Electronic Properties of Graphene
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Development of Graphene Manufacturing Technology

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Abstract

The recent discovery of graphene has sparked interest for a variety of applications that may benefit from graphene's highly advantageous properties. Graphene is a single atomic layer of carbon atoms, tightly bonded to one another. It has been shown to be durable, flexible, and impermeable. Graphene has ballistic electron transport has demonstrated exceptionally high electron mobilities. Among the several demonstrated graphene production methods, the techniques of sublimation (from SiC) and chemical vapor deposition appear to hold the greatest promise for production of high quality well controlled thickness graphene films. Our team, SMI and Cornell, has used silicon sublimation and chemical vapor deposition (CVD) to produce single and multi-layer graphene films - we are refining these processes and are developing an array of process specific tools for graphene manufacturing. In this presentation, we review results we have achieved using several of these techniques, and compare reactor designs and process tradeoffs with the different tools.

Sublimation formation of graphene, has been performed in a vertical reactor, and, depending on whether this is performed in ultra high vacuum (UHV) or in an Ar atmosphere, requires heating the SiC wafer in the range of 1300° to 1650°C. Growth on the C face of SiC is dramatically different from growth on the Si face and the growth rate on the carbon face does not appear to be self limited. It has been found that growth of graphene on the Si face is generally self limited to 1 to 4 monolayers (ML).

A variety of dielectric substrates have been investigated for CVD growth of graphene including: CMP polished on-axis 6H-SiC (both Si-face and C-face), SiO_2 (250 nm PECVD oxide) on SiC, and sapphire (0001) substrates. CVD growth has been performed at temperatures ranging from 1000°C to 1650°C using propane as the carbon source with an argon flow; this has been done in horizontal tube and vertical chamber reactors. These films have been analyzed as-grown using Raman spectroscopy with a 488 nm laser. In contrast to the sublimation approach with SiC, this carbon addition technique allows multi-layer graphene formation on both the Si-face and the C-face of SiC, on SiO_2 and sapphire substrates, with thickness (from 3 monolayers to ~100 monolayers) controlled by the growth time, propane flow rate, and growth temperature. Another technique of great promise is CVD deposition of graphene on copper and nickel. The metal substrate material may be a film deposited on a variety of substrate materials, or it may be a metal foil which allows continuous roll-to-roll CVD systems for graphene.

Our team is refining multiple process tools for large area graphene production with several end users and will present an overview of these approaches, results and directions being pursued.

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Graphene Production

Chemical Vapor Deposition (CVD) and Thermal Decomposition (TD) of SiC (also called silicon sublimation) are production scalable techniques of producing graphene. CVD is widely used in the semiconductor industry for research and for production of microscale devices and large area technologies such as photovoltaics and displays.

SMI produces deposition tools and Support Equipment that Enables Novel Next Generation Devices and Advanced Materials R&D

MOCVD • PECVD • ALD

Standard and Custom R&D Tools

Worldwide sales to leading research organizations and developers

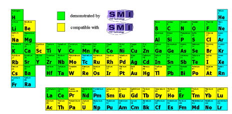
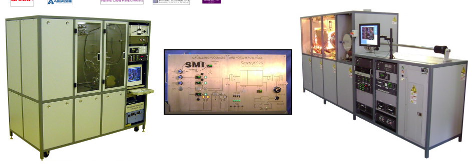


Table of elements showing the range of material compositions that can be deposited using SMI's technology.



Process Comparison

CVD allows the growth of complex layer structures with other materials and doping. TD offers exceptional graphene purity and is compatible with semiconductor production processes.

	SiC Sublimation	CVD on Metal/ ceramic	CVD Tape
Total Area	100mm wafer	Al_2O_3: 150mm wafer Quartz: 300mm wafer	Potentially meters x kilometers
Layer control	1 for Si face, 3-4 for C face	Cu- 1 layer (self limit) Ni- few layers	Cu- 1 layer (self limit) Ni- few layers
Platelet film mobility (cm^2/Vs)	2,000 (Si face), 20,000 (C face)	2,000, maybe higher	~2,000, maybe higher
Growth Rate / Throughput	25 ML/hr 1 wafer/2 hours	1ML/10 minutes ~ 1 wafer/hour	~50 Meters/hour (ultimately)
Process conditions	atmospheric argon 1400-1600°C	hydrogen, methane 1000°C	hydrogen, methane 1000°C
Production system cost	Est: 0.6-1.1M$	Est: 0.7-1.2M$	Est: 1.0-1.5M$
$/$cm^2$ particles	High (substrate)	Medium	Low
$/$m^2$ sheets	Not Possible	Not Possible	Low

Design considerations for the TD tool

Attribute	Value (range)	Considerations
Process temperature	1300 – 1700°C	Substrate dependent
Base pressure	10^{-8} Torr	Minimum contamination
Oxygen pp. control	< 10^{-8} Torr outgassing	Prevent O and H "etching"
Operating pressure	10^{-8} Torr - 760 Torr	Wide Range
Doping	Unlikely	Not an additive process
Load-Lock	Yes	Contamination control

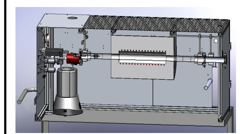
Design considerations for the CVD wafer tool

