

MONASH UNIVERSITY

HONOURS THESIS

Thin oxides in graphene devices

IMAGE
PLACEHOLDER

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Abstract

I present a review of the use of graphene in electronic devices, both in its shortfalls and exciting properties. The electronic structure is detailed, along with various scattering sources that affect electron transport and ultimately the goal of room temperature, electronic devices. Considering heterostructures and the use of other materials to enhance graphene, I discuss the potential use of hafnium dioxide, and other oxides, as an excellent gate dielectric material for potential use in graphene field-effect devices.

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Foreword

This thesis serves the purpose presenting the conclusions of my research into thin oxides on graphene. I will be arguing , and how that fits into a bigger picture of materials science and particular applications.

In chapter 1, I will outline what I hope to achieve in this project. I begin by discussing the theoretical properties of graphene and why it has attracted so much interest as an electronic material. I will also describe some challenges facing new computing technologies, including the use of dielectrics, and how my work contributes to realising solutions to new generations of this technology. I will outline a theoretical and experimental summary of the results to date seen in introducing dielectrics to graphene.

In chapter 2, I describe the various ways of producing and identifying graphene in lab use, and the characterisations I have conducted. This will include our use of atomic force microscopy (AFM), optical microscopy and Raman spectroscopy.

I will then describe the devices and measurements I have made in chapter 3. This will regard connections to devices, which allow the measurements I have perform, and the processes used to fabricate our devices. I have made graphene devices using lithography and evaporation methods, to create electrical contacts. I will also describe the oxides I have investigated in this chapter, and the methods I have used to transfer them.

In chapter 4 I will present the data and results from my measurements of the respective devices which will be placed on SiO_2 . The results to here will be compared alongside data after stamping the same devices with thin oxides in chapter 5.

Chapter 1

Introduction

1.1 Preface

The mechanical exfoliation of atomically thin materials in 2004 sparked a flurry of research into many materials with unique properties. Graphene, the first of these, rose to prominence in research and has begun finding applications in industrial contexts.

Materials that are two dimensional restrict the movement of electrons to a plane. Because of this, these materials exhibit unique electronic properties. A clear example of this is a hexagonal lattice of carbon atoms, or graphene, which gives rise to a 'dirac' point in the band structure (see section 1.3.1).

1.2 Transistors - the field effect

1.2.1 Conductivity in FETs

1.2.2 Mobility in FETs

1.3 Graphene

1.3.1 Electronic properties

Why is it a good conductor?

Hybridisation

Electronic dispersion

Charged puddling

1.4 Transport and scattering in graphene

1.4.1 Charged impurities

1.4.2 Phonon scattering

1.4.3 Dielectric screening

Charge screening

Fine structure constant

Tuning the fine structure constant

High κ materials

1.4.4 Remote phonon scattering

1.5

Chapter 2

Production & identification of graphene

2.1 Production

Since graphene's realisation in 2004^[1], much research has been focused to finding efficient ways of producing large amounts of graphene^[2]. Originally, the first samples ever created which have primarily been used for sensitive measurements have been conducted using a method of exfoliation (section 2.1.1). These samples typically exhibit better electronic properties than those produced by other methods. Since 2008/2009, CVD (section 2.1.2) of carbon to create graphene films has provided another prominent method to produce large films for industrial scale applications. In particular, growth of graphene on copper sheets^[3] has been a reliable way producing these large uniform sheets.

There are other methods not used in this thesis, such as epitaxial growth of graphene via SiC uses heating to boil off silicon atoms to form a layer of graphene on its surface.

2.1.1 Exfoliation

Originally made famous in the breakthrough method by Giam and Novoselov^[1;4], a mechanical exfoliation technique allowed for the isolation of atomically thin crystals of various materials. They reported the use of scotch tape to cleave thin layers from a larger crystal.

The common procedure involves pressing tape/surfaces against a bulk crystal (such as highly orientated pyrolytic graphite (HOPG), Kish graphite, natural graphite, or graphenium). Due to van der Waals interactions, layers of graphite are transferred to the desired surface. By repeated peeling of the same tape, a thin coverage can be obtained and then transferred onto substrates, such as SiO₂.

Thermal enhancement

Drawing on the methods described in Huang *et al*^[5], we developed a reliable method of exfoliation. Using

When bringing the tape with graphite flakes into contact with the SiO₂ wafer, we use Huang *et al*'s method they use an annealing process of heating the tape and wafer for 2-5m at $\sim 100^{\circ}\text{C}$ on a conventional lab hot plate. After allowing cooling to room temperature, the tape is removed. They find under optical microscopy that graphene flakes with uniform thickness routinely range from $\sim 20\mu\text{m}$ to above $100\mu\text{m}$. The two additional steps to regular exfoliation methods were oxygen plasma cleaning and temperature annealing. Annealing is expected to increase traction due to the removal of gas molecules trapped between SiO₂ and graphite. Oxygen plasma is expected to remove adsorbates on the substrate surface.

Huang *et al* suggest part of their success comes from applying larger uniform coverage on tape. They suggest that because the exfoliation comes from the competition of forces between the substrate and the other graphene layers in multilayer graphite, using thinly covered tape is detrimental to the transfer.

Extra details Huang *et al* also specified further details about the parameter spaces they search for optimising their exfoliation.

- Only apply tape exfoliation maximum 3 to 4 times after removal from bulk graphite.
- Annealing time nor temperature not strongly affected coverage, but optimal at $\sim 100^{\circ}\text{C}$ & 2 mins. Longer time also implied more glue residue from the tape.

Rough surface adhesion

2.1.2 CVD

Dry transfer

2.2 Identification of Graphene

2.2.1 Optical Microscopy

2.2.2 Raman Spectroscopy

2.2.3 Atomic Force Microscopy Imaging

Chapter 3

Devices

To create devices where we can measure the electronic properties referenced in sections 1.2 and 1.3.1, metallic contacts need to be added to the graphene to measure electronic flow through the device.

To do this, lithography can be used to create polymer structures that allow the deposition of desired material in 2D geometries. This process and the adjustments made for fabricating our devices are described in the sections below.

3.1 Lithography

Lithography typically consists of three steps.

1. Spin coating - covering your sample with a uniform layer of polymer.
2. Exposure - exposing the polymer to light changes the chemical compounds and properties. This differentiates exposed areas to those unexposed.
3. Developer solution - developer solution removes indented areas of photoresist to create structures.

3.1.1 Spin coating photoresists

A spin coater is used to deposit thin films of materials. A vacuum is used to hold a sample horizontally on the spinner, before drops of photoresist are dropped onto the sample. The sample is then spun over sometime to achieve a uniform thickness of the photoresist, before baking on a hotplate occurs to set the sample.

Photoresists vary in their spinning thickness, but also their exposure rates. Positive photoresists dissolve in developer when exposed to light, while negative photoresists dissolve if not exposed to light. We have only used positive photoresists, as we have primarily been creating structures for deposition, and not etching material (protect your sample, but remove everything else).

HMDS & AZ-1512

Initially devices were fabricated using the AZ-1512 polymer, with the additional use of hexamethyldisilazane (HMDS) as an adhesion promoter between SiO_2 and AZ-1512. Devices were spun initially for 10 s at 1000 rpm, before being spun between 2000 and 3000 rpm for 30 s, per resist layer. This leaves a thickness of $1.7\text{ }\mu\text{m}$ to $1.39\text{ }\mu\text{m}$ ^[6]. Devices were then baked at $100\text{ }^\circ\text{C}$ for 1 minute.

