Enhanced Interfacial Transport using Carbon Nanotube Arrays

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Outline

- Background
- Thermal Interfaces
- Electrical Interfaces
- Improved CNT Synthesis
- Conclusions and Acknowledgments
Interfacial Resistance

- Contact resistance
  - Exacerbated by microscopic asperities between contacting surfaces
    \[ R_c = \frac{Q \cdot A}{T_1 - T_2} \]
  - Existing thermal interface materials (TIMs)
    - Solders, thermal greases, phase change materials (PCMs), composites
    - More compliant than the contacting surfaces themselves
    - Displace air gaps under applied pressure to increase the extent of contact
    - Dry-out/pump-out and mechanical fatigue
    - Low thermal conductivity

![Diagram depicting constant and uniform heat flow Q(W) and nominal contact area A(m²)]
Motivation

- Reduction of chip-package interfacial thermal resistance is a major challenge in the thermal management of semiconductor devices
  - Projected 2018 single-chip power dissipation levels*
    - 1.08 W/mm² for “cost-performance”
    - 0.64 W/mm² for “high-performance”
- Individual CNTs exhibit extremely high, phonon-dominated thermal conductivities
  - 5000-8000 W/(mK) for individual single-walled carbon nanotubes (Maruyama, 2003; Yu et al., 2003)
  - 3000 W/(mK) for multi-walled carbon nanotubes (Kim et al., 2001)
- Enhanced thermal contact conductance with carbon nanotubes could help to meet the challenge of increasing power dissipation

*International Technology Roadmap for Semiconductors (ITRS) 2004 Update
Prior Work

- Typical performance of traditional thermal interface materials
  - Solder, 5mm$^2$K/W (*Chung*, 2001)
  - Thermal grease/gel, 40-100mm$^2$K/W (*Blazej*, 2003)
  - Phase change material, 30-70 mm$^2$K/W (*Blazej*, 2003)

- Carbon nanotube/nanofiber arrays
  - CNT array, 200-350mm$^2$K/W (*Sample et al.*, 2004)
Nanoscale Thermo-Fluid Lab Research Objectives

- Develop and demonstrate processes for synthesis of well anchored carbon nanotube arrays with controlled patterning and alignment over relevant substrate surfaces
- Establish an experimental rig to characterize thermal contact conductance of carbon nanotube arrays of varying density, diameter, and alignment
- Develop a model of thermal conductance and optimize the effective thermal conductance of carbon nanotube interfaces
Well Anchored CNT Array Growth with PECVD

Student: Jun Xu

- Plasma enhanced chemical vapor deposition system
  - High-quality CNT synthesis
  - Controllability of PECVD
    - Typical substrate temperature 600-1000°C
    - Max. 1.5 kW microwave source (2.5 GHz)
    - Max. 600VDC substrate bias
    - 3 to 200 torr chamber pressure
    - Feed gases: H₂, CH₄, and N₂
Tri-layer Catalyst and Substrates

- 30nm-Ti/10nm-Al/6nm-Ni
- CNT arrays synthesized on:
  - polished silicon
  - copper
  - quartz
  - diamond
General Characteristics of CNT Arrays

- Full CNT coverage over the sample (macroscopic)
- Uniform CNT layer thickness for each array (array height ≈ 8 to 16µm)
- Dense and vertically oriented CNT ‘forest’
  - Density ≈ several hundred million CNTs/mm²
  - Multi-walled carbon nanotubes
  - CNT diameters ≈15 ~50 nm
Well Anchored CNT Arrays

- Strong bonding between CNTs and substrates

CNT array substrate surface after scratching

Broken stems of CNTs
Experimental Setup for Thermal Contact Resistance Measurements

- Testing rig – 1D reference bar method*

*adapted from ASTM D 5470

Nanoscale Thermo-Fluids Laboratory
Measurements of Temperature Difference $\Delta T$ and Gradient $G$
Temperature Calibration

- Thermal camera readings are linear with actual temperatures

Tested materials
- Graphite bars (NIST SRM 8426)
- MIKRON M310 blackbody source
- Aluminum bar (Rustoleum flat black painted)

Reference sensors
- Pt RTD (4-wire)
- Blackbody built in sensor
- T-type thermocouples

Environments
- In air
- High vacuum
- With or Without Ge window

\[ y = 0.5389x + 15.563 \]
\[ R^2 = 0.9994 \]
Test Column Resistance Network

- **Contact Resistance Measurement**

\[
R_{total} = R_{Cu} + R_{c1} + R_{Si} + R_{c2}
\]

\[
q = -G \cdot k_{Cu} \cdot A
\]

\[
R_{total} = \frac{\Delta T}{q}
\]
Experimental Uncertainty

- Uncertainty analysis (*Holman, 1994*)

\[
\delta R_{c1} = \left[ \sum_{i=1}^{n} \left( \frac{\partial R_{c1}}{\partial X_i} \delta X_i \right)^2 + (\delta R_{c2})^2 \right]^{1/2}
\]

- \( \delta \Delta T \approx \pm 0.2 \, \text{K} \) (\( \Delta T = 20 \sim 30 \, \text{K} \))
- \( \delta A \leq \pm 0.004 \, \text{cm}^2 \) (\( A = 1 \, \text{cm}^2 \))
- \( \delta L \approx \pm 0.18 \, \text{mm} \) (\( L \approx 42 \, \text{mm} \))
- \( \delta G \approx \pm 2 \sim \pm 3 \, \text{K/m}^* \) (\( G \approx 100 \sim 450 \, \text{K/m} \))
- \( \delta R_{c2} \), uncertainty from control experiment

*Bowker and Lieberman, 1972.*
Results: Single-sided CNT Interfaces

- Copper-silicon interfaces with CNTs grown on Si
  - Significant enhancement
  - Less pressure dependence and much smaller contact resistances with larger array height

![Graph showing interface resistance vs pressure for different array heights and bare Si wafer.](image)

Results: CNT-PCM Interfaces

- Combinations of CNT array with phase change material
  - Preformed PCM* thin film on Cu @313K, much lower resistance than that of PCM alone
  - Strong pressure effect with an inflection point near 0.28MPa
  - Lowest resistance: 5.2mm²K/W @ 0.35MPa

*Honeywell PCM45

Two-sided CNT Interfaces

- CNT arrays synthesized on both sides of a Si chip
- CNT array synthesized on a surface of 1cm x 1cm x 1cm copper block
Results: Two-sided CNT Interfaces

- Resistances below 5mm$^2$K/W under the tested pressures
- A negative value of (-3.9mm$^2$K/W) under a pressure of 0.24MPa caused by the relatively large experimental errors
- Improved accuracy required for the measurements of resistance values of order 1mm$^2$K/W

Xu and Fisher, to appear, ISHMT, 2006
Diamond-CNT Combinations

- Diamond-CNT combination intended to enhance lateral heat spreading near the interface
  - High-quality PECVD diamond
    - Good electrical insulator
    - High surface hardness and chemical inertness
    - Excellent heat spreader with a thermal conductivity >1000W/(mK)
  - CNT array
    - Thermal contact conductance enhancement
Diamond-CNT Combinations

- Polycrystalline diamond thin films deposited on polished silicon wafers
  - PECVD
  - Full coverage
  - Nucleation layer
  - Columnar growth
- CNT array on diamond

Diamond-CNT Combinations

- Deformation of silicon substrate after diamond deposition
  - Different thermal expansion coefficients
  - Strong bonding between diamond film and substrate
- Possible method to obtain flat samples
  - Deposit the films on a larger substrate and then trim it to the final size with laser cutting techniques so that the deformed area is removed
  - Deposit the films on a circular disc substrate in which edge effects should be less prominent.

