Lecture 9
Other Thin-Film Semiconductor Materials

Announcements

Homework 2/4:
• Due Today. Please hand it in to me.
• I will return it on the day of the midterm (October 25th).
Additional Information

• Today we are talking about new and unconventional semiconductor systems. No single book exists covering these topics, Brotherton does not.
• Review articles are best source of information:

  http://pubs.rsc.org/en/Content/ArticleLanding/2013/CS/C2CS35335K#!divAbstract

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http://science.sciencemag.org/content/327/5973/1603
Lecture 9

- Midterm Information.
- Graphene.
- Fullerenes.
- Carbon Nanotubes.
- Hybrid Halide Perovskites.
- Chalcogenides.
- Silicon (again).

Information on Midterm Examination
Midterm Exam Details

- Thursday October 25th at 10:00am in STAG 211
- Exam will last 80 minutes.
  - The exam will start exactly at 10:00am!
- Closed book and closed notes.
  - You can, and are expected to, use a calculator.
- Choose 2 out of 3 questions.
  - If you answer 3 I will take best 2 scores.
- It will contribute 30% of overall grade for class.
- The exam will material covered in lectures 1-9 (inclusive).
- There will be 25 marks per question. 50 total.

Midterm Exam Details

- The format will be similar to homeworks.
  - Several sub-questions per question.
- The number of marks will be shown at the end of every sub-question.
- Read through all questions before deciding which 2 you wish to answer.
- There will be a mixture of descriptive and quantitative questions.
- I will not expect you to conduct any numerical methods (e.g. numerical differentiation / fitting).
- I would provide the results of such a method.
Front Page of Midterm

• This is the front page of a previous exam:

There will be 25 marks per question

You have 80 minutes to complete the exam

• Our exam will be similar.

Equations

• All constants will be provided.
• All relevant formulae will also be provided.
• Parameters will be labeled as clearly as possible.

**Diffusion Length**

\[ L = \sqrt{D \tau} \]

- \( L \) is the carrier diffusion length.
- \( D \) is the carrier diffusion coefficient.
- \( \tau \) is the recombination lifetime.

**Lorentz Force on a charge particle**

\[ F = q(E + v \times B) \]

- \( E \) is the electric field.
- \( v \) is the velocity of the particle.
- \( B \) is the magnetic field vector.
- \( q \) is the charge on the particle.

**Cross Product of two vectors**

\[ \mathbf{a} \times \mathbf{b} = |\mathbf{a}| |\mathbf{b}| \sin \theta \mathbf{n} \]

- \( \mathbf{a} \) is a vector
- \( \mathbf{b} \) is a vector
- \( \theta \) is the angle between vectors \( \mathbf{a} \) and \( \mathbf{b} \)
- \( \mathbf{n} \) is the unit vector in the direction perpendicular to vectors \( \mathbf{a} \) and \( \mathbf{b} \).
Equations Not Provided

- You will be given most equations. However, simple relationships you would be expected to know.

- Examples:
  - Density:
    \[ n_{2D} = \frac{1}{A} \quad n_{3D} = \frac{1}{V} \]
  - Area:
    \[ A = \pi r^2 \]
  - Surface area of sphere:
    \[ A = 4\pi r^2 \]

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- Examples:
  - Chain rule:
    \[ \frac{df}{dx} = \frac{df}{dg} \frac{dg}{dx} \]
  - Standard derivatives:
    \[ \frac{d}{dx} (ae^{bx}) = a e^{bx} \quad \frac{d}{dx} (\ln(ax)) = \frac{1}{x} \]
    \[ \frac{d}{dx} (\sin(ax + b)) = -a \cos(ax + b) \]
    \[ \frac{d}{dx} (\cos(ax + b)) = -a \sin(ax + b) \]
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- Examples:

  - Velocity: \( v = \frac{x}{t} \)
  - Current from charge: \( I = \frac{Q}{t} \)
  - Ohm’s Law: \( V = IR \)
  - Kinetic Energy: \( E = \frac{1}{2}mv^2 \)
  - Momentum: \( p = mv \)
  - Mass density: \( \rho = \frac{m}{V} \)

Equations Not Provided

- You will be given most equations. However, simple relationships you would be expected to know.
- Examples:
  - Limits of exponentials:
    \[
    e^0 = 1 \quad e^{-\infty} = 0 \\
    e^{\pm 1/\infty} = e^0 = 1
    \]
  - Unit conversions
    \[1\text{Å} = 10^{-10}\text{m}\]
    \[1\mu\text{m} = 10^{-6}\text{m}\]
    etc...
Grading

- Hopefully I will not have to curve.
- But it depends on results.
- I may try to ~match grade distributions from previous years.
- Although if everyone does well the mean will be higher.
  - The course contains a lot of material.
- I will return your examinations 1 week later (Thursday November 1\textsuperscript{st}).

Practice Questions

- We do not have a lecture on Tuesday (October 23\textsuperscript{rd}).
- Instead, I will make available some practice questions.
- These will not be graded, but will allow you to practice the type of questions that could be asked.
- I will upload the solutions at the same time.
- I strongly suggest that you attempt the questions first, before looking at the solutions.
Graphene

Carbon Allotropes

• What do we mean by a carbon allotrope?
• Last lecture we talked about organic semiconductors.
  • We broadly defined these as molecules that contain at least one carbon.
• Today we are talking about materials that are exclusively carbon.
• It turns out that pure carbon can take many different forms (allotropes).
Carbon

- Carbon, like silicon, is a group 14 element, and shared some properties.
- Has 4 electrons in outer shell.
- Tends to bond covalently, via hybridized orbitals.

Diamond

- One of the best known allotropes of carbon is diamond:
- The “diamond” crystal structure is the same as that adopted by crystalline silicon.
- Each atom has 4 nearest neighbors.
- Tetragonal bonding.
Diamond

- Diamond has a very low electrical conductivity, and a very high thermal conductivity.
- Diamond transistors have been demonstrated:

![Diamond transistor diagram](image)

- The band gap of diamond is wide: 5.5 eV.
- It could be of interest for high-temperature electronics (e.g. inside reactors).
- Nitrogen defects add an electron.

- These centers are potentially of interest for quantum computing.
Diamond

- People have prepared diamond thin films by CVD
- But the cost is likely to be prohibitive for what we want to achieve.

Graphite

- Another form of carbon is graphite:
  - The carbon atoms form layers, with each atom covalently bonded to 3 others in the layer.
  - The layers are weakly (π) bonded.
  - Graphite conducts electricity in plane.
Graphene

• Graphite is just multiple stacked layers of graphene.

• Graphene is a single atomic layer of carbon.

• For a long time it was considered a hypothetical material. It was isolated in 2004.\[1\]


Graphene

• The reason why graphene is (semi)-conducting is similar to organic semiconductors (last lecture).

• Carbon has 4 outer electrons, yet in graphene only 3 participate in bonding.
**$sp^2$ Hybridization**

- The ground state of carbon is:
  \[ C = [\text{He}]2s^22p^2 \quad \text{Or} \quad C = 1s^22s^22p^2 \]
- In graphene, one electron is excited from the 2s to the 2p state the configuration becomes:
  \[ C^* = [\text{He}]2s^12p^3 \quad \text{Or} \quad C^* = 1s^22s^12p^3 \]
- In this case we now have **one** 2s electron and **three** 2s electrons to participate in bonding

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**$sp^2$ Hybridization**

- As with organic semiconductors, these electron states **hybridize** into a linear combination of orbitals.
- **Two of the three** 2p orbitals, and the **one** 2s orbital, hybridize into **three** $sp^2$ orbitals:

![Hybridization Diagram]

- Or, in Dirac Notation, each electron is described as:
  \[ |sp^2\rangle = \frac{1}{3}|2s\rangle + \frac{2}{3}|2p\rangle \]
$sp^2$ Hybridization

- These three orbitals are highly directional.
- It is energetically favorable for the three $sp^2$ orbitals to form a planar structure with $120^\circ$ between each lobe.
- This explains the three valence electrons, but recall we have 4 valence electrons in carbon:
  \[ C^* = 1s^22s^12p^3 \]
- We have one extra $2p$ orbital.

$sp^2$ Hybridization

- It turns out the remaining $p$ orbital will orientate with lobes above and below the plane of the $sp^2$ orbitals.
- These $p$-orbitals are completely free to move throughout the honeycomb lattice.
- In graphite they are involved in $\pi$-bonding.
Charge Transport in Graphene

- The honeycomb lattice is ordered, with carbon atoms in **regular positions**.
- This is unlike organic semiconductors that have molecular order, but **long-range disorder**.

http://reichmanis.chbe.gatech.edu/research.html

- So electrons are coherent and delocalized across the sheet.
- We will not derive it, but the band structure of graphene turns out to look like the following:
- The points at which the bands touch are called the **Dirac Point**.
- The surface here is called the **Dirac Cone**.

