CNT/Graphene Technologies for Advanced Interconnects and TSVs

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1. Advantages of nano carbon as wiring materials.

2. Previous study: CNT via interconnect
   @MIRAI-Selete, Fujitsu

3. Dense Vertical and Horizontal Graphene (DVHG) for CNT via interconnect and TSV

4. Multilayer graphene for horizontal interconnect

5. CNT/Graphene contact for 3D interconnects
## Physical properties of CNT

<table>
<thead>
<tr>
<th>Multi wall CNT (MWNT)</th>
<th>Single wall CNT (SWNT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>![MWNT Image]</td>
<td>![SWNT Image]</td>
</tr>
</tbody>
</table>

- **High current density**
  - $>10^9$ A/cm² (Cu ~$10^6$ A/cm²)
- **Ballistic transport** (6.45 kΩ/tube)
- **High carrier mobility**
  - $\approx 100,000$ cm²/Vs (Si ~450 cm²/Vs)
- **High thermal conductivity**
  - $\approx 3,000$ W/Km (Cu ~400 W/Km)
- **High Young’s modulus**
  - $\approx 1000$ GPa (Cu ~130GPa)
- **Energy band-gap changeable**

### Material Types

<table>
<thead>
<tr>
<th>Metallic</th>
<th>Semiconductive/Metallic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interconnect</td>
<td>Transistor</td>
</tr>
</tbody>
</table>

### Graphene Band Gap vs Diameter

![Graphene Band Gap vs Diameter Graph]
Physical properties of graphene

- High current density: $10^8$ A/cm$^2$ (CNT $\sim 10^9$ A/cm$^2$, Cu $\sim 10^6$ A/cm$^2$)
- Ballistic transport (CNT $6.45$ k$\Omega$/tube)
- High carrier mobility: $\approx 200,000$ cm$^2$/Vs (CNT $\sim 100,000$ cm$^2$/Vs, Si $\sim 450$ cm$^2$/Vs)
- High thermal conductivity: $\approx 5,000$ W/Km (CNT $\sim 3000$ W/Km, Cu $\sim 400$ W/Km)
- Energy band-gap changes depending on the ribbon width

B. Obradovic et al., APL, 88, 142102, 2006.
Difficulties in LSI interconnect

- **Current density issue:**
  Deterioration of reliability due to electro-migration

- **Resistance issue:**
  Increase of resistivity due to width-dependent scattering

<table>
<thead>
<tr>
<th>Metal 1 ½ Pitch (nm)</th>
<th>54</th>
<th>38</th>
<th>27</th>
<th>21</th>
<th>16.9</th>
<th>13.4</th>
<th>10.6</th>
</tr>
</thead>
</table>

Solutions are not known

Interconnect (Cu wire)

Conventional Cu wire

Electro-migration problem

Resistivity (μΩcm)

ITRS2009 Edition
Solution to the current density issue

Experimental

Cu \sim 10^6 \text{ A/cm}^2

CNT: \sim 10^9 \text{ A/cm}^2

Graphene: > 10^8 \text{ A/cm}^2

B. Q. Wei, et al.,

R. Murali, et al.,
Solution to the resistance issue

Simulation
A. Naeemi et al., IEEE-IITC2008

Experimental
R. Murali et al., EDL, 30 (2009) 611.

Resistance of SWNT and graphene can be lower than that of Cu wires at the line width below 100 nm.
Solution to the LSI chip temperature issue

Power density in the LSI chip is increasing......

Thermal conductivity
Si: 168 W/mK
Cu: 398 W/mK
CNT: ~3000 W/mK

Simulation
N. Srivastava et al., IEDM (2005)
Our task is developing CNT/graphene technologies for
- Interconnect
- TSV (through silicon via)
- TIM (thermal interface material)

Low resistance
High reliability

Low-power consumption, high-performance LSI
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Trial of applying CNT bundles for via interconnects

Succeeded in showing the superior potential of using CNT.

Nature Digest, June 2007, vol. 4, pp48

Growth temperature: 450ºC

CNT density: $10^{11} \sim 10^{12}$ cm$^{-2}$

SiOC (k=2.9)

Cu

160 nm

MWNT

Normalized resistance

$\approx 10^8$ A/cm$^2$ per tube

• Sub. Temp.
  105ºC in vacuum

5.0 x $10^6$ A/cm$^2$

100hrs

0 20 40 60 80 100 120

Time (hr)

0 0.5 1.0 1.5

Normalized resistance

10 nm
The processes were mostly compatible with conventional Si process.

CNT via interconnect fabrication processes

M. Nihei et al., IITC2007
CNT growth system

Thermal CVD

- Lamp heater 400-800°C
- C$_2$H$_2$ diluted by Ar

Low temperature processes are needed for CMOS LSI (≈400°C)
Demonstration of CNT contact plugs on CMOS

The bundles of MWNTs were grown directly on nickel silicides by low-temperature thermal CVD.

