Chapter 3

Nanocavities created by high energy ion irradiation

3.1. Introduction

High energy ion irradiation onto a solid causes structural and chemical changes, which are called radiation damage. All macroscopic ion irradiation effects are produced by electronic excitations and elastic atomic collisions [1]. Electronic excitations lead to ionization of the atoms in the solid, and the resulting electron-hole pairs do not create lasting damage. In elastic collision process, ions transfer their kinetic energy to lattice atoms. If the transferred energy exceeds a material-dependent threshold energy \( E_d \), displacement damage is created in the crystal; as discussed in chapter 0, the threshold energy for Ge is \( \sim 13 \) eV. Recoiled atoms with the energy of \( E_d < T < 2.5E_d \) produce just one displacement (a pair of individual interstitial and vacancy or Frenkel pair), and recoiled atoms with the energy larger than \( 2.5E_d \) can produce a number of displacements [1]. Transferred energy of \( \sim 1-10^3 \) keV produces thermal spikes [1]; the ions slow down over distances much larger than a lattice constant and can displace many lattice atoms which also will displace other lattice atoms, leading to thermal spikes and damaged regions [1-8].

Inert gas precipitates and cavities are formed in solids during high energy inert gas ion irradiation [2,9-25]. The term cavities encompasses bubbles containing inert gases and voids that are three dimensional aggregate of vacancies; thus the cavities with typical radius \( \sim 1-10 \) nm that are reported below will be called nanocavities. The
behavior of inert gas precipitates and nanocavities has been extensively studied driven by technological concerns related to inert gases in semiconductors and materials problems associated with nuclear reactors. Inert gas precipitates and nanocavities have been experimentally observed in Ni [9,10], Zr and Zr alloys [11,12], Nb [12], Al [9,13], mica [14], amorphous Ge [15,16] and Si [17-20].

Inert gas precipitates are formed due to low solubility of inert gases in solids. Nanocavities are formed through aggregation of irradiation-induced and thermal vacancies and inert gas atoms. Establishing vacancy supersaturation is critical in the formation of nanocavities. Nucleation of nanocavities during ion irradiation under vacancy supersaturation resembles nucleation of islands during thin film growth under adatom supersaturation and can be elucidated in the context of classical steady state nucleation theory [26]. In the case of Xe ion implantation in Ge, because of the strain energy associated with large Xe atoms in the crystal lattice, Xe atoms are likely to relax the strain by capturing vacancies much like Xe atoms in Cu [2].

Nucleation rate of nanocavities \( I \) is given approximately as

\[
I = \frac{B}{\int s(x)n(x)^{-1} \, dx},
\]

where \( B \) is the vacancy flux to nanocavities, \( s(x) \) is the surface area of nanocavities containing \( x \) vacancies, and \( n(x) \) is the number of nanocavities containing \( x \) vacancies [9]. \( n(x) \) is strongly affected by the ratio of vacancy flux and interstitial flux to nanocavities and also by the vacancy supersaturation [9]. Therefore, nucleation rate of nanocavities diminishes at low temperatures since vacancies of low mobility are more likely to be
annihilated through recombination with interstitials before reaching nanocavity nuclei. Nucleation rate of nanocavities also diminishes at high temperatures due to reduced vacancy supersaturation resulting from the increased vacancy mobility. Therefore nucleation of nanocavities occurs in limited temperature range. At the temperatures the experiments reported in this chapter are performed, both vacancies and interstitials are mobile; however, since \( n(x) \) is strongly dependent on the ratio of vacancy flux and interstitial flux to nanocavities and also proportional to \( \exp(-\Delta G^*/kT) \), where \( \Delta G^* \) is the free energy change for the nucleation, nucleation rate of nanocavities will be varied at different temperatures. In the early life of a nanocavity, implanted inert gas atoms stabilize the nanocavity against the collapse to a vacancy loop [11].