Diagonal scans over both sides of a double-side diamond coated specimen (with arbitrary zero height).
Preliminary Electrical Testing

Collaborators: Prof. Hyonny Kim, Prof. Thomas Siegmund
Students: Myounggu Park, Baratunde Cola, Chongbae Park

- Sample Structure
- Macroscopic view of sample
  - CNT array covered Cu block uniformly

Sample structure

Fabricated Sample (Unit; cm)
Experimental Setup

- Cu Nail Probe
- Upper Grip with Insulation
- Multimeter
- Glass Plate
- Lower Grip
- CCD Camera
- MWNT layer on Cu Block
Preliminary Results

- Electrical resistance as a function of contact force
Preliminary Contact Conductance Model for CNT Array Interfaces

- Tall, dense CNT array forms a highly conforming, rough surface under moderate pressures
  - Conforming rough limit (microcontacts only*)
  - Assumes that resistances of array itself and well anchored side are small

\[ R_q = 0.5 \mu \text{m} \]

AFM scan of post-experiment CNT array

*T= T_{source}
T = T_{i,1}
body 1
R_{s,1}

T = T_{i,2}
body 2

R_{s,2}

T = T_{sink}

R_j = R_s

*Bahrami et al., 2004
Preliminary Contact Conductance Model for CNT Array Interfaces

Parameters of the CNT array-Cu contact

<table>
<thead>
<tr>
<th></th>
<th>$E \times 10^9$Pa</th>
<th>$\nu$</th>
<th>$H \times 10^9$Pa</th>
<th>$k$ (W/(mK))</th>
<th>$R_a$ ($\mu$m)</th>
<th>$\tan(\theta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OHFC bar (pre-exp.)</td>
<td>117.2</td>
<td>0.34</td>
<td>&gt;0.784</td>
<td>390</td>
<td>1</td>
<td>0.36</td>
</tr>
<tr>
<td>CNT array (post-exp.)</td>
<td>80</td>
<td>0.19</td>
<td>0.5</td>
<td>80</td>
<td>0.5</td>
<td>0.14</td>
</tr>
<tr>
<td>Effective values</td>
<td>51</td>
<td>\</td>
<td>0.5</td>
<td>132.8</td>
<td>1.12</td>
<td>0.386</td>
</tr>
</tbody>
</table>

Contact conductance estimated with Mikic’s relation (1974)

$$h = \left[1.13k \cdot \tan(\theta)/R_a\right](P/H)^{0.94}$$

*Values in red are rough estimates, based on preliminary values in the literature
Predictions of the Present Model

- RMS difference between the model and measurement is 25.2%
- Control experiment in Cu-CNT-Si interface resistance measurement is a source of large uncertainty
- Many CNT properties are uncertain
- Present model is not able to account explicitly for effects of CNT array density, height and diameter

![Graph showing interface resistance vs. pressure](image)
Improved Modeling

- Constriction resistance at interfaces of CNT roots to their substrate
  - Model the constriction resistance between individual CNTs to the growth substrate as constriction bounded by semi-infinite cylinders
  - Substrate taken to be a cluster of cylinders with various diameters
  - Assume the contact sizes to be the sizes of CNTs
  - Uniform a/b ratio
  - CNT density and diameter distribution
  - Resistance

\[
R_{\text{CNT-sub}} = \left( \sum_i R_{cs} \left( \frac{a_i}{b_i} \right)^{-1} n_i \right)^{-1}
\]

(Madhusudana, 1996)
Improved Modeling, cont’d

- Contact resistance at CNT free tips to the opposite substrate surface
  - Study CNT diameter and density effects implicitly through the values of surface roughness and mean surface slope
    - Number of contact points not explicitly specified or fixed
    - Additional AFM examinations
  - Study the contact between individual CNTs and the opposite substrate surface, then sum these contact conductances
    - Gaussian distribution of asperities with a small mean surface slope $\tan(\theta)$
    - Flat and circular microcontacts, with Hertz theory to determine contact size
    - Number of contact points related to CNT density
    - Constriction modeled with bounded semi-infinite cylinders
CNT Array Synthesis: Parameter Optimization

- Variation of CNT diameter and density
  - Reported thermal conductivity of aligned SWNTs larger than 200W/(mK) (Hone et al. 2000)
  - CNT array with good anchoring to the substrate and high density of oriented, small-diameter, high-quality nanotubes
  - Reduced nickel layer thickness
    - High density (3 to $10^9$ CNTs/mm²) and small CNT diameters (5 to 20nm) achieved
    - Difficult to achieve full CNT coverage over the substrate and large array height
Catalyst Variation

- Iron and cobalt
- CNT arrays synthesized with iron
  - Dense and well aligned CNT array with large height (≈60µm)
  - Large CNT diameter (50~200nm)
- Variations of plasma power and substrate bias
CNT Synthesis at Reduced Temperatures

- Fe@dendrimer
  (with Dr. Placidus Amama)
  - Easily processed aqueous solution catalyst
  - Iron nanoparticles encapsulated in a polymer with very order structure
  - Allows for improved control over tube diameter and array density

Collaborator: Dr. Placidus Amama

CNTs used for later test
Conventional Temperatures for CNT Growth

Raman spectra of CNTs synthesized using Mo/Co (4:1) supported on MgO (98%)
The catalyst was supplied by Prof. Iqbal Zafar, NJIT

What is a Dendrimer?

Discovered in the early 1980’s by Dr. Don Tomalia

- Discrete, well-defined polymers
- Synthetic three dimensional macromolecule
- Synthesized in a series of repetitive reactions from simple monomer units

Attributes of Dendrimers

- Uniform composition and structure
- Nanoparticles are stabilized by encapsulation
- The core or peripheral functional groups can be tailored
- Encapsulation of metal nanoparticles occurs mainly by steric effects

http://www.ninger.com/dendrimer/
Growth at 600°C

Exposed catalyst

Shielded catalyst

Graph 1: Raman shift vs. intensity for shielded and exposed catalysts at 600°C.

Graph 2: Raman shift vs. intensity for shielded and exposed catalysts at 600°C.
Raman Spectra of CNTs Synthesized at Low Temperatures

- Shielded catalyst produces CNTs
- Exposed catalyst produces mostly CNFs
- Single-walled signatures for most conditions

Plasma Sample

Mo Puck

Exposed

- 300 °C
- 400 °C
- 500 °C

Shielded

- 300 °C
- 400 °C
- 500 °C

Intensity (arb. u.)

Raman shift (cm$^{-1}$)
<table>
<thead>
<tr>
<th>Substrate Temperature (°C)</th>
<th>Plasma Power (W)</th>
<th>Pyrometer Temperature (°C)</th>
<th>Carbon Species (FESEM, Raman spectroscopy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>200</td>
<td>880</td>
<td>SWNTs, MWNTs</td>
</tr>
<tr>
<td>800</td>
<td>300</td>
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<tr>
<td>600</td>
<td>500</td>
<td>777</td>
<td>CNFs, SWNTs, MWNTs</td>
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<tr>
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<td>500</td>
<td>CNFs, MWNTs</td>
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<td>500</td>
<td>540</td>
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<tr>
<td>300</td>
<td>500</td>
<td>n.d.</td>
<td>CNFs, SWNTs</td>
</tr>
</tbody>
</table>
Conclusions

- CNT arrays can produce outstanding thermal interface performance
  - Resistance reduction of two orders of magnitude compared to bare interfaces
  - CNT size, quality, and anchoring appear to be significant factors

- Preliminary electrical resistance results are positive
  - Approximately one order of magnitude improvement to date
  - Improved CNT density and quality are needed in future studies

- Improved direct CNT synthesis routes needed
  - As-deposited arrays can be well anchored
  - Low-temperature growth of high-quality CNT arrays remains an area of ongoing study and progress
Acknowledgements

- Funding from the Cooling Technologies Research Center at Purdue University is gratefully acknowledged