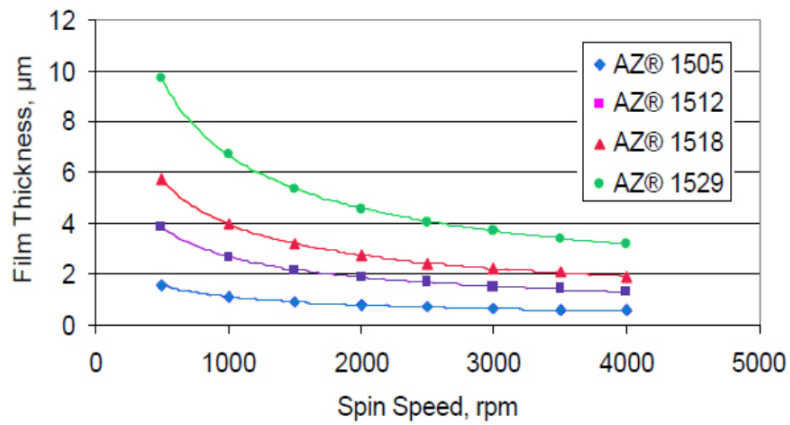


Figure 3.1: Spin curve of AZ-1512 (Source: EMD Performance Materials^[7])

Skin issues with HMDS

When using HMDS and AZ-1512 in conjunction,

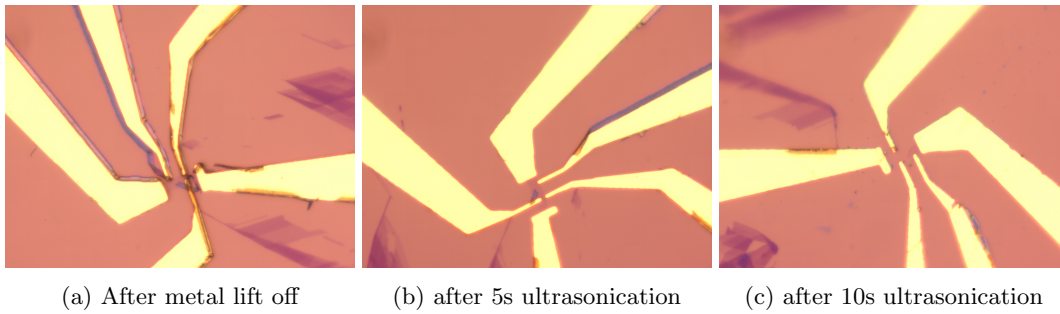


Figure 3.2: Material remanants from lithography

LOR-1A & AZ-1512

3.1.2 Exposure

Photo mask writer

3.1.3 Developer

3.2 UV Ozone surface preparation

3.3 Deposition

3.3.1 Oxide

3.4 Lift-off

3.4.1 Ultrasonication

3.5 Oxide transfer

3.5.1 Printing

Al_2O_3

SnO

Bi_2O_3

3.5.2 Smearing

Ga_2O_3

Chapter 4

Bare graphene

4.1 CVD

4.2 Exfoliated

4.2.1 hBN transfer

Chapter 5

Thin oxide graphene

5.1 CVD

5.2 Exfoliated

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References

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. Electric Field Effect in Atomically Thin Carbon Films. *Science*, 306(5696):666–669, October 2004.
- [2] Yi Zhang, Luyao Zhang, and Chongwu Zhou. Review of Chemical Vapor Deposition of Graphene and Related Applications. *Accounts of Chemical Research*, 46(10):2329–2339, October 2013.
- [3] Xuesong Li, Weiwei Cai, Jinho An, Seyoung Kim, Junghyo Nah, Dongxing Yang, Richard Piner, Aruna Velamakanni, Inhwa Jung, Emanuel Tutuc, Sanjay K. Banerjee, Luigi Colombo, and Rodney S. Ruoff. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science*, 324(5932):1312–1314, June 2009.
- [4] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim. Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences*, 102(30):10451–10453, July 2005.
- [5] Yuan Huang, Eli Sutter, Norman N. Shi, Jiabao Zheng, Tianzhong Yang, Dirk Englund, Hong-Jun Gao, and Peter Sutter. Reliable Exfoliation of Large-Area High-Quality Flakes of Graphene and Other Two-Dimensional Materials. *ACS Nano*, 9(11):10612–10620, November 2015.
- [6] Az1500 series technical datasheet.
- [7] EMD performance materials. Az 1500 series technical datasheet.