After nucleation, each nucleus can act as a sink for vacancies and interstitials. Each nucleus must receive a net influx of vacancies to grow, and hence in general interstitials produced in number equal to vacancies during ion irradiation must be preferentially absorbed into other sinks such as dislocations or grain boundaries [9]. Referring to the Eq. (1-22) and (1-23), the growth rate of a nanocavity is determined by the net influx of vacancy volume per unit nanocavity area per unit time [10,23,25]

\[
\frac{dR}{dt} = \frac{\Omega}{R} [Z_v^\circ D_v C_v - Z_i^\circ D_i C_i - Z_v^\circ D_v C_c],
\]

where

\[
C_c = C_v^\circ \exp\left\{ \left( \frac{2\gamma}{R} - P_s \right) \frac{\Omega}{kT} \right\}
\]

is the thermal release rate of vacancies from the nanocavity. Thermal release rate of vacancies from a nanocavity is an exponential function of nanocavity radius and
decreases with increasing radius. There is therefore a critical nanocavity radius, \( R_e = 2\gamma / P_g \), above which thermal vacancy release from nanocavities is weaker than the net vacancy influx and below which the reverse is true.

Nanocavities can grow by either of two mechanisms. First, in the bias driven growth mechanism, a nanocavity can grow beyond its critical radius or equilibrium size, \( R_e = 2\gamma / P_g \), once the vacancy concentration gradient is introduced near the nanocavity. Vacancies near the nanocavity are likely to migrate and be absorbed to the nanocavity. Therefore a vacancy concentration gradient is introduced near the nanocavity, and the net vacancy influx will be greater than thermal vacancy release from the nanocavity. Second, at high temperatures where nanocavities are mobile, nanocavities can grow through coalescence with other nanocavities.

3.2. Results and discussion

3.2.1. TEM observation of nanocavities

Cross section TEM micrographs of Ge(111) irradiated by 5 keV Xe ions with the ion fluence of \( 1.8 \times 10^{16} \) ions/cm\(^2\) are shown in Fig. 3.1; the temperatures during ion irradiation are 400 °C for Fig. 3.1(a) and 500 °C for Fig. 3.1(b). More and larger nanocavities are formed at 500 °C than at 400 °C. No clearly faceted nanocavities are observed unlike in Zr and Zr alloys [11,12] and Ni [9,10,12]; surfaces of nanocavities are often composed of \{100\} and \{111\} planes in fcc metals, and of \{110\} and \{100\} planes in bcc metals [9]. Facetted nanocavities have been observed in Si implanted at room temperature with 30 keV He ions with the ion fluence of \( 1.0 \times 10^{17} \) ions/cm\(^2\) and
subsequently annealed at 900 \(^\circ\)C for 1 hour [17]. Wang and Birtcher observed the change from circular shaped nanocavities to irregular shaped nanocavities in Ge after the ion fluence of \(6.0 \times 10^{15}\) ions/cm\(^2\) during 1.5 MeV Kr ion irradiation at room temperature [15]. They also observed spherical shaped nanocavities in Ge after the ion fluence of \(2.0 \times 10^{16}\) ions/cm\(^2\) during 200 keV Kr ion irradiation while the Ge remains crystalline [15]. Even though nanocavities are formed inside the crystal, Ge(111) surfaces irradiated at temperatures higher than 400 \(^\circ\)C do not show noticeable surface defects other than steps much like Fig. 2.3(a).

Diameters of the nanocavities can be measured using TEM micrographs and are plotted as a function of depth in Fig. 3.2. Also, density of the nanocavities is plotted as a function of diameter in Fig. 3.3. In Ge(111) irradiated at 500 \(^\circ\)C, 56 nanocavities with average diameter of 10 nm are observed below the surface area of \(1.1 \times 10^4\) nm\(^2\), whereas 31 nanocavities with average diameter of 2.9 nm are observed below the surface area of \(1.0 \times 10^4\) nm\(^2\) in the Ge(111) irradiated at 400 \(^\circ\)C; the surface area is determined by TEM measurement of horizontal length scales using a buildup of deposited carbon in the sample as a reference; the thickness of TEM foils is 83 nm for the sample irradiated at 400 \(^\circ\)C and 75 nm for the sample irradiated at 500 \(^\circ\)C. As will be reported below in section 3.2.4, the areal density of Xe atoms remaining in the Ge(111) irradiated at 500 \(^\circ\)C is \(1.6 \times 10^{15}\) cm\(^{-2}\) and that in the Ge(111) irradiated at 400 \(^\circ\)C is \(1.2 \times 10^{15}\) cm\(^{-2}\). The areal density of Xe atoms at 400 \(^\circ\)C and 500 \(^\circ\)C is different by about 30 \%, but the difference in the number and size of nanocavities results in the difference in the total volume of nanocavities of a factor of 50.
Assuming all the remaining Xe atoms are contained in the observed nanocavities, the average density of Xe atoms at 400 °C is $1.7 \times 10^{23} \text{ cm}^{-3}$, which is about one order of magnitude larger than the density of solid Xe which is $2.0 \times 10^{22} \text{ cm}^{-3}$, and the average density of Xe atoms at 500 °C is $3.3 \times 10^{21} \text{ cm}^{-3}$. Therefore, not all the Xe atoms remaining in the crystal at 400 °C are within the observed nanocavities; due probably to low mobility of Xe atoms and vacancies at 400 °C, small Xe precipitates or nanocavities are formed but may not be detected by TEM. However, due to higher mobility of Xe atoms and vacancies at 500 °C, almost all the remaining Xe atoms are likely to be contained in the observed nanocavities.

The estimated gas pressure inside the nanocavities is 0.035 GPa compared to the equilibrium pressure $P_e = 2\gamma/R = 0.38 \text{ GPa}$; the gas pressure of 0.035 GPa was obtained by using ideal gas law of $P_g = N kT/V$, where $N$ is the total number of Xe atoms remaining in the Ge(111) and $V$ is the total volume of the nanocavities. The van der Waals equation of state is expressed as

$$P_g = \frac{N kT}{V (1 - \frac{N}{V} B)} \approx \frac{N kT}{V} \left(1 + \frac{B}{(V/N)} + \frac{C}{(V/N)^2}\right).$$

(3-4)

The virial coefficients $B$ and $C$ for Xe gas at 500 °C are $–0.13 \text{ cm}^3/\text{mol}$ and 1130 $\text{ cm}^6/\text{mol}^2$ [27], and thus the van der Waals gas pressure is 0.036 GPa.

In estimating gas pressure above, I assumed that the density of Xe atoms in each nanocavity is the same. Thus fluctuation in the density of Xe atoms among nanocavities can lead to different gas pressure. Since I cannot measure the number of Xe atoms in each nanocavity, I cannot estimate the pressure of Xe gas in each nanocavity. However,
assuming that each nanocavity has gas pressure of the same fraction of equilibrium pressure, the gas pressure in each nanocavity can be estimated: \( P_g = CP_e \) for each nanocavity, where \( P_e \) is the equilibrium pressure \( 2\gamma R \). Using ideal gas law \( P_g = nkT/V = nkT/(4\pi R^3/3) \), where \( n \) is the number of Xe atoms in a nanocavity with radius \( R \),

\[
\frac{3nkT}{4\pi R^3} = C \cdot \frac{2\gamma}{R},
\]

\[
n = C \cdot \frac{8\pi\gamma R^2}{3kT} = (790 \text{ nm}^2) \cdot CR^2.
\]  

(3-5)

Therefore, summing the number of Xe atoms in all the nanocavities and equaling the sum to \( 1.8 \times 10^5 \) Xe atoms estimated from RBS data gives \( C = 0.13 \), which agrees relatively well with the ratio of estimated gas pressure inside nanocavities 0.035 GPa and equilibrium pressure 0.38 GPa, 0.092. The error introduced by the size distribution of nanocavities is \((0.13/0.092) - 1 \approx 40 \%\), and therefore I believe all the nanocavities are underpressurized at 500 °C.

The average density of the nanocavities is plotted as a function of depth in Fig. 3.4. The nanocavities closest to the surface are observed ~ 3-4 nm below the surface, which is approximately the predicted penetration depth of 5 keV Xe ions in Ge(111). The average separation of the nanocavities are 37 nm at 500 °C and 19 nm at 400 °C; the total density of the nanocavities \( n \) can be calculated as \( (\text{total number of the nanocavities})/(\text{total volume where the nanocavities are formed}) \), and the average separation between the nanocavities can be approximately estimated as \( n^{-1/3} \) - (average diameter of the nanocavities). Therefore, the denuded zone of the nanocavities below the surface may not be unexpected since the average separation between the nanocavities is much larger than
the width of the denuded zone; the small width of the denuded zone compared to the 
average separation between the nanocavities may indicate that the Ge surface is a sink 
weaker than nanocavities for the absorption of vacancies. Another possible formation 
mechanism of the denuded zone is that the nanocavities formed in the denuded zone are 
annihilated on the surface due to the interaction with the thermal spikes, leaving behind 
the denuded zone with the width of about an average penetration depth of 5 keV Xe 
atoms, 3.5 nm; as will be discussed in chapter 4, the same mechanism results in the 
formation of surface pits.

3.2.2. Nucleation of nanocavities

Nanocavities are observed as deep as 550 nm from the surface at 500 °C and 32 
nm from the surface at 400 °C as displayed in Fig. 3.2 and 3.4. The reduced density of the 
nanocavities near the surface is probably due to the diffusion of Xe atoms and migration 
of nanocavities out of the crystal. There are two possible scenarios for the nucleation of 
nanocavities: (1) nanocavities are nucleated near the surface and then thermally migrate 
into the bulk and (2) Xe atoms diffuse inside the crystal and then nucleation of the 
nanocavities takes place. When the nanocavities are nucleated near the surface, the 
nucleation process can be enhanced by thermal spikes [21]. The first scenario will be 
discussed below, whereas the second scenario cannot be tested since RBS data do not 
give Xe atom density profile as precise as TEM data of density of nanocavities. Since 
nucleation of nanocavities requires at least two Xe atoms, nucleation of nanocavities 
should strongly depend on density of Xe atoms. Therefore, from Fig. 3.4 where the
average nanocavity density varies a factor of 10 between the peaks and minima over the depth where the nanocavities are observed, I believe nucleation of nanocavities must occur near the surface.

In the first scenario, the activation energy for the migration of nanocavities can be approximately estimated as follows. Assuming the nanocavities nucleated 4 nm (approximate average penetration depth of 5 keV Xe ions in Ge(111)) below the original surface at the start of the ion irradiation migrated the farthest and also assuming the mobility of nanocavities is unchanged throughout migration, those initially nucleated nanocavities at 500 °C traveled 558 nm compared to 40 nm at 400 °C, considering the eroded surface thickness of 12 nm. Since the duration of the ion irradiation is the same,

\[ d = \sqrt{4Dt} = \sqrt{4D_0t \exp(-\frac{E_a}{2kT})} = C \exp(-\frac{E_a}{2kT}), \]

\[ 558 \text{ nm} = C \exp(-\frac{E_a}{2k(773K)}) = C \exp(-7.5E_a), \]

\[ 40 \text{ nm} = C \exp(-\frac{E_a}{2k(673K)}) = C \exp(-8.6E_a), \]

where \( d \) is the depth traveled by nanocavities, \( D_0 \) is the prefactor of the mobility, \( E_a \) is the activation energy for the migration of nanocavities in Ge in unit of eV, and \( C \) is a constant. Solving the Eq. (3-6), \( E_a = 2.4 \text{ eV} \) and \( D_0 = 1.9 \times 10^3 \text{ cm}^2/\text{s} \); the mobility of nanocavities is therefore \( 1.9 \times 10^{-15} \text{ cm}^2/\text{s} \) at 400 °C and \( 4.0 \times 10^{-13} \text{ cm}^2/\text{s} \) at 500 °C.

The activation energy of 2.4 eV agrees relatively well with the activation energy 1.8 eV for surface diffusion due to step mobility [28]. Goodhew and Tyler obtained \( D_0 = 1.15 \times 10^4 \text{ cm}^2/\text{s} \) for He nanocavities migration in Nb via surface diffusion mechanism.
compared to previously known \( D_o = 0.43 \text{ cm}^2/\text{s} \), and interpreted the discrepancy in terms of interstitial impurity level of the samples [12]. Goodhew and Tyler also measured \( D_o = 0.18 \text{ cm}^2/\text{s} \) for He nanocavities migration in Nb-1% Zr alloy via surface diffusion mechanism [12]. For Kr nanocavities migration in Al via volume diffusion mechanism \( D_o = 1.71 \text{ cm}^2/\text{s} \) [29]. Therefore, the estimated \( D_o = 1.9 \times 10^3 \text{ cm}^2/\text{s} \) for Xe nanocavities migration in Ge seems large, and I do not know if the level of point defects in my Ge samples is responsible for this large prefactor as Goodhew and Tyler proposed.

Assuming the same number of nanocavities is formed during each bilayer removal, the density of nanocavities can be obtained with the boundary condition that the density of nanocavities is 0 at each bilayer surface; the boundary condition stems from that the nanocavities can escape through the surface. The dotted plots in Fig. 3.4 are the density of nanocavities thus calculated; the parameters used in this calculation are the mobility of nanocavities, which is \( 1.9 \times 10^{-15} \text{ cm}^2/\text{s} \) at 400 °C and \( 4.0 \times 10^{-13} \text{ cm}^2/\text{s} \) at 500 °C, and the generation rate of nanocavities, which is \( 2.6 \times 10^{11} \) nanocavities/cm² per bilayer removal at 400 °C and \( 6.2 \times 10^{11} \) nanocavities/cm² per bilayer removal at 500 °C. The measured average density of nanocavities agrees well with the calculated density of nanocavities at 500 °C, while those two densities do not agree well near the surface at 400 °C. This discrepancy at 400 °C may result from the annihilation of more nanocavities, migrating slower at 400 °C than at 500 °C, through the interaction of thermal spikes with nanocavities.
3.2.3. Growth mechanism of nanocavities

The nanocavities formed at 500 °C are underpressurized since the average pressure inside the nanocavities is about one order of magnitude smaller than the equilibrium pressure, and this result implies that the nanocavities grow beyond the equilibrium size. There are two possible mechanisms for the growth of nanocavities: one is growth due to the coalescence of nanocavities and the other is the bias driven growth of nanocavities. However, I do not yet know which mechanism is responsible for the growth of nanocavities in this experiment, but I believe probably both mechanisms contribute to the growth of nanocavities.

TEM micrographs in Fig. 3.1 do not reveal bulk defects that can act as biased point defect sinks other than the nanocavities. Therefore, possible mechanisms for the bias are (1) that the Ge surface may act as the biased interstitial sink, (2) that the nanocavities may act as the biased vacancy sinks, and (3) that the vacancy clusters produced by thermal spikes may act as the biased interstitial sinks.

3.2.4. Content of Xe atoms measured by RBS

RBS data of the Ge(111) irradiated by 5 keV Xe ions at 400 °C, 500 °C and 600 °C are plotted in Fig. 3.5; the ion fluence is $1.8 \times 10^{16}$ ions/cm$^2$, and Ge surface peak and Xe bulk peak are marked by arrows. The amount of Xe atoms remaining in the bulk is $1.2 \times 10^{15}$ cm$^{-2}$ at 400 °C, $1.6 \times 10^{15}$ cm$^{-2}$ at 500 °C and less than $1.0 \times 10^{14}$ cm$^{-2}$ at 600 °C. Fitting the sharp Xe peak at 400 °C as shown in Fig. 3.6, the depth of Xe distribution is estimated 32 nm, which agrees well with the depth of the nanocavity distribution from
the TEM results in Fig. 3.2 and 3.4. Due to the broadened Xe peak at 500 °C, however, estimating the exact depth of Xe atom distribution is not possible, and only the lower limit for the depth is estimated 140 nm. At 600 °C, high mobility of Xe atoms leads to rapid distribution of Xe atoms in the bulk as well as high rate of desorption of Xe atoms through the surface, resulting in no peak corresponding to Xe.
Fig. 3.1. Cross section TEM micrographs of Ge(111) irradiated by 5 keV Xe ions with the ion fluence of $1.8 \times 10^{16}$ ions/cm$^2$ at (a) 400 °C and (b) 500 °C. Ge(111) surfaces are marked by arrows.
Fig. 3.2. Diameters of the nanocavities observed in Fig. 3.1 as a function of depth. 56 nanocavities with average diameter of 10 nm are observed at 500 °C while 31 nanocavities with average diameter of 2.9 nm are observed at 400 °C.
Fig. 3.3. Density of nanocavities as a function of the diameter of nanocavities in Ge(111) irradiated at 400 °C and 500 °C.
Fig. 3.4. Average density of the nanocavities observed in Fig. 3.1 as a function of depth. The dotted plots are fits for density of the nanocavities as discussed in section 3.2.2.
Fig. 3.5. RBS data of the Ge(111) irradiated by 5 keV Xe ions at 400 °C, 500 °C and 600 °C with the ion fluence of $1.8 \times 10^{16}$ ions/cm$^2$. Ge surface and Xe bulk peaks are marked by arrows.
Fig. 3.6. Fitting (smooth plot) of the RBS spectrum (noisy plot) of the Ge(111) irradiated at 400 °C shown in Fig. 3.5. The fitting was performed by trial and error independently of the TEM data of nanocavities. However, the depth of Xe distribution from the fit agrees well with the depth of nanocavity distribution from the TEM data.
3.3. References


