Fundamental Concepts of Ion-Beam Processing

R.S. Averback and P. Bellon

Department of Materials Science and Engineering, University of Illinois at Urbana Champaign, Urbana, IL, 61801, USA, e-mail: averback@uiuc.edu

Abstract. The basic concepts underlying the response of materials to ion-beam irradiation are outlined. These include the slowing of energetic ions, the creation of defects, sputtering, ion-beam mixing, the acceleration of kinetic processes, and phase transformations. Several examples are cited to illustrate how each of these concepts can be exploited to modify materials in ways not easily achieved, or not even possible, by more conventional processing methods. The chapter attempts to provide a physical understanding of the basic effects of ion-beam irradiation on materials, to enable readers in other areas of research to better understand the more technical chapters that follow, and to develop ideas relevant to their own disciplines. We provide references to more quantitative treatments of the topics covered here.

1 Introduction: Basic Mechanisms of Ion–Solid Interactions

The underlying principles guiding the design and processing of engineering materials have traditionally been based on the equilibrium properties of solids, gradients in the chemical potential, and atomic mobilities. Typically, a material is first excited above its ground state by such means as quenching from high temperatures, plastic deformation, vapor deposition, or even ion implantation. The material is subsequently annealed according to a predetermined time–temperature program designed to select a kinetic pathway toward a desired metastable, or even unstable, state. A specific example illustrating this concept is the processing of age-hardening alloys such as Al–Cu. In this example, the alloy is homogenized at elevated temperatures and subsequently quenched to low temperatures, where the Cu exceeds its solubility limit. Upon subsequent aging at elevated temperature, the Cu precipitates out of solution in a series of metastable phases before arriving at the equilibrium \( \approx \text{CuAl}_2 \), body-centered tetragonal phase. The microstructure of the alloy is thus controlled by applying specific heating programs to take advantage of different nucleation barriers of the metastable phases and their growth kinetics. Notably, the processing is irreversible and once the alloy is overaged, there is no possibility to recover the previous microstructure. Vapor deposition, mechanical processing, powder metallurgy and in-
deed some elements of ion implantation all involve these common principles. While ion-beam processing of materials of course shares many of these same ideas, the introduction of persistent displacement damage, or driving forces, into the processing scheme greatly enriches the materials science and provides new opportunities for synthesizing materials with unique microstructures and properties. The reasons for this will become evident later in this chapter and throughout this volume; however, a simple example will serve at present to illustrate this key point.

The example considers ion irradiation of dilute $\text{Ni}_{(1-x)}\text{Si}_x$ alloys at elevated temperatures. Assume $x < .10$ and so under equilibrium conditions the alloy forms a homogeneous single phase. The effect of irradiation is to produce vacancies and interstitials in large supersaturations, and as a result they flow to sinks, such as dislocations, grain boundaries, and surfaces, to restore equilibrium concentrations. It is well documented that interstitial atoms in Ni have a strong binding energy with Si solute, and as a consequence, the migration of an interstitial to a point defect sink drags a Si atom along with it, enriching the local concentration of Si at these sites. The system is thus driven away from equilibrium. Eventually this enrichment leads to precipitation of the $\text{Ni}_3\text{Si}$, $\gamma'$ phase, and a two-phase alloy is formed. If the irradiation is switched off, the point-defect fluxes quickly die out, and the precipitates redissolve in the matrix by ordinary diffusion mechanisms, and equilibrium is restored.

In the remainder of this chapter, we will develop the theoretical framework to understand this example, and other materials problems involving irradiation. The discussion will center on metals, but the concepts are general and apply to most solid materials.

1.1 Electronic Excitation

As an ion impinges on a solid it begins a series of collision with both the electrons and the ion cores of target atoms. The collisions with electrons are more numerous owing to their larger number and cross section, but since their mass is small they do not much alter the trajectory of the incoming ion, nor do they usually result in atomic displacements. In most materials, therefore, these inelastic collisions can be treated simply by assuming that the electrons form a viscous background that extracts energy from the fast-moving ions and slows them down [1]. In a few special cases, however, such as swift ions (i.e., heavy ions with GeVs of energy) the high density of energy deposited along the ion track, often tens of keV per nanometer, can have significant consequences. For example, the traversal of such ions can produce a linear track of damage in various materials. These tracks can be later etched to form pores for various applications, most often in insulators [2]. In high-$T_C$ superconductors, the damage tracks themselves can pin fluxoids, which greatly increases critical currents [3]. The energy loss of ions due to these inelastic excitations is characterized by the electronic stopping power, $S_e(E)$. 
Figure 1 illustrates the electronic stopping as a function of energy for a few representative ion-target combinations. Notice that the maximum in $S_e(E)$ and the energy where the maximum is reached both increase with the atomic masses of the ion and target atoms.

### 1.2 Nuclear Collisions

**Defect Production**

Ions are also slowed in a solid by the elastic collisions between the projectiles and target atoms; this slowing can also be characterized by a stopping power, $S_n$, as shown in Fig. 2. These collisions, however, can lead to displacement damage, whereby a knocked-on atom recoils away from its initial lattice site. Typically, an atom must receive $\approx 25\,\text{eV}$ of energy to create a stable interstitial–vacancy (Frenkel) pair. Many recoil atoms receive much higher energies, as discussed below, and these recoils can undergo a series of secondary recoils with target atoms displacing them as well, and indeed, many of these secondary recoil atoms can create yet additional displacements in tertiary recoils, and so on. In this way, a displacement cascade evolves. When the energies of recoil atoms fall below $25\,\text{eV}$, the atoms continue to
be displaced from their lattice sites, however, the separation between the interstitial–vacancy pair is too small to avoid spontaneous recombination owing to the strong elastic interaction between the two defects. The number of Frenkel pairs produced by a projectile of energy, $E_1$, $\nu(E)$, can be estimated using the expression [5]:

$$
\nu(E_1) = \int_{E_1}^{E_1} \frac{dE}{S_n + S_e} \int_{E_d}^{T_{\text{max}}} dT \frac{d\sigma(E, T)}{dT} \nu(T),
$$

(1)

where $d\sigma(E, T)/dT$ is the differential scattering cross section for an ion of energy $E$ to produce a recoil of energy $T$, $T_{\text{max}}$ is the maximum energy transfer in a single collision, and $\nu(T)$ is the damage function given by [6, 7],

$$
\nu(T) = \begin{cases} 
0, & T < E_d, \\
1, & E_d < T < 2.5E_d, \\
\frac{0.8\xi(T)E_D(T)}{2E_d}, & 2.5E_d < T,
\end{cases}
$$

(1.a)

where $\xi(T)$ is the efficiency function, $E_D$ is the total energy of the cascade less that lost to electronic excitation, and $E_d$ is the displacement energy, on the order of 25 eV in metals, 60 eV in ionic crystals, and 15 eV in semiconductors. For most metals, $\xi(T)$ is unity at low energies and drops smoothly to $\approx 1/3$ at energies above 1–2 keV [5, 8]. $E_D$ can be found from simulation.\(^1\)

**Sputtering**

Atoms located in the first layer or two of the surface that receive recoil energies greater than the sublimation energy, $\approx 5$ eV, with momentum directed away from the surface can be sputtered into the vacuum. As a consequence, the surface continually erodes during irradiation. Under prolonged irradiation at temperatures where defects are immobile, therefore, a system reaches a steady state in terms of damage and changes in alloy composition when the thickness of sputtered material is roughly equal to the depth of the implanted ions. It is easily shown from conservation of mass, moreover, that the steady-state concentration of an implanted ion, $X_{\text{max}}/(1-X_{\text{max}}) \approx 1/(S-1)$, where $S$ is the number of sputtered atoms per incident ion. This expression assumes that the partial sputtering yields of different alloy components are the same, i.e., proportional to the surface composition. In general, partial sputtering yields are different, and this leads to surface compositions that differ from the bulk composition [9, 10]. For low-energy ion sputtering of an alloy target, these composition fluctuations are confined to a depth of $\approx 2$ nm, i.e., the penetration depth of the ion, which is in strong contrast to thermal evaporation. Once sufficient material has been removed and steady state achieved, the alloy compositions are constant in time, albeit inhomogeneous just below the surface. In steady state, the alloy components must sputter at rates proportional to their bulk compositions (not their surface compositions). This

\(^1\) See [4] for details of SRIM.
has practical significance for the growth of alloy films by sputter deposition, since it guarantees that the film composition will equal that of the sputtering target after a short transient.

**Ion-Beam Mixing**

One of the consequences of the displacement process is that several atoms in the vicinity of the recoil location exchange lattice sites with neighboring atoms. A simple estimate of this ballistic mixing rate can be obtained by considering the mixing in terms of a diffusion process, \( \langle r^2 \rangle = n\lambda^2 \), where \( n \) is the average number of random jumps each atom performs, and \( \lambda \) is the jump distance [11]. If we assume that \( s \) atoms each jump one atomic distance in creating a Frenkel pair, then using (1), the mean square displacement of all atoms per incident ion is simply,

\[
\langle R^2 \rangle = \frac{0.8E_D s\lambda^2}{2E_d}. \tag{2}
\]

After irradiation to dose \( \phi \), the total *damage energy per atom* is \( E'_D = N_0\phi F_D \), where \( N_0 \) is the atomic density, \( F_D = dE_D/dx \) and \( x \) is measured normal to the surface. \( F_D \) is usually obtained by computer simulation.\(^2\) The mean square displacement per atom, \( \langle r^2 \rangle \), normalized by damage energy, can thus be written,

\[
\xi = \frac{\langle r^2 \rangle}{\phi F_D} = \frac{0.8s\lambda^2}{2N_0E_d} \tag{3}
\]

Evaluation of (3) illustrates that each atom in a displacement cascade undergoes \( \approx 0.1–1 \) jumps on average.

### 1.3 Thermal Spikes

The displacement cascade just described evolves in time over a period of a few tenths of ps. Beyond this period the atomic energies fall below 5 eV and the collisions can no longer be considered as two-body events, but rather many-bodied. An atom with \( \approx 5 \) eV, notably, has a velocity on the order of the speed of sound in crystals. Indeed, as a molecular dynamics simulation of a 10-keV collision event in the ordered \( B_2 \) phase of NiAl shows in Fig. 3a, all of the atoms localized in a small volume are set into motion. Plotting the energy distribution in Fig. 3b for various instants of time illustrates that after a few tenths of a ps, the distribution becomes Maxwellian, with the maximum temperature exceeding 3000 K at this time. Depending on the energy density in this locality, the local temperature can therefore rise significantly above the melting temperature for several ps, giving rise to liquid-like diffusion and defect clustering on subsequent cooling [12]. Notice in Fig. 3a the rather well-defined solid–liquid phase boundary. At the end of the recoil event shown in

\(^2\) See footnote 1.
Fig. 3a. Position of atoms in a cross-sectional slice, one lattice parameter thick, during a 10-keV event in β-NiAl. After [13]

Fig. 3a–f, only 25 Frenkel pairs are created ($\xi(10\text{ keV}) = 0.27$) while $\approx2000$ atoms relocate from their initial lattice sites.

A brief comment is in order concerning the analysis of thermal spikes, either theoretically or through MD simulations. Most thermal spike models do not include heat loss from the cascade that arises from thermal conduction by electron carriers. This omission assumes that equilibration times for the phonon and electron systems are long compared to the lifetimes of the thermal spikes. In most metals, however, these times are comparable, and therefore the models should be considered approximate. Attempts have been made to include the electronic system [14–16], but at present, their accuracy has not been determined.
Fig. 3b. Distribution of atomic energies for different times during the evolution of a 10-keV cascade event in $\beta$-NiAl. o – actual distribution; x – Maxwellian distribution. $N$ is the number of atoms within the cascade and $T$ represents the average kinetic energy. After [13]

From this brief description of the implantation of an energetic ion in a solid, it is apparent how processing of materials with ions differs from that by traditional methods. Consider first the displacement process during the early phases of the cascade. The energies required to create a Frenkel pair exceed $\approx 25$ eV, and therefore defect production is not sensitive to the thermochemical properties of the material. Typical point-defect concentrations at the end of cascade events are highly supersaturated, $\approx$ one per cent, which at room
temperature corresponds to a chemical potential on the order of one eV for vacancies and four eV for interstitials. Atomic motion during this phase of the cascade is ballistic, i.e., atoms relocate randomly, driven by gradients in their concentrations rather than gradients in their chemical potentials. As a consequence, solubility limits are greatly extended, and ordered alloys disorder. Later in the cascade development, during the thermal spike, thermodynamic forces can become relevant. From the perspective of forming alloy phases, displacement cascades with high energy densities can be qualitatively described as rapid quenching from the melt with a quench speed on the order of \( \approx 10^{14} \text{s}^{-1} \).

### 1.4 Radiation-Enhanced Diffusion

At elevated temperatures the high concentrations of defects produced in the cascade can migrate throughout the material and begin to restore equilibrium. Again, this has similarities to quenching in point defects from high temperatures. For example, supersaturations of quenched in vacancies can enhance low-temperature diffusion and therefore accelerate kinetic processes, at least until the excess concentration of vacancies dissipates. There are two important differences, however. First, irradiation produces vacancies and interstitials in equal numbers, whereas quenching only produced vacancies in metals. As noted before, the interstitial supersaturation is far greater than that of vacancies, and thus the alloy can explore far larger regions of phase space. During continued irradiation, moreover, the supersaturations of point defects are continually replenished, leading to persistent net defect fluxes to sinks. These in turn can result in radiation-induced segregation (as discussed in the introduction), disordering/ordering of ordered alloys, and dimensional instabilities such as creep and void swelling.

Radiation-enhanced diffusion is typically treated within a mean-field theory approach using chemical rate equations. Within this framework the rate equations for the concentrations of vacancies and interstitials are \([17]\):

\[
\frac{\partial c_i}{\partial t} = \sigma \dot{\phi} - \frac{4\pi r}{\Omega_0}(D_i + D_v)c_i c_v - \left( \sum_j K_{i,j} \right)D_i c_i + D_i \nabla^2 c_i, \quad (4a)
\]

\[
\frac{\partial c_v}{\partial t} = \sigma \dot{\phi} - \frac{4\pi r}{\Omega_0}(D_i + D_v)c_i c_v - \left( \sum_j K_{v,j} \right)D_v c_v + D_v \nabla^2 c_v, \quad (4b)
\]

where \(\sigma\) is the cross section for producing Frenkel pairs, \(\dot{\phi}\) is the ion flux, \(r\) is the capture radius for interstitial-vacancy recombination \(\Omega_0\) is the atomic volume, \(D_{v,i}\) are the diffusivities of vacancies and interstitials, respectively, and the \(K_{j,k}\) are the strengths of the various sinks (grain boundaries, surfaces, etc.) for interstitials and vacancies. The atomic diffusion coefficient is thus obtained as,

\[
D = f_i c_i D_i + f_j c_v D_v, \quad (5)
\]
where $f_j$ are correlation factors, which are of order unity. During irradiation at elevated temperature, the defect concentrations typically reach their steady states long before the phase transformations take place, and spatial variations in the steady-state concentrations often remain small, so that the defect concentrations are easily obtained. Figures 4a and b show schematically the concentration of point defects and the temperature dependence of the radiation-enhanced self-diffusion coefficient. At low temperature, the migration of defects is negligible and the diffusion is controlled by ion-beam mixing. As the temperature is increased, defect diffusivities increase. The concentration of point defects in this regime is controlled by the production rate and recombination, giving rise to a temperature-dependent diffusion coefficient. At still higher temperatures, the point defects migrate to sinks, rather than recombining. While the defect diffusivities continue to increase with temperature, as before, the concentrations of defects in this sink-limited regime correspondingly decrease and the diffusion coefficient becomes independent of temperature. The reason for this behavior is simply that in the sink-limited regime, each irradiation-produced defect undergoes a fixed number of jumps to reach a sink, and this number is independent of how fast the defects perform these jumps. This behavior is very different from that arising from thermal diffusion, which is included in Fig. 4 for comparison. While (4) provides a convenient first approximation for treating alloy evolution under irradiation, many complexities arise in inhomogeneous alloys where defect and solute mobilities depend on local environments. Moreover, the assumption that the different terms in (4) act independently breaks down for inhomogeneous sink structures, such as grain boundaries and surfaces [19, 20].

In many applications irradiations are conducted at room temperature, where defects are immobile, and subsequently the implanted material is annealed to remove implantation damage, such as excess point defects and defect clusters. When these defects become mobile, they mediate diffusion, often referred to as transient-enhanced diffusion (TED) [21]. As pointed out earlier, once these defects produced at room temperature have migrated to sinks, no additional diffusion takes place, similar to rapid quenching. Since the maximum concentrations of defects that are stable in crystals do not exceed $\approx 1 \text{ at.\%}$, TED is usually not overly significant for phase transformations in concentrated alloys. As discussed in chapter on Transient enhanced diffusion (S. Libertino & S. Coffa, U. of Catania & ST Microelectronics, Catania, Italy), however, TED can play an important role in the semiconductor industry since it leads to precipitation (and loss of electrical activity) and broadening of the depth distribution of shallow implanted dopants.

1.5 Primary Recoil Spectrum

While the preceding discussion has described irradiation effects in general terms, a material’s response depends sensitively on the choice of ion mass and energy as well as the specific target. For example, irradiating a target
Fig. 4. (Left) Concentration of point defects in Cu as a function of temperature at constant flux $10^{-6}$ dpa s$^{-1}$, and a dislocation density of $10^9$ cm$^{-2}$. (Right) Diffusion coefficient shown in an Arrhenius plot for the conditions in (left), but with different dislocation densities. After [18]

with high atomic number and low melting temperature, such as Au or PbTe, with energetic heavy ions creates cascades with high energy densities and extreme thermal spike effects. As a consequence, defect production results in high densities of point defects that often condense into immobile clusters and dislocation loops. Ion-beam mixing is extensive due to the local melting, and the surface is pocked with craters and mounds. At the other end of the spectrum, irradiation of a low-Z material such as Ti or Si with a light ion such as He results in isolated point defects, little atomic mixing, and sputtering yields much less than unity. The difference between these two irradiations arises primarily from the difference in the screening of the Coulomb interaction between the ion and target atom.

For high-energy, light ions, the screening is minimal and the interaction can be described by Rutherford scattering. The scattering cross section in this case is given by,

$$\frac{d\sigma(E_1, T)}{dT} = \frac{\pi m_1 Z_1^2 Z_2^2}{m_2 E_1} \cdot \frac{1}{T^2},$$

where $Z_{i(j)}$ and $m_{i(j)}$ are the atomic number and mass of the projectile (target atom), respectively. The average recoil energy, therefore, is,

$$\langle T \rangle = T_{\min} \ln \frac{T_{\max}}{T_{\min}},$$

where $T_{\max} = 4m_1 m_2 E_1 / (m_1 + m_2)^2$ and $T_{\min} \approx E_1$. For 1-MeV proton irradiation of Cu, for example, $\langle T \rangle \approx 200$ eV. For heavy-ion irradiations of
targets with high atomic weights, screening is strong and the interaction can be approximated reasonably well by hard-sphere collisions. The scattering cross section in this case is,

\[ \frac{d\sigma(E_1, T)}{dT} = \frac{\pi \rho_0^2}{T_{\text{max}}}, \]  

where \( \rho_0 \) is the hard-sphere radius, and

\[ \langle T \rangle = \frac{T_{\text{max}}}{2}. \]

The average recoil energy is thus seen to increase logarithmically with energy for light ions but linearly with energy for heavy ions. The primary recoil spectrum for any particular irradiation is usually obtained by computer simulation [4], which employs the so-called universal potential to describe the two-body interactions [22]. Physical insight into the primary recoil function can be obtained by considering the related function, \( W(T) \), which is the integral fraction of damage energy (and thus also the fraction of defects, atomic mixing, or sputtered atoms) associated with cascades of all energies up to energy, \( T \). This function thus weights the different recoils by how much damage they produce. It is plotted in Fig. 5 for various 1-MeV ions in Ni. A useful single-parameter characterization of a recoil spectrum is provided by \( T_{1/2} \), defined by \( W(T_{1/2}) = 0.5 \), since it yields the recoil energy at which half the defects are produced in cascades of energy greater than \( T_{1/2} \) and half in cascades with energies less than \( T_{1/2} \). Notice that \( T_{1/2} \) increases from 500 eV to over 10 keV on switching the incident ion in Ni from protons to Xe. An interesting comparison shown in Fig. 5 is the \( W(T) \) functions for protons and neutrons since the projectiles have the same masses and energies. Since the former undergoes nearly purely Rutherford scattering while the latter undergoes hard-sphere scattering, the \( W(T) \) are very different, with \( T_{1/2} \) changing from \( \approx 400 \) eV to 40 keV. Lastly, we consider the spatial distribution of recoil events. Shown in Fig. 6 is a simulation of a 200 keV Cu event in Cu. The figure illustrates that the energy is distributed inhomogeneously along the path of the projectile, but with local regions of high energy density. These local regions are denoted as subcascades, suggesting that high energy events can be considered as a series of isolated, smaller events of energy \( E_C \) or less. \( E_C \) marks the energy at which cascades begin to split into subcascades. For recoils in Si, Ni, and Au, for example, \( E_C \approx 5 \) keV, 20 keV, and 50 keV, respectively.

## 2 Irradiation-Induced Stresses and Surface Effects

Changes in the state of stress in materials under irradiation derive from a number of mechanisms: accumulation of defects, the redistribution of material near surfaces, and phase transformations. We do not discuss phase
transformations in this section, since their effect on stress will be apparent after discussing the other mechanisms.

2.1 Defect Accumulation

Irradiation of materials at low temperatures produces point defects and defect clusters. In order/disorder alloys, antisite defects can also be produced. Associated with each of these defects is an excess (relaxation) volume,\(^3\) thus creating internal stress. For example, the relaxation volume of a Frenkel pair in metals is \(\approx 1 \ \Omega_0\) (atomic volume), i.e., \(\approx 1–2 \ \Omega_0\) for the interstitial and \(\approx -0.3 \ \Omega_0\) for the vacancy [23]. As defects cluster and “collapse” into dislocation loops, the relaxation volumes for interstitials and vacancies become symmetric, \(\approx +1\) or \(-1 \ \Omega_0\) for the two defects, respectively. The implanted ion also creates stress since it contributes one excess atom to the sample.

\(^3\) The relaxation volume is the change in sample volume when an atom is removed or added to the interior of a crystal. It differs from the formation volume by one atomic volume.
Measurements of strain, either by lattice parameter measurements or wafer bending, in fact, provide sensitive measures of defect concentrations [24, 25].

An important example of irradiation-induced stress concerns the implantation of hydrogen atoms into Si. It has long been known that implantation of many materials with H or He ions results in high-pressure bubbles and eventually to void formation (see chapter “Voids and Nanocavities in Silicon” by Williams and Wong-Leung), blistering and exfoliation of the surface. It is now recognized that this seemingly detrimental effect can be utilized to good purpose, such as the slicing of thin plates from a thick wafer of single-crystalline material, a process called “ion cut” [26]. Typically, hydrogen is implanted at room temperature to high doses. Subsequently, the material is annealed at elevated temperatures, allowing the hydrogen to coalesce into bubbles with very narrow depth distribution. As the pressure builds, the surface layer fractures parallel to the surface, providing a thin slice of material. The implantation damage, moreover, is removed by the annealing process. By first oxidizing the wafer before slicing, the method can be used to fabricate single-crystalline Si wafers on SiO$_2$ for SOI devices.

2.2 Collective Behavior: Irradiation-Induced Viscous Flow

Irradiation of materials under an applied stress at elevated temperature can lead to enhanced creep rates and stress relaxation owing to the increased concentrations of point defects. While this result is not surprising in light of Sect. 1.5 on radiation-enhanced diffusion, rather unusual plastic deformation has also been observed during irradiation at temperatures where defects are immobile. Such behavior was first observed during swift ion, i.e., GeV energies, irradiation of silicate [27] and metallic [28] glasses. These studies showed anisotropic deformation in irradiated glasses; i.e., they elongate in directions perpendicular to the direction of an energetic ion beam and shrink parallel to it, conserving volume in the process. Using ions with much lower energies, Volkert noticed that epitaxial stresses in amorphous Si underwent stress relaxation during irradiation and showed that relaxation in amorphous Si followed Newtonian viscous flow [29]. Similar behavior has been observed in metallic glasses [30] and amorphous SiO$_2$ [31]. These behaviors are usually attributed to thermal spike effects [32, 33], although alternative mechanisms have been suggested in these glasses [34]. Before going into further detail, it is illuminative to examine the near-surface of an irradiated material during ion irradiation.

Figure 7 shows snapshots obtained from a MD simulation of 10-keV self-ion bombardment of Au at different instants of time. As the cascade event evolves, the local volume heats above the melting temperature and pressures of $\approx$1–10 GPa develop in the core. The pressure associated with the thermal expansion and the solid–liquid transformation causes mass to flow onto the surface. With time, the pressure relaxes and a small volume of liquid is left in the surface region. When the liquid cools and resolidifies, however, atomic
mobility becomes negligible and many atoms are left frozen on the surface. As a consequence, there is a net flux of mass onto the surface, leaving a many vacancies below the surface, which condense into dislocation loops. Since the relaxation volume of each vacancy in a loop is $\approx 1\, \Omega_0$, a permanent biaxial tensile stress is created in the surface region of the films.

While this example uses a relatively low-energy ion and the penetration is shallow, the same basic mechanism has been shown to operate during MeV irradiations as well, and in a variety of different materials [36]. It is also observed in Fig. 7f, that a mound forms on the surface around each impact, owing to the excess material. In some cases craters are also formed, surrounded by a rim. These features add roughness to an irradiated surface and generally they contribute far more roughness to a film than simple sputtering [37, 38]. Lastly, we remark that low-energy sputtering (0.5–5 keV ions) is

![Fig. 7. Evolution of a 10-keV cascade in Au. This event is initiated by a Au impinging on the surface at 0 K. Atoms located within a cross-sectional slab 0.4 nm thick are shown. After [35]](image-url)
often used in processing materials. This procedure can induce tensile stress in films due to the process just described, but it can also create compressive stress owing to end-of-range defects and the addition of the implanted atom. This idea has been used for controlling the radius of curvature of Si components employed in MEMS technology [39].

We return now to the question of anisotropic deformation in metallic glasses during swift ion irradiation. As seen in Fig. 1, the electronic stopping power for swift ions is several keV nm$^{-1}$, which can heat a material within a cylindrical region surrounding the track to temperatures far in excess of the glass temperature. As pointed out by Trinkaus [40], the thermal expansion creates stress within the cylinder, but owing to the elongated asymmetry, the strain is not homogeneous, but rather larger in the direction radial to the beam than parallel to it, as illustrated schematically in Fig. 8. The cylinder of material thus deforms. When the local region cools to below the glass temperature, the anisotropic deformation becomes frozen in, similar to the situation described for mound formation at surfaces. Subsequent tracks add to the deformation. This model is applicable for glasses, but not crystalline material, since for the latter, lattice sites must be conserved during crystallization of the melt. In crystals, therefore, surfaces or other sources and sinks for mass are required for the macroscopic flow described above.

3 Phase Transformations

3.1 Order-Disorder Alloys: Cu$_3$Au

Cu$_3$Au provides a model system for illustrating how ion beams can be employed to control phase stability in order–disorder alloys since the equilibrium thermochemical properties of this alloy are well established. The effect of irradiation on the order of Cu$_3$Au at 80 K is illustrated in Fig. 9 [41]. Here, the long-range order parameter decreases nearly exponentially with ion fluence. This behavior is understood on the basis that atomic mixing arises solely from the ballistic mixing in cascade events and that no reordering is possible during diffusion of vacancies at this low temperature. Interstitial atoms are mobile at 80 K, but their interstitialcy diffusion mechanism does not promote
ordering. Since the disordered arises only from mixing within cascades, the disordered rate in this situation can be written \[42\],

\[
\frac{dS}{d\phi} = -\alpha S,
\]

and

\[
S = S_{eq} \exp(-\alpha \phi),
\]

where \(S\) is the long-range order parameter and \(\alpha\) represents the initial disordering rate of a fully ordered alloy. For doses measured in displacements per atom (dpa), \(\alpha = 24\) for the data shown in Fig. 9. One dpa is the dose required to create a Frenkel pair on every lattice site one time (see (1)); it is a convenient measure of dose since it is independent of the type of ion employed, and it provides physical insight into the damage level.

The behavior is very different at elevated temperatures. As shown in the lower inset of Fig. 10, a short pulse of irradiation (1 s) with He ions at 635.5 K or 607.7 K results in a rapid change in the order parameter, as monitored here by the change in electrical resistivity, \(\Delta R\). At the end of the pulse, reordering takes place. The time constants for reordering are shown in an Arrhenius plot in the same figure for various ion irradiations. At low temperatures the relaxation times show a linear behavior, whereas near the order–disorder temperature in equilibrium, \(T_c\), the times become much longer owing to the reduced driving force for ordering. The curves fit well to an equation of the form,

\[
\tau^{-1} \propto D \tanh \left[ \frac{\varepsilon_a}{2T} \left( \frac{T_0 - T}{T_0} \right) \right],
\]

where \(\varepsilon_a \approx 1000\) K and is related to the ordering energy, and \(T_0 = T_C \pm 2\) K \[43\], illustrating that recovery in this case is due primarily to equilibrium.
kinetics. The excess vacancies produced by the short pulse of irradiation find sinks in times far shorter than $\tau$, and thus cause little reordering. Also shown in this plot is the feature that the time constants become significantly longer as the primary recoil is shifted to higher energies. From these times, the average number of jumps each atom undergoes during the reordering process may be deduced. For He irradiation, at the lowest temperatures, reordering can be achieved with only a few atomic jumps, whereas with Kr irradiation, also at low temperatures, the number increases by a factor of three. The low number for He shows that the disorder is comprised predominantly of isolated antisite defects and that no large volumes of disorder are present. For Kr, the number is increased, showing that small volumes of disorder are created by the cascades and these regions require more atomic motion to reorder.

Figure 11 illustrates the ordering kinetics under continuous irradiation. Initially, the order increases with He ion fluence until the ordering/disordering processes come into steady state. At temperatures well below $T_c$, the kinetic equations for this case can be approximated by [44],

$$\frac{dS}{dt} = -K\phi S + K_1 D (S_{ss} - S)^2.$$  \hspace{1cm} (12)

The reordering process is mediated, as before, by vacancy diffusion, but under persistent irradiation the vacancy concentration is comprised of both equilibrium and excess vacancies. Notice in Fig. 11 that when the irradiation intensity is increased the balance between ordering and disordering is upset and the order parameter decreases and a new steady state is achieved. If the irradiation is reduced to its original intensity, the previous degree of order is restored. The process is reversible, illustrating that the steady state of the system is independent of the starting point and thus represents a state characterized by the temperature and ion flux, as will be described in fuller detail below in Sect. 4. When the irradiation is switched off, the equilibrium state of order is obtained. Notice, however, that the time constants for the system order to change from one state to another is longer when the irradiation is switched off compared to that when the irradiation is only reduced from $\phi + \Delta \phi$ to $\phi$. The difference arises primarily from the excess vacancies in the system during irradiation. When the irradiation is switched off, the recovery is due only to equilibrium vacancies. By comparing these relaxation times, the concentrations of vacancies in the system can be accurately measured, relative to the equilibrium concentration, for any temperature and irradiation intensity [43]. In terms of materials processing, this study illustrates that the irradiation flux, $\phi$, provides an independent control variable, like temperature and pressure, for materials processing.

It is noteworthy that in Cu$_3$Au, $T_c \approx 380^\circ C$, or approximately 3/8 the melting temperature ($T_m$). Since diffusion is sluggish at this temperature, it is very difficult to reach high degrees of order without extensive thermal annealing. In such cases irradiation can prove very helpful, since it enhances diffusion. For example, the L1$_0$ ordered phase of equiatomic Fe–Ni, which has a
critical temperature of 320°C, was discovered after irradiation with neutrons at 295°C [45]. More recently, interest has arisen in achieving high degrees of order in thin films such as FePt for high-density magnetic recording media, since the ordered phase has a high magnetic anisotropy. The required temperature for ordering is far too high for manufacturing thin-film devices, however, as discussed in chapter “Magnetic Properties and Ion Beams: Why and How” by Devolder and Bernas, ion irradiation can be employed to accelerate the ordering kinetics, as illustrated for Cu₃Au in Fig. 10 [46].

3.2 Phase-Separating Alloys: AgCu

Similar behavior is observed in phase-separating alloys, such as the eutectic alloy, AgCu, as shown in Fig. 12. Here, X-ray diffraction patterns from a
multilayer thin-film sample are shown following irradiation with 1.8-MeV Kr ions to a dose of \(1 \times 10^{16} \text{cm}^{-2}\) at various temperatures. At this dose, the microstructure reaches a steady state and the diffraction patterns no longer change. The diffraction pattern obtained from the as deposited sample shows pure phases of Cu and Ag. The peak widths are quite broad since each layer is only 10 nm thick. The absence of (200) peaks indicates strong preferential alignment of the films. Curve F, obtained after irradiation at room temperature, shows that this immiscible alloys has been forced into a homogeneous AgCu alloy due to ion-beam mixing. The peak width has sharpened considerably, illustrating that the grain size is much larger than the initial layer thickness and that phase boundaries are no longer present. Irradiation at higher temperatures results in two-phase alloys, but now with the solubility limits in the steady state being greatly extended.

Similar to the results on ordered alloys, the solubility limits at steady state are independent of the sample history as illustrated in Fig. 13. Diffraction patterns D and A derive from Cu–Ag multilayers irradiated at room temperature and 368 K, respectively, to a dose of \(1 \times 10^{16} \text{cm}^{-2}\). Curves B and C are diffraction patterns from samples first irradiated at room temperature and subsequently reirradiated at 368 K to doses of \(1 \times 10^{16}\) and \(7 \times 10^{16} \text{cm}^{-2}\), respectively. Independent of the initial microstructure, therefore, the solubility limits of the alloy reach the same values for a given irradiation flux and temperature.

A large number of different alloy systems have been irradiated at room temperature to explore the extension of solubility limits in immiscible alloys. Similar to CuAg, several of these alloys form single-phase solid solutions, while many do not. For example, irradiation of AgNi at temperatures as low as \(\approx 80 \text{K}\) shows a maximum solubility of 16 at.% Ag in Ni, but only 4 at.% Ni

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**Fig. 12.** X-ray diffraction patterns of multilayer Cu–Ag samples after irradiation to a dose of \(1 \times 10^{16} \text{cm}^{-2}\) with 1.0-MeV Kr ion at (A) as deposited; (B) 473 K; (C) 423 K; (D) 398 K; (E) 348 K; (F) 298 K. From [47]
Fig. 13. X-ray diffraction patterns of multilayer Cu–Ag samples after irradiation to a dose of $1 \times 10^{16}$ cm$^{-2}$ with 1.0-MeV Kr ion at (A) 398 K; (D) 298 K; (B) 398 K – reirradiation of the sample shown as (D); (C) 398 K – but irradiated to $7.4 \times 10^{16}$ cm$^{-2}$ K. From [47]

in Ag [48]. This result may appear surprising at first since radiation-enhanced diffusion is negligible at this low temperature. This example illustrates, however, that atomic mixing in cascades is comprised of both purely ballistic mixing, where solutes flow down their concentration gradients, and thermal spike mixing where atoms move in the liquid state flow down gradients in their chemical potentials. Noteworthy is that the solubility limit of Ag in Ni just above $T_m$(Ni) = 1453°C is $\approx$5 at.%, while that for Ni in Ag is 1 at.% just above $T_m$(Ag) = 961°C, suggesting that equilibrium is not attained during the short lifetime of the thermal spike, but see Sect. 4, below, for further details.

3.3 Amorphization

Many irradiated materials have been shown to undergo a crystalline to amorphous transition during irradiation at temperatures sufficiently far below the crystallization temperature of the amorphous phase. Covalently bonded systems are particularly conducive to amorphization, with even pure elements Si and Ge undergoing amorphization during irradiation. In contrast, no pure metal undergoes amorphization under irradiation, nor do alloys that form solid solutions, even at irradiation temperatures below 10 K. Several intermetallic compounds, on the other hand, have been amorphized [49]. A review of the models for amorphization under irradiation can be found in [50]. In the present work, we concern ourselves only with how this phase transition depends on the conditions of the irradiation, and therefore we will simply assume that the accumulation of defects and disorder eventually leads to amorphization. We note, however, that in pure metals the largest concentration of point defects and defect clusters that can be accumulated is $\approx$0.1 at.%%
even at temperatures where point defects are immobile. At higher concentrations, the Frenkel pairs recombine and defect clusters collapse into dislocation loops, which have much lower energies. Owing to these relaxation mechanisms, amorphization is prevented. In many intermetallic compounds both defect accumulation and chemical disorder are introduced, enabling amorphization. Simulations suggest that in some intermetallic compounds either chemical disorder or point defects are sufficient for amorphization, but not always [50].

Figure 14 schematically illustrates the effects of primary recoil spectrum and temperature on the critical ion dose required for amorphization, while Fig. 15 shows a similar plot obtained from experiments on CuTi [51]. At low temperatures, amorphization is achieved at approximately the same irradiation dose (measured in dpa), regardless of primary recoil spectrum. At higher temperatures, however, the critical dose for amorphization increases.
owing to the onset of thermally activated recovery mechanisms. Presumably recovery of order and defect annealing is mediated predominantly by vacancy migration. The situation for amorphization thus very much resembles the behavior shown in Fig. 10, for the order–disorder alloy, Cu$_3$Au. For Cu$_3$Au it was pointed out that the relaxation time of the order parameter increases markedly on increasing the mass of the irradiation ion. If we assume that similar mechanisms control amorphization, the data shown in Fig. 13 follow directly, but see [50] for details.

4 Phase Transformations: Effective Temperature Model

Sustained irradiation can lead to the dynamical stabilization of nonequilibrium phases at steady state, as illustrated in Sect. 3. In order to assess the radiation resistance of materials, for instance in nuclear reactors or in matrices for radioactive waste immobilization, it is of high practical interest to be able to rationalize or even predict the phases eventually stabilized by a given irradiation environment. An important observation in that respect is that, in almost all experiments, these steady states are observed to be independent of the initial state of the alloy, and that the transformation from one steady state to another occurs reversibly as the irradiation parameters are varied. Furthermore, small changes in the irradiation conditions can lead to drastically different steady states. For instance, during 1-MeV electron irradiation of the ordered alloy Ni$_4$Mo, a temperature drop from 470 K to 450 K results in a transition from a chemically long-range ordered to a disordered steady state [52].

This general behavior suggests that it may be possible to recast the problem of phase stability under irradiation into a framework resembling equilibrium thermodynamics, and thereby place ion-beam processing on the same footing as more conventional processing. Earlier attempts were made to rationalize radiation-induced phase transformations using free energies constrained by high point defect supersaturations. This approach, however, fails to reproduce experimental results, in particular transitions from one steady state to another. As initially proposed by Adda et al. [53], one should instead consider an alloy under irradiation as a system subjected to several dynamical processes in parallel, which can be synergistic or competing. For such a dynamical system, one could envision constructing a steady-state phase diagram that yields the most stable steady state under specified irradiation conditions, thus extending the concept of equilibrium phase diagram. Clearly, axes in such a diagram need to include the irradiation flux, or the displacement rate, in addition to common thermodynamic variables such as composition and temperature. The experimental results reviewed above indicate that, in these steady-state diagrams, one expects to find phase boundaries, which correspond to dynamical phase transitions. A fundamental and practical question is then to determine the location of these dynamical phase
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boundaries. Although there is no general proof that an effective free energy can be derived for dissipative systems [54], a simplified but powerful approach was introduced by Martin in the mid-1980s [55], leading to the so-called effective temperature criterion. We now review this criterion and illustrate its application to various phase transformations.

4.1 Phase Decomposition

Consider the case of an alloy such as Cu–Ag subjected to sustained irradiation, as illustrated in Figs. 12 and 13. In order to distinguish solid solution from phase-separated steady states, Martin proposed to write the evolution of the composition profile in such an alloy as

$$\frac{\partial c(r, t)}{\partial t} = -M' \nabla \mu + D_b \nabla c,$$  \hspace{1cm} (13)

where $M'$ is the atomic mobility, enhanced by the point-defect supersaturation, $\mu$ the equilibrium chemical potential of the alloy, and $D_b$ a ballistic diffusion coefficient that takes into account the random mixing forced by the nuclear collisions discussed in Sect. 2. Two important approximations are made in writing (13). First, the forced mixing is assumed to be random, and second, this mixing is assumed to be short-range and thus it can be described by a diffusive process. Using a regular-solution model for the chemical potential of the alloy, including a Cahn–Hilliard inhomogeneity term, Martin showed that the stable steady state reached under irradiation at the temperature $T$, corresponds to the equilibrium state that the same alloy system would have reached at an effective temperature,

$$T_{\text{eff}} = T \left(1 + \frac{D_b}{D_{\text{th}}'}\right),$$  \hspace{1cm} (14)

where $D_{\text{th}}'$ is the radiation-enhanced interdiffusion coefficient due to thermally activated atomic transport.

Figure 16 illustrates how the effective temperature $T_{\text{eff}}$ varies with the actual irradiation temperature $T$ and the irradiation flux $\phi$. At elevated temperatures, $T_{\text{eff}} \rightarrow T$, irradiation accelerates the thermal kinetics but without much affecting the alloy state. At low temperatures, $T_{\text{eff}}$ becomes very large since ballistic effects dominate. In fact, if one retains only the ballistic term on the RHS of (14), the alloy reaches an infinite temperature state. At a given intermediate temperature, the higher the irradiation flux, the higher the effective temperature. For a model alloy simply displaying a miscibility gap at equilibrium, the application of the effective temperature criterion leads to the dynamical phase diagrams shown in Fig. 17 [56]. Experimental results discussed in Sect. 3.2 for the Cu–Ag system under irradiation are in good agreement with such diagrams.
4.2 Order–Disorder

Although it is not possible to derive an exact expression for an alloy undergoing an order–disorder transition under irradiation, the effective temperature criterion provides a very good approximation of the steady-state degree of order parameter reached under irradiation [55]. From a qualitative perspective, it reproduces very well the features discussed in Sect. 2 for irradiated Cu₃Au. For ordered phases that remain ordered up to their melting point, T_M, such as NiTi, by extension of the T_eff criterion, one could suggest that, when T_eff > T_M, the alloy would reach an amorphous steady state. Certain compounds, however, such as Ni₃Al, while fully disordered by low-temperature irradiation, do not transform to amorphous phases, even at cryogenic temperatures [57]. It should be kept in mind, however, that the effective temperature model refers to diffusion and chemical compositions, it does not consider free energies of competing structures.

4.3 Beyond the Effective Temperature Criterion

While the effective-temperature criterion captures the dynamical competition between the rates of irradiation-induced mixing or disordering and ther-
mally activated relaxation toward a low free-energy state, it does not take into account the fact that these processes may operate at different length scales. Irradiation with heavy and energetic ions in particular leads to the formation of dense displacement cascades, thus introducing two new length scales in the problem, the cascade size, $\approx 1$ to $10$ nm, and the average relocation distance of atoms within the cascade, $\approx 1$ to $10$ Å. Recent analytical and simulation works have shown that a general property of systems where dynamical processes compete at different length scales is the propensity to self-organize in space into patterns. Self-organization of composition fields in the bulk and patterning of surface morphology, for instance, are covered in detail in chapters “Precipitate and Microstructural Stability in Alloys Subjected to Sustained Irradiation” by Bellon and “Spontaneous Patterning of Surfaces by Low-Energy Ion Beams” by Chason and Chan.

5 Conclusions

The underlying principles of ion-beam processing are now well understood, and it is possible to design ion-beam processing schemes to achieve desired structures. Many challenges, however, remain in predicting the response of more complex materials that are of interest for engineering applications. The difficulties arise because ion irradiation drives materials far from their equilibrium states and this opens many pathways for the material to respond. For example, prolonged irradiation of metals creates point defects that can form defect clusters, and these clusters may be immobile or mobile, they may trap other defects and solute, and they alter the properties of the material, such as conductivity and strength. Accounting for these defect interactions is difficult, particularly in concentrated, multiphase alloys. Another example where ion-beam processing is proving a promising processing tool concerns the synthesis of nanostructured materials. As was noted in this chapter, the dimensions of the displacement cascades, or diameter of ion tracks are ideal for forming nanostructures both in the interior and at the surfaces of materials. The irradiation process, however, is stochastic and it remains challenging to create nanostructures that are spatially organized in patterns. Progress in achieving self-organization and patterning in irradiated materials is discussed in chapters “Precipitate and Microstructural Stability in Alloys Subjected to Sustained Irradiation” by Bellon and “Spontaneous Patterning of Surfaces by Low-Energy Ion Beams” by Chason and Chan.

A promising new direction in treating the complexity involved in ion-beam processing of engineering materials involves multiscale computer modeling. Several examples in this article concerning the displacement process in irradiated materials illustrate the power of molecular-dynamics computer simulations for this purpose. With current computing power, and progress in developing accurate yet tractable interatomic potentials, it is indeed now possible to reliably calculate the displacement process in most materials, although
materials where charge exchange is significant remains difficult. The more challenging task of computing the evolution of microstructures at elevated temperatures during prolonged irradiation, or during postirradiation annealing still lies ahead. Advances in such methods as kinetic Monte Carlo [58, 59], accelerated molecular dynamics [60, 61], and phase-field modeling [62, 63], however, appear very promising for this purpose and the field of ion-beam processing.

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References

17. R. Sizmann, J. Nucl. Mater. 69/70, 386 (1978) 8
41. Y.S. Lee, Ph.D. thesis, University of Illinois at Urbana-Champaign 15, 16
42. S. Siegel, Phys. Rev. 75, 1823 (1949) 16
47. L.C. Wei, R.S. Averback, J. Appl. Phys. 81, 613 (1997) 19, 20

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