Charge Transport in Graphene

• Just looking in 1 dimension we can sketch the band structure as:

• Traditionally, effective mass is evaluated from the 2nd derivative of $E$ wrt $k$:

\[ m^* = \frac{\hbar^2}{\left(\frac{d^2E}{dk^2}\right)} \]

• Since for graphene $E \propto k$, the effective mass would here be $\infty$.

• For this reason, charges are described differently for this system.
  • The effects of special relativity need to be considered.
  • However very high mobilities are reported in graphene ($\sim 10^6$ cm$^2$/Vs at low temperatures).
  • There is however one major problem with graphene.
    • It has no band gap.
Graphene TFTs

- The band structure below illustrates that conduction band and valence band touch (at the Dirac Point).

- Graphene TFTs have very low on/off ratios.

2-Dimensional Materials

- Despite graphene failing to find a useful application (yet), it has spawned a new field of electronic materials: 2D Materials.

- Other 2D materials are semiconducting.
Fullerenes

• $C_{60}$ (fullerene) is a rolled-up sheet of graphene, consisting of 60 carbon atoms.
• In the shape of a soccer ball.
• As with graphene, each carbon is covalently bonded to another 3 carbon atoms.
• Leave one $p$-orbital free for transport.
Fullerene Transistors

- $C_{60}$ has been shown to enable n-type charge transport.
- Mobility $\mu \sim 5 \text{ cm}^2/\text{Vs}$.
- These are disordered films, deposited by vacuum deposition.
- $C_{60}$ is not soluble in common organic solvents.
- Fullerenes are generally referred to in the same class as organic semiconductors.

Aside: Dual Slit Experiment

- This is not examinable, but it is interesting to note that the dual-slit experiment has been carried out using $C_{60}$ molecules instead of electrons.
Fullerenes

- Other fullerenes exist


Soluble Fullerenes

- Standard fullerene molecules are not soluble in common solvents.
- By adding a functional group to the fullerene cage, the molecule can be made soluble.
- The most common soluble fullerene derivative is Phenyl-C_{61}-butyric acid methyl ester (PCBM).
- The mobility of PCBM TFTs is a little lower than C60 TFTs (typically 0.1 cm^2/Vs).
- Due to less favorable packing of spheres.
Soluble Fullerenes

- Soluble fullerene derivatives can be blended with soluble polymers for use in organic solar cells.

http://www.rcas.sinica.edu.tw/~cwpao/node16.html

Soluble Fullerenes

- There are a wide range of fullerene derivatives, with various adducts.

- Properties are broadly similar, with small differences in energy levels and packing properties.
Carbon Nanotubes

- Carbon nanotubes (CNTs) are basically sheets of graphene rolled up.
- Their aspect ratio (length to diameter ratio) is typically $\sim 10^2$ to $10^7$.
- Unlike graphene, there are many forms of CNTs.
Multiple Walled CNTs

- Carbon nanotubes do not need to consist of a single layer of carbon.
- Carbon nanotubes can be multi-walled:

  ![Image of multi-walled CNTs]

- The following acronyms are often used:
  - SWCNT: Single walled carbon nanotube.
  - MWCNT: Multi-walled carbon nanotube.

Chirality

- The diameter and arrangement of carbon atoms can be varied.

  ![Images of CNTs with different chiralities]

- The chirality of the carbon nanotube will determine the electronic properties.
Charge Transport in CNTs.
- As with other carbon systems, transport takes place through $p$-orbitals left over from $sp^2$ hybridization.
- We are not going to derive electronic structure for CNTs.
- But the properties depend on diameter and chirality.
- CNTs can be either metallic or semiconducting.

Band Structure of CNTs.
- Some CNTs have band gaps, other are like graphene.
- The density of states has a series of discontinuous spikes (Van Hove singularities).
Purification

• For electronic applications, we require semiconducting CNTs.
• During synthesis, a wide range of diameters and chiralities are formed.
• So semiconducting CNTs need to be separated from a mixture of metallic and semiconducting CNTs.
• Even a small amount of metallic CNT in the mixture can cause devices to short circuit, or have low on/off ratios.
• To be effective this is generally a costly procedure.
• See: https://www.nature.com/articles/nnano.2008.135

Single CNT Transistors

• Transistors can be made using just a single CNT as the channel.
• These devices exhibit high mobilities (~10^5 cm^2/Vs).
• But are not scalable for large-area TFTs.
Thin-Film CNT Transistors

- Transistors can also be made using a random CNT network.
- Because of percolation effects, the mobility is lower in these random networks than single CNTs.
- There is also an observed trade-off between mobility and on-off ratio.

