ECE 488: Compound Semiconductors

M,W,F 11:00 – 11:50, 3013 ECEB
Professor John Dallesasse
2114 Micro and Nanotechnology Laboratory
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E-mail: jdallesa@illinois.edu
Office Hours: Tuesday 13:00 – 14:00
Lecture 25: October 21st, 2016
Assignments

• Reading from “Compound Semiconductors and Devices – An Introduction”
  – Mon 10/17: §’s 6.4, 6.5, 6.5.1, 6.5.2, 6.5.3, 6.5.4
  – Wed 10/19: §’s 7.1, 7.1.1, 7.1.2
  – Fri 10/21: §’s 7.2, 7.2.1, 7.2.2

• Homework: Will be assigned Friday, due Friday October 28th
Today’s Agenda

• Group IV Materials
• Bulk Crystal Growth
<table>
<thead>
<tr>
<th>SEP 26: Doping and Deep Levels</th>
<th>SEP 28: The Fermi Integral, Free Carrier Concentration, Surface States</th>
<th>SEP 30: III-V Semiconductor Lattice Constant and Bandgap</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCT 3: III-N and Group IV Semiconductors</td>
<td>OCT 5: Crystal Growth, Phase Diagrams **</td>
<td>OCT 7: Midterm Exam (Tentative) **</td>
</tr>
<tr>
<td>OCT 10: Energy Band Alignment, Model-Solid Theory</td>
<td>OCT 12: Strained Layer Structures</td>
<td>OCT 14: Strain Effects on Band Edges</td>
</tr>
<tr>
<td>OCT 24: Realistic Finite Quantum Wells</td>
<td>OCT 26: Superlattices and Minibands</td>
<td>OCT 28: Heterostructures in Electric Fields and the Franz-Keldysh Effect</td>
</tr>
</tbody>
</table>

**Guideline Only: Subject to Change**
Group IV Compounds: SiGe Alloys and SiC
Group-IV elements can be mixed to form alloys just like III-V compounds. They can form heterostructures with silicon using silicon as the substrate. These alloys include $Si_{1-x}Ge_x$, $Si_{1-y}C_y$, and $Si_{1-x-y}Ge_xC_y$. By adding Ge and C to the alloy can increase and decrease the lattice constant, respectively. By adjusting the amounts of Ge and C properly, a lattice matched $Si_{1-x-y}Ge_xC_y$ alloy can be grown on silicon substrates.

<table>
<thead>
<tr>
<th>Property</th>
<th>Diamond</th>
<th>$\beta$-SiC</th>
<th>Si</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent radius (Å)</td>
<td>0.077</td>
<td>—</td>
<td>0.117</td>
<td>0.122</td>
</tr>
<tr>
<td>Lattice constant (Å)</td>
<td>3.567</td>
<td>4.36</td>
<td>5.431</td>
<td>5.657</td>
</tr>
<tr>
<td>Lattice mismatch to Si</td>
<td>—0.52</td>
<td>—0.246</td>
<td>—</td>
<td>0.040</td>
</tr>
<tr>
<td>$f = (a_{film} - a_{Si})/a_{film}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bandgap at 4.2 K (eV)</td>
<td>5.48</td>
<td>2.2</td>
<td>1.19</td>
<td>0.66</td>
</tr>
<tr>
<td>Thermal conductivity (W/cmK)</td>
<td>20</td>
<td>5</td>
<td>1.56</td>
<td>0.6</td>
</tr>
<tr>
<td>Saturation drift velocity (10^7 cm/s)</td>
<td>2.7</td>
<td>2.5</td>
<td>1.0</td>
<td>0.6</td>
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<tr>
<td>Electron mobility (cm²/Vs)</td>
<td>1800</td>
<td>—</td>
<td>1500</td>
<td>3900</td>
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<tr>
<td>Hole mobility (cm²/Vs)</td>
<td>1600</td>
<td>—</td>
<td>450</td>
<td>1900</td>
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<tr>
<td>Dielectric constant</td>
<td>5.66</td>
<td>6.5</td>
<td>11.9</td>
<td>16</td>
</tr>
</tbody>
</table>
Lattice Constant of Group IV Alloys

Again, the lattice constant of group-IV alloys follows Vegard’s law.

- $Si_{1-x}Ge_x$:
  \[ a_o(x) = a_{Si} + (a_{Ge} - a_{Si})x = 5.431 + 0.226x \]
  Due to the $\sim 4\%$ lattice mismatch, $Si_{1-x}Ge_x$ grown on Si will take either a psuedomorphic (strained) thin layer form or form relaxed thick film with misfit dislocations at the interface.

