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General features and fundamental concepts

1.1 Introduction

Ion beam processing of materials results from the introduction of atoms into the surface layer of a solid substrate by bombardment of the solid with ions in the electron-volt to mega-electron-volt energy range. The solid-state aspects are particularly broad because of the range of physical properties that are sensitive to the presence of a trace amount of foreign atoms. Mechanical, electrical, optical, magnetic, and superconducting properties are all affected and, indeed, may even be dominated by the presence of such foreign atoms. The use of energetic ions affords the possibility of introducing a wide range of atomic species, independent of thermodynamic factors, thus making it possible to obtain impurity concentrations and distributions of particular interest; in many cases, these distributions would not be otherwise attainable.

Recent interest in ion beam processing has focused on the studies of ion implantation, ion beam mixing, ion induced phase transformations, and ion beam deposition. These interests have been stimulated by the possibilities of synthesizing novel materials with potential applications in the semiconductor, tribological, corrosion, and optical fields.

Ion beam processing provides an alternative and non-equilibrium method of introducing dopant atoms into the lattice. In typical applications, a beam of dopant ions is accelerated through a potential of 10–100 kV. The implantation system shown in Fig. 1.1 illustrates the basic elements required in this technique: ion source, acceleration column, mass separator, and target chamber. With different types of ion sources available, a wide variety of beams may be produced with sufficient intensity for implantation purposes for integrated circuit technology; 10^{14}–10^{15} ions/cm^2 (less than a 'monolayer'; see Section

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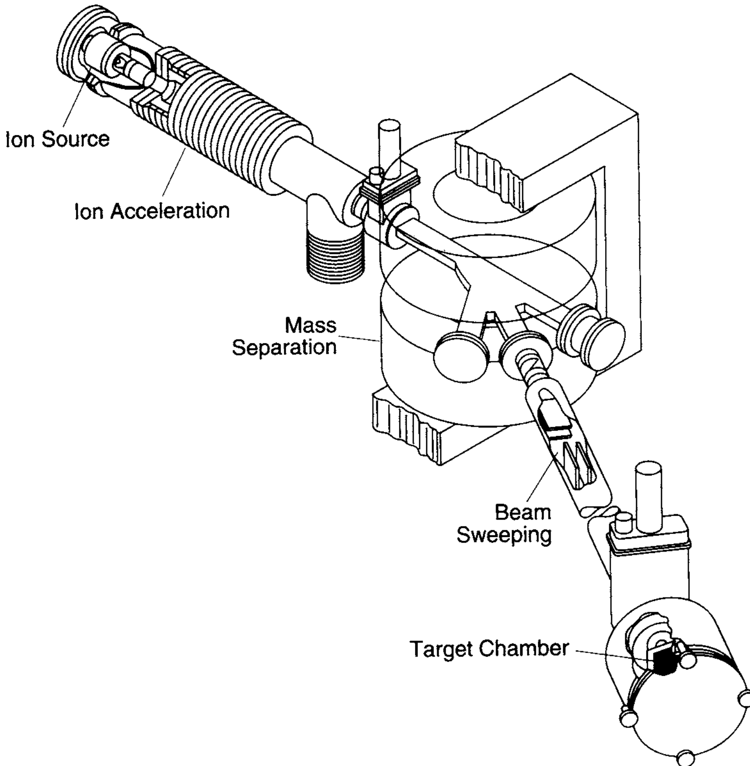

Fig. 1.1. Schematic drawing of an ion implantation system. A mass-separating magnet is used to select the ion species (element and isotopes) of interest. Beam-sweeping facilities are required for large-area uniform implantations.

1.4) is a representative ion dose. Ion dose is defined as the number of ions per centimeter square implanted into the sample. Alternatively, the term fluence is used instead of dose. The ion beam current density is expressed in units of ampères per centimeter squared. The dose rate or flux is given in units of ions per second per centimeter squared.

A mass-separating magnet is almost mandatory for semiconductor processing to eliminate unwanted species that often contaminate the extracted beam. However, for metallurgical processing, mass separation is not important, and as a result the basic instrumentation can be quite simple.

Two ion implantation systems which do not use mass separation and are capable of extremely high ion currents are the broad-beam ion source and the plasma ion source. Broad-beam ion sources, Fig.

