Subash Mahajan • K.S. Sree Harsha

PRINCIPLES OF GROWTH AND PROCESSING OF SEMICONDUCTORS

Principles of Growth and Processing of Semiconductors

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To our families and parents

PREFACE

Fabricating state-of-the-art integrated circuits is a joint endeavor between chemists, chemical engineers, electrical engineers, materials scientists, and physicists. Each group's expertise is not broad enough to appreciate all the interdisciplinary issues in the microelectronics industry. For example, electrical engineers and physicists, though familiar with semiconducting materials and devices, are not exposed to defects in solids or crystal growth. This book builds bridges across various disciplines. We begin with the physics of semiconductors and devices, and follow with the growth and processing of semiconductors. We emphasize how defects arise during growth and processing and what effects these defects have on the device behavior. This approach will help prepare students for the eclectic microelectronics industry.

In planning this book, we asked ourselves the following question: What is a suitable background for a student intending to join the microelectronics industry? It became apparent that chemists, chemical engineers, and materials scientists need exposure to the physics of semiconductors and principles of semiconducting devices, so we decided to discuss these topics in Chapters 1 and 2. Even though materials scientists are familiar with defects in solids, they do not learn specific characteristics of defects in semiconductors. We cover these characteristics in Chapter 3, which also includes the necessary background on various types of defects for students from other disciplines. Since real materials contain defects and since semiconducting behavior is affected by impurities, evaluation of semiconductors is essential. Therefore, we cover structural, chemical, and electrical evaluations of semiconductors in Chapter 4. To illustrate the salient features of each technique and its limitations, we have included one or two examples in each case. Furthermore, semiconducting devices require doped single crystals because grain boundaries act as carrier recombination centers. We cover crystal growth in Chapter 5. In particular, we emphasize the reduction of dislocation densities in as-grown crystals, the precipitation of oxygen in Czochralski silicon, and the formation of impurity striations. For efficient operation, most devices require epitaxial growth, a topic we cover in Chapter 6, along with the introduction of defects during epitaxy and heteroepitaxy.

To convert the crystal into a device requires several fabrication steps. These steps include oxidation, diffusion, ion implantation, metallization, lithography, and etching. The growth of a thermal oxide on silicon forms the backbone of ULSI technology. We cover oxide growth kinetics, thermodynamics, structure and oxidation-induced stacking faults in Chapter 7. The fabrication of several devices requires a local change in carrier concentration and conductivity type using diffusion and ion implantation. We cover these processes in Chapters 8 and 9. External and interdevice communication requires metal contacts and interconnects. We consider the techniques available for depositing contacts and interconnects and other relevant issues in Chapter 10. Circuit fabrication requires transferring a circuit pattern on a

wafer using lithography and etching. We discuss the principles of these two technologies and their limitations in Chapter 11. In Chapter 12, we cover some of the future challenges in growth and processing of semiconductors.

To flesh out the concepts being developed, we have provided problems and their solutions within each chapter, as well as problem material at the end of each chapter. Furthermore, the approach underlying this book has been tested at Carnegie Mellon University and San Jose University, and the student response has been very encouraging.

The authors are grateful to Professor D. W. Greve, Professor M. E. McHenry, and Professor H. Temkin for their feedback on some of the chapters. To assess the student's reaction, some of the chapters were critiqued by Sanjoy, Sunit, and Ashish Mahajan, and their contribution is much appreciated. The authors are also very much obliged to Mrs. Valerie Thompson for her impressive word processing effort and to Mr. Kelly Young for his meticulous illustrations. Finally, they are very grateful to their families for their support and patience through this arduous endeavor.

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Dr. Mahajan has lectured and published extensively on origins of defects in semiconductors and their influence on device behavior and deformation behavior of solids. He has received several honors, such as the John Bardeen Award of the Minerals, Metals and Materials Society (TMS) (and the Albert Sauveur Achievement Award of the American Society at Metals (ASM) International. In addition, Dr. Mahajan consults nationally and internationally and is a member of several leading materials societies.

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Semiconductors: An Introduction

This chapter develops an introductory framework for understanding the behavior of semiconductors. It introduces the concepts of band gaps and charge carriers in semiconductors, that is, electrons and holes, discusses the changes in carrier concentration due to the addition of dopants, and correlates the conductivity of a semiconductor with the mobilities of the carriers. These concepts underlie the operation of semiconducting devices covered in Chapter 2.

1.1 BEHAVIOR OF FREE ELECTRONS

We show later in this chapter that the conduction in semiconductors occurs by the migration of two types of charge carriers, one of them being electrons. The presence of two types of carriers produces interesting effects in semiconductors. Therefore, we first discuss the properties of free electrons, that is, electrons that exist outside a solid—and progressively add more realism to this model so that it represents a semiconductor.

1.1.1 Particle-Wave Duality

Free electrons exhibit particle-wave duality. Figure 1.1 shows a setup to demonstrate the particle-like behavior. The electrons from a hot cathode overcome the surface potential barrier when a suitable potential is applied between the cathode and an anode. The anode has a pinhole that collimates the free-electron beam emitted from the cathode. When this beam hits a target metal, it ejects core-shell electrons from the atoms. An outer-shell electron rapidly fills the resulting vacancy in the core shell. The difference in the energies between the two electronic levels is given off as an X-ray photon. This behavior is consistent with the particle-like nature of electrons.

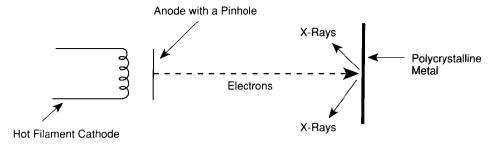


FIGURE 1.1 Schematic of a setup that can demonstrate the particle-like behavior of free electrons.

Now consider the setup shown in Figure 1.2. The electron beam defined by magnetic lenses traverses a very thin, single crystal sample and is Bragg diffracted. The diffraction produces a large number of diffraction spots on a fluorescent screen as shown in Figure 1.2. The pattern is best understood if the electrons behave as waves.

The equivalence between the particle- and wavelike behaviors of free electrons is provided by the Planck and de Broglie relations. According to Planck, electron energy E is related to its frequency ν by

$$v = \frac{E}{h},\tag{1.1}$$

where h is Planck's constant. This relation is applicable to all types of electromagnetic radiation. On the other hand, de Broglie hypothesized that the wavelength λ of a wave associated with an electron is related to its momentum p by

$$\lambda = \frac{h}{p}.\tag{1.2}$$

Every particle can exhibit the particle- and wavelike behaviors. Whether the wavelike nature of a particle is experimentally discernible depends on the wave-

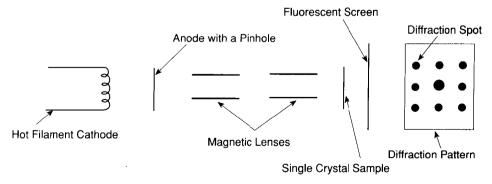


FIGURE 1.2 Schematic of a setup that can demonstrate the wave-like behavior of free electrons.

length of the wave associated with the particle relative to the dimension of the experiment. For electrons the mass is extremely small (9.11 \times 10⁻³¹ kg). Therefore, for reasonable values of velocities, as shown in Example 1.1, the values of momentum are fairly small, resulting in associated wavelengths of waves that can be discerned by their diffraction from a grating consisting of lattice planes within a crystal.

EXAMPLE 1.1. Electrons are excited from a hot wire cathode at a potential of 100 kV. Calculate the wavelength of the electrons.

Solution

E = the kinetic energy of the accelerated electrons =
$$\frac{1}{2}$$
 mv²
= 100 keV
= 1.6×10^{-14} J.

 $E = \frac{1}{2} \text{ mv}^2$ is reasonable because E is much less than the rest energy mc² (500 keV), where c is the velocity of light. For higher energies you need to use the relativistic formulas.

 $p = momentum of the electrons = \sqrt{2mE}$, where m is the mass of the electron (9.11 \times 10⁻³¹ kg).

Thus
$$p = \sqrt{2 \times 9.11 \times 10^{-31} \times 1.6 \times 10^{-14}} \text{ kg-m/sec}$$

= 1.7 × 10⁻²² kg-m/sec.

According to de Broglie

$$\lambda = \frac{h}{p}$$
.

Substituting for p and $h = 6.6 \times 10^{-34} \, J$ sec, we obtain

$$\lambda = \frac{6.6 \times 10^{-34}}{1.7 \times 10^{-22}} = 0.004 \text{ nm}.$$

Waves having the preceding wavelength can be diffracted from various lattice planes within silicon and gallium arsenide whose lattice parameters are 0.543 and 0.565 nm. Diffraction occurs because the electron wavelength is considerably smaller than the separations between different gratings formed by different crystal planes.

1.1.2 Uncertainty Principle

We cannot describe the events involving atomic particles with absolute precision. Instead, we must think of the average values of position, momentum, and energy of a particle such as an electron. According to Heisenberg, the uncertainties in the measurements of position Δx and momentum Δp are related by the uncertainty relation

$$(\Delta x)(\Delta p) \ge \hbar, \tag{1.3}$$