- $Si_{1-x-y}Ge_xC_y$:
  \[ a_o(x) = a_{Si} + (a_{Ge} - a_{Si})x + (a_{C} - a_{Si})y \]

- $Si_{1-y}C_y$:
  There is no reliable experimental data for this material system.
SiGe Bandgap

Using the virtual-crystal approximation (VCA), the physical properties of the alloy are interpolated between the two end elements. The derived bandgap-composition plot and the band structure of $Si_{0.5}Ge_{0.5}$ are shown.

$\Delta$ is along the $<100>$ toward $X$ (100), $L$ is at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$.
Si/SiGe Heterostructures

The $Si/Si_{1-x}Ge_x$ heterostructure is a strained system for thin $Si_{1-x}Ge_x$ epitaxial layers grown on silicon substrate, the strain effect has to be included. The following figure shows the band gap variation of strained (thin) and relaxed (thick) $Si_{1-x}Ge_x$ layers as a function of Ge composition.
Materials Technology
Binary Phase Diagrams: Basics

- **Solidus**: The phase boundary between the solid and liquid or semi-liquid states
- **Liquidus**: The phase boundary between the liquid and semi-liquid or solid states
- **Solvus**: The phase boundary showing the limit of solubility of one phase in another, also, the boundary between a single solid phase region and a mixed solid phase region
- **Eutectic Point**: A point on the phase diagram where the liquid state exists below the melting point of either constituent. Also the point where the maximum number of phases are in equilibrium (invariant point)
- **Peritectic Point**: A point on the phase diagram where a first solid phase plus liquid react to form a second solid phase (invariant point)
- **Congruent Melting**: Melting where a phase melts to a liquid with the same composition as the solid
- **Incongruent Melting**: Melting where a phase melts to a liquid with a composition different than the solid and produces a solid with a different composition during cooling
- **Lever Law**: Used to determine the fraction of a given phase in a given region of interest
- **Tie Line**: Used to determine the composition of each phase present
5.1.1. Phase equilibrium

The temperature-composition phase diagram of a binary compound describes the equilibrium compositions between solid and liquid as a function of temperature. At a fixed composition, say $x_2$, the solid will be completely dissolved into liquid at a temperature $T_2$. At $T<T_2$, some binary compound AB will precipitate out from the liquid. At very low temperature, the liquid-solid mixture will be completely solidified into a mixture of solid A plus compound AB. At a composition of 50%, the equilibrium solid-liquid temperature is the congruent melting temperature $T_F$. 
Binary Phase Diagrams: Lever Rule

Lever Rule:

\[ X_a = \frac{c - b}{a - b} \]

\[ X_a \equiv \text{Weight percentage in alpha phase} \]

\[ a \equiv \text{Weight percentage of element "B" in the alpha phase} \]

\[ b \equiv \text{Weight percentage of element "B" in the beta phase} \]

\[ c \equiv \text{Weight percentage of element "B" (total)} \]

Example:

Weight percent of solid phase:

\[ X_s = \frac{w_o - w_l}{w_s - w_l} \]

Weight percent of liquid phase:

\[ X_l = \frac{w_s - w_o}{w_s - w_l} \]
Congruent Melting Point

The melting point at which the solid and liquid have the same composition is called the *congruent melting point*. The congruent point of some materials may not always happen at a fixed composition of 50%. There is a range of composition around 50% which defines the extent of the solid phase called *existence region*. The enlarged existence region of GaAs is show on the right. The congruent melting point occurs slightly to the Ga-rich side of the stoichiometric composition.

For crystal grown with compositions in the existence region different from 50% value, the formed solid will contain non-stoichiometric crystal defects. These defects such as vacancies, interstitials, and antisite defects can have profound influence on the electrical properties.
Phase Diagram: Contacts

Source: http://www1.asminternational.org/asmenterprise/APD/SearchAPD.aspx
Phase Diagram: Crystal
Other Phase Diagrams
Vapor Pressure of GaAs

- Vapor pressure of GaAs:
  Near the congruent melting temperature, the binary dissociates into elements. The vapor pressure at this temperature is determined by the more volatile group-V element. The equilibrium vapor pressure of Ga, As$_1$, As$_2$, and As$_4$ over the GaAs liquidus are shown. The equilibrium vapor pressure required at the melting temperature of GaAs ($T_L=1238{\degree}C$) over a Ga+As liquidus is ~1atm, which is dictated by the high vapor pressure of As$_4$. It also displayed the very different vapor pressures for each species over Ga- or As-rich liquidus. For practical purpose, a group-III-rich liquid is commonly used for crystal growth from the melt.
Vapor Pressure of the InP System

Near the congruent melting temperature, the vapor pressure over InP is dominate by the high vapor pressure of phosphor tetramers, $P_4$. The equilibrium group-V vapor pressure of InP at the melting temperature ($T_F=1062^\circ C$) over the InP liquidus is $\sim 27$ atm. The high equilibrium pressure required for the growth of bulk InP from the liquid limits the selection of crystal growth methods.
Crystal Growth Techniques

(a) Horizontal gradient freeze method
- Static growth method - melt is gradually solidified by the movement of a temperature gradient along the melt.
- Sources - Ga in high temp zone; As in low temp (620°C) zone.
- Seed crystal - to initiate single crystal growth along <111> orientation.
- Slow cooling rate to reduce thermal stress induced dislocations.
- InP growth requires a two-step process; synthesis polycrystalline InP first; single crystal growth in the second solidification cycle.
- Forms semi-circular or D-shape crystals.

(b) Horizontal Bridgman method:
- Similar to HGF except now the furnace is moved along the quartz ampoule.
(c) Vertical growth methods

- **Vertical Bridgman growth method** -
  Similar to the horizontal Bridgman method except the crucible and furnace moving relatively in a vertical arrangement.

- **Vertical gradient freeze (VGF) method** -
  This is a stationary growth method like horizontal gradient freeze method. Only the temperature gradient is slowly adjusted to cool the melt for crystal growth. Due to the reduced axial and radial temperature gradients, the convective melt flow and thermal stress can be minimized. Therefore, large crystals (>3") with very low dislocation density (≤100cm⁻²) are obtained in GaAs and InP.
(d) Crystal Growth by Pulling from a Crucible

Czochralski (CZ) pulling method:
A seeded single crystal is withdrawn from the melt and is rotated to maintain thermal uniformity and cylindrical geometry of the crystal.

- Seed is dipped into the melt at a temperature slightly higher than the melting temperature.
- The melt temperature is reduced to enhance oriented crystal growth.
- The rotating seed is withdrawn from the melt at a slow rate of 1-10mm/h.
- The crystal diameter is increased by lowering the melt temperature. Once the desired diameter is reached, the lowering of the melt temperature is stopped.
- Inert gas environment is used to prevent oxidization of the melt.

http://www.youtube.com/watch?v=xftnhfa-Dmo&feature=related
Liquid Encapsulated Czochraski (LEC)

- Using CZ pulling method to grow compound semiconductors having volatile elements such as As and P in GaAs and InP, respectively, faces the problem of decomposition of the melt.
- LEC technique was developed to prevent loss of group-V element from the melt by covering the melt with a thin layer of $B_2O_3$. A counter pressure of an inert gas is maintained above $B_2O_3$.
- Attributes of $B_2O_3$:
  - Low vapor pressure (0.1mm Hg at 1238°C)
  - Low viscosity
  - Density lower than the melt (1.5 g/cm³)
  - Does not react with the melt and the crucible
  - Lower melting temperature (softens and starts to flow at 450°C)
  - Water content can be reduced by vacuum baking at ~1000°C.
- LEC growth techniques
  - **Two-step method**: The III-V compound source materials are prepared separately outside the LEC system. The synthesized source materials was then used for LEC growth.
  - **High-pressure LEC method**: The source materials are synthesized from elements directly inside the LEC chamber. It generally associate with very high pressure, e.g., it needs 60atm to synthesize GaAs directly.
LEC - System

Liquid Encapsulated Czochraski (LEC) method:

The LEC growth system is very similar to a CZ pulling system. In order to handle the high vapor pressure, the whole growth apparatus is enclosed in a high pressure chamber. An excess As or P source is provided inside the chamber to replenish group-V loss in the melt during the growth.
Crystal Imperfections

- Concentration of EL2 level control (point defects)
- Non-uniform heat flow during solidification and ensuing thermal stress causing plastic deformation. The generated dislocation distribution of a LEC GaAs crystal has a W-shape and been verified theoretically as well as experimentally. The VGF growth method provides a better solution.
- Propagation of dislocations from defective seed crystal, inclusions, and foreign particles.
Boules
Agenda for Next Class

• Epitaxy
• Electrical Properties of Heterstructures
Thank You!
# Final Exam

<table>
<thead>
<tr>
<th>Course</th>
<th>Section</th>
<th>CRN</th>
<th>Date</th>
<th>Day</th>
<th>Start Time</th>
<th>End Time</th>
<th>Room</th>
<th>Exam Type</th>
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<tbody>
<tr>
<td>ECE 488</td>
<td>C</td>
<td>66375</td>
<td>12/12/2016</td>
<td>M</td>
<td>7:00 PM</td>
<td>10:00 PM</td>
<td>3017 Electrical &amp; Computer Eng Bldg</td>
<td>Extra Space</td>
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## Periodic Table of the Elements

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<th>6</th>
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<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
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<tbody>
<tr>
<td>H</td>
<td>He</td>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td>Ne</td>
<td>Na</td>
<td>Mg</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Helium</td>
<td>Lithium</td>
<td>Beryllium</td>
<td>Boron</td>
<td>Carbon</td>
<td>Nitrogen</td>
<td>Oxygen</td>
<td>Fluorine</td>
<td>Neon</td>
<td>Sodium</td>
<td>Magnesium</td>
</tr>
</tbody>
</table>

### Periodic Table Notes

- **C**: Solid
- **Hg**: Liquid
- **H**: Gas
- **Rf**: Unknown

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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Common Semiconductors

```
<table>
<thead>
<tr>
<th>Material</th>
<th>Bandgap Energy (eV)</th>
<th>Lattice Constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>3.4</td>
<td>4.3</td>
</tr>
<tr>
<td>GaN</td>
<td>3.4</td>
<td>3.4</td>
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<tr>
<td>ZnS</td>
<td>3.6</td>
<td>4.2</td>
</tr>
<tr>
<td>MgS</td>
<td>3.6</td>
<td>4.2</td>
</tr>
<tr>
<td>MgSe</td>
<td>4.0</td>
<td>4.6</td>
</tr>
<tr>
<td>MgTe</td>
<td>4.0</td>
<td>4.6</td>
</tr>
<tr>
<td>Diamond</td>
<td>5.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>
```

“*Italic*” = indirect gap
“*Roman*” = direct gap

○ hexagonal structure
□ cubic structure

Fig. 21.4. Room-temperature bandgap energy versus lattice constant of common elemental and binary compound semiconductors.
Contact Information & Website

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jcarls21@illinois.edu

Website:
https://courses.engr.illinois.edu/ece488/
Course Objectives
Course Objectives

• Develop a working knowledge of compound semiconductor materials and devices
• Provide a foundation for future advanced physical electronics courses
• Provide basic device knowledge to support a career in wireless communications or photonics
• Provide sufficient background such that you can begin to read and understand the literature on compound semiconductor materials and devices
Course Outline
Course Outline

• Review of semiconductor fundamentals
  – Elementary quantum mechanics
  – Atomic bonding and crystal structures
  – Electronic band structures of solids

• Compound semiconductor materials
  – Compound semiconductor crystals
  – Material technologies

• Properties of heterostructures
  – Basic heterostructure properties
  – Electrical properties of heterostructures
  – Optical properties of heterostructures

• Heterostructure devices
  – High-speed electronic devices
  – Semiconductor lasers
  – New device development
Course Description (Detailed)

- Review of quantum, mechanical basics including wave-particle duality, Schroedinger wave equation, one-dimensional free and bounded particles in quantum wells
- Introduction to compound semiconductor crystals, structural and electrical properties, free carrier concentration and Fermi-Dirac integral, III-V alloys
- Phase equilibrium, growth of bulk crystals and phase equilibrium, liquid phase epitaxy, vapor phase epitaxy, metalorganic chemical vapor deposition, molecular beam epitaxy
- Basic heterostructure properties, energy band alignment models, strain effect on the bandgap energies, abrupt p-n heterojunction in equilibrium, heterojunction under bias
- Electronic properties of real quantum wells, potential barrier and tunneling, superlattices and miniband, quantum wells in electric fields, modulation doping and two-dimensional electron gas
- Optical properties of dielectrics, absorption, radiative transitions - Einstein relations, stimulated emission, absorption and emission rates in semiconductors, transitions in degenerated semiconductors, nonradiative recombination processes
- Metal-semiconductor field-effect transistors, pseudomorphic high-electron mobility transistors, heterojunction bipolar transistors, transfer electron devices, resonant tunneling devices
- Photodetectors, solar cells, light-emitting diodes (LEDs), dielectric waveguide and heterostructure laser theories, quantum well lasers, distributed feedback lasers, vertical cavity surface emitting lasers
Prerequisites

• ECE340 or equivalent basic semiconductor course
• Physics background – Basic modern physics
• Math background – differential equations
## Tentative Schedule [1]

