A Course in Electronic Materials:

PROCESS TECHNOLOGY OF SOLID-STATE MATERIALS AND DEVICES

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THE CHEMICAL ENGINEER is making an increasing number of contributions to solid state industries, from ultrapurification and single crystal production to process engineering in semiconductor integrated electronics. The rapidly-evolving technological requirements of the highly competitive electronic materials and device industries are creating new horizons for well trained chemical engineers with specialization in solid state engineering: a working knowledge of solid state chemistry, basic device physics and process chemical engineering. In response to the importance of contributing to solid state engineering education, a new course has been introduced into the chemical engineering curriculum at the University of California, Berkeley.

The foundations of the modern solid state industries developed slowly in the early 1900's. Among the most important concepts was that of crystal lattice defects introduced by Frenkel in 1926. Schottky and Wagner, Fowler and others then developed the statistical mechanics of crystals to describe states of disorder in a nearly perfect lattice. Wilson also contributed to this development with the band theory of solids which was based on quantum mechanics. The recognition of the importance of defects in solids has had a profound influence on our current understanding of many diverse phenomena including solid state reactions, heterogeneous catalysis, semiconductor electronics, photography and laser physics. The defect chemistry of solids is of such continuing importance in solid state engineering that this subject, including the supporting basics of solid state chemistry were chosen for the basis of the new course.

The beginning of electronic device technology began in earnest with the disclosure of the Schottke-barrier field-effect transistor in 1940. At that time the device operated at a net power loss, and it was evident that new experimental technologies were needed for ultrapure single crystal production and device processing. New purification procedures such as zone refining were introduced, as well as techniques able to control surface defects. The new approaches ultimately climaxed in power gain with the Bardeen-Brattain point contact transistor in 1947. Since that time advancements in process technology of solid state devices have appeared at an ever accelerating rate. In recent years, planar processing, large scale integration, and single crystal film processing have expanded the techniques and needed expertise of the process engineer. The basis for understanding these developments in process technology, and techniques for applying them in current applications, form the latter part of the new course.

COURSE OBJECTIVES

THE MAIN PURPOSE of this course then is to provide students with an introduction to and working knowledge of (a) the chemistry of the solid state, (b) theory and practice of single crystal growth and (c) process operations and technologies for solid state device fabrication. An important theme is that the attainable physical properties of electronic, magnetic and optical materials are often limited by process-induced defects, and as a consequence, fabrication processes must be designed to control materials properties so as to optimize the performance of the final device. The student acquires an understanding of the methods for control of electrically, magnetically and optically active defects and gains insight into the effect of processing variables on materials and defect-related device properties.

The course is a chemical engineering elective designed for senior and first year graduate students of chemical engineering who are interested in a materials engineering option. Nevertheless, this one-quarter course has attracted students from departments of electrical engineering, chemistry and materials science. A prerequisite for enrollment is a basic course in materials science or materials engineering; most of the chemical engineering seniors at Berkeley, and many entering graduate students have completed this prerequisite. In addition, some chemical engineering students concurrently enroll in an electrical engineering course in Electronic Circuits designed specifically for non-majors.

The new course complements several electronic materials and related curricula within the university. The chemical engineering courses in Mass Transfer, Transport Phenomena and Chemical Processing of Inorganic Compounds coordinate with the sections on crystal growth, chemical vapor deposition, oxidation and diffusion. The course treatment of silicon is extended in the electrical engineering courses Processing and Design of Integrated Circuits, and Semiconductor Devices; also, the treatment of point defect thermodynamics provides a basis for advanced physical property studies offered in Physics and Chemistry of Semiconductors. Two complementary courses in physical properties are offered in materials science: Thermal and Optical Properties of Materials and Electrical and Magnetic Properties of Materials. Nevertheless, the treatment of the defect chemistry of solids and relation to chemical phenomena in solid state materials and device processing remains unique to the new course.

Table I.

OUTLINE OF COURSE ON ELECTRONIC MATERIALS

		Ref.
1.	Introduction: Solid-State Engineering; Materials and Devices; Process Technologies.	1, 2
2.	Crystal Chemistry: Crystal Structures and Bonding; Energetics of Defects; Point Defect Equilibria; Laser Crystal Chemistry.	1, 3-5
3.	Electronic Defect Structure: Equilibria with Impurities; Transport Properties and Lattice Defects.	1, 3, 4
4.	Ultrapurification: Purification Schemes; Halide Transport; Zone Refining.	6, 7, 8
5.	Crystal Growth: Use of Phase Equilibria; Czochralski Crystal Growth; Growth from Solution.	1, 9, 10
6.	Chemical Vapor Deposition: Kinetic Mechanisms; Chemical Transport; Vapor Phase Epitaxy of Silicon and Gallium Arsenide-Phosphide.	11, 12
7.	Processing of Silicon Devices: Photoresist Technology; Chemical Etching; Oxidation; Diffusion.	2, 11
8.	Discrete Component Processing: MOS Technologies; Packaging.	11, 13
9.	Electro-optical Device Processing: Solar Cells; Light-Emitting Diodes; Heterostructure Devices.	14, 15
10.	Magnetic Device Processing: Magnetic Thin Films; Garnet Film Memories.	16, 17

The main purpose of the course is to provide a working knowledge of solid-state chemistry, theory and practice of single crystal growth and process operations and technology for solid state device fabrication.

COURSE CONTENT

THE TEN TOPICAL sections shown in Table I comprise the course content. The student is introduced to the field of solid state engineering and shown how materials purification, crystal growth and select processing steps influence the performance of solid state devices. Single crystals and working devices serve as in-class examples: 3" dia. germanium crystals, ultra-high purity compound crystals, and silicon memory chips, light-emitting diodes and magnetic thin film memories in different stages of fabrication.

The fundamentals of crystal chemistry are explored in the next section beginning with a review of Bravais lattices and bonding. Magnetic and ferroelectric crystal structures are examined from an ion-centered approach, while optical, semiconducting and superconducting crystals are examined in terms of bonding and band structure. Defects in solids are introduced, and mass action relations between point defects solved by matrix methods to obtain defect equilibria. Factors influencing substitutional ion solubilities in laser crystals are explored. Defect equilibria between electronic defects and impurities are then introduced and related to electronic transport properties.

Section four presents ultrapurification schemes for elements and compounds. The selected removal of electrically active impurities is emphasized. Two purification processes are examined in detail: halide transport purification and zone refining, using a case study approach for silicon and group III-V compounds.

Crystal growth fundamentals are presented in Section five, where phase equilibrium requirements and non-stoichiometry consequences are explored for different growth methods. Interface attachment kinetics and defect densities are related to crystallization driving forces for different growth mechanisms. Czochralski crystal growth of silicon and III-V compounds and solution growth of garnets are treated as extended examples. Interesting interactions are explored between crystal growth phenomena and lattice defects which influence both impurity solubility and growth rates. A typical problem is shown in Homework Example 1.

Reactor design and chemical reaction processes of chemical vapor deposition are presented in Section six, beginning with a discussion of kinetic mechanisms and rate control regimes. Closed system chemical transport crystal growth fundamentals are explored. Finally, commercial reactors, chemical reactions and growth conditions for silicon and gallium arsenide-phosphide are explored. An illustrative problem treated is described in Homework Example 2.

Section seven is devoted to unit processes for solid state device fabrication. For several processes, chemical etching, oxidation and diffusion, there exists a wealth of literature, and easily identified rate dependence on lattice defects. Consequently, these processes serve to exemplify the influence process variables have on physical properties of solid state materials.

In Sections eight through ten, process technologies of selected devices are presented: bipolar and metal-oxide-silicon (MOS) transistors, solar cells and light-emitting diodes and magnetic thin film memories. For each, the sequence of process operations is identified and the process conditions and critical properties are outlined. The unit processes examined earlier in the course are drawn on as a basis for this section. In homework problems the processing conditions needed to achieve a final device of given characteristics are sought in terms of rate processes and process alternatives.

Demonstrations supplement the lecture and reading material, and provide closer contact with industrial processes.* Czochralski crystal growth is demonstrated, and melt convection simulated. Chemical vapor deposition is demonstrated with a graduate research reactor. The current-voltage characteristics of electronic devices are demonstrated with a semiconductor curve tracer.

A term paper was an integral part of the course during the first two years of development. This project served to integrate the course material with a specific topic of interest to each student. The conditions and deadlines for this assignment were presented at the beginning of the course, with a topic approved and abstract written by mid quarter. The most successful topics chosen are listed in Table II. In the last

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Table II.

TERM PAPER TOPICS

- MOS Processing Techniques.
- Ion Implantation Techniques for the Manufacture of New Semiconductor Devices.
- Recent Innovations in Zone Refining.
- Photoresist Properties and Use in Semiconductor Processing Operations.
- Light Emitting Diode Processing.
- Laser Crystals: How they work and Some Preparative Methods.
- Modification of Solvent Compositions for Liquid Phase Epitaxial Growth of Magnetic Thin-Film Garnets.

year, this assignment was omitted to allow greater development of device process technologies with illustrative, extended homework assignments.

There exist no comprehensive text able to cover the broad subject matter treated in the course. Consequently, an extensive set of course notes is provided. The book **Solid-State Chemistry** by Hannay[1] has served as an introductory text, with reading assignments drawn from the reference list. Slides are used as a part of many lectures to present examples from the reading. Although the course material appears extensive, experience has shown that well directed homework and reading assignments enable the conscientious student to handle the material without difficulty.

SUMMARY

IN THE THREE YEARS during which this course has been given the emphasis has expanded from the fundamentals of solid state chemistry and control of electrically active defects toward a fuller explication of unit processes and technologies for currently important electronic devices such as bipolar and MOS integrated circuits, light-emitting devices, and "bubble domain" magnetic memories. Whereas the former emphasis is more important for materials engineers, this subject causes chemical engineers the most difficulty. The exploration of basic processes such as crystal growth, oxidation and diffusion provides students with a better understanding of the effect of process variables on defect-related physical properties. Coverage of the process technologies for specific solid state devices tends to kindle the most interest and is more important for preparing chemical engineers for roles in solid state industries. Many alumni of this course have already launched successful careers in local electronics and solid state materials industries, where the demand for the chemical engineer with specialized skills in materials is increasing. □

HOMEWORK EXAMPLE 1:

Neodemium Distribution in Czochralski Grown $CaWO_4$

The addition of Na_2O to the melt significantly affects the solubility of Nd^{3+} ions in $CaWO_4$ through charge compensation with Na^+ ions. In this problem the distribution of Nd^{3+} along a $CaWO_4$ crystal grown by the Czochralski method is to be calculated from distribution coefficients for Nd and Na and from properties of the diffusion boundary layer at the crystallizing interface. The instantaneous ion concentrations in the crystal are calculated by solving mass action relations for Schottky defect formation, Nd substitution on a Ca site with Ca vacancy formation, Na substitution on a Ca site with formation of an oxygen vacancy, and the time-dependent Na_2O and Nd_2O_3 concentrations in the melt. This problem demonstrates the interdependence of defect mass action relationships with crystal growth conditions.

HOMEWORK EXAMPLE 2:

Chemical Vapor Deposition of $GaAS_{1-x}P_x$

Phase equilibrium temperatures and deposition rates are explored within a barrel reactor in which gallium arsenide-phosphide solid solutions are deposited from GaCl, As_4, P_4 and HCl source vapors transposed by H_2. The vapor-solid reaction equilibria are solved simultaneously to deduce the equilibrium temperature and solid solution composition for the overall reaction. Side reactions are omitted in this simplified analysis. The deposition rates at lower temperatures are determined by solving the set of component molar flux equations for a film boundary layer. This problem provides useful criteria for understanding commercial reactors for electro-optical film deposition.

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occurrence of a van der Waals "loop" in the region of coexistence is a manifestation of the approximate nature of the equation of state.[7]

Diffusional stability, or immiscibility phenomena, is presented in a manner abstracted from Prigogine and Defay.[8] Margules solution models, starting with the "regular," are adequate to demonstrate a broad spectrum of possible immiscibility behavior. Prausnitz's discussion of the subject[9] is a good complement to this topic.

6. Thermodynamics of Mixtures (2 weeks, or whatever time remains).

Obviously, two weeks is not enough to do any justice to the practical aspects of the thermodynamics of mixtures, such as the fugacity and activity concepts. Often, these few lectures are given in a qualitive way to provide an overview of what is presently relevant in chemical thermodynamics. This is generally all that the non-chemical engineers will desire while the chemical engineers have refuge in a second course for which this course is a prerequisite. The second course is a course in phase equilibria and uses Prausnitz[9] as a text. It will not be discussed here.

In closing, it is satisfying to note that Equation (3.1-8)—(3.1-14) and Equation (3.4-9)—(3.4-17) of Prausnitz,[9] equations for the properties of mixtures with independent variables (P,T) and (V,T) relative to an ideal gas basis (T = T, P = 1 atm absolute), are derivable by students of the core course without recourse to the work of Beattie.[10] □

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