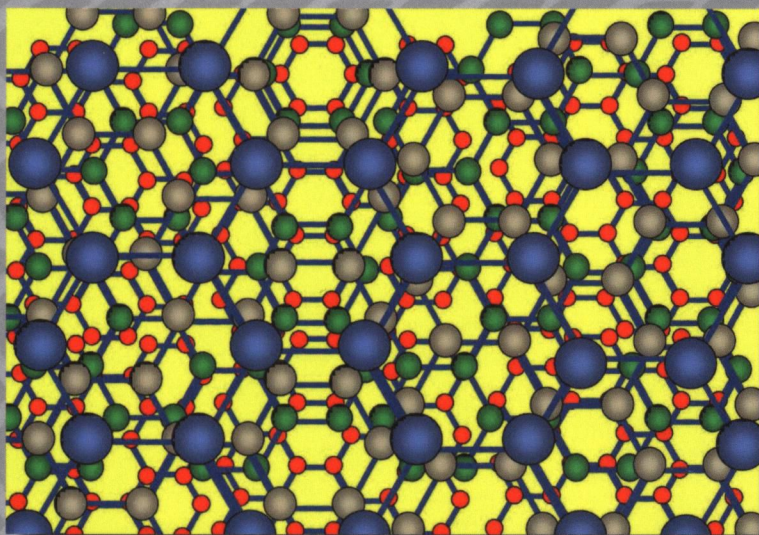


Elemental Graphene Analogues



David J. Fisher

M|R|F

ISBN 9781945291302



9 781945 291302

90000 >



ISBN: 978-1-945291-30-2

Materials Research Foundations, Vol. 14, 2017, ISSN 2471-8890

<http://www.mrforum.com>

Elemental Graphene Analogues

David J. Fisher

Elemental Graphene Analogues

David J. Fisher

Copyright © 2017 by the authors

Published by **Materials Research Forum LLC**
Millersville, PA 17551, USA

All rights reserved. No part of the contents of this book may be reproduced or transmitted in any form or by any means without the written permission of the publisher.

Published as part of the book series

Materials Research Foundations

Volume 14 (2017)

ISSN 2471-8890 (Print)

ISSN 2471-8904 (Online)

Print ISBN 978-1-945291-30-2

ePDF ISBN 978-1-945291-31-9

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Distributed worldwide by

Materials Research Forum LLC

105 Springdale Lane

Millersville, PA 17551

USA

<http://www.mrforum.com>

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Elemental Graphene Analogues

David J. Fisher

One of the greatest revolutions in materials science in recent years has been the literal renaissance of age-old materials in new and unexpected guises and possessing correspondingly astounding properties. There was once a time, for instance, when textbooks declared that only metals could offer any progress in superconduction. Since then, familiar perovskites – and even humble magnesium boride – have been recognised as being so-called ‘room-temperature’ superconductors. Carbon in particular has benefited from this revolution and has now found application as routinely deposited diamond coatings and as C60 ‘buckyballs’.

The most recent innovation has been the discovery and preparation of graphene; single-monolayer carbon having a remarkable strength. This success has naturally led researchers to ask whether other materials might also be prepared in an analogous monolayer form and offer similarly amazing properties.

The present monograph summarizes all of the work carried out on such monolayer materials up to the beginning of 2017, with attention being restricted to those, like graphene, being composed of a single element. Most of the work done so far on these ‘elemental graphene analogues’ has been theoretical, but the existing experimental data suggest that they may well become as useful as graphene.

Introduction

Graphene has entered the public consciousness as few other ‘non high-street’ materials have done in the recent past; even being mentioned in the TV comedy series, *The Big Bang Theory*¹. Engineers already dream² of using super-strength graphene to realize science-fiction writer Arthur C. Clarke’s ‘space elevator’³. Much of the initial public interest in graphene was probably piqued by the fact that its discovery earned a Nobel prize for Andre Geim and Konstantin Novoselov.

But scientists never rest on their laurels, and it was only natural to seek other analogous materials which might offer similarly spectacular properties. In barely more than half a decade, this search has already yielded a large amount of information; albeit much of it based upon computer modelling rather than experimental investigation. Density-functional theory computations in particular are a powerful tool for investigating the electronic structure (especially the ground state) of nanomaterials. By using this method, many graphene-like materials have been explored, and amazing properties have been revealed.⁴

Monolayer materials in general have been among the ‘hottest’ topics in condensed-matter physics ever since the experimental fabrication of graphene. The new classes of monolayer materials to be manufactured experimentally include the group-IV elements (yielding ‘silicene’, ‘germanene’ and ‘stanene [tinene]’), the group-V elements (yielding ‘phosphorene’) and transition-metal dichalcogenides. The group-IV monolayers are predicted to be topological insulators⁵, while the transition-metal dichalcogenides are potentially useful for valleytronics. Monolayer materials can be used as field-effect transistors and are expected to be a key feature of future nano-electronic devices.

Opto-electronic applications require materials having suitable band-gaps and high mobilities. The broad range of band-gaps and high mobilities offered by two-dimensional semiconductors composed of monolayers of group-15 elements (phosphorene, arsenene, antimonene, etc.) thus offers great promise. The calculated binding energies and phonon band dispersions of these allotropes reflect thermodynamic stability. The energy band-gaps range from 0.36 to 2.62 eV, and phosphorene, arsenene and bismuthene in particular have carrier mobilities which are as high as several thousand cm^2/Vs .⁶

This work is summarised in the present book. The contents are however restricted to analogues consisting of a single element, thus being closest to graphene in nature, and so the transition-metal dichalcogenides will not be covered here.

Table of Contents

Introduction

Silicene.....	1
1.1 Mechanical Properties	6
1.2 Preparation and Structure	14
1.3 Composites	17
1.4 Substrate Interaction	19
1.5 Thermoelectricity	40
1.6 Thermal Conductivity	46
1.7 Magnetoresistance	50
1.8 Valley and Spin Phenomena.....	53
1.9 Magnetic Properties	65
1.10 Optical Properties	70
1.11 Electrical Conductivity	73
1.11.1 Superconductivity	77
1.11.2 Hall Effect.....	78
1.11.3 Semiconductivity and Band Structure	80
1.12 Surface Interaction.....	107
1.13 Defects	122
1.13.1 Line Defects	123
1.13.2 Point Defects.....	124
1.13.3 Stone-Wales Defect	128
1.13.4 Miscellaneous	131
1.14 Diffusion Processes	132
1.15 Applications	133

1.15.1 Transistors.....	133
1.15.2 Spintronics	138
1.15.3 Environmental Protection	141
1.15.4 Sensors	141
1.15.5 Gas Purification	143
1.15.6 Hydrogen Storage	143
1.15.7 Energy Storage.....	145
1.15.8 Catalysis.....	147
Germanene.....	149
2.1 Preparation	149
2.2 Structure.....	152
2.3 Mechanical Properties	155
2.4 Semiconduction and Band Structure	156
2.5 Substrate Interaction	158
2.6 Surface Interaction.....	163
2.7 Defects	170
2.8 Thermal Conductivity	171
2.9 Thermo-Electricity.....	172
2.10 Optical Properties	173
2.11 Composites	174
2.12 Applications.....	175
2.12.1 Solar Energy	175
2.12.2 Energy Storage.....	176
2.12.3 Catalysis.....	176
2.12.4 Transistors.....	176

2.12.5 Optical Devices.....178

2.12.6 Spintronics178

Stanene (Tinene).....180

3.1 Structure.....181

3.2 Preparation.....182

3.3 Mechanical Properties182

3.4 Substrate Interaction.....183

3.5 Surface Interaction.....184

3.6 Superconductivity186

3.7 Defects188

3.8 Diffusion.....189

3.9 Magnetism189

3.10 Band Structure.....189

3.11 Thermal Conductivity.....192

3.12 Applications.....193

Antimonene.....195

4.1 Preparation.....196

4.2 Composites197

4.3 Substrate Interaction.....198

4.4 Surface Interaction.....199

4.5 Defects199

4.6 Thermal Conductivity.....200

4.7 Optical Properties201

4.8 Semiconduction201

4.9 Applications.....201

Indiene.....	203
Arsenene.....	204
6.1 Mechanical Properties	205
6.2 Semiconduction	205
6.3 Composites	208
6.4 Surface Interaction.....	209
6.5 Magnetism	211
6.6 Thermal Conductivity.....	212
Phosphorene	213
7.1 Preparation	213
7.2 Structure.....	216
7.3 Mechanical Properties	217
7.4 Diffusion	221
7.5 Magnetism	222
7.6 Semiconduction and Band Structure	226
7.7 Surface Interaction.....	241
7.8 Substrate Interaction	246
7.9 Optical Properties	247
7.10 Defects	249
7.11 Composites	254
7.12 Superconductivity.....	256
7.13 Thermal Conductivity.....	257
7.14 Applications.....	259
7.14.1 Solar Power.....	259
7.14.2 Sensors	259