There is an observed trade-off between mobility and on-off ratio.
- This can be tuned through areal density.
- Current records are approximately:
  - $\mu \sim 300 \text{ cm}^2/\text{Vs}$ with $I_{on}/I_{off} = 10$.
  - $\mu \sim 10 \text{ cm}^2/\text{Vs}$ with $I_{on}/I_{off} = 10^5$.
Thin-Film CNT Transistors

• The reason the mobility in random network CNT transistors is lower than in single CNT transistors is:
  • Due to contact resistance / charge hopping between CNTs.
  • Traditional parallel-plate capacitor models overestimate the areal capacitance.
  • Mobility can be improved by aligning CNTS in direction of channel.


In general CNTs have good mobility and are ambipolar.

• The real issue with CNTs is their purity, which remains a problem.
• To be useful in low-cost electronics, the purification process needs to be significantly cheaper to be considered for commercialization.
• Mark Hersam’s review article on carbon systems is very good:
  • [http://pubs.rsc.org/en/Content/ArticleLanding/2013/CS/C2CS35335K#!divAbstract](http://pubs.rsc.org/en/Content/ArticleLanding/2013/CS/C2CS35335K#!divAbstract)
Hybrid Perovskites

Hybrid Semiconductors

- Last time we briefly mentioned these “hybrid” compounds.

- They have recently (re)-emerged in the last decade.

Perovskite Crystal Structure

- Perovskite is a crystal structure: ABX₃.
- Methylammonium Lead Iodide = (MA)PbI₃.

Solar Cell Efficiency
Hybrid Halide Perovskites

- Processable from solution.
- At low temperature (>100°C).
- At ambient pressure.
- With low cost precursors.

Remarkable Properties

- Low effective mass: \(m_e^* \sim m_h^* \sim 0.1m_e\).\(^\,[1]\)
- High in-grain structural order.\(^\,[2]\)
- Small Urbach tail energy (~15 meV).\(^\,[3]\)
- Low density of trap states (~10\(^{10}\) cm\(^{-3}\)).\(^\,[3]\)
- High carrier mobilities (~100 cm\(^2\)/Vs).\(^\,[4]\)

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\(^\,[1]\) Miyata et. al. Nat. Phys. 11 (2015) 582
\(^\,[2]\) Ergar et. al. JACS 134 (2012) 17396
\(^\,[4]\) Semonin et. al. JPCL 7 (2016) 3510
Photon Recycling

• This is the observation that in some systems (including perovskites) photons emitted via radiative recombination (bimolecular) are not always lost.

Perovskite Transistors

• TFTs have been demonstrated, but mainly only at low temperature:

• It is likely there is some ionic screening effects taking place in these compounds.
Perovskite Transistors

- If ions are mobile, they may end up screening the semiconductor-dielectric interface and stopping electronic charge from accumulating.

- In the late 1990s there were reports of TFTs based on similar, perovskite-like materials.

  - A mobility of $0.5 \text{ cm}^2/\text{Vs}$ was reported at the time.
Perovskite Transistors

- With improvements in device design, the same material has been demonstrated with 15 cm$^2$/Vs.

Perovskite Transistors

- Material instabilities, lead content, and ionic effects mean for now it is not competitive with metal oxides, organics for flexible electronics.
- However, it does have very impressive optical absorption and emission properties.
- So some people are interested in it for light-emission and light-detection.
- This field is very young, so we will see what happens.
Chalcogenides

- Another class of materials, mainly studied for solar cell applications.
- Chalcogenides of at least one chalcogen anion and at least one more electropositive element.
Chalcogenides

- Cadmium telluride (CdTe) is a well known solar material.
- They have efficiencies about 20%.

Chalcogenide TFTs

- There are not many examples of TFTs based on this class of materials.
- SnS$_{2-x}$Se$_x$ is one example.
Chalcogenide TFTs

• SnS$_{2-x}$Se$_x$ can be processed from solution, and has a hole mobility $\sim 10$ cm$^2$/Vs.

[Graph Image]

• The main problem is the use of hydrazine as a solvent.

Chalcogenide TFTs

• A recent paper has demonstrated TFTs based on a range of solution-processed chalcogenides (with no hydrazine).

[Graph Image]

Chalcogenide TFTs

- Their paper claims high mobilities.

Silicon (Again)
Stretchable Silicon

- One approach is to use traditional crystalline silicon and flexible interconnects.

Next Time...

- Gate Dielectrics: