

Materials Science and Engineering PhD Qualifying Exam

WRITTEN EXAM: Tuesday, January 18, 2022 9:00AM-1:00PM.
Virtual, see Zoom and Blackboard info below.

ORAL EXAM: Friday, January 21, 2022, 10:30AM-2:30PM
Virtual, see Zoom info below.

General Instructions:

- Calculators are allowed.
- Only the books indicated will be allowed.
- NO INTERNET (other than the Blackboard/Zoom connections if offered remote)

Complete the topical sections as instructed.

Section I: Answer MS 577 Problems

- **Problem 1:** Electrical, Optical, Magnetic Properties of Matls (MS 577, Swan)
CLOSED BOOK. NOTES ALLOWED (3 pages, double-sided). If remote, no internet or people. Calculator permitted.

Section II: Answer 3 out of 4 Problems

- **Problems 1 and/or 2:** Thermodynamics and Statistical Mechanics (MS 505, Pal)
CLOSED BOOK, OPEN NOTES (1 pg, double sided), bring ruler to the exam, graphing calculator optional.
- **Problems 3 and/or 4:** Kinetic Proc. in Matls (MS 503, Basu)
CLOSED BOOK, NO NOTES.

Section III: Answer 1 out of 2 Problems

- **Problem 1:** Computational Methods of Materials (MS 508, Coker).
CLOSED BOOK, NOTES ALLOWED (one page, double-sided).
- **Problem 2:** Physics of Semiconductor Materials (MS 574, Bellotti)
CLOSED BOOK, NOTES ALLOWED (one page, double-sided).

General Written Exam Guidance on Page 2.

Oral Exam Schedule, Friday, January 21.

Virtual. You MAY have the option of using a division conference room for white board access. Please confirm your preference with eflagg@bu.edu.

<https://bostonu.zoom.us/j/98626793973?pwd=eFZGQzNpelUxMUdUZW5IREk4S3Bndz09>

Meeting ID: 986 2679 3973

Passcode: 028894

Oral Schedule	Student	Advisor	Room (optional)	Zoom Room
10:30-11:30	Wadehra	Ludwig	121	1
11:30-12:30	Quinn	Brown	105	2
12:30-1:30	Morey	Ryan	121	3
1:30-2:30	Exam Committee		Virtual	5

General Written Exam Guidance

- **8:30AM, Tuesday, January 18.** This is the time recommended to arrive in the virtual settings; links below in the text box.

General Guidelines

- Calculators are permitted.
- Bathroom breaks are permitted. You don't need to ask permission.
- No other smart devices are permitted (i.e., no cell phones except if used for Zoom connection)
- Only books and notes permitted as indicated on exam cover sheet.
- **You must sign the honor code on each exam question.** Just write the words "Honor Code" at the top of each section's answer sheet (just first page) and sign. You should not write this, but the honor code is:
 - Honor Code Statement: I have not received nor given any unauthorized aid during this exam in accordance with the indicated rules outlined above. I further certify that all work is entirely my own and does not violate the Boston University Academic Conduct Code.Signature and UID:
- **Exam Responses**
 - Make sure your handwriting is clear and legible.
 - Only write on one side of each exam response sheet.
 - Number the pages by question.
- **Clarification Needed During the Exam?** Alert the Exam Proctor if clarification is needed on anything.
 - Please include your cell phone number.
 - The Exam Proctor will contact the faculty and the faculty will send clarification via the Proctor in most cases.
 - The faculty member may call you or chat with you in a Zoom breakout room.

Remote Details. Enter the Zoom meeting and Blackboard so that you can ask the Proctor questions and be ready for the questions which will be released automatically at 8:55AM and close at 1:00PM (will allow upload until 1:30PM; later only if you have an accommodation).

- **Blackboard**
 - [Materials PhD Written Qual](#)
- **Zoom**
 - <https://bostonu.zoom.us/j/92623560436?pwd=akpPMzB3UGc2dGIBK2FXK0hGakpLQT09>
 - Meeting ID: 926 2356 0436
 - Passcode: 996153
 - The Zoom session will be recorded.
 - Your camera should show your face and your work surface.
 - Virtual backgrounds are not permitted.
- **Exam timeframe:** 9:00AM-1:00PM
- **Exam Responses** must be uploaded to Blackboard by 1:30PM (later if you have an accommodation). (Use a cell phone app or scanner to pdf responses and upload or email to instructor for grading.)

Carriers in semiconductors. In semiconductor device physics, we want to control current flows through carrier densities and (built-in) voltages. The three questions below pertain to intrinsic carrier concentrations, how we calculate carrier concentrations, and doping. To your aid, you have a figure showing the measured number of intrinsic carrier density as a function of temperature, properties of Si, Ge, GaAs, and a couple of relevant formulas.

a) Intrinsic carrier density and effective density of states for Si, Ge and GaAs at Room Temperature (RT)

- Use the diagram to find the intrinsic carrier concentrations for Si, Ge and GaAs at RT (RT: $1000/T = 3.3$). (Mark the levels on the graph too)

Si:

Ge:

GaAs:

- Si, Ge and GaAs have the same lattice structure, very similar number density, and are Group IV (Si, Ge) and III-V (GaAs). Why the large differences in intrinsic carrier density?

b) An approximation we use with abandon to calculate semiconductor carrier densities relies on approximations: the effective Density of states, N_c and N_v , and Maxwell Boltzmann (MB) statistics. This approximation works very well if the doping is an order of magnitude below the effective DOS.

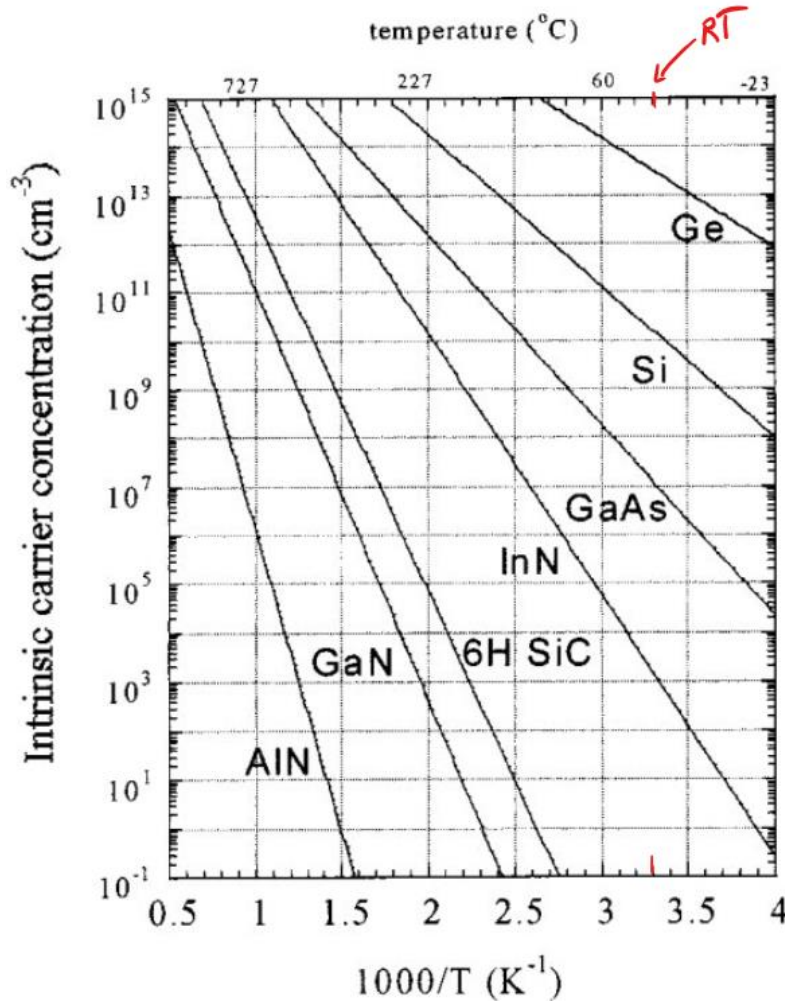
- How does N_c and N_v relate to the actual density of states and the carrier statistics? Use a drawing of the density of states and the carrier statistics to illustrate your answer for an intrinsic semiconductor.
- Why does the MB approximation of the Fermi-Dirac distribution no longer work so well for high doping levels? Illustrate your answer.

c) Doping, Fermi levels and diodes in Si at RT with $N_A = N_D = 10^{16} \text{ cm}^{-3}$.

- Use the above doping and draw the pn junction band-diagram at zero volt external bias. What is the built-in voltage V_{bi} ?

- Use the above doping and draw the pn junction band diagram at external forward bias $V = V_{bi}$. Comment of the I-V characteristics; Is the diode equation valid at this voltage?

Properties	Si	Ge	GaAs
Atoms/cm ³	5.0 x 10 ²²	4.42 x 10 ²²	4.42 x 10 ²²
Atomic Weight	28.09	72.60	144.63
Breakdown Field	approx. 3 x 10 ⁵	approx. 1 x 10 ⁵	approx. 4 x 10 ⁵
Crystal Structure	Diamond	Diamond	Zincblende
Energy Gap at 300K (eV)	1.12	0.66	1.424



$$n = n_i \exp((E_F - E_i)/kT) \quad \text{and} \quad p = n_i \exp((E_i - E_F)/kT) \quad pn = n_i^2$$

$$n = N_c \exp\left(-\frac{E_C - E_F}{kT}\right) \quad p = N_v \exp\left(-\frac{E_F - E_V}{kT}\right)$$

Diode equation: $J = J_{sat} (e^{\frac{eV}{kT}} - 1)$

Materials Ph.D. Qualifying Examination
Thermodynamics
(Allowed 1-page formula sheet and a calculator)

1. The following expression provides the internal energy of a one-component system:

$$U = \frac{V_0 \theta S^3}{NVR^2}$$

Where V_0 , θ and R , are constants. S , V , N are entropy, volume, and number of moles in the system, respectively.

- a. Write three other equations of state.
 - b. Show that temperature, pressure, and chemical potential are all intensive properties.
 - c. Write the differential form of the internal energy, dU .
 - d. How does the above system differ from an ideal gas?
2. By how much does the melting point of silver change as a result of the solution of 0.16 g of oxygen in 100 g of liquid silver? Neglect the solubility of oxygen in solid silver. Please note that the oxygen dissolves in the monoatomic form and the solution is ideal. Please use the following data to solve the problem:

Pure silver melts at 961.8 C. The heat of melting of silver is 11,255 J per mole of silver and assume that it does not change with temperature. Atomic weight of silver and oxygen are 108 and 16, respectively.

Hint: You may assume that the product of the new melting point with dissolved oxygen and the original melting point of pure silver (with no oxygen) is approximately equal to the square of the original melting point of silver (with no oxygen).

January 2022 MSE Qualifier Questions: MS 503

Closed book, NO additional notes

Some physical constants and kinetics formulas that may or may not be relevant:

Gas constant, $R = 8.314 \text{ J/mole-K}$

Avagadro's constant, $N_{Av} = 6.023 \times 10^{23} \text{ mole}^{-1}$

Plank's constant, $h = 6.626 \times 10^{-34} \text{ J-s}$

Boltzman's constant, $k = 1.381 \times 10^{-23} \text{ J/K}$

Charge of an electron, $e = -1.602 \times 10^{-19} \text{ Coulombs}$

$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

$$c(x,t) = \frac{S}{\sqrt{4\pi Dt}} \exp(-x^2/4Dt), \quad c(x,t) = A + \text{Berf}(x/2\sqrt{Dt}),$$

$$c(x,t) = \frac{4c^0}{\pi} \sum_{j=0}^{\infty} \frac{1}{2j+1} \sin\left(\frac{(2j+1)\pi x}{l}\right) \exp\left(-\left(\frac{(2j+1)\pi}{l}\right)^2 Dt\right)$$

$$\bar{c}(t) = \frac{8c^0}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp\left(-\left(\frac{(2j+1)\pi}{l}\right)^2 Dt\right)$$

$$D(\text{vacancy mechanism}) = \gamma a^2 \nu_D P_v \exp\left(-\frac{\Delta G_m^v}{RT}\right),$$

$$D(\text{interstitial mechanism}) = \gamma a^2 \nu_D \exp\left(-\frac{\Delta G_m^i}{RT}\right),$$

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

$$\Delta G = V\Delta G_v + V\Delta G_s + A\sigma$$

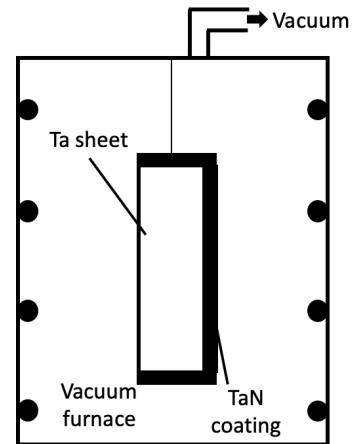
$$G = H - TS$$

$$\frac{\varepsilon}{2} = \frac{L_S}{ZN_{Av}}$$

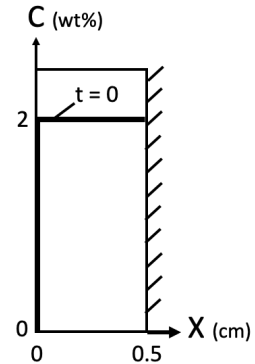
$$\text{For FCC: } \sqrt{2}a = 4r$$

Problem 1

The solubility limit of atomic H in Ta at 1000°C is 2wt%. A 5mm thick Ta sheet at 1000°C, is saturated with H. The sheet is coated on one side and the edges with a TaN coating. Since H diffuses rapidly in Ta, the sheet is subjected to a degassing anneal by placing in a vacuum furnace at 1000°C. This causes H atoms in the sheet to diffuse to the exposed surface, and quickly desorb as gas phase H₂ which is quickly removed by the pump (see figure on right, where the sheet is shown in cross-section).



Since the desorption step is much faster than the diffusion step, it can be assumed that the concentration of the exposed surface of the sheet is maintained at 0wt% at all times. Further, assume that the diffusivity of H in TaN is many orders of magnitude slower than in Ta, so the coated surfaces can be considered to be effectively zero flux planes. The initial concentration profile in the sheet is shown in the figure to the right. Note that $x = 0$ is at the exposed surface of sheet. **Please use this axis system for all your answers.**



a) If the activation energy, Q , of diffusion of atomic H in Ta is 1eV, and $D_0 = 0.913 \text{ cm}^2/\text{s}$, calculate diffusivity of hydrogen, D_H , at 1000°C.

b) Sketch qualitatively, the change in the concentration profile in the sheet as a function of time, assuming 1-D out-diffusion of H. The profile at $t = 0$ is shown.

c) How long will it take for the concentration at a depth of 1mm from the exposed surface to reach 1wt%? There is more than one way you can solve this. State (without solving) two ways you can approach this problem. **Justify** which approach you have chosen, and answer the question (solve) using that approach. Assume error tolerance is 1%.

d) How long will it take to remove 90% of the initial H in the Ta? **Justify** any assumption you make.

Problem 2

The hypothetical metal Photonium (Po) transforms from a higher temperature β -phase to a lower temperature α -phase by nucleation of **cubic** shaped α precipitates with $\{100\}$ surfaces. The equilibrium temperature for this transformation is 1200K. Consider the following experiment: a sample of Po is rapidly quenched from 1300K to a temperature T below 1200K. The sample is then held isothermally at that temperature for nucleation of α -Po to occur

a) If a is the side of the cubic solid, show that if strain energy is neglected, then:

$$a^* = -\frac{4\gamma}{\Delta G_V}, \Delta G^* = \frac{32\gamma^3}{\Delta G_V^2}$$

where γ is the surface energy and $\Delta G_V (= G_V(\alpha) - G_V(\beta))$ is the free energy change per unit volume.

- b) If it is assumed that changes in enthalpy and entropy per unit volume, ΔH_V (defined as $\Delta H_V(\alpha) - \Delta H_V(\beta)$) and ΔS_V (defined as $\Delta S_V(\alpha) - \Delta S_V(\beta)$) are independent of T, show that:

$$\Delta G_V = \frac{\Delta H_V \Delta T}{T_E}, \text{ where } \Delta T = T_E - T \text{ and } T_E \text{ is the equilibrium temperature.}$$

- c) The crystal structure of α -Po is FCC. Based on the broken bond model, **derive** an expression relation bond energy, ϵ , to the latent heat of sublimation, L_S , in an FCC metal. Using the broken bond model, show that the $\{100\}$ surface energy of incoherent α Po precipitates, γ_{incoh} , is 0.4 J/m².

DATA: Latent heat of sublimation of α -Po is 90 KJ/mole. The lattice parameter of the FCC α -Po unit cell is 5Å.

NOTE: The energy of a broken bond is $\epsilon/2$, and the coordination number, Z, of atoms in FCC metals is 12.

- d) There is a question of whether the nuclei of α -Po precipitates are coherent or incoherent. Derive the expression for a^* and ΔG^* when strain energy is involved. Over what range of T will i) coherent and ii) incoherent precipitation of α -Po occur?

DATA: $\Delta H_V = -1.5 \times 10^8 \text{ J m}^{-3}$, $\gamma_{\text{incoh}}/\gamma_{\text{coh}} = 10$ (use γ_{incoh} from part c))

Strain energy/unit volume for coherent precipitates = $7 \times 10^6 \text{ J m}^{-3}$

Strain energy/unit volume for incoherent precipitates = 0 J m^{-3}

Consider a simple 3D cubic lattice with lattice constant a and one basis atoms at $\vec{b} = 0$.

- Sketch the Wigner-Seitz, compute the reciprocal lattice vectors, sketch the Brillouin zone.
- Using the tight binding method derive an expression for the energy bands as a function of k_x , k_y and k_z .
- Compute the effective masses along $[111]$ and $[100]$ directions.