for low energy ions or

\[ x_{\text{min}} = 18.8 \, N \delta t_1 \]

for high energy ions.

\( N \) is the number of atoms per unit volume, other quantities are in Å, MeV or degrees.

**REFERENCES**


**Chapter 4**

**Radiation Damage**

**4.1 INTRODUCTION**

Ion implantation adds new atoms to the surface of a material but in addition introduces property changes by disrupting the existing atomic order of the surface layers. This is to be expected since even a light ion will deposit energy at an average rate of 10–100 eV per Å and a heavy ion near the end of its range can lose keV per Å. The atoms of the solid are displaced and whole regions around the track may be treated as though the solid were molten, this is the concept of the thermal spike. If many atoms are displaced then they in turn may displace further atoms, it is customary to refer to this highly disordered region as a collision cascade.

Whilst these dynamic effects are transient, the perturbed structures may re-order into characteristic arrangements of atoms to include vacancies, interstitials and other defects. For the sake of completeness we will list the more common defects, describe their structure and indicate their stability during thermal annealing of the solid in typical situations.

Disorder introduced by ion implantation is called radiation damage or lattice imperfection. One should repeat that the prejudice invoked by the words damage or defects is unfortunate since the changes in structure produced by the passage of fast ions enables us to make materials which were not obtainable by normal thermodynamic processes. It is also true that the “damaged” material may have superior properties to the original solid. Most text books which discuss radiation damage mention defect structures in terms of crystal lattices, because this simplifies both the theoretical and experimental analyses. The major difference between crystals and amorphous solids is that in the former there is long range order of the atoms whereas in amorphous systems the order (i.e. bond length, direction and type of neighbouring atom) exists over a small region. However defect properties also influence a limited region of the solid so their effects are likely to be similar in both crystalline and amorphous solids.

We shall first discuss defects which involve one or two atypical atomic sites and then consider extended defects.
4.2 VACANCIES AND INTERSTITIALS

An unoccupied lattice site is termed a vacancy and an extra atom forced into some region of the lattice is an interstitial. Since these involve relatively small distortions of the original lattice they may exist in "normal" solids and be generated by thermal fluctuations in the lattice. We will first consider the energy required to form an interstitial–vacancy pair in the most favourable case when the lattice can relax during the formation of the defects.

If the solid is ionic or covalent, with directional bonds, then we may consider forming a vacancy by breaking the bonds around an ion and placing it on the surface of the crystal. A surface atom will have about half the normal bond directions satisfied by the lattice so the net expenditure of energy is the energy required to break half the bonds but this is also the sublimation energy of a surface atom. Hence the energy of formation of a vacancy is around 1 eV in an insulator.

In the case of a metal we can make an estimate of the energy for vacancy formation by considering a spherical crystal in which we form a small cavity (the vacancy). Because conduction band electrons spread throughout the solid we can think of the cohesive energy of the metal as being amorphous so the material from the vacancy \( (4/3) \pi r_v^3 \) can be added uniformly over the outside of the sphere. The total surface area of the metal has increased (by \( \approx 4 \pi r_v^2 \)), and we can determine the surface energy, \( S_v \), of a metal so the energy required to make a vacancy is \( U_v \approx 4 \pi r_v^2 S_v \). Numerically this is between 1 and 2 eV for most metals. More sophisticated models predict similar energies of vacancy formation.

We may now calculate the equilibrium vacancy concentration and note that the change in free energy of a material containing vacancies is

\[
F = n_v U_v - TS_v
\]

where \( S_v \) is the entropy change associated with vacancy formation and there are \( n_v \) defects. If there are \( N \) lattice sites and \( n_v \) identical defects the number of different configurations is

\[
W = \frac{N!}{n_v!(N - n_v)!}
\]

and the entropy of the disorder is \( S_v = k \ln W \).

Defects also modify the lattice vibrations. Normally the thermal entropy is

\[
S = 3Nk \ln (h v / k T)
\]

where \( v \) is a vibrational frequency but this will be modified to \( v_v \) near a vacancy.

If each vacancy influences \( x \) normal lattice sites the total change in free energy is

\[
F = n_v U_v - k T \ln \frac{N!}{n_v!(N - n_v)!} - 3k x \left[ \ln \frac{kT}{h v_v} - \ln \frac{kT}{h v} \right]
\]

At equilibrium \( \partial F / \partial n_v = 0 \), so on substituting the Stirling approximation, \( \ln N! \approx N \ln N \), we obtain

\[
\frac{n_v}{N} = \left( \frac{v_v}{v} \right)^3 \exp \left( - \frac{U_v}{kT} \right)
\]

\( n_v/N \) is the vacancy concentration. The pre exponential term is not important since \( v \) and \( v_v \) will differ by only a few per cent and the number of perturbed atoms, \( x \), is generally less than 10. (These statements can be justified experimentally by infra-red spectroscopy, electron spin resonance, field ion microscopy etc.) Thus the Boltzmann factor dominates the defect concentration. The formation energy is important, for in a material at 1000 K the concentration would vary from \( 10^{-5} \), if \( U_v \sim 1 \) eV, to \( 10^{-50} \) if the \( U_v \) were 10 eV.

A concentration of \( 10^{-4} \) defects per normal lattice site is significant as it can represent \( 10^{14} \) centres per cm\(^3\). For comparision we may note that impurity atom concentrations are rarely as low as \( 10^{-5} \) and even in semiconductor materials a higher purity may only refer to electrically active impurities and not the total impurity concentration. In situations where one can distinguish between the different types of defect or impurity a specific concentration of \( 10^{-10} \) may be detectable (e.g. by ESR or luminescence).

![Fig. 4.1. Simple defects in an ordered and an amorphous solid. A is a vacancy, B, C, D are the body centred, split and crowdon models for an interstitial, E is probably interstitial-like in behaviour.](image)
The vacancy concentration introduced in thermodynamic equilibrium at high temperature is not trivial and it is important to note that this concentration may be frozen into the solid by rapid cooling. This situation exists in the formation of many materials. The calculation also indicates the vacancy concentration which could be “frozen” from a thermal spike.

In our estimate of the vacancy concentration we did not distinguish between Frenkel and Schottky vacancy–interstitial pairs. Frenkel defects are those in which both the vacancy and interstitial are included in the bulk of the specimen whereas in Schottky defects the interstitial is considered as being added on to the surface. Figure 4.1 offers some models for vacancy and interstitial sites. The vacancy, A, is an unoccupied lattice site and although some relaxation may occur near the site only short range order is affected, therefore the defect is basically stable and could exist in either a lattice or an amorphous material.

The choice of models for an interstitial is not so obvious nor are the calculations of its stability. Figure 4.1 shows three ways the extra atom may be included in a lattice. Example B is termed a body centred site; C is a split interstitial, that is two atoms sharing a single site and D is a crownion. Crownion describes an ion which has been inserted into a normal row of atoms and produces a perturbation over several lattice sites. More realistic sketches of ions in a lattice should include an indication of finite atomic radii. When this is considered, Fig. 4.2, some interstitial models look less promising. In the figure the crosses represent original ion sites. By assuming a hard

![Simple defect models with ions of finite size. The crosses represent the perfect lattice sites.](image)

sphere type ionic potential only the vacancy and the split interstitial could be readily accommodated in this picture.

Even if the defects are formed we should consider if they are thermally stable or if they anneal. The rate of migration will be of the form \( \nu \exp (-U_{\text{mass}}/kT) \) where the vibrational frequency, \( \nu \), is the lattice frequency (\( \sim 10^{13} s^{-1} \)) and the migration energy will differ for the various defects.

In an annealing experiment where the temperature is being steadily increased there will be temperature regions where particular defects anneal.

Table 4.1 indicates the calculated energies of formation and migration for some simple defects in metals together with the temperature at which annealing might occur. As a guideline it is frequently convenient to relate the annealing temperature to the activation energy for migration by \( U_m \approx 25 kT_{\text{anneal}} \). This estimate is equally useful in insulators or semiconductors where the probability of transition between two electron levels is also significant if \( E \sim 25 kT \). Such a guideline is inappropriate if the pre-exponential factor is noticeably different from the lattice vibrational frequency (\( 10^{13} s^{-1} \)). These data were selected from a review of annealing calculations and measurements in the book by Thompson (1969).

### Table 4.1

<table>
<thead>
<tr>
<th></th>
<th>Copper</th>
<th>Silver</th>
<th>Gold</th>
<th>Annealing temperature (( U_m/25k ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancy formation</td>
<td>1:2</td>
<td>1:1</td>
<td>1:0</td>
<td></td>
</tr>
<tr>
<td>Di-vacancy formation</td>
<td>2:2</td>
<td>2:1</td>
<td>1:9</td>
<td></td>
</tr>
<tr>
<td>Vacancy migration</td>
<td>1:0</td>
<td>0:9</td>
<td>1:0</td>
<td>~ 460K</td>
</tr>
<tr>
<td>Di-vacancy migration</td>
<td>0:6</td>
<td>0:5</td>
<td>1:0</td>
<td>~ 230K</td>
</tr>
</tbody>
</table>

Theoretical estimates of interstitial formation and migration energies in copper, eV.

<table>
<thead>
<tr>
<th></th>
<th>Body-centre</th>
<th>split-interstitial</th>
<th>Crownion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation energy</td>
<td>4:0</td>
<td>3:9</td>
<td>4:7</td>
</tr>
<tr>
<td>Migration energy</td>
<td>0:05</td>
<td>0:05</td>
<td>0:25</td>
</tr>
<tr>
<td>Annealing temperature (( U_m/25k ), K)</td>
<td>~ 23</td>
<td>~ 23</td>
<td>~ 115</td>
</tr>
</tbody>
</table>

This data was selected from a review of annealing calculations and measurements in the book by Thompson (1969).

The precise values of these theoretical estimates are open to some debate but they suggest that only vacancy type defects would be generated by thermal processes in these face centred cubic metals. Vacancy or interstitial
defects produced during ion implantation will require more energy than the equilibrium calculation since the lattice does not relax during the displacement event. A "standard" estimate of the displacement energy (Section 4.3) is 25 eV rather than the 1 or 4 eV of the equilibrium case. However such quantities of energy are readily available, so all types of defects could be produced. Whether or not they will be stable depends on their migration energy and here the normal lattice calculation is still applicable. The Table 4.1 indicates that vacancy type defects could exist at room temperature but to preserve interstitial defects the damage must be produced and maintained near liquid helium temperature.

![Graph](image)

Fig. 4.3. Pulse annealing curves for several metals. The curves record the recovery of radiation induced resistivity after bombardment with 1.5 MeV electrons at 20 K (from Walker, 1962). Measurements were made at 20 K. The structure in the first major annealing stage is shown in more detail for copper.

4.2 VACANCIES AND INTERSTITIALS

Typical annealing curves for the annealing of radiation damage in metals is shown in Fig. 4.3 (Walker, 1962). For simplicity the damage was introduced by relativistic electrons (1.5 MeV) which have sufficient momentum to produce point defects but cannot disturb larger regions of the solid. In this example the changes in defect concentration are sensed by electrical resistivity measurements, however, all defects contribute to electron scattering so one cannot distinguish between different species by a resistivity measurement. To separate thermal and defect scattering the resistivity measurements were made at 20 K after successive 10 minute anneals at progressively higher temperatures. The data are presented as the fractional recovery of the resistivity introduced by radiation damage.

This family of curves has the major annealing stage at very low temperatures which is consistent with the theoretical estimates of interstitial migration and the assumption that the bulk of the interstitials anneal by recombining with vacancies. In particularly detailed studies of point defects in copper (e.g. see Corbett and Walker, 1959; Sosin and Neely, 1962 or the review by Walker, 1962) the first annealing stage (16–55 K) has been subdivided into five substages which can be associated with (i) correlated diffusion of interstitials to the adjacent vacancy (ii) random diffusion to other vacancies and (iii) interstitials stabilised by impurities. (Diffusion kinetics will be discussed in Chapter 5.)

Not only do the general features of the annealing curves look similar for all the metals (Fig. 4.3) but also these comments on defect stability are equally applicable to insulators. Once again the interstitial type defects become mobile at much lower temperatures (<50 K) than vacancies (< 500 K). One should note that in non-metallic systems the stability of a defect will also depend on the electronic charge state relative to its surroundings. For example in alkali halides the halogen vacancy is stabilised by an electron and can exist up to 500 K whereas without the electron the system is unstable above 50 K.

Whilst it is clear that imperfections exist, together with changes in properties of the solid, it is always a major problem to decide the detailed structure of the defect and its contribution to a particular property. Few measurements discriminate between different defects and one normally resorts to an indirect identification via a bulk property change (e.g. resistivity, friction, length) by comparison with a theoretical model. Some atomic sites may be located by Rutherford backscattering (see Chapter 8).

In non-metals the directional nature of the ionic or covalent bonds together with the optical transparency of solids which have empty conduction bands combine to make defect identification more positive. The powerful techniques of electron spin resonance (ESR) or electron nuclear double resonance (ENDOR) probe the electron density around a defect and sense
the minor shifts in energy levels produced by interactions with nuclear spins.
In the classic case of the F-centre in alkali halides (an electron in a halogen vacancy) some 90\% of the electron density is seen to be confined to the vacancy. However the technique can still note interactions with neighbours up to six lattice sites from the vacancy. Even if ESR is not applicable the dispersive measurements of optical absorption or luminescence provide some insight into the behaviour of different defect types.

| Table 4.2 A summary of defects in alkali halides which involve halogen lattice sites. The defects used to be labelled in terms of the optical absorption bands $\alpha$, $F$, $M$, $R$, etc. but it is now customary to indicate the number of vacancies and the charge state relative to the perfect lattice (i.e. $F^+$, $F$, $F_2$, $F_3$). |

<table>
<thead>
<tr>
<th>Band</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ band ($F^+$)</td>
<td>A halogen ion vacancy which modifies electronic transitions of the lattice.</td>
</tr>
<tr>
<td>$F$ band ($F$)</td>
<td>A halogen ion vacancy that has trapped an electron. The transitions to higher states are also evident as the bands labelled $K$, $L_1$, $L_2$, $L_3$.</td>
</tr>
<tr>
<td>$F_A$, $F_B$ bands</td>
<td>(Sometimes labelled $A$ and $B$)—absorption bands which arise from impurity alkali ions at one of the six neighbouring metal ions sites of an $F$ centre. (There are two bands because of the reduced symmetry of the centre, and the dipole may lie along the axis through, or perpendicular to, the impurity ion.)</td>
</tr>
<tr>
<td>$F'$ band ($F^-$)</td>
<td>A halogen ion vacancy that has trapped two electrons.</td>
</tr>
<tr>
<td>$M$ band ($F_2$)</td>
<td>A pair of adjacent $F$ centres.</td>
</tr>
<tr>
<td>$R$ bands ($F_3$)</td>
<td>A triangular array of three $F$ centres. Although possible arrangements are a linear chain of three vacancies, an L-shaped set in the (100) plane or a triangular set in the (111) plane, the model currently believed is the latter (111) arrangement.</td>
</tr>
<tr>
<td>$N$ bands ($F_4$)</td>
<td>Four $F$ centres linked together. Two possible configurations are a parallelogram of vacancies in the (111) plane which may produce the $N_1$ absorption and a tetrahedron of vacancies which may give the $N_2$ absorption.</td>
</tr>
<tr>
<td>$M'$, $R'$, $N'$ bands ($F_2^-$, $F_3^-$, $F_4^-$)</td>
<td>By analogy with the $F$ centre the $M$, $R$ or $N$ centres may trap an additional electron. Some absorption bands have been associated with these defect models.</td>
</tr>
<tr>
<td>$U$ band</td>
<td>A hydride ion substituting for a halogen ion on a lattice site. (Hydrogen negative ions may form in interstitial sites (the $U_4$ band) and hydrogen atoms in interstitial sites (the $U_2$ band).</td>
</tr>
</tbody>
</table>

represents some 30 years of world wide research. There are many more defects, particularly impurity related centres, for which a “first-guess” model exists. One may ask why no point defects were mentioned for the cation sub-lattice since ion implantation or energetic electrons will certainly produce displacements. It appears that the migration energy is so low that the defects anneal or form into extended defects such as platelets or colloidal metal aggregates. Indeed optical scattering from metal colloids has been observed and one may note that the development of a grain in a photographic emulsion requires the precipitation of a small metallic cluster.

Further examples of the analysis and identification of point defects are given in the general references listed at the end of this chapter. The role of defects in device applications is specifically mentioned in the book by Townsend and Kelly (1973).

To summarise, we are at the stage in point defect studies where we can predict the general behaviour of vacancies and interstitials and in a few materials offer quite detailed justification for the models. However, many defect structures, particularly in metals, can only be surmised from indirect evidence. A realistic view is that we may utilise the property changes of defects introduced by ion implantation without a detailed knowledge of the defect structure. This pragmatic approach is not limited to ion beam technology as the conventional preparation of semiconductors, phosphors, metallic alloys etc. abound with similar uncertainties.
4.4 ALTERNATIVE PROCESSES IN DEFECT PRODUCTION

where

\[ b = \frac{2Z_2e^2}{m_0c^2}; \quad \beta = \frac{v}{c}; \quad \alpha = \frac{Z_2e^2}{\hbar c} \approx \frac{Z_2}{137}; \]

\[ E_D \] is the threshold energy for displacement and \( E_m \) the energy transferred from the relativistic electron is

\[ E_m = \frac{2E_r(E_1 + 2m_0c^2)}{M_2c^2} \]

In an ordered lattice the displacement energy will be sensitive to the direction in which the ejected atom attempts to escape. Such effects have been recorded and in Fig. 4.5 the computed curves for \( E_D = 20 \) and \( 30 \) eV are compared with the resistivity changes produced in thin oriented layers of iron (Lomer et al., 1967) and it is apparent that the theory describes the experimental data. An average \( E_D \) of 25 eV seems justified.

For a more extensive treatment of the subject the reader is referred to the book by Corbett (1966). One should realise that electron bombardment is, in terms of property change, just a special case of ion implantation. It has the advantages that defects are produced without any additional ions and the electron range is long compared with the range of an energetic ion, so a larger volume of material may be modified. Range expressions, for unit density material, are given empirically by Glendenin (1948) as

\[ R = 407 \, E^{1.38} \quad 0.15 < E < 0.8 \text{ MeV} \]

\[ R = 542 \, E - 133 \quad E > 0.8 \text{ MeV} \]

where \( R \) is in mg cm\(^{-2}\) and \( E \) in MeV.

4.4 ALTERNATIVE PROCESSES IN DEFECT PRODUCTION

AND SEPARATION

It was assumed, in all the discussions so far, that atomic displacements were the result of elastic collisions and that electronic effects were unimportant. Indeed, elastic collisions are the major reason for defect formation but it should be pointed out that in non-metallic systems defect production rates are influenced by the charge state of the lattice. In particular we must realise that electronic and nuclear losses are not independent events and the state of ionisation of the struck atom and the surrounding lattice atoms may significantly change the energy required for displacement. For example if the ion becomes multiply charged the electrostatic repulsion between it and its neighbours may assist in the removal from the original site. It is also apparent that a multiply charged positive ion will be physically smaller than the singly
charged ion and so may require less energy to force its way out from the lattice site. Such an argument implies that the time required for ejection is less than the time needed to recapture electrons and return to the ground electronic state. Defects generated by ionisation have been discussed by Pabst and Palmer (1974) to explain defects induced in silicon during proton and helium irradiation.

We have also assumed that the interstitial–vacancy separation was achieved by a series of displacement events. However a stable separation of the pair can be produced with a smaller expenditure of energy if the lattice will support a focussed replacement sequence (Silsbee, 1957). Figure 4.6(a) describes a row of atoms in which atom B has been struck and received momentum as indicated by the vector. This is sufficient to displace atom C which in turn strikes atom D. The linear progression can be assisted by the ordered nature of the surrounding lattice. Eventually we reach the situation of Fig. 4.6(b) where there is a vacancy at the original site of atom B and the interstitial appears between D and F (in this example as a crowdon).

The process is important because the equilibrium concentration of defects will be higher since correlated recombination of interstitial–vacancy pairs is less likely. In the case of a collision cascade it might also leave the central core rich in vacancies. A situation in which the vacancies might cluster independently of the interstitial processes.

In some materials purely electronic mechanisms can lead to atomic movements. Classic examples are the photographic process in silver halides and colour centre formation in alkali halides. The latter is interesting because it is proposed (Pooley, 1966, Hersh, 1966, Itoh and Saidoh, 1973, Toyozawa, 1974) that the energy is coupled into the halogen sub-lattice by the transient formation of an excited halogen molecule. When this relaxes and then dissociates the energy is directed along a close packed row (110) of halogens by a replacement collision sequence. To make the process more efficient (i.e. increase the length of the sequence) it was assumed that the collisions occur between small neutral halogen atoms and halogen ions, rather than between pairs of large halogen ions (Smoluchowski et al., 1971). The effective ionic transport is achieved by a parallel process of electronic tunnelling along the collision chain. In alkali-halides the existence of the crowdon interstitial is positively established and there is considerable evidence for this low energy model of defect formation (e.g. Townsend and Kelly, 1973, Townsend, 1973, Saidoh and Townsend, 1976).

In materials which allow these alternative mechanisms of defect production the volume of the solid containing defects may be greater than that expected from the simple elastic collision process.

4.5 DEFECT CONCENTRATIONS

In Chapter 2 we discussed the spatial distribution of the defects produced by ion implantation and realised that it was similar to the concentration profile for implanted ions; and also the ion range and the defect distribution are sensitive to $M_2/M_1$. Although we discussed the distribution we made no attempt to quantify the number of vacancies and interstitials that were produced, and in the light of the comments in this chapter on the thermal equilibrium of point defects at various temperatures it is not possible to do so without considering a specific example. We could, however, estimate the number of atoms that will be initially disturbed from their original sites, this may not predict the equilibrium concentration of defects, but it is useful (i) in setting an upper limit to the primary defect concentration, (ii) in considering whether or not sufficient disorder is introduced that the solid may undergo a crystalline to amorphous transition, and (iii) the number of displacements near the surface is related to the number of atoms ejected from the surface (i.e. sputtering).

In essence the early models of Kinchin and Pease (1955) Snyder and Neufeld (1955) assumed that no atoms were displaced unless a minimum displacement energy $E_p$ was transferred to the struck atom. If more than $2E_p$ energy were available this would produce a multiplicity of displacements proportional to the energy in excess of $2E_p$. This suggests that a function $v(E_2)$, which measures the number of displacements, has the form of Fig. 4.7. The maximum slope is $E_2/2E_p$, assuming there are no alternative sources of energy loss. The total number of displacements which are made, $C_D$, is related to the flux, $\Phi$, and irradiation time, $t$, by

$$ C_D = \Phi \int_{E_p}^{E_p} v(E_2) \frac{d\sigma}{dE_2} dE_2, $$

Fig. 4.6. A replacement collision sequence which leads to a vacancy and an interstitial in the row of atoms.
where \( T_{\text{max}} = \frac{4M_1(M_2E_1)}{(M_1 + M_2)^2} \). This equation can be integrated if we specify \( \text{d}E/\text{d}E_z \). With the usual assumptions about the nature of the repulsive potential for ion pairs (see Chapter 2) the inverse square potential leads to

\[
C_D = \Phi t \frac{\pi M_1 Z_1^2 Z_2^2 e^4}{2M_1 E_1 E_D} \log \left( \frac{4M_1 M_2 E_1}{(M_1 + M_2)^2 E_D} \right)
\]

for energetic light ions. Note that \( C_D \), in this case is approximately proportional to \( E_1^{-1} \). For heavy ions we approach

\[
C_D = \Phi t \frac{\pi^2 (0.885)^2 M_1 e(Z_1 Z_2)^{7/6}}{4(M_1 + M_2) (Z_1^{2/3} + Z_2^{2/3}) E_D},
\]

which is independent of \( E_1 \). We would therefore expect a fairly constant density of defects along the track of the implanted ion.

### 4.6 Extended Defects

Disordered regions, which extend over a large region of a solid, will occur in the form of grain boundaries, dislocations, impurity clusters and crystalline or amorphous inclusions. In compound systems there can also be localized variations is stoichiometry. Such arrays of defects are certainly not passive and, as is explained in undergraduate text books of the solid state, dominate the mechanical properties of solids. Both implanted ions and atomic defects interact with the existing network of extended defects and contribute to their production or removal. Additional large scale features develop in the form of bubbles, if the implanted ions are inert or are gaseous and exceed the solubility conditions existing in the material. The migration of vacancies can generate vacancy "bubbles" called voids, the parallel effect of a solid implant would be termed precipitation. The possible interactions are so diverse and a function of so many parameters that one can only mention typical interactions and leave specific problems for more detailed thought when one knows the defect mobility, alternative phases, sample temperature (see Nelson, 1968).

In the controlled situations of ion implantation these effects can be studied after their production whereas in the similar situation of defects and fission fragments injected by a nuclear reactor it is essential to predict the consequences. The situation is more difficult because in the working life of a reactor one might easily expect every atom to have been displaced as often as 100 times. Ignorance of the consequences, or inability to control them, has led to reactor materials which distorted or failed. Fortunately it has now been realised that reactor conditions can be simulated by ion beam implantation at high dose rates. The radiation damage of the reactor's operating lifetime can then be assessed in days, rather than years.

### 4.7 Fission Fragments and Fission Tracks

The fission of uranium produces energetic neutrons, alpha particles and heavy fission fragments. Initially one considers that the neutrons and alpha particles generate point defects over much of their path and extended defects will occur as a secondary process. For example the inert gaseous helium (\( A = 4 \)) krypton (\( A = 84 \)) and xenon (\( A = 131 \)) produced by fission may cluster to form gas bubbles (see Section 4.9). Such effects are only important after prolonged irradiations. However the fission fragments are both heavy and enormously energetic. The fission fragment spectrum (Glasstone and Edlund, 1952) peaks near masses 96 and 137 and the ions share up to 200 MeV. The rate of energy dissipation from these highly ionised atoms can be keV per Ångstrom and result in as many as \( 10^3 \) target atoms being displaced per fragment. Not surprisingly there is so much damage that a single event leaves an extended defect in the form of a fission track. The disorder and associated strains make the track viewable by chemical etching or electron microscopy. A brief introduction to the subject is given in the book by Chadderton and Torrens (1969).
are generated they can form or remove dislocation lines in the following way.
For example a large number of interstitial atoms which form into an inter-
planar “raft”, Fig. 4.8(b), may bond as a normal atomic plane in the middle
of the raft. However the edge of the plane cannot match the surrounding
lattice so an edge dislocation forms. Similarly a raft of vacancies may collapse
over the central region which again produces an edge dislocation. The size
of the loops can change as interstitials or vacancies migrate in the solid. It is
frequently useful to distinguish between the different dislocations and specify
the direction and number of extra planes which are involved. This is done
by considering a vector path around the region of the dislocation, Fig. 4.10.
In a perfect solid the sum of the vectorial steps is zero, but here the resultant
is a measure of the dislocation and is called a Burgers vector. For an edge
dislocation the vector is perpendicular to the direction of the dislocation.

Fig. 4.9. A screw dislocation. The figure shows how a surface step would be generated if
part of the crystal is displaced by a lattice unit.

and 4.9. An edge dislocation is the line which separates the parts of a crystal
which contain a normal number of atomic planes and a different number of
planes (normally ± 1 extra plane). In the sectional view of the solid, Fig.4.8(a),
the dislocation line emerges normal to the plane of the paper. Such a dis-
continuity can only exist in a lattice structure if the line emerges at the surface
or forms a closed path within the solid. (A similar situation of a crack in an
amorphous material would not have this restriction.) If many point defects

Fig. 4.10. A vectorial path which encloses a dislocation determines the Burgers vector.

In the other basic type of dislocation, the screw dislocation, the Burgers
vector is parallel to the dislocation. It can be visualized with the aid of Fig.
4.9, in which part of the crystal has been displaced by an atomic layer. When
a screw dislocation intersects the surface there is a surface step and, of course,
an atomic site of different chemical stability from the rest of the surface plane.
Such sites are readily resolved in crystals by an electron microscope. In addition they provide sites for whisker growth from the vapour phase and lead to growth spirals around the point of enhanced chemical stability.

One can consider the interaction of dislocations in terms of the vector properties of the Burgers vector. For example a pair of extra planes at one dislocation can be separated to form two separate, or partial, dislocations, each having a halved Burgers vector. Such movement reduces the elastic strain in the lattice so dislocation motion is an energetic possibility. It is this freedom of movement which is so important in mechanical properties of solids. One would expect that shear could take place in a perfect crystal if all the bonds between adjacent planes were disrupted simultaneously. However this would require an enormous energy and the material strength would be some $10^3$ greater than is normally observed. This reduction in the strength of normal materials occurs because the dislocation lines allow sideways motion of adjacent layers (Fig. 4.11). Only in dislocation free materials do theoretical strengths approach the observed strengths.

The sideways motion of dislocations is termed slip and the plane in which it moves is the glide plane (Fig. 4.8). As a general rule slip occurs on the plane of densest atomic packing. If the dislocation moves parallel to the

![Perfect lattice and Lattice with a dislocation](image)

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**Fig. 4.11.** The strength of perfect and faulted material is seen for lattices under shear. The perfect lattice requires simultaneous breaking of all bonds between adjacent layers whereas the dislocation region allows the shearing faces to cross one atomic plane at a time.

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extra atomic plane it is called climb. This is only possible if the dislocation is a source or a sink for point defects, such as those generated during ion implantation. Studies of dislocations made in an electron microscope during ion bombardment (Nelson and Mazey, 1973) reveal rapid activity in the dislocation network as existing lines sweep through the sample and new dislocations are generated.

Not all parts of the dislocation line are equally mobile and the line may be pinned at nodes where dislocation lines intersect. These points may then act as sources of vacancies or interstitials if the line is forced to bow through the crystal whilst anchored at fixed points. Pinning may also occur by the presence of impurity atoms. The strain field around a dislocation together with the altered chemical stability make dislocation lines favoured sites for the accretion of lattice impurities.

If a segment of a dislocation line is strongly pinned then applied stresses may make it the source of dislocation loops. Such a mechanism suggested by Frank and Read (1950) is illustrated by Fig. 4.12. Here the pinned segment bows under the stress across the slip plane and expands by the inclusion of more material. Once the line reaches a semicircular shape it will expand beyond the pinning points so as to enclose them. However if the sections

![Fig. 4.12. A mechanism proposed by Frank and Read (1950) for a strongly pinned region of a dislocation line to act as a source for dislocation loops.](image)
from each side of the loop intersect they will annihilate since they have opposite Burgers vectors. This will leave a complete loop and the original pinned segment. One can therefore generate a series of loops based on the central segment and examples are frequently observed. In crystalline materials the strain energy modifies the circular loops into a series of lines which follow low energy crystallographic directions. Loops formed from a Frank–Read source will be inhibited once the outer loops pile up at a grain boundary.

It is clear that in repeated stress cycles dislocations will be generated which can form a network and so “work harden” the material. Ion implantation and the associated radiation damage can play a role in controlling the rate of hardening in a surface layer. Generally one would expect the dislocation network to be more heavily pinned in the implanted region and to provide a toughened surface.

If a high concentration of ions are injected into the solid it may be appropriate to think of the system as an alloy. Whilst a discussion of metallic alloys is outside the scope of this book the general features of alloy hardness may be appreciated. If the additional ions are randomly distributed then the strength of the material is similar to the pure system. This situation can be achieved during implantation without perturbing the original phase of the solid whereas random impurity dispersion by thermodynamic means (i.e. solution) may require a quenching procedure from a high temperature phase.

If the alloy is maintained at a temperature where the impurities can migrate then they may cluster, move to dislocations, or form new alloy phases. Such effects are referred to as ageing. In the case of precipitation hardening the first stage may be the formation of small precipitates which pin the dislocation network, and so increase the hardness. However prolonged ageing can cause the precipitate regions to grow and then the dislocation lines can effectively pass between these “islands” and the material is again reduced in strength. Annealing of alloy systems must be carried out with these possibilities in mind. The main advantage of ion implantation over chemical alloying is that the solubility phase diagram can be bypassed to a large extent. It also allows one to harden just the surface layers of a solid without a high temperature heat treatment.

### 4.9 Bubbles and Voids

The migration energy for clusters of vacancies is higher than for point defects so if a high vacancy concentration is produced in a solid there is a tendency to form large empty volumes, or voids. Similarly, insoluble gas atoms diffuse to these voids. If there is gas contained within these volumes then they are referred to as bubbles. The shape of the bubble is determined by the surface energy of the walls so in a crystalline structure they are polyhedral. Because bubble formation requires nucleation sites the bubble density will vary with the impurity content of the solid. It is also obvious that the competitive process of vacancy capture at nucleation sites, or annihilation by interstitial recombination, etcetera, will produce different equilibria under different conditions of temperature and irradiation flux. Hence bubble formation will also depend on the rate of defect production.

A bubble contains many more vacancies than gas atoms because the walls are stabilised against collapse by the gas pressure. Barnes (1963) suggested that if the bubble had an internal pressure, \( p \), volume \( v = 4/3 \pi r^3 \), a surface area \( a = 4\pi r^2 \) and a surface energy \( \gamma \) per unit area, then in equilibrium the changes in surface energy equals the work done in changing the volume,

\[
p\ dv = \gamma \ da
\]

or

\[
p4\pi r^2 = \gamma 8\pi r \ dr
\]

so

\[
p = \frac{2\gamma}{r}.
\]

If the bubble behaves as a perfect gas \( pv = \frac{3}{2} mk T \) so

\[
m = \left(\frac{8}{3} \frac{\pi r^2}{kT}\right).
\]

Barnes and Mazey (1973) justified this relationship by noting that when \( n \) bubbles coalesced the initial and final radii satisfied the equation

\[
\Sigma_n r_n = r_{final}^2.
\]

As a result of either ion implantation or nuclear fission the total number of ions in the solid is increased. There is therefore an expansion of the solid with the fractional change in volume being proportional to the mean bubble radius (e.g. Thompson, 1969). To minimise the amount of swelling it is essential to have the gas contained in a large number of small bubbles. This is possible if the initial material contains suitable impurities which can act as nucleation sites.

Bubbles may diffuse through the material and coalesce so the problem of swelling is increased at higher temperatures where this movement occurs. At very high temperatures the problem is reduced, in part because more of the irradiation damage anneals before bubbles form (Mazey et al., 1971).

If bubbles diffuse to the surface then the internal gas pressure can cause them to burst and fragments of the surface are removed. This is termed blistering. Such problems may not seem relevant to normal ion implantation
work except in the simulation of reactor damage, however, blistering does occur under certain circumstances even if small quantities of implanted material are involved. The problem can arise when a masking or encapsulating layer has been deposited on the surface. If the specimen is annealed after implantation the trapped gas, or gas evolved from decomposition of the substrate, will attempt to diffuse from the specimen. If the encapsulating layer stops the diffusion of the gas, or the layer to substrate adhesion is poor, then the gas will collect at this interface. The resultant bubbles and surface blistering can then destroy the encapsulating layer.

4.10 SUMMARY

In this chapter we have made a rapid survey of typical point and extended defects which are likely to be encountered in the course of ion implantation. Whilst it was possible to indicate a few general consequences of the defect interactions one must specify many parameters before making predictions for a particular system. The literature of radiation damage, dislocations, metallic alloys etcetera is very extensive and a few general references are included with this chapter.

REFERENCES

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REFERENCES