7.14.3Catalysis.....261

7.14.4Energy Storage.....262

7.14.5Energy Harvesting263

7.14.6Thermoelectricity.....264

7.14.7Electronics265

7.14.8Biological.....270

Bismuthene271

Borophene272

9.1 Structure.....272

9.2 Defects273

9.3 Mechanical Properties273

9.4 Composites275

9.5 Superconductivity276

9.6 Magnetism276

9.7 Applications.....276

9.7.1 Energy Storage.....276

9.7.2 Hydrogen Storage278

9.7.3 Sensors.....278

9.7.4 Catalysis.....279

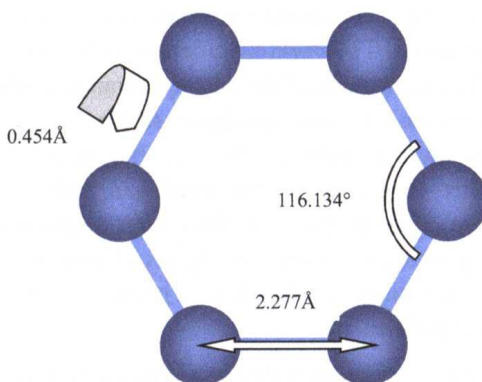
9.7.5 Biological.....279

References280

Keywords365

Chapter 1

Silicene



The advent of graphene ushered-in a new era in materials science. Graphene is a two-dimensional planar honeycomb array of carbon atoms in sp^2 -hybridized states. A natural question to ask was whether other elements of the group-IV elements of the periodic table, such as silicon and germanium, could also form graphene-like structures. Silicene was theoretically predicted in 1994 and has been created experimentally much more recently, in the face of some skepticism⁷. Like graphene, silicene exhibits electronic and mechanical properties that can be exploited in nano-electronic applications. That is, silicene shares many of the intriguing properties of graphene; such as so-called Dirac electronic dispersion. The different structure, compared to that of graphene, also offers the ability to open a band-gap in the presence of an electric field, or when deposited onto a substrate. These are important properties from the viewpoint of digital electronics applications. Experimental evidence nevertheless indicates that silicene is very different to graphene in terms of its stability, atomic structure, electronic properties and processing. Some of these differences impair the use of silicene for practical application. It is necessary to consider the tendency of silicene to exhibit multiple structural forms, and the role played by strong hybridization with substrates with regard to the electronic band structure of silicene.

There was once doubt over whether graphene could be prepared, because its existence contradicted the Landau-Peierls-Mermin-Wagner predictions that there could exist no

stable flat form of such crystals⁸. The so-called flat shape of graphene arises due to microscopic buckling at the finest interatomic scale. There were similar misgivings over the feasibility of silicene and other analogues.

As long ago as 1994, the possibility of corrugation in the silicon analogue of graphite had already been theoretically examined. There was however very little study of silicene before 2009, when silicene with a low-buckle structure was proved to be dynamically stable using *ab initio* calculations. The buckling amounts to 0.454Å, as indicated in the figure at the head of this chapter. In spite of the buckled geometry, silicene exhibits most of the good electronic properties of planar graphene: such as a high Fermi velocity, a Dirac cone (figure 1) and carrier mobility. Silicene moreover offers some distinct advantages. There is better tunability of the band gap, which will facilitate the preparation of an effective room-temperature field effect transistor. It has a much stronger spin-orbit coupling which thus promises the occurrence of a quantum spin Hall effect at experimentally useful temperatures. Silicene permits easier valley polarization, and this aids valleytronics experimentation.

It can be shown however that silicene and other two-dimensional crystals are stable due to transverse short-range displacements of certain atoms. The distortions are small and form various patterns. As the temperature decreases, two transitions - disorder to order and order to disorder - can occur. The ordered state of graphene takes the form of stripes, where carbon atoms are shifted regularly with respect to the plane. The flat graphene, silicene and germanene planes look like microscopic so-called washboards with a wavelength of a few interatomic spacings. Because of an up-down asymmetry in such two-dimensional crystals, deposited on a substrate, a mini band-gap can appear. Mini-gap formation is related to the buckling and to interaction with the substrate.

Molecular dynamics simulations, using the Lennard-Jones potential, of a two-dimensional array of silicon atoms at various temperatures and densities shows that the radial distribution function does not change as the parameters change, and resembles the corresponding (111) surface of the face-centered cubic structure. The liquid phase appears at very high temperatures, suggesting that the system is very stable in the solid phase.⁹

For silicon, which is usually sp^3 -hybridized, silicene is an unusual and rare structure. Silicene was theoretically proposed and its structure was subsequently calculated as a possible candidate for nanoribbons of silicon grown onto the anisotropic Ag(110) surface. Since 2012, monolayer silicene sheets with various superstructures have been synthesized on many substrates, including Ag(111), Ir(111), $ZrB_2(00\cdot1)$, $ZrC(111)$ and MoS_2 . Multilayer sheets have also been grown onto Ag(111). A silicene field effect transistor