<table>
<thead>
<tr>
<th>Date</th>
<th>Topic</th>
<th>Date</th>
<th>Topic</th>
<th>Date</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>AUG 22</td>
<td>Introductions, Objectives, Class Outline, Policies</td>
<td>AUG 24</td>
<td>Motivation, Intro to Quantum Theory</td>
<td>AUG 26</td>
<td>Infinite Square &amp; Triangle Wells</td>
</tr>
<tr>
<td>AUG 29</td>
<td>Potential Steps, Coulomb Well (Hydrogen Atom), Atomic Bonding</td>
<td>AUG 31</td>
<td>Crystal Structures, Diffraction</td>
<td>SEP 2</td>
<td>Reciprocal Space, Diffraction Condition</td>
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<tr>
<td>SEP 5</td>
<td>LABOR DAY NO CLASS</td>
<td>SEP 7</td>
<td>The Brillouin Zone, Band Structures, Density of States</td>
<td>SEP 9</td>
<td>Bloch Theorem, Empty Lattice Model</td>
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<tr>
<td>SEP 12</td>
<td>Band Gaps</td>
<td>SEP 14</td>
<td>Kronig-Penny Model</td>
<td>SEP 16</td>
<td>Effective Mass, Bloch Oscillations, Band Structure</td>
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<tr>
<td>SEP 19</td>
<td>Compound Semiconductor Crystals</td>
<td>SEP 21</td>
<td>Phonons</td>
<td>SEP 23</td>
<td>Electrical Properties, Gap, Effective Mass, Mobility</td>
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</tbody>
</table>

**Guideline Only: Subject to Change**
<table>
<thead>
<tr>
<th>Date</th>
<th>Topic</th>
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<tbody>
<tr>
<td>OCT 31:</td>
<td>Optical Properties of Dielectric Media</td>
</tr>
<tr>
<td>NOV 2:</td>
<td>Absorption in Semiconductors</td>
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<tr>
<td>NOV 4:</td>
<td>Transitions Between Discrete States</td>
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<td>NOV 7:</td>
<td>Radiative and Non-Radiative Transitions Between Bands</td>
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<tr>
<td>NOV 9:</td>
<td>Introduction to Heterojunction Devices, MESFETs</td>
</tr>
<tr>
<td>NOV 11:</td>
<td>Modulation Doping</td>
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<tr>
<td>NOV 14:</td>
<td>High Electron Mobility Transistors (HEMTs)</td>
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<td>NOV 16:</td>
<td>High Electron Mobility Transistors (HEMTs)</td>
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<tr>
<td>NOV 18:</td>
<td>GaN High Electron Mobility Transistors; NOV 21-25: Thanksgiving</td>
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<tr>
<td>NOV 28:</td>
<td>Heterojunction Bipolar Transistors (HBTs)</td>
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<td>NOV 30:</td>
<td>Heterojunction Bipolar Transistors</td>
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<tr>
<td>DEC 2:</td>
<td>Heterostructure Lasers</td>
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<tr>
<td>DEC 5:</td>
<td>Heterostructure Lasers</td>
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<tr>
<td>DEC 7:</td>
<td>Photodiodes and Solar Cells; Last Lecture</td>
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<tr>
<td>FINAL EXAM:</td>
<td>Per Registrar’s Office</td>
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Grading and Policies
# Grading

<table>
<thead>
<tr>
<th>Grading Category</th>
<th>Percentage of Grade</th>
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<tbody>
<tr>
<td>Homework &amp; Class Participation</td>
<td>30%</td>
</tr>
<tr>
<td>Quizzes (Dates Will be Announced)</td>
<td>10%</td>
</tr>
<tr>
<td>Mid-Term Exam</td>
<td>20%</td>
</tr>
<tr>
<td>Final Exam</td>
<td>40%</td>
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</table>

**Homework:**
- Due 1 week after assigned, due in class, no late homework accepted

**Quizzes:**
- 2 quizzes, dates will be announced ahead of time, 20 minutes

**Exam(s):**
- Calculator allowed
- 8.5 X 11, hand-written, double-sided formula sheet

**Key Points:**
- Come to class
- Do your homework
- If you’re having problems attend office hours
Other Comments

• Ask questions if you have them
• Don’t miss quizzes, exams, or homework
• Turn off your cell phones
• No video recording or photography in class
• Include name and NetID on all documents turned in for credit
• Class notes (required) can be purchased from the ECE Supply Center
• Additional reading materials will be distributed in class or through the course website
• Reference for further reading (NOT required):
  • Solid state physics:
  • Semiconductor physics and devices:
    – S.L. Chuang, *Physics of Semiconductor Devices*
  • Quantum wells and heterostructures:
  • Compound semiconductor materials: