension of gallium hydroxide and gallium oxide nanoflakes without the use of any toxic chemicals or surfactants. This two-step synthesis method was based on sonicating liquid
gallium droplets immersed in DI water and subsequent annealing of the detached native hydrated oxide skin. The synthesized nanoparticles were thoroughly investigated revealing the presence of porous hexagonal $\alpha$-Ga$_2$O$_3$ nanoflakes with plate and rod like structures. The obtained nanoflakes proved to be promising for application as a functional material for the mitigation of organic pollutants under solar irradiation. It was shown that the as-synthesized porous Ga$_2$O$_3$, despite its relatively wide band-gap (4.7 eV), exhibited enhanced photocatalytic performance under simulated solar light irradiation to degrade complex organic dyes like Congo red and Rhodamin B. The key factors behind the enhanced photocatalytic performance were the high surface area of the porous 2D nanosheets and the presence of trap states that reside within the electronic band-gap. It was revealed that the superior photocatalytic performance emerged from the narrowed optical band-gap caused by the raised valance band maximum owing to the development of trap states inside the band-gap. These trap states effectively reduced the optical band-gap to 1.65 eV and enhanced light absorption of the material by shifting its photo-response towards the visible range. The findings suggest that there is significant potential for the synthesized 2D Ga$_2$O$_3$ nanosheets in various environment friendly solar light driven photocatalytic applications. Overall, this work led to a facile and inexpensive route for synthesizing oxide nanostructures that can be extended to other low melting temperature metals and their alloys. The gallium oxide nanostructures may furthermore be exploited as precursor for other gallium based compound semiconductors such as GaP, GaN or GaS, which may lead to further improvements of the activity. The developed method is particularly appealing due to it great potential for scaling up, high yields and simple approach rendering it to be a synthesis route that may enable future practical applications.

6.1.2 Synthesis of large area 2D GaPO$_4$
While the previous stage of the thesis was designed to lead to a high yield synthesis approach to obtain 2D Ga₂O₃ nanoflakes, it did not produce nanosheets with large lateral dimensions and hence it was found to be inadequate for the application of “wafer-scale” semiconductor processing. Since liquid gallium undergoes a Cabrera-Mott oxidation in air creating self-limiting 2D surface oxides on its surface, the second stage of this project focused on exploiting these interfacial oxide skins. The grown 2D surface oxide exhibits minimal adhesion to the liquid parent metal, offering a unique pathway to synthesize different 2D materials. Therefore, the next stages aimed to design new synthetic techniques to harvest large area, ultra-thin nanosheets of 2D gallium compounds, employing liquid gallium as a convenient precursor.

In this section of the thesis, a novel synthesis approach was proposed for depositing large area 2D GaPO₄, which is an archetypal piezoelectric material in its bulk form. Firstly, the ultra-thin 2D gallium oxide skin was delaminated from parent metal and transferred onto various suitable substrates following a previously devised van der Waals printing technique. A subsequent low temperature vapour phase phosphatization process lead to the formation of 2D GaPO₄ nanosheets of unit-cell thickness, while featuring lateral dimensions reaching several millimetres. There are several advantages of the proposed synthesis method including the low temperature process, cost effectiveness, scalability and simplicity. In this work, the first experimental evidence of strong out-of-plane piezoelectricity of 2D GaPO₄ sheets was demonstrated, which was further confirmed by DFT simulations. The out-of-plane piezoelectricity for a unit cell thick GaPO₄ nanosheet was relatively high, with the experimental and theoretical piezoelectric coefficient being determined as 7.5 ± 0.8 pm V⁻¹ and ~8.5 pm V⁻¹, respectively. The vertical piezoelectric behaviour of 2D GaPO₄ nanosheets with different thicknesses was also explored, identifying a decrease of the coefficient towards that of the bulk value with increasing thickness. The developed process was also found to be suitable for the
fabrication of free-standing GaPO₄ membranes with a piezoelectric response similar to that of the supported GaPO₄ films. The findings highlight that ultra-thin GaPO₄ is a very promising 2D material for piezotronic sensing and energy harvesting. The developed synthesis method is compatible with existing industrial processes and may be adapted to offer deposition of 2D piezoelectric material on a wafer scale. Moreover, the proposed synthetic route is likely also transferable to other gallium based materials as well as to the development of materials based on other low melting point metals.

6.1.3 Synthesis of centimetre-scale 2D GaN

The final part of this thesis focused on producing ultra-thin 2D gallium nitride nanosheets which has been predicted to be a promising material for various opto-electronic devices. The developed deposition technique for 2D GaN relies on a facile two-step liquid metal based synthesis process. Centimetre-scale 2D gallium oxide nanosheets were first harvested from the surface of liquid metal gallium using a squeeze printing technique. The exfoliated oxide films were subsequently transformed to GaN using a vapour phase ammonolysis reaction process. The deposition process offers the successful growth of few atoms thick, wurtzite 2D GaN nanosheets with lateral sizes reaching several centimetres. The unique characteristics of the synthesized GaN were investigated at the 2D limit. The nanosheets were found to be oxygen doped leading to a narrower than expected band-gap. The fabricated 2D GaN nanosheet shows a high carrier mobility of 21.5 cm² V⁻¹ s⁻¹. The proposed exfoliation approach paves a scalable and low cost route to produce 2D GaN nanosheets with an ultra large lateral size and intriguing characteristics diverging from its bulk counterpart. To enhance the versatility of the proposed deposition technique, an adapted synthesis process utilizing liquid indium instead of liquid gallium was explored in order to obtain 2D InN nanosheets. Moreover, this work provides a route towards integrating 2D morphologies of well-known
semiconductors into emerging 2D material based electronic and optoelectronic devices using a liquid metal based techniques.

6.2 Future Work

The research conducted in the context of this thesis has led to the development of novel synthesis routes for ultra-thin 2D materials, taking advantage of the bulk and surface properties of liquid gallium. Liquid metals have been identified as a promising platform for the synthesis of large area 2D materials and as a result there are still abundant opportunities to expand the scope of this research further, enabling future discovery based on the presented PhD research.

6.2.1 Two-dimensional metal oxide and hydroxide nanoflakes of other material

In chapter 3, liquid gallium droplets were used as a reaction environment to synthesize high yield gallium oxide and hydroxide nanoflakes. The process outlined in chapter 3 could potentially be expanded to produce 2D nanoflakes based on other low melting point metals (i.e. In, Sn, Bi) or metal alloys. Changing the composition of the used metal may lead to the creation of binary and ternary metal oxide nanoflakes. Furthermore, the properties of the resulting nanoflakes can be investigated and optimized for different reaction environments. Replacing the oxygen containing reaction environment with a sulphur containing solution may lead to the synthesis of metal sulphides. Similarly, other reactions may be realized using different precursors. The as-synthesized metal compounds can then be explored for different functional applications in sensing and catalysis.

6.2.2 Synthesis of large-area nanosheets of new 2D metal compounds utilizing other molten metals
The work presented in Chapters 4 and 5 has been limited to liquid gallium, while other low melting point metals may provide access to additional 2D compounds. Moreover, the use of various low melting point alloys may also allow expanding the synthesis scheme to obtain binary or ternary metal oxides, and oxides of higher melting point metals. Hence, there are still plenty of opportunities to synthesize a range of metal oxides in 2D sheet morphology using the developed synthesis protocol. These oxides can also potentially be converted to various metal compounds such as sulphides, selenides, nitrides and other pnictogenides through suitable chemical post-processing, which will further expand the library of accessible 2D compounds. Modifications of the fundamental properties of the as-synthesized 2D metal compounds through doping, functionalization, strain engineering and hetero-structuring are also important avenues for further investigation.

6.2.3 Functional applications of the large area 2D metal compounds

The as-synthesized piezoelectric 2D GaPO₄ can likely be utilized for applications in piezoelectric energy harvesting in nano-generators or in piezo-catalysis. The developed 2D GaN nanosheets may be a favourable building block for many future applications in optoelectronics such as lasers, LEDs, and solar cells. The flexible nature of 2D materials may ultimately enable new products and devices that take advantage of the electronic properties of these traditional ceramic materials and their superior mechanical properties arising from the ultimate tenuity of 2D materials. Considering the simplicity of the synthesis scheme compared to other thin-film deposition techniques, the future realization of various electronic, optoelectronic and piezoelectric devices based on the liquid metal exfoliated 2D nanosheets may ultimately have an extraordinary impact on the future of nanodevices in general. Other prospective applications of these synthesized 2D nanosheets may involve the development of
van der Waals hetero-structures tailored towards specific target applications. Overall, the opportunities emerging from the developed low melting point liquid metal based synthesis approaches are plenteous and may span across a range of research fields.