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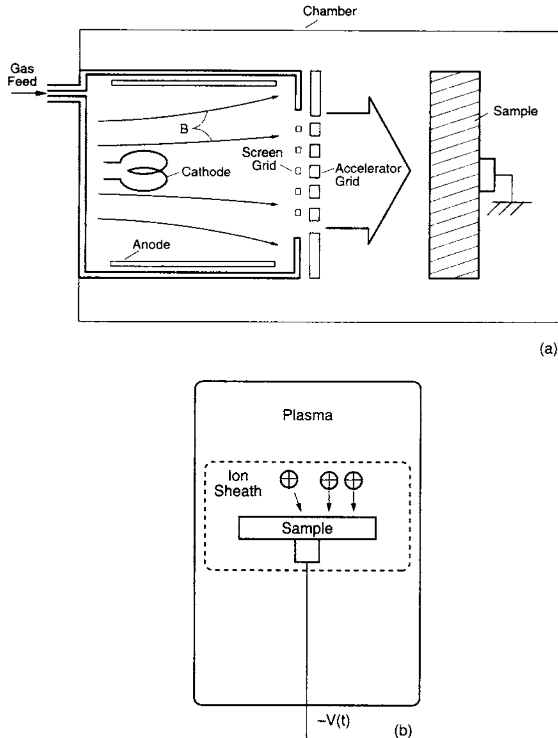

Fig. 1.2. (a) A typical discharge-chamber design for broad-beam gridded ion sources used in close proximity to a sample. (b) A schematic of plasma immersion ion implantation (PIII) geometry.

1.2(a), typically employ grids at the front end of the source to obtain electrostatic acceleration of ions. These sources originated in research programs in the early 1960s as a technology for space propulsion. Since that early work, broad-beam systems have been successfully used in the areas of ion implantation, ion beam deposition, and ion beam assisted deposition, where the ions employed are in the low-energy range of a few tens to several thousand electron-volts.

The plasma-source system does not use an extraction and acceleration scheme found in traditional mass-analyzing implanters (Fig. 1.1), but rather the sample to be implanted is placed inside a plasma (Fig. 1.2(b)). The sample is repetitively pulsed at high negative voltages (typically -100 kV) to envelop the surface with a flux of energetic plasma ions. Because the plasma surrounds the sample, and because the ions are accelerated normal to the sample surface, plasma-source

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implantation occurs over the entire surface, thereby eliminating the need to manipulate non-planar samples in front of the ion beam.

The major features governing the successful exploitation of ion beam processing are the range distribution of the energetic ions, the amount and nature of the lattice disorder that is created, and the location of the energetic ions in the crystal lattice. We will consider all of these factors briefly in the present chapter; subsequent chapters will then treat each one in detail. At high dose levels (used to incorporate greater than 5–10 at.% of implanted species to modify the composition of the target), other phenomena become important: sputtering, ion induced phase formation, and transformations. We will discuss these in later chapters.

1.2 Range distributions

One of the most important considerations in any description of ion–solid interactions is the depth (range) distribution of the implanted ions. A large amount of experimental and theoretical work has been devoted to the task of understanding the energy-loss processes that govern the range distribution, and it is now possible to predict fairly accurately most of the factors involved. For example, a typical range distribution in an amorphous substrate from monoenergetic ions at moderate ion doses is approximately Gaussian in shape, and may therefore be characterized by a projected range, R_p, and a straggling, ΔR_p, about this mean value, as depicted in Fig. 1.3. The notation uses

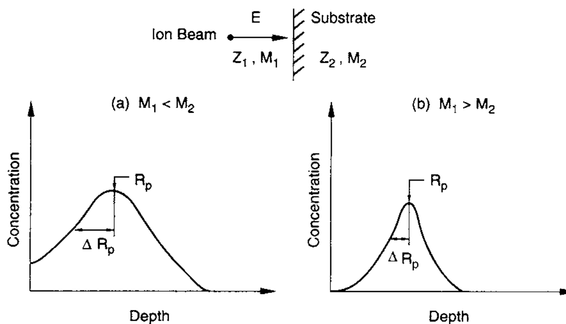

Fig. 1.3. The depth distribution of implanted atoms in an amorphous target for the cases in which (a) the ion mass is less than or (b) greater than the mass of the substrate atoms. To a first approximation, the mean depth, R_p, depends on ion mass, M_1, and incident energy, E, whereas the relative width, $\Delta R_p/R_p$, of the distribution depends primarily on the ratio between ion mass and the mass of the substrate ion, M_2.

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Z and M for atomic number and atomic mass, respectively, with subscript 1 denoting the incident ions (Z_1, M_1), and subscript 2 denoting the ion bombarded sample (or target). By convention, the energy of the incident ion is denoted by E_0 or by E without a subscript.

1.3 Lattice disorder

Lattice-disorder and radiation-damage effects are produced in the substrate by the incident ion. As an implanted ion slows down and comes to rest, it makes many violent collisions with lattice atoms, displacing them from their lattice sites. These displaced atoms can in turn displace others, and the net result is the production of a highly disordered region around the path of the ion, as shown schematically in Fig. 1.4 for the case of a heavy implanted atom at typically

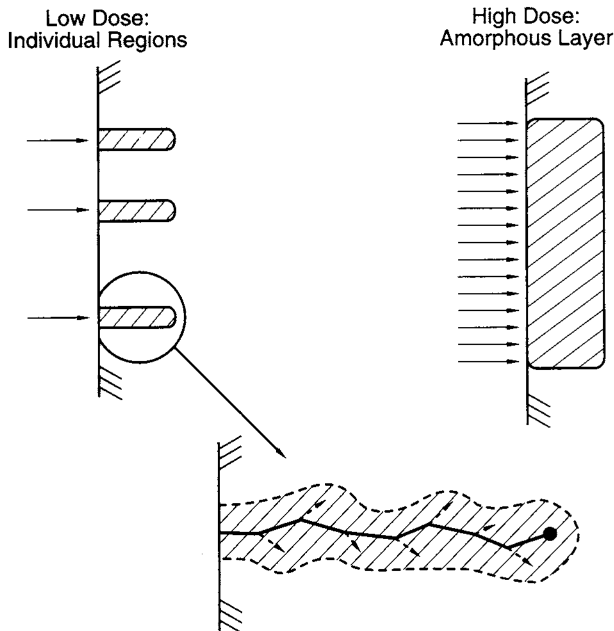

Fig. 1.4. A schematic representation of the disorder produced in room-temperature implantations of heavy ions at energies of 10–100 keV. At low doses, the highly disordered regions around the tracks of the ions are spatially separated from each other. The volume of the disordered region is determined primarily by the stopping point of the ion and the range of the displaced lattice atoms (dashed arrows) At high doses, the disordered regions can overlap to form an amorphous layer.

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10–100 keV. At sufficiently high doses, these individual disordered regions may overlap, and an amorphous or metastable crystalline layer may form.

Fig. 1.5 shows the schematic atomic arrangement for a crystalline solid (a) and an amorphous solid (b). A crystalline solid has long-range atomic order; an amorphous solid has short-range order (the order among the nearest neighbors) but no long-range order. In a single crystal, the entire sample is composed of atoms placed on well-defined planes and rows. Fig. 1.6(a) shows a side view of a single crystal, where the planes of atoms are depicted by parallel pairs of lines. A polycrystalline sample is made of small single crystal regions, called crystallites, whose planes and atomic rows are misaligned with respect to those in neighboring crystallites. A polycrystalline layer on a single crystal substrate is shown in Fig. 1.6(b).

1.4 Atomic and planar densities

The description of ion implantation and ion doses requires knowledge of the atomic density interplanar distance between planes and the

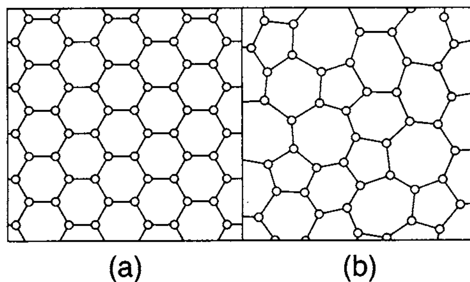

Fig. 1.5. Schematic atomic arrangement of (a) a crystalline solid and (b) an amorphous solid.

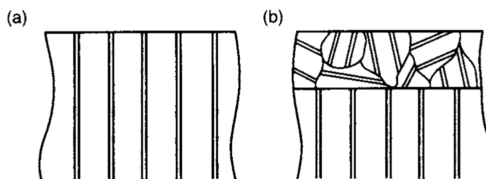

Fig. 1.6. Schematic representation for (a) a single crystal with crystallographic planes perpendicular to the surface and (b) a polycrystalline layer on a single crystal.

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number of atoms per centimeter squared on a given plane. The distance between planes labeled by the Miller indices is d_{hkl}. In cubic systems with an atomic density of N atoms/cm^3, the crystal lattice parameter a_c is given by

$$a_c = \left(\frac{\text{atoms/unit cell}}{N}\right)^{1/3} \tag{1.1}$$

where, for systems with one atom per lattice point, the number of atoms per unit cell equals four for a face-centered-cubic lattice (Al, Ag, Au, Pd, Pt) and is eight for the common semiconductors germanium and silicon, which have the diamond cubic structure. Aluminum has an atomic density of 6.02×10^{22} atoms/cm^3 so that the lattice parameter is

$$a_c = \left(\frac{4}{6.02 \times 10^{22}}\right)^{1/3} = 4.05 \times 10^{-8}\ \text{cm}$$

For Al with a lattice parameter of 4.05×10^{-8} cm = 0.405 nm, the (1 1 0) interplanar spacing determined by Eq. (A.4) is 0.286 nm. A summary of the conventions used to indicate directions and planes in crystallography is given in Table A.2, Appendix A. The interplanar spacing equations for all crystallographic systems are also given in Appendix A.

The atomic volume can be calculated without use of crystallography. The atomic density N atoms/cm^3 is given by

$$N = \frac{N_A}{A}\rho \tag{1.2}$$

where N_A is Avogadro's number, ρ is the mass density in grams per centimeter cube and A is the atomic mass number. Taking Al as an example, where ρ is 2.7 g/cm^3 and A is 27, the atomic density is $N = (6.02 \times 10^{23} \times 2.70)/27 = 6.02 \times 10^{22}$ atoms/cm^3. The semiconductors Ge and Si have atomic densities of about 4.4×10^{22} and 5.0×10^{22} atoms/cm^3, respectively, and metals such as Co, Ni, and Cu, have atomic densities of about 9×10^{22} atoms/cm^3. The volume Ω_V occupied by an atom is given by

$$\Omega_V = \frac{1}{N} \tag{1.3}$$

with a typical value of 20×10^{-24} cm^3.

The atomic density can also be determined for intermetallic compounds and alloys. For the alloy A_xB_y, replace A in Eq. (1.2) with A_c = molecular weight/$(x + y)$ and use the mass density of the alloy.

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For example, the intermetallic alloy Fe_2Al has a mass density of 6.33 g/cm^3. The variable $A_c = (2 \times 55.8 + 27)/3 = 46$ g/mol of atoms. Thus, $N_{Fe_2Al} = 8.29 \times 10^{22}$ atoms/cm^3. The Ω_V calculated from the alloy atomic density using Eq. (1.3) is an average atomic volume.

The average areal density of a monolayer, N_s atoms/cm^2, can also be estimated without use of crystallography by taking the atomic density N to the 2/3 power:

$$N_s \cong N^{2/3} \tag{1.4}$$

Eq. (1.4) gives the average areal density of one monolayer for a material with an atomic density N. However, to calculate the areal density for a specific set of planes in a crystal requires knowledge of the planar spacing for that set of planes; for this, see Appendix A. For the specific crystallographic case we have

$$N_s^{hkl} = N d_{hkl} \tag{1.5}$$

where d_{hkl} is the interplanar spacing for the (hkl) plane of interest (see Appendix A). For example, for the case of (1 1 0) planes in Al we know from the example above and Appendix A that $d_{110} = 0.286$ nm $= 2.86 \times 10^{-8}$ cm and that the atomic density is 6.02×10^{22} atoms/cm^3. From Eq. (1.5) the areal density for one monolayer of Al on the (1 1 0) plane is 1.72×10^{15} atoms/cm^2.

1.5 Energy and particles

In the SI (or MKS) system of units, the joule (J) is a unit of energy, but the electron-volt (eV) is the traditional unit used in ion–solid interactions: 1 eV is defined as the kinetic energy gained by an electron accelerated through a potential difference of 1 V. The charge on the electron is 1.602×10^{19} coulombs, and a joule is a coulomb-volt, so that the relationship between these units is given by

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} \tag{1.6}$$

Commonly used multiples of the electron-volt are the kilo-electron-volt (10^3 eV) and the mega-electron-volt (10^6 eV).

Energy density units for problems involving thermodynamic analysis are typically of the form of kilojoules per mole in MKS units, where a mole (mol) represents Avogadro's number of particles or molecules, i.e., $N_A = 6.02 \times 10^{23}$ particles/mol. The energy unit in the cgs (centimeter-gram-second) system is the calorie, with the relationship between joules and calories given by

$$1 \text{ cal} = 4.186 \text{ J} \tag{1.7}$$

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Other thermodynamic energy density units are in the form of energy per gram and energy per centimeter cube. Values in energy per gram are converted to energy per mole by multiplication by the atomic weight or molecular weight. In a similar way, energy per centimeter cube can be converted to energy per gram by dividing through by the mass density

$$\frac{\text{energy}}{\text{mole}} = \frac{\text{energy}}{\text{gram}} \times \frac{\text{gram}}{\text{mole}} \tag{1.8a}$$

$$\frac{\text{energy}}{\text{gram}} = \frac{\text{energy}}{\text{cm}^3} \bigg/ \frac{\text{gram}}{\text{cm}^3} \tag{1.8b}$$

Another typically observed energy density unit is energy per gram-atom. The connection between gram-atom and mole will be explained by use of an example involving the intermetallic compound Ni_3Al.

1 mol of Ni_3Al represents 1 mol of the molecule Ni_3Al, which is composed of 4 mol of atoms, 25% of which are Al and 75% of which are Ni. Another representation of the 4 mol of Ni_3Al atoms is 4 gram-atoms of Ni_3Al. Thus, in 1 gram-atom of Ni_3Al there is 1 mol of atoms, while in 1 mol of Ni_3Al there are 4 mol of atoms. Thus, *1 gram-atom refers to 1 mol of atoms.*

The distinction between mole and gram-atom is important when considering heat of reaction or heat of formation data. For instance, the experimentally reported heat of formation for Ni_3Al is −41 kJ/gram-atom. The heat of formation value in terms of moles is −164 kJ/mol, a factor of four larger, because Ni_3Al has four atoms per molecule.

The typical energy density unit when examining thermodynamic processes on an atomic level is electron-volts per atom. The useful conversion factors when translating from molar to atomic quantities are

$$1\ \text{eV/atom} = 23.06\ \text{kcal/gram-atom} \tag{1.9a}$$

$$1\ \text{eV/atom} = 96.53\ \text{kJ/gram-atom} \tag{1.9b}$$

In ion–solid interactions it is convenient to use cgs units rather than SI units in relations involving the charge on the electron. The usefulness of cgs units is clear when considering the Coulomb force between two charged particles with Z_1 and Z_2 units of electronic charge separated by a distance r,

$$F = \frac{Z_1 Z_2 e^2 k_c}{r^2} \tag{1.10}$$

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where the Coulomb law constant $k_c = 1/4(\pi\varepsilon_0) = 8.988 \times 10^9$ m/F in the SI system (where 1 farad ≡ 1 A s/V) and is equal to unity in the cgs system.

The conversion factor follows from:

$$e^2 k_c = (1.6 \times 10^{-19}\ \mathrm{C})^2 \times 8.988 \times 10^9\ \mathrm{m/F} = 2.31 \times 10^{-28}\ \mathrm{C^2\,m/F}$$

The conversions 1 coulomb ≡ 1 ampère second and 1 joule ≡ 1 coulomb-volt lead to the units of the farad:

1 farad ≡ 1 ampère second per volt

so that

$$1\ \mathrm{C^2\,m/F} \equiv 1\ \mathrm{C^2\,Vm/A\,s} \equiv 1\ \mathrm{J\,m} \equiv 10^9\ \mathrm{J\,nm}$$
$$= \frac{10^9\ \mathrm{J\,nm}}{(1.6 \times 10^{-19}\ \mathrm{J/eV})} = \frac{10^{28}}{1.6}\ \mathrm{eV\,nm}$$

and

$$e^2 k_c = 2.31 \times 10^{-28}\ \frac{\mathrm{C^2\,m}}{\mathrm{F}} = \frac{2.31}{1.6}\ \mathrm{eV\,nm} = 1.44\ \mathrm{eV\,nm}$$

In this book we will follow the cgs units for e^2 with $k_c = 1$ so that

$$e^2 = 1.44\ \mathrm{eV\,nm} \tag{1.11}$$

Each nucleus is characterized by a definite atomic number Z and a mass number A; for clarity, we use the symbol M to denote the atomic mass in kinematic equations. The atomic number Z is the number of protons, and hence the number of electrons, in the neutral atom; it reflects the atomic properties of the atom. The mass number gives the number of nucleons, protons, and neutrons; isotopes are nuclei (often called nuclides) with the same Z and different A. The current practice is to represent each nucleus by the chemical name with the mass number as a superscript, e.g. ^{12}C. The chemical atomic weight (or atomic mass) of elements as listed in the periodic table gives the average mass, i.e., the average of the stable isotopes weighted by their abundance. Carbon, for example, has an atomic weight of 12.011, which reflects the 1.1% abundance of ^{13}C. Appendix B lists the elements and their relative abundances, atomic weights, atomic densities, and specific gravities.

The masses of particles may be expressed as given in Table 1.1 in terms of energy through the Einstein relation

$$E = Mc^2 \tag{1.12}$$

which associates 1 J of energy with $1/c^2$ of mass, where c is the velocity

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