Attribute	Value (range)	Considerations
Process temperature	900 – 1400°C	Substrate dependent
Base pressure	10^{-8} Torr	Minimum contamination
Oxygen pp. control	< 10^{-11} Torr outgassing	Prevent O and H "etching"
Operating pressure	10^{-8} Torr - 760 Torr	Wide Range
Doping sources	gas, metal organics	Advanced processes
Rotation	Available	Temperature uniformity
Load-Lock	Yes	Contamination control

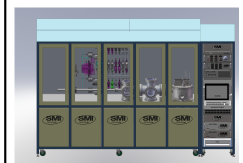
Design considerations for the CVD tape tool

Attribute	Value (range)	Considerations
Process temperature	900 – 1050°C	Substrate restricted
Base pressure	10^{-2} Torr	Minimum contamination
Oxygen pp. control	< 10^{-8} Torr outgassing	Prevent O and H "etching"
Operating pressure	1 Torr - 760 Torr	Wide Range
Doping sources	gas, metal organics	Advanced processes
Rotation	No	No possible with tape.
Load-Lock	No	But sealed for bake-out.

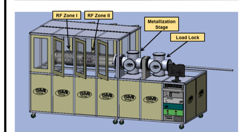
Tool Designs



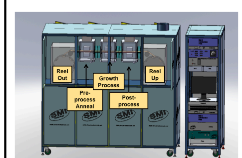
Desktop Tool – R&D reactor
Horizontal Tube
CVD, PECVD Graphene/CNT.
Metal substrates.
1200°C



Vertical RDR Tool –
Primarily CVD, TD possible.
Wafer growth, doping.
1700°C

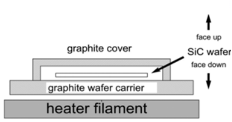


Horizontal Tube Tool –
CVD, TD, SiC CVD. Multizone.
To 1200°C, 1700°C, or 2200°C.
Wafer growth.

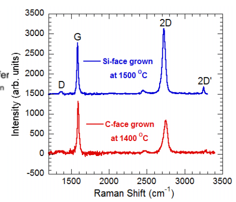


Tape Tool –
CVD on roll-to-roll metal tape for continuous graphene.
Multizone for foil prep and post-process.
To 1100°C, doping optional.

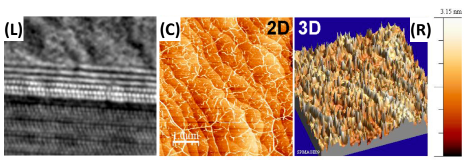
Graphene Fabrication by Thermal Decomposition of SiC.



Graphite wafer holder used for thermal decomposition of SiC.



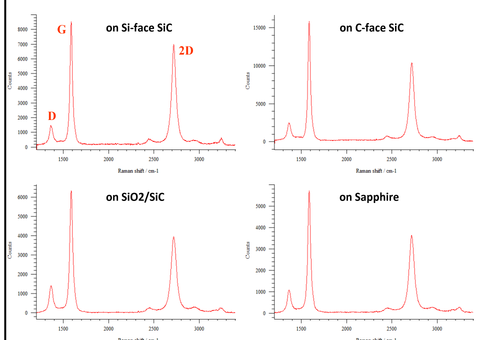
Raman spectrum for epitaxial graphene films grown on the Si-face and C-face of 6H-SiC.

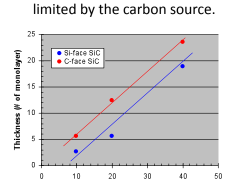


(L) TEM micrograph showing the cross section of graphene layers grown on (0001) SiC. (C and R) AFM of graphene 1400°C 30 minutes, 5-8 MLs (5x5 µm image).

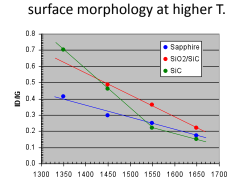
Graphene Fabrication by CVD on SiC, Al_2O_3, and SiO_2

Raman spectra of multi-layer graphene/graphite grown on Si-face SiC, C-face SiC, Al_2O_3, and SiO_2 by carbon addition CVD. All samples were under the same conditions: 1650° C, 600 Torr, 40 sccm propane flow.



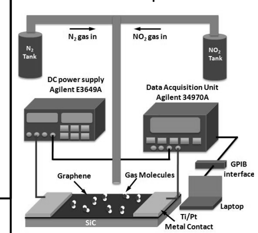


Thickness versus propane flow (growth at 1350° C and 100 Torr for 15 min). Showing growth rate is limited by the carbon source.

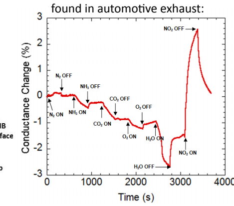


I_D/I_G versus growth temperature with 40 sccm propane flow and 600 Torr. Showing Improvement in surface morphology at higher T.

Graphene Based NO_x Detector



Change in graphene conductance with exposure to interfering gases commonly found in automotive exhaust:



Percentage conductance change at different temperatures, under 18 ppm NO_2, for graphene films grown on 6H-SiC: