Growth of Low-Dimensional Carbon Nanomaterials

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Partially Disordered Interface

1100°C: To form an interface layer

The layer decomposes at 1400°C

1600°C

Atomic Growth Model

1. A carbon rich layer on the SiC surface is formed at high temperature
2. The interaction of the residual oxygen with carbon forms thermally stable oxygen-carbon embedded structures.
3. Depending on environment such structures lead to curvature of hexagonal structures resulting in the formation of CNT nanocaps or planar graphene

Interface transition layer before/after graphene formation
X-Ray Photoelectron Spectroscopy

Sample Composition

- SiC
- Graphene (C-C $sp^2$)
- SiO$_x$C$_y$
  - C 1s $sp^3$
  - Si 2p SiO$_x$C$_y$
  - O 1s C-O
- *O-C (Bulk component)
Role of Oxygen in SiC Decomposition

The Key Issue to produce carbon on SiC
The reaction must be controlled in active oxidation, not forming SiO$_2$


Region 1: Active oxidation, Si(g)/SiO(g)

\[ \text{SiC}(s) + \frac{1}{2} \text{O}_2(g) = \text{SiO}(g) + \text{C}(s) \]

\[ \text{SiC}(s) = \text{Si}(g) + \text{C}(s) \]

Region 2: Active oxidation, SiO(g)

\[ \text{SiC}(s) + \text{O}_2(g) = \text{SiO}(g) + \text{CO}(g) \]

Region 3: Passive oxidation, high O$_2$, SiO$_2$ (s)

\[ \text{SiC}(s) + 3/2 \text{O}_2(g) = \text{SiO}_2(s) + \text{CO}(g) \]
Growth by Interface Decomposition


Thermally stable O-C compounds

Goal to understand the thermal stable O-C compounds by TEM, TPD, and modeling

Thermal desorption spectra of CO (a) and CO₂ (b) after oxygen implantation for various carbon materials. (EK98: pure graphite, and USB15: 15%B in C),

Temperature region for CNT and graphene growth

Graphene Growth Conclusions

- Graphene is formed above \(~1400^\circ\text{C}\)
- Oxygen may play a role in the initial growth of graphene on SiC
- XPS shows oxy-carbides, $sp^3$ and $sp^2$ carbon structures
- Proposed growth model with oxygen
  \[ \text{SiC (s)} + \text{O}_2 (\text{g}) \rightarrow \text{SiC}_x\text{O}_y (\text{s}) \rightarrow \text{SiO} (\text{g}) + \text{C} (\text{s}) \]
- The controlling steps:
  \[ \text{SiC} \rightarrow \text{SiO}_x\text{C}_y \rightarrow \text{SiO} + \text{C} \rightarrow \text{C} \: sp^3 \rightarrow \text{C} \: sp^2 \]
Low-D Carbon Nanostructures on SiC

**Growth of graphene/SiC**
- Growth at 1200-1500°C in UHV, or at 1600-1800°C in Ar for 1-30 min

**Growth of SWNTs/SiC structure**
- Growth in high vacuum at $10^{-6}$ to $10^{-7}$ torr ~1400°C

**Growth of MWNTs/SiC structure**
- Growth in high vacuum at $10^{-3}$ to $10^{-5}$ torr at 1400-1700°C up to 2 um long

**Standard growth conditions and results**
- Annealing from 1400-1700°C
- Vacuum from $10^{-2}$ to $10^{-10}$ torr
- Products: SWNTs, MWNTs and graphene.
- No amorphous carbon and no Si in the products
- Metal-free and well aligned structures

*An ideal space for studying mechanism/kinetics of Low-D materials*
Metal-free SWNTs on SiC

- Si-face SiC, at 1400°C, 10^{-6-7} Torr
- Radial breathing mode centered at 191 cm\(^{-1}\)
- Diameter of SWNT is 1.3 nm

Other diameters demonstrated by:
Metal-free MWNTs on SiC

- **Metal-free CNTs**
- **Well-aligned on SiC**
- **Low structural defects**

Oxygen is at $10^{-8}$ torr when the total pressure is at $10^{-5}$ torr
Atomic growth model of CNTs

- A graphene layer is formed on the SiC surface at high temperature.
- Interaction of residual oxygen with graphene to form thermally stable oxygen embedded structures.
- Embedded structures lead to curvature of hexagonal structure and result in the formation of CNT caps.

Heptagon defect on graphene

Heptagon/pentagon defects resulting in curvature
Carbon on SiC: Summary

- Complex growth process
  - Difficult environment for in-situ tools
  - Use modeling to assist in understanding
- We predict oxygen plays critical role in controlling growth
  - Need to know residual gas levels in system
  - Can be used for preferential structure growth
  - Evaluating model to study molecular oxygen adsorption
- Graphene
  - Layer control reasonable
  - Electronic quality improvements still needed
- CNT’s
  - Structurally attached to the SiC substrate
  - Vertically aligned to SiC substrate
  - Non-metal catalyst method
Outline

• Introduction
• Atomic scale growth of Low-D carbon/SiC
• Growth of 3-D carbon nanostructures for potential thermal applications
• Conclusions/Acknowledgements
Pillared Carbon Architecture

- Bottom-up approach: 3-D Pillared Architecture
- Thermal transport limited by CNT-graphene junction
- Variations by changing CNTs density and distance between graphene layers
- Growth based on theory of oxygen atomic catalysis for Low-D carbon

Pillared Carbon Structures on SiC

- Pillared graphene-CNTs on SiC can be produced
- Great for modeling
- Excellent structures for investigating thermal nano-science

**Goal**

To control the growth of low-dimensional carbon nanostructures enabling application specific materials to be produced.
**Processing 3-D Structures**

**Low-D Carbon Patterning**

- Masking: Si₃N₄, SiO₂
- Control of Growth environment

- Oxide/Nitride
  - SiC
  - Wet Etch
  - Anneal for graphene

- Repeat

**SiC Substrate Patterning**

- Reactive Ion Etching
- Gases: CF₆, CHF₃, NF₃, SF₆, O₂
- Masking: Au, Al, Cr, Ni, or ITO

- SiC substrate

Anneal for CNTs
Preliminary Conclusions

**Approach**
- Evaluate the atomic structures by TEM, SEM, Raman, and IR
- Understand the structures of CNTs-graphene junctions and correlate with phonon properties

**Result**
- The first group to grow Pillared graphene structures at the atomic scale
- A new high performance thermal material with promising applications

IR microscopy (x12)
120°C on the substrate (unpublished data)
Outline

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• Conclusions/Acknowledgements
Conclusions

- Focus on chemistry and atomic catalysis for growth from atomic to nano scale and beyond
- A preliminary atomic oxygen catalytic growth mechanism for low-D carbon nano-structure growth
- Experimental data has shown that the proposed mechanism could be applied to growth of pillared graphene architectures
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Carbon Research Group

Transport Measurements
MBE, SE
Raman
X-ray
Transport/Devices/EBIC
Raman, XPS, Growth
MBE, XPS

Device Fabrication

Device Testing

Device Development

AFM, STM

Sample Preparation
SIMS, XPS

Transport Measurements

RT Transport

Raman