- There are no damages to CMOS
- Issues: low density \((3 \times 10^{11} \sim 1 \times 10^{12} \text{ tubes/cm}^2)\)
Benchmarking of CNT via resistance

Resistance @20nmφ (Ω)

- VIACARBON (2010)※3
- IMEC (2011)※4
- KAIST (2011)※2
- MIRAI-Selete (2009)※1
- Calculated

<table>
<thead>
<tr>
<th>CNT density (tube/cm²)</th>
<th>1.E+11</th>
<th>1.E+12</th>
<th>1.E+13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

※1 M. Katagiri et al., IITC2009, pp. 44
※2 S. Lee et al., Journal of The Electrochemical Society, 158 (2011) K193
※3 J Dijon et al., IEDM2010, p760
※4 N. Chiodarelli et al., IITC2011
Outline

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Dense Vertical and Horizontal Graphene (DVHG)

Growth condition
Source gas: C₂H₂/Ar
Catalyst film: Co 4nm/Ti 1 nm
Growth temperature: 450°C

Carbon density 1.4 g/cm³ (63% of the 2.2 g/cm³ of graphite)

A. Kawabata et al., SSDM2012
Electrical resistance of DVHG

Ar etching: 0.5 Pa, 400 W, 120sec

Ar plasma etching was used to remove the horizontal graphene.

M. Nihei et al., ICSICT2012

*Initial thicknesses are different for each samples.
Temperature dependence of electrical resistance

With Ar etching
⇒ Vertical graphene contact
⇒ Metallic behavior

Without Ar etching
⇒ Horizontal graphene contact
⇒ Carrier conduction barrier

M. Nihei et al., ICSICT2012
Thermal conductivity of DVHG

Picosecond thermoreflectance measurement

\[ b = \sqrt{\lambda c \rho} \]

- \( b \): Thermal effusivity
- \( \rho \): Density
- \( l \): Thermal conductivity
- \( c \): Specific heat capacity

Ar etching time 300 sec

Improved

\( \lambda \approx 10 \text{ W/mK} \)

\( \lambda \approx 1 \text{ W/mK} \)

A. Kawabata et al., SSDM2012
Applying to via interconnect, TSV

Optimizations are needed.

DVHG: growth temp. 450ºC

- Extremely high density,
  - but, short length, poor quality.

CNT bundle: growth temp. ~800ºC

- Long length, better quality,
  - but, low density.
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Annealing sputtered amorphous carbon with catalyst

Other study

Graphene on the top surface of a catalyst

Our study

Multi-layer graphene can be obtained directly on SiO$_2$.

Cross-sectional TEM images after annealing

Grown by a solid-state transformation of sputtered amorphous carbon with catalyst

Cross-sectional TEM image after annealing at 800°C

C(30nm)/SiO₂

Co(50nm)/C(30nm)/SiO₂

Networked nanographite (NNG)

SiO₂

5nm

Co

Multi-layer graphene (MLG)

SiO₂

5nm

Graphite sheets formed between the Co catalyst and SiO₂ dielectric, aligned to the Co (111) fcc structure.

Graphite structure still remained after the Co removal.

M. Sato et al., IITC/MAM2011

Resistivity of multi-layer graphene films

- Resistivity of annealed carbon film with Co is one order of magnitude higher than that of HOPG (Highly Oriented Pyrolytic Graphite).
- Grain size may be small, and grain boundaries have higher resistance.

Grain size of multi-layer graphene films

HOPG

Annealing sputtered amorphous carbon: Co/C/SiO₂/Si (after Co removal)

Grain size ~ 5 µm

5 µm

Grain size ~ 400 nm

5 µm

EBSP: Electron Backscatter diffraction Pattern

M. Sato et al., SSDM2012
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Contact between CNT and multilayer graphene

TEM-EELS measurement

Diffusion of Co and Ti into multilayer graphene

This may contribute to the reduction of contact resistance between CNTs and multilayer graphene by forming the vertical graphene contacts.
Summary

1. With the aim of achieving low-power consumption, high-performance LSIs, our work focuses on the development of carbon nanotube(CNT)/graphene technologies for interconnect and thermal application.

2. For vertical via interconnects and TSVs, we report on a dense vertical and horizontal graphene (DVHG) structure, which is expected to lead to a low electrical resistance and high thermal conductivity.

3. Although the DVHG showed poor properties at this point, we found that the vertical graphene contact formation can be an important technology to realize high electrical and thermal conductivity.

4. For horizontal interconnects, we have succeeded in forming multi-layer graphene directly on SiO₂ by annealing sputtered amorphous carbon.

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