Structural Characterization of Germanium and Gold - Germanium Nanoclusters Embedded in Silica

by

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Abstract

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The fabrication and structural characterization of ion beam synthesized Ge and Ge-Au nanoclusters embedded in silica is presented. The theory of nanocluster size distribution from ion beam synthesis is discussed and a processing route to narrow the size distribution is investigated. Transmission electron microscopy is used to determine the size distribution of ion beam synthesized Ge nanoclusters embedded in silica. It is demonstrated that implantation at room temperature, liquid nitrogen (LN₂) or ramping temperature, i.e., half dose at LN₂ temperature immediately followed by half dose at increasing temperature until room temperature is reached, results in a narrow size distribution of particles. However, it is determined that post-growth thermal annealing broadens the size distribution regardless of the implantation condition. High resolution transmission electron microscopy is used to evaluate the crystallinity of the nanoclusters before and after thermal annealing.

Ge-Au nanoclusters embedded in silica are fabricated by co-sputtering Au and silica followed by Ge implantation and thermal annealing. Scanning transmission electron microscopy, Raman spectroscopy, and synchrotron X-ray diffraction are used to demonstrate a reversible phase transition in the system. The bi-lobe structure observed after annealing is switched to a homogeneously mixed structure using a 30 ns UV laser pulse. The structure is
switched back to bi-lobe by heating at 80 °C. The bi-lobe/homogeneously mixed switching can be performed at least 10 times. The phases present in the bi-lobe and homogeneously mixed structures are evaluated by synchrotron X-ray diffraction. The melting behavior of the Ge-Au nanoclusters is explored by in-situ transmission electron microscopy.
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Chapter 1

Introduction

The synthesis and characterization of nanoscale materials has been the subject of extensive investigations over the past few decades [1-8]. In this size regime, mechanical [9,10], physical [11,12], and optoelectronic properties [13,14] distinct from those of the corresponding bulk materials are observed [15]. For example, the bandgap of CdS nanoclusters can be tuned between 2.6 and 4.2 eV by varying the size of the particles [16]. This system also shows a size-dependent melting point up to 1105 K lower than the bulk melting point [17]. There are two fundamental reasons why the properties of nanoscale materials are different from their bulk counterparts: surface effects and quantum confinement. Due to the high surface to volume ratio observed in nanoclusters, a large number of atoms are located on the surface giving rise to significantly different thermodynamic properties compared to the bulk [18]. Quantum confinement occurs when one or more dimensions of a structure become comparable to the exciton Bohr radius [19]. As a result, the minimum energy of the electron increases and its excited state energies become quantized [20] and shift to higher energy [21]. In the present study, quantum dots or nanoclusters, that exhibit quantum confinement in all three dimensions, are investigated.

A wide range of techniques have been developed to fabricate nanoclusters including chemical [22,23], physical [24], and biological methods [25]. Chemical methods are frequently used to synthesize nearly monodispersed semiconductor and metal nanoclusters. Unfortunately, these methods are incompatible with current microfabrication techniques. Ion implantation, on the other hand, is commonly used in the microelectronics industry for semiconductor doping. As a result, nanostructures fabricated by high-dose \(10^{16} - 10^{18} / \text{cm}^2\) ion implantation or ion beam synthesis (IBS) can be readily integrated into semiconductor devices using current production techniques. In addition, IBS provides excellent control over the quantity, purity, and isotopic mass of the implanted species. This process, which has area and depth selectivity, can be used to
form metal [26-28] and semiconductor [29-31] nanoclusters embedded in a wide range of host matrices [26,27,30-33]. The nanoclusters investigated in this work were fabricated by IBS.

IBS has been used to fabricate both elemental and compound semiconductor nanoclusters [34-37]. The former are easier to fabricate because they contain only one element. In addition, they are relatively inexpensive, and compatible with current technologies. It is well established that Ge possesses a higher dielectric constant and lower electron and hole effective masses compared to Si [38]. Therefore, the exciton Bohr radius of Ge is larger than Si resulting in stronger quantum confinement effects. For example, Takagahara et al. showed in their theoretical work that the increase in exciton energy with decreasing nanocluster size begins to appear in Ge quantum dots with larger size compared to Si quantum dots [39]. In this dissertation, Ge nanoclusters embedded in silica are investigated.

One of the main drawbacks of IBS is the wide size distribution of nanoclusters [40,41]. For technological applications requiring narrow optical emission and predictable charge storage, the size distribution must be significantly narrowed [42]. In Chapter 2, the theory of nanocluster size distribution from IBS is described and a processing route to narrow the size distribution of Ge nanoclusters embedded in silica is discussed. In Chapter 4, the size distribution of ion beam synthesized Ge nanoclusters embedded in silica is investigated and the processing route suggested in Chapter 2 is used to fabricate nanoclusters with a narrow size distribution. This chapter also contains a description of the effects of annealing temperature and annealing time on the size distribution and crystallinity of the Ge nanoclusters.

Memory devices are one of the promising applications of semiconductor nanoclusters [43]. For example, Tiwari and colleagues fabricated metal oxide semiconductor field effect transistors (MOSFETs) containing Si or Ge nanoclusters in the gate oxide and investigated their feasibility for nonvolatile memory applications. They determined that these devices possess long retention time, smaller operating voltages, lower power dissipation, and faster write and read operations compared to the most popular form of nonvolatile memories [44,45]. Furthermore, it has been demonstrated that memory devices containing Ge nanoclusters have superior write / erase times and operating voltage compared to Si nanoclusters [46]. Recently, embedded binary eutectic alloy nanostructures (BEANs) have emerged as a new class of phase change materials with potential applications in phase change memory [47]. In this approach, nanoparticles composed of a binary eutectic alloy are embedded in a silica matrix. When the BEANs are heated above their melting point, they form a liquid with homogeneous composition. Slow cooling of the liquid leads to the formation of the equilibrium structure (bi-lobe). Fast cooling, on the other hand, yields a metastable amorphous structure with homogeneous composition. This structure can be transformed to bi-lobe by heating at low temperature. The first investigation of BEANs was performed using Ge-Sn nanoclusters embedded in silica. In Chapter 5, a new system: Ge-Au nanoclusters embedded in silica is investigated. The melting behavior of this system is explored in Chapter 6.
Chapter 2

Theory of Nanocluster Size Distribution from Ion Beam Synthesis

2.1 Introduction

Ion beam synthesis (IBS) has been used successfully to fabricate a wide variety of structures from thin films [48-50] to nanoclusters [32,34,51] and nanowires [52]. In IBS, one or more low-solubility species are embedded into a suitable matrix through implantation of energetic ions. This process has several advantages over other methods to synthesize embedded nanoclusters. For example, an excellent control over the quantity, purity and isotopic mass of the implanted species can be achieved with IBS. In addition, this process has area and depth selectivity, and it can be seamlessly integrated into industrial wafer fabrication lines. However, synthesizing embedded nanoclusters using IBS has drawbacks such as a broad size distribution of particles [33,53,54]. It is well established that semiconductor nanoclusters possess size dependent optoelectronic properties [13,21]. Therefore, controlling the size distribution of nanoclusters is of paramount importance [55]. In this chapter, a model to describe the size-distribution evolution of ion-beam-synthesized nanoclusters in silica, developed by Chun-Wei Yuan and Diana O. Yi [56-58], former graduate students in the group of Prof. Daryl C. Chrzan, is discussed. In addition, a processing route to narrow the size distribution of embedded nanoclusters synthesized by IBS is described [59].
2.2 Rate-Equations Model

In the mean-field approach to model the evolution of the nanocluster size distribution during IBS, all interactions are characterized by mean-field quantities averaged over all space. In contrast, the kinetic Monte Carlo (KMC) model presented in the next section simulates a series of random processes that are inherently local. The quantity of interest in the rate equations model is the average density of clusters containing $s$ atoms, $\langle n_s \rangle$, because the size distribution of the nanoclusters can be determined from the value of $\langle n_s \rangle$ as a function of $s$. However, we are interested in the evolution of the size distribution during the implantation process. Therefore, the rate of change of $\langle n_s \rangle$ with time, i.e., $\frac{d\langle n_s \rangle}{dt}$, must be determined. Yuan et al. [57] found the set of coupled rate equations describing the evolution of the size distribution to be:

$$\frac{d\langle n_1 \rangle}{dt} = F - 2D\sigma_1\langle n_1 \rangle^2 - D\sum_{j>1} \sigma_j \langle n_j \rangle \langle n_1 \rangle + 2\frac{\langle n_2 \rangle}{\tau_2} + \sum_{j>2} \frac{\langle n_j \rangle}{\tau_j} + F\Omega \sum_{j>1} \langle n_j \rangle(j + 1)K_1(\alpha, j), \quad (2.1)$$

$$\frac{d\langle n_s \rangle}{dt} = D\sigma_{s-1}\langle n_{s-1} \rangle\langle n_1 \rangle - D\sigma_s\langle n_s \rangle\langle n_1 \rangle - \frac{\langle n_s \rangle}{\tau_s} + \frac{\langle n_{s+1} \rangle}{\tau_{s+1}} - F\langle n_s \rangle\Omega(s + 1) + F\Omega \sum_{j>s} \langle n_j \rangle(j + 1)K_s(\alpha, j), \quad (2.2)$$

where $D$ is the effective diffusivity of the implanted species within the matrix, $\sigma_s$ is the capture length of a diffusing monomer by a cluster of size $s$, $\tau_s$ is the desorption time for an atom to leave a cluster of $s$ atoms, $F$ is the volumetric flux rate, and $\Omega$ the atomic volume.

Typical results from the rate equations model are shown in Figure 2.1. Specifically, the average radius of the clusters $\langle R \rangle$ as a function of time is plotted in Figure 2.1 (a) while the cluster density as a function of time is shown in Figure 2.1 (b). Three different stages are observed in the evolution of the size distribution. First, a nucleation stage characterized by a small average radius and a rapidly increasing cluster density is observed during times lower than 0.1 s. This is followed by a growth stage between 0.1 and 30 s where monomers attach to the existing clusters, leading to a rapid increase in the average cluster size and a slow increase in the cluster density. In the third stage, cluster fragmentation by the implanted species becomes significant. This occurs when both the cluster density and the average cluster radius are large, i.e., for times larger than 30 s. As a result, the average cluster radius starts to decrease and it approaches a steady-state value. In addition, the cluster density increases rapidly filling the volume.
Figure 2.1. Average cluster radius (a) and cluster density (b) as a function of time for typical growth conditions, obtained using the rate-equations model [56].
2.3 Kinetic Monte Carlo Model

In kinetic Monte Carlo (KMC) simulations, all key kinetic processes that drive the system forward in time are identified and rates of occurrence are assigned to these processes. To model the evolution of the size distribution of ion-beam-synthesized nanoclusters embedded in silica, six kinetic processes were identified by Yuan et al. [57]:

(i) Ion implantation into an amorphous silica matrix.
(ii) The off-lattice random walk of implanted atoms.
(iii) The attachment of atoms to each other and existing clusters.
(iv) Relaxation of all clusters to a spherical shape.
(v) The thermally driven detachment of atoms from existing clusters.
(vi) The ion damage induced fragmentation of clusters.

To carry out the implantation process, atoms were made appear in randomly selected locations within the simulation cell at a rate $F$, derived from experiments. The off-lattice random walk of the implanted atoms was described as thermally activated hoping events characterized by a relaxation rate proportional to the diffusivity of the implanted atoms [57]. The attachment of atoms to each other and existing clusters took place instantly whenever the distance between the surfaces of the particles was 0. Relaxation of all clusters to a spherical shape was assumed in order to minimize the surface energy of the system. The shape relaxation time was assumed to be short so that when two atoms or an atom and a cluster made contact, the cluster became spherical immediately. The thermally driven detachment of atoms from existing clusters was described by a local equilibrium approximation [60]. Finally, the ion damage induced fragmentation of clusters was modeled by extending the approach of Heining and co-workers [61].

The KMC simulations were carried out within a cubic supercell 30 nm on an edge and periodic boundary conditions were imposed. Statistics were obtained by averaging over 30 simulations. The parameters considered for an initial calculation were based on the room temperature implantation of $^{74}$Ge$^+$ ions into amorphous SiO$_2$ at 120 keV. Typical results of the KMC simulations are shown in Figure 2.2. After implanting for up to 0.1 s, there is a large number of nucleation events and therefore the number of clusters increases rapidly. Between 0.1 and 30 s of the implantation process, the clusters begin to coarsen resulting in a rapid increase of the average radius and a slow increase in cluster density. At this point, the nanoclusters have a low concentration and a small size as shown in Figure 2.2(a). As a result, the effect of cluster fragmentation is negligible compared to the nucleation and growth processes. However, as the size and concentration of clusters increase, the probability an ion impinging on a cluster increases. This leads to a peak in the average radius of the distribution and then the average radius starts to decrease. As the implantation process continues, more clusters are added to the system which leads to larger fragmentation from ion impingement. After implanting for 30 s or longer, cluster damage continues to occur, the average radius of the distribution decreases, and
Figure 2.2. Structural evolution of Ge nanoclusters embedded in silica after 30 (a), 300 (b), and 3000 s (c) of ion implantation obtained by KMC simulations [57].
the volume fills with clusters as shown in Figures 2.2(b) and 2.2(c). The average radius approaches a steady-state value in the final stages of growth.

Now, the evolution of the nanocluster size distribution during implantation obtained from the KMC and rate equations simulations are compared. The two models display good agreement during the various stages of growth as shown in Figure 2.3. After implanting less than 1% of the total dose, the nucleation and growth processes dominate the evolution of the size distribution since there is a negligible effect of cluster fragmentation as shown in Figure 2.3(a). As the implantation process continues, the clusters coarsen and the fragmentation effect increases resulting in a bimodal size distribution [Figure 2.3(b)]. Then, the bimodal distribution becomes wider and more weighted towards the smaller clusters as shown in Figure 2.3(c). Finally, the peak at large sizes disappears leading to a unimodal log-normal-like distribution as shown in Figure 2.3(d).

Figure 2.3. Size distributions of Ge nanoclusters embedded in SiO$_2$ obtained using both KMC (blue) and rate-equations models (orange). 0.27 % of the experimental final density has been reached in (a), 1.49 % in (b), 2.70 % in (c) and 27.0 % in (d). A bin size of 1 Å was used [57].
2.4 Processing Route for Size Distribution Narrowing

In this section, a processing route to narrow the size distribution of ion beam synthesized nanoclusters developed by Yuan et al. is presented [59]. Specifically, the KMC model described in the previous section will be used to explore IBS during atypical conditions and design processing routes to narrow the width of the size distribution. Empirically, Yuan et al. determined that the steady-state shape of the nanocluster size distribution is influenced only by the characteristic length, \( L \) given by

\[ L \equiv \sqrt{\frac{Dn_\infty}{F}}. \]  

(2.9)

Here, \( D \), \( F \), and \( n_\infty \) are the effective diffusivity during implantation, the volumetric implantation flux, and the solubility of the implanted species, respectively. In addition, they observed that the width of the size distribution decreases by decreasing \( L \). This can be achieved by increasing the flux of ions and/or by decreasing the product of the transient enhanced diffusion coefficient and the solubility. Once the shape of the size distribution is determined, the average cluster radius is influenced by the cluster-matrix interface energy, \( \gamma \).

Using parameters near those appropriate for the implantation of Ge into amorphous silica at 120 keV [33], the following processing route to narrow the size distribution of the nanoclusters can be suggested. First, Ge is implanted into amorphous silica at liquid nitrogen temperature to a dose of \( 5 \times 10^{15} \text{ cm}^{-2} \). This is immediately followed by a warm implant at 340 K to a dose of \( 4 \times 10^{16} \text{ cm}^{-2} \). It is assumed that the temperature increases linearly from liquid nitrogen to the final temperature during the initial stage of the warm implant over a span of 30 min. Typical microstructural images illustrating the evolution of the size distribution as a function of time are shown in Figure 2.4. Starting the implant at liquid nitrogen temperature leads to a large number of nucleation events, as shown in Figure 2.4(a). A subsequent increase in temperature while continuing the implantation leads to the rapid growth of these clusters from monomers located in the matrix, without the accompanying coarsening that broadens the cluster size distributions as seen in Figure 2.4(b). However, as implantation continues at the final temperature, larger clusters form. These large clusters have a higher probability of ion-cluster collisions. When a collision occurs, the impacted cluster becomes a smaller cluster surrounded by fragments, as illustrated in Figure 2.4(c). As implantation continues, the average size increases, while the size distribution width remains practically unchanged as shown in Figure 2.4(d). After the implantation process is completed, a slight thermal annealing step leads to the coalescence of small fragments with the large particles. This results in a size distribution with a width of 20 % compared to the typical 70 % observed after room temperature implantation. The processing route recommended to narrow the size distribution is analogous to the colloidal methods employed to fabricate nearly monodisperse nanoclusters. These methods involve
temporally discrete nucleation events followed by relatively rapid growth from monomers located in the solution and finally slower growth by Ostwald ripening.

Figure 2.5 plots the scaled size distribution of the suggested processing route, traditional coarsening theory, and the predictions for the constant temperature implantation typically used in IBS. It can be observed that the predicted distribution is significantly narrower than the steady state and coarsening cases.

Figure 2.4. Structural evolution of Ge nanoclusters embedded in silica obtained by KMC simulations after implanting Ge into SiO$_2$ at liquid nitrogen temperature to $5 \times 10^{15}$ cm$^{-2}$ (a) immediately followed by $2.7 \times 10^{15}$ cm$^{-2}$ (b), $2.2 \times 10^{16}$ cm$^{-2}$ (c), and $4 \times 10^{16}$ cm$^{-2}$ (d) at 340 K [59].
Figure 2.5. Size distributions for the current processing route (Narrowed), traditional coarsening theory (Coarsening), and the predictions for constant temperature IBS (Steady state). The small peaks close to the origin would not be visible in a typical experiment to measure size distributions [59].
Chapter 3

Synthesis and Structural Characterization

3.1 Ion Beam Synthesis

In this investigation, ion beam synthesis (IBS) was used to fabricate Ge and Ge-Au nanoclusters embedded in silica. The motivation for using this fabrication technique was discussed in Chapter 1. In the previous chapter, the theory of nanocluster size distribution from IBS was presented. In addition, it was discussed that by initiating the implant at low temperature followed by a temperature increase while continuing the implantation will result in a narrow size distribution of particles. Therefore, the following procedure was followed. First, float zone (FZ) p-type (100) Si wafers with a resistivity of 10 kohm-cm were purchased from Topsil. Then, a 500 nm layer of amorphous SiO$_2$ was thermally grown by Process Specialties in a chemical vapor deposition reactor. This was followed by $^{74}$Ge implantation into the 500 nm thick layer of SiO$_2$ at 150 keV to 2 x $10^{16}$ cm$^{-2}$. The implantation was performed at three different temperatures, i.e., liquid nitrogen (LN$_2$) temperature, room temperature (RT), and ramping temperature (RampT). The temperature ramp consisted of implanting 1 x $10^{16}$ cm$^{-2}$ at LN$_2$ temperature immediately followed by 1 x $10^{16}$ cm$^{-2}$ at increasing temperature until room temperature was reached, approximately at the same time the implant was completed. After the implantation process was completed, the samples underwent rapid thermal annealing (RTA) or thermal annealing in a tube furnace following the procedure described in section 3.3.

IBS was also used to fabricate Ge-Au nanoclusters embedded in silica. However, the mass of the only stable Au isotope, 197 amu, exceeds the limits of the Varian CF300 ion implanter used in this work. As a result, Au$^+$ ions could not be implanted into thermally grown silica and an alternative processing route was developed. Specifically, Au-doped silica films were prepared by co-sputtering as described in the next section. Then, 3.5 x $10^{16}$, 4.7 x $10^{15}$, and 7.0 x $10^{15}$ cm$^{-2}$ $^{74}$Ge was implanted into the co-sputtered Au-doped silica film, with energies of 150, 90, and 50 kV, respectively. The multiple energies and doses were used in order to achieve
a more homogeneous Ge to Au ratio throughout the sample. After Ge implantation, the samples were annealed in sealed ampoules, prepared as described in section 3.3, at 900 °C for 1 h followed by quenching from the annealing temperature to room temperature using cold running water.

3.2 Sputtering

In this investigation, Au-doped silica films were prepared by co-sputtering since the mass of Au exceeds the limits of the implanter used in this work. Sputtering is widely used in the semiconductor industry for surface cleaning and etching, thin film deposition, surface layer analysis, and sputter ion sources [62]. Advantages of this fabrication technique include: uniform deposition rate over very large areas, stoichiometric volatilization of compounds, and ability to deposit both metals and insulators [63]. Sputtering was discovered by accident in 1852 when William Robert Grove first observed metal deposits at the cathode surface of a DC gas discharge tube. This phenomenon was undesirable at the time because the cathode and grid in the gas discharge tube were destroyed. The first application of sputtering was for coating mirrors as early as in 1887. In 1920s and 1930s, sputtering was used for coating fabrics and phonograph wax masters [64]. Today, sputtering systems are found in virtually all micro fabrication facilities. In this section, the basics of sputtering and the process developed to synthesize Au-doped silica films are described.

Sputtering is a process in which one or more atoms are ejected from a target during bombardment by energetic particles (50 – 1000 eV). Several systems have been developed for the deposition of thin films by sputtering. DC sputtering, also known as cathodic sputtering, is the simplest system and it is shown schematically in Figure 3.1. In DC sputtering, the target is connected to a negative voltage supply, the substrate is placed on the anode facing the target, and a DC voltage, generally between 1 and 5 kV, is applied across the electrode. A gas or gas mixture is introduced into the previously evacuated sputtering chamber with a pressure typically ranging from a few mTorr to several hundred mTorr. Inert gasses such as Ar, Kr, and Xe are generally used in sputtering. After introducing the gas into the chamber, a glow discharge is initiated and the positively charged ions are accelerated towards the target. When these ions impinge on the target material, secondary electrons are generated and accelerated, and they collide with atoms from the sputter gas. These collisions generate new ions and maintain the glow discharge [65]. When the positive ions arrive at the target, one or more atoms (usually
neutral) are dislodged from the surface by a momentum and energy transfer process. Finally, the neutral atoms arrive at the substrate where a film is formed.

Radiofrequency (RF) sputtering is typically used when insulating targets are required. This occurs because in DC sputtering charge is built up on the surface of the insulating target during ion bombardment. Such charge buildup can be avoided by simultaneously bombarding the insulator with ions and electrons. In RF sputtering, an RF potential with a frequency of 13.6 MHz is applied to an electrode placed behind the insulating target. This potential causes the electrons to oscillate and ionize atoms from the sputter gas which maintains the glow discharge. Since electrons have much higher mobilities than the ions, more electrons will reach the surface of the target compared to positive ions during a complete cycle. Therefore, the surface of the target will be negatively biased and such bias will repel electrons from the vicinity of the surface. Consequently, a layer rich of ions will form in front of the target; these ions will be accelerated towards the target and sputtering will be achieved [66].

In reactive sputtering, a reactive gas is added to the typical Ar sputtering gas in order to deposit a compound film from an elemental target, or to modify the stoichiometry of a film.
formed using a compound target. The later application arises from a tendency for the electronegative element to become depleted in compound sputtering. This substoichiometric deposition is due to the likely lower sticking coefficient of the electronegative element at the substrate [63]. Reactive sputtering has been used to synthesize films of oxides, nitrides, borides, carbides, among others [67].

In this work, Au-doped silica films were prepared by reactive RF sputtering. Specifically, the films were fabricated by co-sputtering Au and Si under a 90% Ar - 10% O atmosphere onto Si (111) substrates using a 2400 Perkin-Elmer RF sputtering system. The sputtering target consisted of an 8-in Si disk with one 3 x 3 mm$^2$ Au piece attached. The sputtering system was pumped down to a pressure of $\sim 3 \times 10^{-6}$ Torr and sputtering was performed with RF power of 200 W and a gas pressure of $30 \times 10^{-3}$ Torr. In order to achieve a more uniform Au to Ge ratio after Ge implantation, approximately 60 nm and 30 nm of silica were sputtered before and after the Au-doped silica film, respectively. Figure 3.2 shows Rutherford backscattering spectrometry (RBS) measurements of the Au-doped silica film. The Au concentration was found to be 1.2 at. % from approximately 40 to 150 nm from the surface.

![Figure 3.2](image.png)

**Figure 3.2.** Concentration profile of Au in silica from a sputter-deposited Au-doped silica film obtained using Rutherford backscattering spectrometry.
In order to verify the formation of Au nanoclusters in the silica matrix, the Au-doped silica films were annealed at 900 °C for 1h in air and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) experiments were performed. Indeed, Au nanoclusters embedded in silica formed after annealing are shown in Figure 3.3. In addition, the size distribution of the nanoclusters was measured and it was determined that the Au particles have an average diameter of 5 nm.

Figure 3.3. HAADF-STEM image of the Au-doped silica film annealed at 900 °C showing the formation of Au nanoclusters.
3.3 Thermal Annealing

Thermal annealing is required for the crystallization and growth of ion beam synthesized nanoclusters and to recover the damaged oxide. This process must be carried out in a moisture and oxygen free atmosphere in order to avoid the oxidation of Ge [68]. In this section, the process employed to anneal the samples is described.

Thermal annealing was performed in sealed quartz ampoules. The ampoules consisted of a 1.2 and a 0.9 cm outer diameter semiconductor grade silica tubes purchased from GM Associates Inc. The tubes had a wall thickness of 2 mm and were closed on one end using a hydrogen/oxygen torch (Figure 3.4). They were thoroughly cleaned using acetone and DI water followed by a 3 min. etch using 5% HF. Then, the tubes were rinsed with DI water and methanol. The samples were carefully cleaned using acetone, DI water, and methanol before being placed inside of the ampoule. The loaded ampoule was placed in the setup shown in Figure 3.5 and evacuated to a pressure of approximately $5 \times 10^{-6}$ Torr using a turbomolecular pump. When this pressure was reached, the ampoule was moderately heated using a hydrogen torch in order to evaporate the moisture and solvents remaining in the inner walls of the ampoule. After pumping down for 10 more min., the ampoule was isolated from the pump system using a gate valve and backfilled with high purity Ar to a pressure of about 0.7 atm. Finally, the ampoule was sealed with a hydrogen/oxygen torch.

![Figure 3.4. Photograph of the tubes used for thermal annealing of the samples in a tube furnace. After thoroughly cleaning the ampoule and the sample, the latter was placed inside of the larger tube followed by the smaller tube. Then, the ampoule was evacuated, backfilled with Ar, sealed, and annealed at the desired temperature.](image)
Figure 3.5. Photograph of the setup used to evacuate, backfill with Ar, and seal the ampoules. The main components are shown.
Thermal annealing was carried out in a Lindbergh/Blue HTF55322A tube furnace at temperatures between 900 and 1200 °C for times ranging from 5 to 180 min. The temperature was measured using a S-type thermocouple encased in a tube and placed next to the sample. Annealing was terminated by removing the ampoule from the furnace with a quartz rod and quenching to room temperature using cold running water.

3.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is arguably the most powerful technique for the characterization of nanoscale materials. With this technique, information about morphology, internal structure, bandgap, local chemical environment, among others, can be obtained. In this investigation, TEM was used to determine the size distribution, crystallinity, melting point, and structure of the Ge and Ge-Au nanoclusters. In this section, the procedures used for TEM sample preparation are presented. Then, the specific TEM techniques used in this work are described.

3.4.1 Sample Preparation

Plan-view specimens were used to investigate the structure and the melting behavior of the Ge-Au samples. The fabrication of plan-view samples is simpler compared to cross-sectional specimens. In addition, plan-view samples do not require glue which can contaminate both the specimen and the TEM column when heating to high temperature.

To prepare plan-view TEM specimens the following procedure was followed. First, the sample was cleaned thoroughly using acetone, DI water, and methanol (Figure 3.6.a). Then, the sample was mounted on a glass slide with the silica film facing down using Crystalbond™. A 3 mm disk was cut with a South Bay Technology 360 Rotary Disc Cutter and abrasive slurry (Figure 3.6.b). The disk was removed from the glass slide, cleaned with solvents, and glued to a round piece of glass. This was followed by thinning with a VCR 500i dimpler. Three different wheels and slurries were used during the dimpling process. The first 420 μm of Si were removed using a metal wheel and 3 μm diamond slurry. The next 55 μm of Si were taken off using a Texmet cloth and 3 μm diamond slurry. An additional 5 μm of Si were removed using the same cloth and 1 μm slurry. A final polishing step was performed using a polishing cloth and 0.5 μm slurry until no scratches or pits were observed on the surface of the sample. After cleaning the specimen with acetone and ethanol, it was ion milled at liquid nitrogen temperature using a Fischione Model 1010 ion mill and 5 kV Ar⁺ ions until a hole was made as shown in Figure 3.6.c.
Figure 3.6. Photograph of the sample at different stages of the plan-view TEM sample preparation process. The sample is shown after cleaning (a), cutting a 3 mm disk (b), and dimpling and ion milling until perforation occurs (c).
Cross-sectional TEM specimens were fabricated to determine the size distribution and crystallinity of the ion beam synthesized Ge nanoclusters discussed in Chapter 4. The following procedure was followed to prepare the cross-sectional TEM specimens. First, two samples were cleaned thoroughly using acetone, DI water, and methanol. Then, the samples were glued using M-bond 610 and sandwiched between two pieces of dummy Si. Curing was performed in a furnace for 2 h at 175 °C. A slow-speed diamond saw was used to cut cross-sectional slices approximately 500 μm thick (Figure 3.7.a). Then, each slice was mounted on a glass slide with Crystalbond™ and 3 mm disks were cut with a South Bay Technology 360 Rotary Disc Cutter and abrasive slurry (Figure 3.7.b). After gluing the sample to a round piece of glass, it was dimpled on one side until 100 μm were removed. The second side was dimpled until approximately 20 μm were left as shown in Figure 3.7.c. After cleaning the specimen with acetone and ethanol, it was ion milled at liquid nitrogen temperature using a Fischione Model 1010 ion mill and 5 kV Ar⁺ ions until a hole was made as shown in Figure 3.7.d. The sample was rotated by 60 ° during ion milling and two ion guns at a 7° angle were used.
Figure 3.7. Photograph of the sample at different stages of the cross-sectional TEM sample preparation process. The sample is shown after gluing and cutting a cross section (a), cutting a 3 mm disk (b), dimpling (c), and ion milling until a hole is made (d).
3.4.2 Techniques

A wide range of TEM techniques like bright field (BF), high resolution TEM (HRTEM), electron diffraction, and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were used in this investigation. This section discusses the differences between the various techniques.

When electrons in the TEM interact with the specimen, both the amplitude and phase of the electron wave can change resulting in amplitude contrast and phase contrast. There are two main types of amplitude contrast: diffraction and mass-thickness contrast. In diffraction contrast, coherent elastic scattering of the electrons occurs when Bragg’s law is satisfied. This depends on the wavelength of the electrons as well as the crystal structure and orientation of the specimen. This type of contrast was used in this work to obtain diffraction patterns at different temperatures and explore the melting behavior of the Ge-Au nanoclusters (Chapter 6). Mass-thickness contrast is largely due to elastic scattering from individual atoms, where the incident electrons are deflected by Coulomb interactions as they pass through the atom (Rutherford scattering) [69]. Therefore, the number of scattered electrons increases as the thickness and mass (i.e., atomic number) of the specimen increases, all other factors being constant [70]. Mass-thickness contrast is the most important type of contrast in amorphous materials like the silica matrix and the as-implanted Ge nanoclusters presented in Chapter 4. Z-contrast or HAADF-STEM is a high resolution mass-thickness imaging technique where scattering arises from columns of atoms and even single atoms! In this technique, images are formed using incoherent electrons elastically scattered at a high angle, > 50 mrad, in order to minimize the contribution of Bragg scattering. The contrast in HAADF-STEM images is proportional to the square of the atomic number, $Z^2$, according to the Rutherford formula for scattering from an unscreened nucleus [71]. Since Ge, Au, and silica have significantly different Zs, this technique was used to investigate the structure of the embedded Ge-Au nanoclusters discussed in Chapter 5. Finally, it is possible to have both mass-thickness and diffraction contrast in a TEM image. This is the case for the BF images of crystalline Ge nanoparticles presented in Chapter 4.

Phase contrast is due to the phase differences of the electrons which are scattered elastically and coherently through a thin specimen. This type of contrast is used in HRTEM to form images of atomic columns. Contrary to BF images where the objective aperture is used to select only one beam, phase-contrast images require the selection of multiple beams. The forward-scattered beam is required to provide a reference phase of the electron wavefront. In addition, at least one diffracted beam is needed to interfere constructively and destructively with the forward-scattered beam [69].

The operating conditions of the TEM are significantly different for the various techniques used in this work. For example, in BF, HRTEM and electron diffraction the specimen is illuminated with a parallel beam of electrons as shown in Figure 3.8.a. On the other hand, a convergent beam is required for HAADF-STEM (Figure 3.8.b). To obtain electron diffraction
patterns, the lenses of the imaging system are adjusted so that the back focal plane of the objective lens becomes the object plane for the intermediate lens as shown in Figure 3.9.a. When the TEM is operated in imaging mode to acquire BF and HRTEM images, the intermediate lens is adjusted so that its object plane is the image plane of the objective lens as shown in Figure 3.9.b. BF images are formed with one beam, i.e. the forward scattered beam. As a result, a small objective aperture is used to select this beam. However, an objective aperture large enough to enclose multiple beams is required in HRTEM [72].
Figure 3.9. Ray diagrams illustrating the operating conditions of the TEM to form diffraction patterns (a) and images (b) [70].
3.5 Rutherford Backscattering Spectrometry

The concentration profiles of Ge and Au in silica were determined by Rutherford backscattering spectrometry (RBS) both before and after thermal annealing. In RBS, a beam of collimated He\(^+\) ions with typical energies of 2 to 4 MeV impinges perpendicularly on a target. Most of the ions are implanted into the target and do not escape since the space between nuclei is about 10\(^4\) times larger than the diameter of the impinging particle. Nonetheless, a small fraction of the incident particles undergo collisions with the nuclei of single atoms, are scattered backwards, and escape from the target [73,74]. These collisions are due to the Coulombic forces and can be modeled as the collision of two hard spheres using classical physics.

There are three basic concepts which allow RBS analysis to give quantitative depth distribution of targets with different masses. First, the kinematic factor, \(K\), is the ratio of the particle’s energy after a collision to the energy before a collision. \(K\) can be calculated from collision kinematics and it is used for mass determination. Second, the scattering cross-section, \(d\sigma/d\Omega\), is the probability that an elastic collision will result in a detected particle. \(d\sigma/d\Omega\) is used for the quantitative analysis of atomic composition. Third, energy loss is the inelastic energy loss of the He\(^+\) ions during penetration, scattering, and while leaving the target. The energy loss gives a perception of depth [75].

The RBS spectra in this work were obtained by Dr. Kin Man Yu of the Materials Sciences Division (MSD) at the Lawrence Berkeley National Laboratory (LBNL) using a 1.92 MeV He\(^+\) beam. This beam was generated from a 2.5 MeV High Voltage Engineering AK-2500 Van de Graaff accelerator which has a 50° sample tilt for enhanced depth resolution. The backscattered He\(^+\) ions were collected using a Si surface barrier detector at an angle of 165°.

3.6 Raman Spectroscopy

Raman spectroscopy was used to assess the crystallinity and recrystallization temperature of the Ge-Au nanoclusters (Chapter 5). In this technique, monochromatic light impinges on a sample and polarizes the electron clouds making up the chemical bonds in the sample, storing some energy. When the wave passes, the field reverses, the distorted electron cloud relaxes, and the stored energy is reradiated [74]. These reradiated photons have two components. The first component is due to Rayleigh scattering, regarded as elastic scattering, and is the strongest component. This occurs when only electron cloud distortion is involved in scattering. However, if nuclear motion is induced during scattering, energy will be transferred either from the incident photon to the molecule (Stokes scattering) or from the molecule to the scattered photon (anti-Stokes scattering). Raman scattering is a weak process where only one in every 10\(^6\)-10\(^8\) photons which scatter is Raman scattered [76].
A typical Raman setup is shown in Figure 3.10. The setup contains five major components: the excitation source, optics, monochromator, detector, and computer. Excitation sources commonly used for Raman spectroscopy include Ar-ion, Kr-ion, He-Ne, and more recently Nd:YAG (yttrium-aluminum-garnet) lasers. Typically, the shorter wavelengths are used since the intensity of Raman scattering is proportional to the fourth power of the frequency of the scattered light [77]. The optics consists of dielectric mirrors, collecting lenses, and focusing lenses. Since Raman scattering is weak, the scattered light must be collected efficiently. In addition, the incident beam should be properly focused onto the sample. This can be readily achieved since the laser beam has a small diameter. Double and triple spectrometers are often used in Raman spectroscopy in order to suppress the intensity of undiffracted light which overlaps the Raman signal [77]. In the early days, Raman scattering was detected using photographs. Today, photomultipliers, photodiodes, and CCDs are used for that purpose.

![Figure 3.10. Photograph of the Raman setup used in this investigation, showing the different components.](image-url)
The Raman spectroscopy measurements presented in this dissertation were performed in the laboratory of Dr. Joel W. Ager III at the LBNL. The Raman spectra were excited using the 488 nm line of a Lexel Model 95 Ar-ion laser. The scattered light was analyzed by a SPEX 1877 triple spectrometer with a 600 mm focal length and a 1200 cm\(^{-1}\) grating. The signal was collected by a liquid-nitrogen-cooled CCD camera. In addition, optical polarizers were used to suppress the second order Si Raman signal originating from the substrate.

3.7 Synchrotron X-ray Diffraction

X-ray diffraction is the technique of choice in materials science to determine the phases present in a sample. Typically, X-ray diffraction is performed using a diffractometer and Cu K X-rays. Unfortunately, X-ray diffraction from the embedded nanoclusters was not observed after collecting for several hours in a diffractometer. Therefore, synchrotron X-ray diffraction (SXRD) experiments were carried out at the Stanford Synchrotron Radiation Lightsource (SSRL) to assess the crystal structure of the Ge-Au nanoclusters. Synchrotron radiation is produced when electrons or positrons moving at relativistic velocities are deflected along a curved trajectory by a magnetic field [78]. This radiation can be up to 12 orders of magnitude brighter than a conventional X-ray tube [79].

Two different beam lines were used at SSRL. The first beam line was 11-3, which is shown with its main components in Figure 3.11. This beam line is operated at a fixed energy of 12.7 keV and the source is a 26-pole, 2.0-Tesla insertion device. A Rh-coated Si mirror is used to focus the X-ray beam and to remove higher harmonic energies. In addition, the X-rays are detected using an area detector, i.e., a MAR 345 image plate detector. For this work, a beam stop to detector distance of 180 mm was used. The collection time was limited by the strong diffraction from the single crystal Si substrate. As a result, X-rays were collected until approximately 90% of the counts required to saturate the detector were reached. This typically took from 20 to 35 s. A LaB\(_6\) reference was used to calibrate both the wavelength of the X-rays and the exact angle of the detector with respect to the beam. Data analysis, i.e., calibration, averaging, and radial integration, was carried out using the software package BMW Lande [80].
Figure 3.11. Photograph of the synchrotron X-ray diffraction setup used in this work (beam line 11-3 of the SSRL), showing the different components.

The second beam line used in this investigation was 7-2. A photograph of the beam line, indicating its main components, is shown in Figure 3.12. The energy of this beam line can be tuned from 5 to 16 keV. In this work, 10 keV X-rays were used and the signal was collected with a point detector in order to discriminate the signal originating from the Si substrate. In addition, a total scan time of 18 minutes was used.
Figure 3.12. Photograph of the high resolution synchrotron X-ray diffraction setup used in this investigation (beam line 7-2 of SSRL), showing the different components.
Chapter 4

Size Distribution of Germanium Nanoclusters Embedded in Silica

4.1 Introduction

In Chapter 2, the theory of nanocluster size distribution from ion beam synthesis was presented and a processing route for size distribution narrowing was described. Specifically, it was suggested that the size distribution of ion beam synthesized nanoclusters can be narrowed by initiating the implant at low temperature followed by a temperature increase while continuing the implantation. In this chapter, the effect of implantation temperature on the size distribution of Ge nanoclusters embedded in silica is discussed. In addition, the effect of thermal annealing using both a tube furnace and rapid thermal annealing (RTA) on the size distribution and crystallinity of the Ge nanoclusters is described.

4.2 Experimental Procedure

The samples were prepared by ion beam synthesis (IBS) as described in the previous chapter. Then, isochronal annealing of the samples implanted at the three different temperatures was performed for 1 h at 900 and 1200 °C in sealed ampoules as described in section 3.3. In addition, isothermal annealing of the sample implanted at room temperature (RT) was carried out at 1200 °C for 5, 30, 60, and 180 min. After annealing, the samples were quenched from the annealing temperature to room temperature using running cold water. An additional set of
samples, implanted at ramping temperature (RampT), underwent RTA in nitrogen ambient at 600, 800 and 900 °C for 10 s.

Transmission electron microscopy (TEM) studies were carried out using cross-sectional specimens prepared following the procedure described in section 3.4.1. Both bright field (BF) on a JEOL 3010 microscope operated at 300 keV and high resolution transmission electron microscopy (HRTEM) on a 200 keV F20 UT Tecnai were performed. The size distribution of the Ge nanoclusters was determined by Cosima Boswell, a graduate student in the group of Prof. Chrzan, using the image-processing software ImageJ [81,82] and the following analysis technique. First, each TEM image was uploaded to the program and the scale was set using the scale bar included in the image. Then, ellipses of best fit were placed by hand over each nanocluster and the area was measured. After measuring at least 200 nanoclusters, the recorded areas were converted to radii using the following equation

\[ R_{\text{Ell}} = \frac{A_{\text{Ell}}}{\pi} \]  

(4.1)

The radii were binned using a total of eight bins and the bin width was set accordingly. Size distributions can be reported as the radius of the nanoclusters, \( R \), versus the probability, \( P (R) \), which is given by the number of particles contained in a bin divided by the total number of particles. Alternatively, scaled size distributions, i.e., \( R/<R> \) vs. \( P (R) <R> \), can be reported to facilitate the comparison of size distributions with different average sizes. The scaled distributions allow for a prompt determination of the full width at half maximum (FWHM) of the distributions which can be used to establish if narrower distributions are obtained.

The previous procedure introduces two sources of uncertainty to the size distributions. First, it was assumed that the actual size of the nanoclusters was measured. Second, a change in the bin width can alter the appearance of the distribution without altering the data. For example, a very small bin width leads to jagged distributions due to the increasing probability of an empty bin resulting from the finite number of nanoclusters measured. In contrast, a very large bin width leads to the broadening of the distribution. Therefore, the smallest possible bin width which results in a continuous distribution should be used. Instead of setting a bin width, the number of bins was set to eight and the bin width was calculated using the following equation

\[ \text{bin width} = \frac{R_{\text{max}} - R_{\text{min}}}{7} \]  

(4.2)

where \( R_{\text{max}} \) and \( R_{\text{min}} \) are the maximum and minimum radii measured, respectively.

The measurement technique introduces error to the size distribution. The unannealed nanoclusters appear to be elliptical in shape and randomly oriented. Not all particles are oriented such that the axes correspond to the vertical and horizontal axes. Since ImageJ does not allow rotation of the ellipses, error was introduced when fitting ellipses to nanoparticles. As the size of the nanoclusters and the contrast between the nanoclusters and the matrix decreases, the exact location of the particle/matrix interface is more difficult to determine. This introduces additional
error to the size distribution. The following method was used to incorporate error bars to the size distribution plots. First, it was assumed that the measured area follows the equation

\[ A_{Ell} = \pi \left( (R_p + e_1) \cdot (R_p + e_2) \right) \times CF^2 \]  

(4.3)

where \( R_p \) is the radius of the ellipse in number pixels, \( CF \) is a conversion factor which takes the area from pixels\(^2\) to nm\(^2\) and \( e_1 \) and \( e_2 \) are the errors assumed in pixels. It is important to note that a small error in the measurement of small particles can have a significant effect in the size distribution. However, a similar error in the case of large particles does not have a major impact in the size distribution. Using Equation 4.3 and assuming that an error of two pixels in each dimension was introduced during the measurement, i.e., \([e_1, e_2] = [1, 1]\) and \([e_1, e_2] = [-1, -1]\), error bars can be added to the size distributions as shown in Figure 4.1.
Figure 4.1. Unscaled (a) and scaled (b) size distributions of Ge nanoclusters formed by room temperature implantation into silica followed by thermal annealing at 1000 °C for 1 h. Error bars in both axes were added to account for possible sources of error.
4.3 Narrowing the Size Distribution

In this section, the effect of the implantation temperature on the size distribution of the nanoclusters is explored. Figure 4.2 shows BF TEM images of the unannealed nanoclusters implanted at RT, RampT, and LN₂ temperature as well as the corresponding size distributions. The average size of the nanoclusters was found to be 1.67, 2.05, and 1.63 nm for the LN₂, RampT, and RT samples, respectively. Using Equation 4.2, the bin widths of the distributions were calculated to be 0.22 nm for the LN₂ implant, 0.29 nm for the RampT implant, and 0.28 nm for the RT implant. The size distribution of the samples implanted at RampT and LN₂ temperature appears to be narrower than the RT implant. However, the widths of the distributions fall within the error bars of the measurement technique. The LN₂ and RampT implants were found to have a peak in the scaled distribution ranging from 2.1 to 2.9 and a FWHM of approximately 38 %. The RT implant had a FWHM of approximately 47 %. HRTEM experiments of the unannealed samples suggest that the nanoclusters are amorphous prior to annealing.

In Figure 4.2, it can be observed that the sample implanted at RampT appears to have a lower concentration of particles compared to the samples implanted at LN₂ and RT. This is due to the thickness of the TEM sample as illustrated in Figure 4.3 for a sample implanted at RampT and annealed at 1200 °C for 1 h. The thickness of the TEM sample and the concentration of the Ge nanoclusters increase from Figure 4.3(a) to Figure 4.3(d).
Figure 4.2. BF TEM images of Ge nanoclusters embedded in silica after implantation at LN$_2$, RampT and RT. The samples have not been annealed. Also shown are the corresponding size distributions. The blue, purple, and red lines denote the LN$_2$, RampT, and RT implants, respectively.
Figure 4.3. Cross-sectional TEM images of Ge nanoclusters embedded in silica after implantation at RampT and thermal annealing at 1200 °C for 1 h. The glue used for TEM sample preparation can be seen in the top right corner. The thickness of the sample and the concentration of the Ge nanoclusters increases from (a) to (d).
4.4 Effect of Thermal Annealing on the Size Distribution

The effect of thermal annealing using both rapid thermal and tube furnace annealing was investigated. Figure 4.4 shows BF TEM images and the corresponding size distribution of the sample implanted at RampT and RTA at 600 and 800 °C for 10 s. The average size of the nanoclusters was found to be 1.86 and 2.56 nm with increasing RTA temperature. The scaled size distributions after RTA at 600 and 800 °C were found to be very similar. In addition, the FWHM and the peak of the distributions were found to be 52 % and 1.8, respectively. These values suggest that the size distributions after RTA are broader compared to the unannealed distributions presented in section 4.3.

BF TEM images and the corresponding size distribution of the samples implanted at LN2, RampT, and RTA after annealing at 900 and 1200 °C in a tube furnace are shown in Figures 4.5 and 4.6, respectively. The larger size and better contrast of the samples annealed in the tube furnace allow a more accurate measurement of the size distributions. After annealing at 900 °C, the average radius of the nanoclusters has increased. The average sizes of the particles were found to be 2.83, 3.70, and 4.06 nm for the LN2, RampT, and RT implants, respectively. The FWHM for the three implant conditions varied between 55 and 71 % which is wider than the unannealed and RTA samples discussed previously. After annealing at 1200 °C for 1 h, the size distribution was found to be even wider than the previous results. Specifically, the FWHM of the distributions were found to be between 72 and 92 %. In addition, the average radius of the nanoclusters was determined to be 3.59, 3.54, and 3.61 nm for the samples implanted at LN2, RampT, and RT, respectively.
Figure 4.4. BF TEM images of Ge nanoclusters implanted at RampT and RTA at 600, 800, and 900 °C for 10 s. The corresponding size distributions are also shown. Blue, purple and red lines denote the three increasing RTA temperatures.
Figure 4.5. BF TEM images of Ge nanoclusters embedded in silica after implantation at LN$_2$, RampT and RT followed by thermal annealing at 900 °C for 1h. The scaled size distributions for the different implantation conditions look very similar. The blue, purple, and red lines denote the LN$_2$, RampT, and RT implants, respectively.
Figure 4.6. BF TEM images of Ge nanoclusters embedded in silica implanted under various conditions and annealed at 1200 °C for 1h in a tube furnace. The measured size distributions are shown in the graph.

LN$_2$ implant 1200°C 1h

Ramp T imp. 1200°C 1h

RT implant 1200°C 1h

LN$_2$, bw = 0.59 nm
Ramp, bw = 0.58 nm
RT, bw = 0.77 nm
The effect of annealing time on the size distribution of the Ge nanoclusters was investigated by performing isothermal annealing at 1200 °C for 5, 30, 60 and 180 min on the samples implanted at RT. BF TEM images of the samples annealed for 5, 30, and 180 min are shown in Figure 4.7 while the sample annealed for 60 min was shown in Figure 4.6. The average radii of the samples as a function of annealing time were found to be 2.7, 3.4, 3.6, and 4.1 nm, respectively. The FWHM of the distributions after annealing for 5 and 30 min was found to be approximately 64 %. Wider size distributions characterized by a FWHM of 79 % were measured for the samples annealed for 60 and 180 min. The size distributions for the short annealing times were found to be very similar, and those for of the longer annealing time display the same characteristics. This suggests that between 30 and 60 min the coarsening regime of the distributions is reached.
Figure 4.6. BF TEM images of Ge nanoclusters embedded in silica implanted at RT and annealed at 1200 °C for 5 (a), 30 (b), and 180 (c) min. The unscaled (d) and scaled (f) size distributions as well as the average radii as a function of annealing time (e) are also shown.
4.5 Crystallinity of Germanium Nanoclusters

The optoelectronic properties of crystalline and amorphous Ge can be significantly different. For example, the resistivities of amorphous Ge films and intrinsic crystalline Ge differ by 3 orders of magnitude [83]. In addition, the bandgap of near ideal void free amorphous Ge films is 0.33 eV larger than crystalline Ge [84]. Therefore, it is important to determine the temperature at which the Ge nanoclusters begin to crystallize. HRTEM was used to assess the crystallinity of the Ge nanoclusters. The images of the samples implanted at RampT and RTA at 600, 800, and 900 °C for 10 s are shown in Figure 4.8. After RTA at 600 °C for 10 s, lattice fringes are not observed which suggests that the Ge nanoclusters are amorphous. However, after RTA at 800, and 900 °C lattice fringes are visible indicating that the nanoclusters have crystallized.
Figure 4.8. HRTEM images of samples implanted at RampT and RTA at 600, 800, and 900 °C for 10 s. Lattice fringes are not present after RTA at 600 °C suggesting that the nanoclusters are amorphous. However, after RTA at 800 and 900 °C lattice fringes are observed indicating that the nanoclusters have crystallized.
Chapter 5

Reversible Phase Changes in Gold - Germanium Nanoclusters Embedded in Silica

5.1 Introduction

Technological applications like rewritable data storage require reversible phase changes. Also important for data-storage applications are the ability to switch rapidly and repeatedly between states and a large resistance/optical change between states. The prototypical phase change material used in these applications is the chalcogenide alloy Ge$_2$Sb$_2$Te$_5$ (GST). This material can exist at room temperature in either a stable crystalline state (high reflectivity/low resistance) or a metastable amorphous state (low reflectivity/high resistance). In addition, a tailored laser or current pulse can be used to switch between the two states. Specifically, a short high current or high intensity laser pulse can be used to locally melt the material followed by rapid quenching which results in the formation of the metastable phase. Furthermore, a long low current or low intensity laser pulse can be used to obtain the equilibrium phase [85], as shown schematically in Figure 5.1.
Figure 5.1. Phase change materials for rewritable data storage. A short high intensity laser or current pulse can be used to obtain an amorphous phase which has low reflectivity/high resistance. The high reflectivity/low resistance crystalline phase can be recovered using a long low intensity laser or current pulse [85].

In order to minimize the volume of material required for a bit of storage, one-dimensional (1D) and ultimately zero-dimensional (0D) structures are desired. Unfortunately, the short high current or laser pulse cannot be applied to freestanding 0D structures because they do not preserve their shape after melting [17,86,87]. This problem can be overcome by synthesizing capped [88,89] or embedded nanostructures [47,90,91]. Indeed, our group has recently identified a new class of phase change materials consisting of embedded nanostructures, i.e., embedded binary eutectic alloy nanostructures (BEANs). Using Ge-Sn nanoparticles embedded in silica as
an example, it was determined that these particles exhibit an equilibrium bi-lobe structure consisting of phase separated Ge and Sn regions. Furthermore, it was established that after irradiating the bi-lobe structure with a short high power laser pulse, a homogeneously mixed metastable structure formed. Finally, the equilibrium bi-lobe structure was recovered by heating at temperatures as low as ~150 °C for a short time (10 s).

The behavior of the embedded BEANs is shown schematically in Figure 5.2. This behavior can be explained as follows. Above the melting point of the bi-lobe nanoclusters ($T_m$), a liquid droplet of homogeneous composition forms. Two different paths are available for the liquid droplet during cooling. For a slow cooling rate, the equilibrium path (red to dark blue) will be followed and thus the equilibrium bi-lobe structure will form. However, for a rapid cooling rate (red to light blue), the liquid will at first be supercooled, and then will solidify into the homogeneously mixed structure at $T_g$. Upon heating, the metastable homogeneously mixed state may follow the path indicated by the white arrow and crystallize at a temperature $T_{crys}$. In this chapter, reversible phase changes in a new system, Ge-Au nanoclusters embedded in silica, are demonstrated.

Figure 5.2. Schematic of the operating principle of the proposed BEAN. The nanocluster is liquid above its melting point, $T_m$. If the cooling rate is slow, the red to dark blue path will be followed, yielding the equilibrium bi-lobe structure. If the cooling rate is fast, the red to light blue path will be followed and a metastable homogeneously mixed state will form. Upon heating, the amorphous state may follow the path indicated by the white arrow and crystallize at a temperature $T_{crys}$ [88].
5.2 Theoretical Prediction of the Germanium – Gold Structure

Ge-Au nanoclusters embedded in silica could have one of the following equilibrium structures. (1) Separated Ge and Au nanoclusters, (2) Ge core and Au shell nanoclusters, (3) Au core and Ge shell nanoclusters, or (4) bi-lobe nanoclusters. These structures are expected to have significantly different optoelectronic properties. Therefore, predicting the stable structure is of paramount importance. In this section, a simple model developed by Chun-Wei Yuan describing the thermodynamic stability of embedded BEANs is discussed [92].

The model considers eutectic elements A and B embedded within a matrix M. In order to predict the stable structure, the free energies of the four possible structures are calculated and compared. Then, the equilibrium structure minimizing the free energy is determined. The interfacial contribution to the free energy is given by

\[ E_{\text{int}} = \sum_i A_i \gamma_i, \]  

(5.1)

where \( A_i \) is the area of the interface separating the phases and \( \gamma_i \) is the interface energy. For the separated sphere configuration, the interfacial free energy, \( E_{\text{sep}} \), is

\[ E_{\text{sep}} = \sum_i A_i \gamma_i = 4\pi R^2 \gamma_{\alpha/M} + 4\pi R^2 \gamma_{\beta/M}, \]  

(5.2)

where \( R \) is the radius of the sphere, and \( \alpha \) and \( \beta \) are the A-rich and B-rich phases, respectively. Assuming that the total volume of the nanocluster is \( \frac{4\pi}{3} R^3 \) and scaling all interfacial energies by \( 4\pi R^2 \gamma_{\alpha/\beta} \) while defining \( \gamma_1 = \gamma_{\alpha/M}/\gamma_{\alpha/\beta} \) and \( \gamma_2 = \gamma_{\beta/M}/\gamma_{\alpha/\beta} \), one obtains the dimensionless free energy

\[ E_{\text{sep}} = \frac{4\pi R^2 \gamma_{\alpha/M}}{4\pi R^2_0 \gamma_{\alpha/\beta}} + \frac{4\pi R^2 \gamma_{\beta/M}}{4\pi R^2_0 \gamma_{\alpha/\beta}} = \frac{R^2_\alpha R^2_\beta}{R^2_0} \gamma_1 + \frac{R^2_\beta}{R^2_0} \gamma_2 = \left(1 - f_\beta\right)^{2/3} \gamma_1 + f_\beta^{2/3} \gamma_2. \]  

(5.3)

Where \( f_\beta \) is the volume fraction of the \( \beta \) phase.

The interfacial contributions to the free energies for the \( \alpha \)-core/\( \beta \)-shell structure, \( E_{\alphaC/\betaS} \), is given by

\[ E_{\alphaC/\betaS} = \sum_i A_i \gamma_i = 4\pi R^2 \gamma_{\alpha/\beta} + 4\pi R^2 \gamma_{\beta/M}, \]  

(5.4)

and the dimensionless free energy is

\[ E_{\alphaC/\betaS} = \frac{4\pi R^2 \gamma_{\alpha/M}}{4\pi R^2_0 \gamma_{\alpha/\beta}} + \frac{4\pi R^2 \gamma_{\beta/M}}{4\pi R^2_0 \gamma_{\alpha/\beta}} = \frac{R^2_\alpha}{R^2_0} + \frac{\gamma_{\beta/M}}{\gamma_{\alpha/\beta}} = \left(1 - f_\beta\right)^{2/3} + \gamma_2. \]  

(5.5)
Similarly, the dimensionless free energy for the β-core/α-shell structure is

\[ E_{\beta C/\alpha S} = f_B^{2/3} + \gamma_1. \]  

\hspace{1cm} (5.6)

Finally, the free energy for the bi-lobe structure is determined. A typical bi-lobe structure, defining the angles \( \theta_\alpha, \theta_\beta, \) and \( \theta_M \), is shown in Figure 5.3. At the triple point, mechanical equilibrium requires that

\[ \gamma_{\alpha/\beta} = \gamma_{\beta/M} \cos \left(180 - \theta_\beta\right) - \gamma_{\alpha/M} \cos \left(\theta_\alpha\right) \]  

\hspace{1cm} (5.7)

\[ \gamma_{\alpha/M} \sin \left(\theta_\alpha\right) = \gamma_{\beta/M} \sin \left(180 - \theta_\beta\right) \]  

\hspace{1cm} (5.8)

which can be rewritten in dimensionless form as

\[ 1 = -\gamma_2 \cos \left(\theta_\beta\right) - \gamma_1 \cos \left(\theta_\alpha\right) \]  

\hspace{1cm} (5.9)

\[ \gamma_1 \sin \left(\theta_\alpha\right) = \gamma_2 \sin \left(\theta_\beta\right). \]  

\hspace{1cm} (5.10)

Figure 5.3. Cross-sectional view of a bi-lobe structure defining the contact angles \( \theta_\alpha, \theta_\beta, \) and \( \theta_M \).
The angles $\theta_\alpha$, $\theta_\beta$, and $\theta_M$ can be determined using Equations (5.9) and (5.10) if the interface energies $\gamma_{\alpha/M}$, $\gamma_{\beta/M}$, and $\gamma_{\alpha/\beta}$ are known.

The surface area and volume of a spherical cap are

$$A_{cap}(r, \phi) = 2\pi r^2 (1 - \cos \phi)$$

$$V_{cap}(r, \phi) = \frac{2\pi}{3} r^3 (1 - \cos \phi) - \frac{\pi}{3} r^3 \cos \phi \sin^2 \phi,$$

where $r$ is the radius of the sphere and $\phi$ is the polar angle characterizing the volume fraction of the cap to the entire sphere. Since the volume of all structures had been defined as $\frac{4\pi}{3} R_0^3$, the volume of the bi-lobe structure is

$$V_{cap}(r_\alpha, \phi_\alpha) + V_{cap}(r_\beta, \phi_\beta) = \frac{4\pi}{3} R_0^3.$$  

If the interface energies $\gamma_{\alpha/M}$, $\gamma_{\beta/M}$, and $\gamma_{\alpha/\beta}$ and the volume fraction, $f_\beta$, are known, the geometry of the bi-lobe structure can be determined using Equations (5.9), (5.10), (5.12), and (5.13). Then, the total interface energy of the bi-lobe structure can be computed using Equation (5.11).

Finally, using Equations (5.3), (5.5), and (5.6), combined with the numerical solution for the bi-lobe structure, the structure which minimizes the interfacial free energy can be determined. For the case of Ge-Au nanoclusters embedded in silica, the interface energies of interest are $\gamma_{Au/SiO2}$, $\gamma_{Ge/SiO2}$, and $\gamma_{Au/Ge}$. Satpati, et al. estimated the value of $\gamma_{Au/SiO2}$ at 1.36 J/m$^2$ [93], while Biskupek and co-workers found that the value of $\gamma_{Au/SiO2}$ is approximately 1.21 J/m$^2$ [94]. Furthermore, the value of $\gamma_{Ge/SiO2}$ has been determined experimentally to be 0.91 J/m$^2$ [91]. Unfortunately, the value of $\gamma_{Au/Ge}$ is not available in the literature at this time. Therefore, the free energy curves for the four possible structures as a function of the volume fraction of Ge, $f_{Ge}$, is shown in Figure 5.4 using $\gamma_{Au/SiO2} = 1.36$ J/m$^2$, $\gamma_{Ge/SiO2} = 0.91$ J/m$^2$, and four different values of $\gamma_{Au/Ge}$, i.e., 0.5, 1.0, 1.5, and 2.0 J/m$^2$. 
Figure 5.4. Dimensionless free energy curves as a function of the volume fraction of Ge, $f_{Ge}$, for spherical Ge and Au nanoclusters embedded in silica. Four different structures were considered: Separate spheres (black), Au-core-Ge-shell (blue), Ge-core-Au-shell (orange), and bi-lobe (red). The interface energies $\gamma_{Au/SiO_2} = 1.36 \text{ J/m}^2$, $\gamma_{Ge/SiO_2} = 0.91 \text{ J/m}^2$, and $\gamma_{Au/Ge} = (a) 0.5, (b) 1.0, (c) 1.5, and (d) 2.0 \text{ J/m}^2$ were used.

From the previous figure, it can be observed that the equilibrium structure of the Ge-Au nanoclusters embedded in silica is bi-lobe for the four different values of $\gamma_{Au/Ge}$ used. This result still holds if $\gamma_{Au/SiO_2} = 1.21 \text{ J/m}^2$ is used instead of $\gamma_{Au/SiO_2} = 1.36 \text{ J/m}^2$. In addition, it can be seen that the equilibrium structure is not affected by changes in $f_{Ge}$. However, the equilibrium structure does depend on the value of the interface energies. As a result, a structural phase diagram for embedded BEANs can be developed (Figure 5.5). The map contains four regions. In the first region, separated nanoclusters are stable. This occurs when $1 > \gamma_1 + \gamma_2$. On the other hand, when $\gamma_2 > 1 + \gamma_1$, the $\beta$-core/$\alpha$-shell structure is stable. In the third region, the $\alpha$-core/$\beta$-shell is the equilibrium structure. This is observed when $\gamma_1 > 1 + \gamma_2$. For all other values of $\gamma_1$ and $\gamma_2$, the bi-lobe structure is stable.
Figure 5.5. Structural phase diagram of binary alloy nanoclusters with a volume fraction of $f_\beta = 0.5$. The equilibrium structures are located at the respective $\gamma_1$ and $\gamma_2$ coordinates [92].
5.3 Structure of Germanium – Gold Nanoclusters

After showing in section 3.2 that Au nanoclusters embedded in silica can be synthesized in our laboratory, Ge-Au alloy nanoclusters were fabricated by implanting Ge into the unannealed Au-doped silica films. Specifically, $3.5 \times 10^{16}$, $4.7 \times 10^{15}$, and $7.0 \times 10^{15}$ cm$^{-2}$ $^{74}$Ge was implanted into the co-sputtered Au-doped silica film, with energies of 150, 90, and 50 kV, respectively. The multiple energies and doses were used in order to achieve a more homogeneous Ge to Au ratio throughout the sample.

After Ge implantation, the samples were annealed in sealed ampoules at 900 °C for 1 h under an Ar atmosphere followed by quenching from the annealing temperature to room temperature using cold running water. The concentration profiles of both Ge and Au in silica before and after thermal annealing were determined by RBS (Figure 5.6). Prior to annealing, the Au concentration was found to be 1.2 at.% from approximately 40 nm to 150 nm from the sample surface. After annealing at 900 °C for 1 h, the shape of the Au concentration profile remained constant. However, the peak Au concentration in silica decreased from approximately 1.2 to 1.1 at. % and the total Au content decreased from $8.2 \times 10^{15}$ to $7.2 \times 10^{15}$ cm$^{-2}$ after annealing. After implantation, Ge was found to have a peak concentration of approximately 5.5 at.% from about 50 nm to 110 nm from the sample surface. The peak Ge concentration remained constant after thermal annealing. However, Ge diffusion to the silica-Si interface as well as a decrease in the total Ge content from $4.4 \times 10^{16}$ to $4.0 \times 10^{16}$ cm$^{-2}$ were observed after annealing. The reduction in both Ge and Au content after annealing is due to out-diffusion from the surface.
Figure 5.6. Concentration profiles of both $^{74}\text{Ge}$ and Au in silica (a) as-grown and (b) after annealing at 900 °C for 1 h obtained by Rutherford backscattering spectrometry.
The structure of the Ge-Au nanoclusters was characterized by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Plan-view specimens prepared by dimpling and ion milling at liquid-nitrogen temperature were used. After the initial anneal at 900 °C for 1 h, the nanoclusters were found to have a bi-lobe structure (Figure 5.7). This is in agreement with the theoretical predictions discussed in section 5.2. In addition, this is the equilibrium structure expected for strongly segregating alloys that are slowly cooled after melting.

In order to modify the structure of the nanoclusters, pulsed-laser melting (PLM) was performed. This process consists of irradiating the sample with a single pulse from an excimer laser. In this work, a 30 ns pulse from a KrF (\(\lambda = 248\) nm) excimer laser at a fluence of 0.3 J/cm\(^2\) was used. During PLM, the energy of the laser pulse (5 eV) is absorbed by the nanoclusters and not by the silica matrix because its 8.9 eV bandgap is larger than the energy of the laser pulse photons. The absorbed photons are converted rapidly to heat causing the nanoclusters to melt.

![Figure 5.7. HAADF-STEM image of Ge-Au nanoclusters embedded in silica after annealing at 900 °C for 1 h. The nanoclusters have the equilibrium bi-lobe structure predicted theoretically in section 5.2.](image)
Heat is highly localized in the thin implanted layer where the nanoclusters are located and diffuses away rapidly when the laser pulse ends. This leads to a very high cooling rate which can reach $10^9 - 10^{11}$ K/s [95]. As a result, a metastable structure, i.e., mixed structure with no contrast variation [Figure 5.8(b)], forms. To recover the equilibrium bi-lobe structure, rapid thermal annealing (RTA) at low temperature for a short time, i.e., 300 °C for 10 s was performed. Indeed, bi-lobe Ge-Au nanoclusters are observed in HAADF-STEM images after RTA was carried out [Figure 5.8(c)]. This demonstrates that the structural changes in the embedded nanoparticles are reversible.

Figure 5.8. HAADF-STEM images of Ge-Au nanoclusters embedded in silica. After annealing at 900 °C for 1 h, the nanoclusters have the equilibrium bi-lobe structure (a). However, a homogeneously mixed structure is observed after pulsed-laser melting (b). The equilibrium bi-lobe structure is recovered after rapid thermal annealing at 300 °C for 10 s (c).
5.4 Crystal Structure Determination

The crystal structure of the Ge-Au nanoclusters was assessed using synchrotron X-ray diffraction (SXRD) at the Stanford Synchrotron Radiation Lightsource (SSRL). The first set of measurements was performed on beam line 11-3. Figure 5.9 shows typical diffraction data from beam line 11-3 before processing. The Ge reference sample consisted of Ge powder obtained by crushing a single crystal Ge wafer while the Au reference was a piece of polycrystalline Au. Several features can be observed in the Ge-Au annealed sample. First, diffraction spots are

![Image of diffraction patterns]

Figure 5.9. Raw synchrotron X-ray diffraction data collected using an image plate detector. Measurements from the annealed Ge-Au sample as well as the Ge and Au references are shown. Diffraction from Ge, Au, and the Si substrate is observed in the Ge-Au annealed sample.
present. These are due to the single crystal substrate and were also observed in reference samples not containing nanoclusters (not shown). Second, diffraction rings were observed which indicate that both Ge and Au are crystalline. In addition, the presence of rings indicates that the nanoparticles are randomly oriented. Scattering from the amorphous silica matrix was observed at low angles. This feature was also present in a reference sample consisting of SiO₂ thermally grown on Si (not shown).

Figure 5.10 shows the experimental results after calibration and radial integration of the diffraction patterns are performed. After implanting Ge into Au-doped silica (as formed), scattering from the Si substrate as well as the amorphous silica matrix was observed. However, there is no diffraction from either Ge or Au suggesting that they are amorphous. After annealing at 900 °C for 1h, four diffraction peaks assigned to Au and Ge were present. This indicates that the bi-lobe nanoclusters contain crystalline Au and Ge. After PLM, however, the peaks due to crystalline Ge and Au are no longer present. The peaks are observed again after RTA, which is evidence that the crystalline Ge and Au phases are recovered. These results support the findings from the previous section that the phase changes are reversible.

Figure 5.10. Synchrotron X-ray diffraction patterns of the Ge-Au nanoclusters embedded in silica after radial integration. The samples prior to annealing (as formed) and after annealing, PLM, and RTA are shown.
SXRD measurements of the Ge-Au nanoclusters after PLM were performed on beam line 7-2 of SSRL. Six peaks were observed from the PLM sample (Figure 5.11). These peaks were assigned to Ge and the hexagonal close-packed β Ge-Au phase. The amount of the crystalline Ge phase is small and therefore it was not detected in the diffraction experiments performed on beam line 11-3. The presence of the Ge and β Ge-Au phases after PLM was carried out is consistent with quenching experiments performed in bulk samples by Anantharaman and coworkers [96]. It is possible that some crystalline Au remains in the sample after PLM. However, this could not be confirmed with this experiment since the diffraction peaks of Au overlap with the ones of the β Ge-Au phase.

Significant differences in the optoelectronic properties of the equilibrium (bi-lobe) and metastable β Ge-Au (homogeneously mixed) phases are expected, as this is the case in the bulk. For example, Luo and coworkers established that metastable compounds in the Ge-Au system, including β Ge-Au, are superconducting [97].

![Figure 5.11. X-ray diffraction pattern of the Ge-Au nanoclusters after PLM obtained using synchrotron radiation and a point detector. A reference sample of SiO2 on Si was also measured.](image)
5.5 Phase Change Temperature

In sections 5.3 and 5.4, it was established that the bi-lobe structure contains crystalline Ge while the homogenously mixed structure has mostly β Ge-Au. Furthermore, it was found that after RTA at 300 °C for 10 s, the crystalline Ge phase was recovered. In order to determine the exact temperature at which the crystalline Ge phase is recovered, in-situ Raman spectroscopy experiments were performed. The setup used in this investigation consisted of a Lexel Model 95 Ar-ion laser operated at 488 nm. The scattered light was analyzed by a SPEX 1877 triple spectrometer with a 600 mm focal length and a 1200 cm⁻¹ grating. The signal was collected by a liquid-nitrogen-cooled CCD camera. In addition, optical polarizers were used to suppress the second order Si Raman signal originating from the substrate.

The results of the in-situ Raman spectroscopy experiments are shown in Figure 5.12. After annealing at 900 °C for 1h (annealed), a Raman peak from crystalline Ge is observed. This is in agreement with the SXRD experiments. However, after PLM, the Raman peak from crystalline Ge is no longer present. As the temperature is increased from room temperature to 65 °C under an Ar atmosphere, the Raman spectra remain unchanged. However, when the temperature reached 80 °C, the shape of the Raman peak changed and began to look more like the annealed sample. This indicated that a phase change from β Ge-Au to crystalline Ge began to occur at 80 °C.

![Figure 5.12. Raman spectra of Ge-Au nanoclusters after thermal annealing (annealed), PLM, and during in-situ heating. The reference spectra of a highly enriched ⁷⁴Ge single crystal and amorphous Ge are also shown.](image)
5.6 Cycling the Phase Changes

In order to show that Ge-Au alloy nanoclusters embedded in silica are promising phase change materials for rewritable data storage applications, a large cycle number of reversible transitions must be demonstrated (~100,000 cycles). Unfortunately, this large number of cycles is not feasible with the current experimental setup. As a result, only 10 cycles of reversible transitions were carried out to demonstrate proof of concept.

After 1, 5, and 10 cycles ending in both PLM and RTA, the crystallinity of Ge was assessed by ex-situ Raman spectroscopy (Figure 5.13). After the first cycle ending in PLM, the Ge Raman peak looks like the amorphous Ge reference. However, after RTA, a Raman peak from crystalline Ge is observed. This result holds after 5 and 10 cycles are performed. This confirms that the reversible transformation can be performed multiple times.

In order to confirm the previous result and assess the crystallinity of Au after multiple PLM and RTA cycles, SXRD experiments were performed on beam line 11-3 of SSRL (Figure 5.14). After 10 cycles ending in PLM (10 PLM), Ge and Au are not crystalline. This is also the case after PLM only once. However, after 10 cycles ending in RTA (10 RTA), diffraction from crystalline Ge and Au is observed similar to the RTA sample. This is in agreement with the Raman spectroscopy experiments and confirms that the reversible transformation can be performed multiple times.

![Raman spectra of Ge-Au nanoclusters after PLM and RTA once, 5, and 10 times. The reference spectra of a highly enriched $^{74}\text{Ge}$ single crystal and amorphous Ge are also shown.](image-url)
Figure 5.14. Synchrotron X-ray diffraction patterns of the Ge-Au nanoclusters embedded in silica as formed, after annealing, and after PLM and RTA once and 10 times. The reference pattern of SiO$_2$ on Si is also shown.
Chapter 6

Melting Behavior of Germanium - Gold Nanoclusters

6.1 Introduction

Nanocrystalline materials exhibit properties that differ significantly from the properties of these materials in bulk form. For example, thermodynamic analysis predicts that the melting point, one of the most fundamental properties of materials, is inversely proportional to the radius of the particle:

\[ \Delta T \propto \frac{T_m}{L_r} \left[ \gamma_{LV} \left( \frac{\rho_s}{\rho_l} \right)^{2/3} - \gamma_{SV} \right] \]  

(6.1)

where \( \Delta T \) is the difference between the bulk and nanocluster melting point, \( T_m \) is the bulk melting point, \( L \) is the heat of fusion per volume of the solid, \( r \) is the radius of the particle, and \( \gamma_{LV} \) and \( \gamma_{SV} \) are the liquid-vapor and solid-vapor interface energies, respectively. Freestanding nanoclusters exhibit a depression in the melting point relative to the bulk and therefore they exhibit a negative \( \Delta T \) value [11]. However, when the nanoclusters are embedded within a matrix, both positive and negative values of \( \Delta T \) are observed [98-101]. Our group has investigated the melting behavior of ion beam synthesized Ge nanoclusters embedded in silica. It was found that in contrast to the melting point depression reported in nearly all nanocluster studies [102,103], Ge nanoclusters embedded in silica can be both superheated and supercooled by ca. 20% of the bulk melting temperature (\( T_m \)) as shown in Figure 6.1 [91]. However, the melting point hysteresis observed in Ge nanocrystals embedded in silica occurs at a high temperature range for potential technological applications. It is well established that Ge and Au form a eutectic alloy with a eutectic composition and temperature of 28 at. % Ge and 361 °C,
respectively as shown in Figure 6.2 [104]. Therefore, by synthesizing Ge-Au alloy nanocrystals embedded in silica, the melting point of the Ge nanocrystals is expected to be reduced significantly. In this chapter, the melting behavior of Ge-Au nanoclusters embedded in silica is explored.

Figure 6.1. Integrated intensity of the diffraction rings of Ge nanoclusters embedded in silica during in-situ TEM heating. A melting point hysteresis approximately 470 K wide and centered approximately on the melting point of bulk Ge was observed [91].
Figure 6.2. Equilibrium phase diagram for the Ge-Au system in air. A eutectic reaction is observed at a composition of 28 at. % Ge and a temperature of 361 °C [104].

6.2 Experimental Procedure

The Ge-Au nanoclusters embedded in silica were synthesized by co-sputtering Au and silica followed by Ge implantation as described in section 5.3. The ratio of the Ge-Au nanoclusters was modified by varying the amount of implanted Ge while keeping the Au content fixed. Then, the samples were annealed at 900 °C for 1 h under an Ar atmosphere and quenched to room temperature using cold running water as described in section 3.3. The melting behavior of the nanoclusters was investigated by in-situ heating inside a JEOL 3010 transmission electron microscope (TEM) operated at 300 kV. Plan view samples prepared by dimpling and ion milling at liquid nitrogen temperature were used. The samples were placed in a Gatan Ta628 holder containing a tantalum furnace and a pair of calibrated thermocouples. In order to minimize heating and degradation effects from the electron beam, the intensity of the electrons incident on the specimen was minimized. Selected area diffraction (SAD) patterns were obtained in 100 K increments and the measurements were recorded approximately 15 minutes after the temperature was reached. The images were recorded using a Gatan optically coupled TV-rate CCD camera and the more recent experiments with the newly installed Gatan Orius CCD camera. The direct beam is observed in the images taken with the later camera because it is located above the
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viewing screen. ImageJ was used to integrate the intensity of the diffraction patterns circumferentially about the center of the pattern. Then, background subtraction was performed and the melting point was defined as the temperature at which the diffraction pattern disappeared.

6.3 Melting of Germanium - Gold Nanoclusters

Embedded in Silica

Diffraction patterns from a sample containing Ge-Au nanoclusters with a 4 Ge to 1 Au atomic concentration ratio are shown in Figure 6.3. The corresponding plots of the intensity of the diffraction rings after radial integration are shown in Figure 6.4. It is important to note that the nanoclusters exhibit diffraction rings and not spots indicating that the nanoclusters are crystalline and randomly oriented. This result is in agreement with the SXRD experiments discussed in section 5.4. In contrast to the SXRD experiments, diffraction from the Si substrate is not observed in the SAD patterns due to the small thickness of the TEM foils, in the order of 10’s of nm. Diffraction from the nanoclusters is observed from room temperature up to 800 °C as shown in Figures 6.3 and 6.4. However, at 900 °C the diffraction rings are no longer present indicating that the melting point of the particles is between 800 °C and 900 °C for this composition. This temperature is significantly lower than the melting point of Ge nanoclusters embedded in silica (1177 °C). The melting point of bulk the Ge-Au alloy with this composition is 840 °C according to Figure 6.2. Therefore, melting of embedded Ge-Au alloy nanoclusters with a 4 Ge to 1 Au ratio occurs at a similar temperature compared to the bulk.

The diffraction patterns from a sample containing a Ge-Au ratio of 1 to 1 and the corresponding plots of the intensity of the diffraction rings after radial integration are shown in Figures 6.5 and 6.6, respectively. For this composition, significant melting occurs at 700 °C and the diffraction patterns exhibit very weak intensity. When the temperature reaches 800 °C the nanoclusters are completely molten and diffraction from the nanoclusters is no longer observed.
Figure 6.3. Diffraction patterns obtained during in-situ TEM heating of Ge-Au nanoclusters embedded in silica with a 4 Ge to 1 Au ratio.
According to Figure 6.2, bulk Ge-Au alloys with this composition melt at 650 °C. This indicates that the nanoclusters can be superheated between 50 and 150 °C.

Finally, the melting behavior of a sample containing Ge-Au nanoclusters with a 1 Ge to 5 Au ratio was investigated. The SAD patterns taken during in-situ TEM heating are shown in Figure 6.7 and the corresponding plots of the intensity of the diffraction rings after radial integration are shown in Figures 6.8. At a temperature of 700 °C, significant melting has occurred and the following diffraction rings are no longer present: Au 220, Ge 220, and Au 200. The bulk melting point of Ge-Au alloys with this composition is 670 °C which suggests that the melting point of the embedded 1 Ge – 5 Au nanoclusters is higher than the bulk. The melting behavior of the Ge – Au alloy nanoclusters with the different Ge to Au atomic concentration ratios is summarized in Figure 6.9.
Figure 6.5. Diffraction patterns obtained during in-situ TEM heating of Ge-Au nanoclusters embedded in silica. The nanoclusters had a 1 Ge to 1 Au ratio.
Figure 6.6. Integrated intensity plots of the diffraction patterns shown in Figure 6.5 during measurements of the melting point of 1 Ge 1 Au alloy nanoclusters embedded in silica.
Figure 6.7. Diffraction patterns obtained during in-situ TEM heating of Ge-Au nanoclusters (1 Ge to 5 Au ratio) embedded in silica.
Figure 6.8. Integrated intensity plots of the diffraction patterns shown in Figure 6.7 during measurements of the melting point of 1 Ge to 5 Au alloy nanoclusters embedded in silica.
Figure 6.9. Intensity (peak height) of the integrated diffraction rings as a function of temperature during in-situ TEM heating of Ge – Au alloy nanoclusters embedded in silica with different Ge to Au atomic concentration ratios. The height of the 200 Au – 220 Ge peak is presented for the 4 Ge 1 Au (filled squares) sample while the height of the 111 Au peak is given for the 1 Ge 1 Au (filled circles) and 1 Ge 5 Au (filled triangles) samples.
Chapter 7

Conclusions and Future Work

7.1 Conclusions

The work presented in this dissertation was aimed at understanding the structure of ion beam synthesized Ge and Ge-Au nanoclusters embedded in silica. The theory of nanocluster size distributions from ion beam synthesis was presented and a processing route for size distribution narrowing was investigated. Transmission electron microscopy studies revealed that narrow size distributions can be fabricated by implanting at room temperature, liquid nitrogen temperature or using a temperature ramp. Thermal annealing was found to coarsen the size distribution of the Ge nanoclusters. In addition, the nanoclusters began to crystallize after rapid thermal annealing for 10 s at a temperature of 800 °C or higher.

The theory of embedded binary alloy nanoclusters was presented and the structure of Ge-Au nanoclusters embedded in silica was predicted. Since the mass of Au exceeded the limits of the Varian CF300 ion implanter used in this work, a process was developed to incorporate Au into silica, and Ge-Au nanoclusters embedded in silica were fabricated. After thermal annealing, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) experiments revealed that the Ge-Au nanoclusters have a bi-lobe structure. This was in agreement with the theoretical prediction using the proper interface energies. It was demonstrated that a 30 ns laser pulse can be used to obtain a homogeneously mixed structure with no contrast variation in the HAADF-STEM images. The bi-lobe structure was recovered after rapid thermal annealing at low temperature for short time. The transformation between the bi-lobe and homogeneously mixed structures can be cycled at least 10 times. In-situ and ex-situ Raman spectroscopies were used to investigate the crystallinity and recrystallization temperature of Ge. Furthermore, the phases present in the bi-lobe and homogeneously mixed structures were determined using synchrotron X-ray diffraction. The melting behavior of the Ge-Au nanoclusters was investigated using in-situ transmission electron microscopy.

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7.2 Future work

Transmission electron microscopy was used to determine the size distribution of the embedded nanoclusters as described in Chapter 4. However, measuring the size distribution of the unannealed samples using this method is difficult due to the small size of the nanoclusters and the low contrast between the amorphous Ge nanoclusters and the matrix. Therefore, an alternative method like grazing-incidence small-angle X-ray scattering (GISAXS) should be used to verify the size distribution of the unannealed samples. This technique has been used successfully by several groups to determine the size distribution or ion beam synthesized semiconductor nanoclusters [105-107].

One of the crucial properties of phase-change alloys used for non-volatile electronic storage is a large electrical resistance change between the equilibrium and metastable states [85]. This is expected to occur between the bi-lobe and homogeneously mixed structures of the Ge-Au nanoclusters embedded in silica, since this has been reported in the bulk [97]. Scanning tunneling microscopy (STM) is routinely used to measure the current-voltage characteristics of freestanding nanoclusters [108,109]. The Ge-Au nanoclusters can be liberated from the matrix using a process developed in our group [33]. Then, STM can be used to probe the electronic properties of the bi-lobe and homogeneously mixed freestanding Ge-Au nanoclusters.

In Chapter 5, it was demonstrated using both synchrotron X-ray diffraction and electron diffraction that the Ge-Au nanoclusters embedded in silica are randomly oriented. Technological applications may require that the nanoclusters are preferentially oriented in one direction. One way to achieve this could be by heavy ion implantation as demonstrated by Kluth et al. [110]. Preliminary experiments have been performed using Ge-Sn embedded in silica since they have a larger average size [47] compared to Ge-Au. These samples were prepared by implanting $^{120}$Sn at 170 keV to $1 \times 10^{16}$ cm$^{-2}$ followed by $^{74}$Ge at 120 keV to $4 \times 10^{16}$ cm$^{-2}$. The samples were subsequently annealed at 900 ºC for 1 h in a sealed ampoule as described in Chapter 3. After annealing, the Ge-Sn nanoclusters have a bi-lobe structure as shown in Figure 7.1. The annealed samples were irradiated with $^{197}$Au$^{7+}$ at 185 MeV by P. Kluth and colleagues at the Australian National University’s Heavy Ion Accelerator. After irradiation both and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and high resolution transmission electron microscopy (HRTEM) experiments were performed. The HAADF-STEM images shown in Figure 7.2.a and 7.2.b reveal that upon irradiation, the majority of the nanoclusters form nanorods oriented in the direction of the ion beam. These nanorods seem to
Figure 7.1. Bright field transmission electron microscopy image of the 4 Ge to 1 Sn nanoclusters embedded in silica after thermal annealing at 900°C for 1 h. The nanoclusters have a bi-lobe structure.

have a mixed concentration of Ge and Sn atoms. In addition, the particles were found to be amorphous after irradiation as evidenced by a lack of lattice fringes in the HRTEM images shown in Figures 7.2.c and 7.2.d.

After in-situ heating from room temperature to 500 °C inside a 300 kV JEOL 3010 transmission electron microscope (TEM), the specimen was examined by both HAADF-STEM (Figures 7.3.a and 7.3.b) and HRTEM (Figures 7.3.c and 7.3.d). The orientation and morphology of the particles did not seem to change after heating. However, the internal structure appeared to form alternating Ge-rich and Sn-rich regions as shown in the HAADF-STEM images. A similar structure has been observed in Ge-Au nanowires capped with HfO$_2$ with a Au concentration of 29-37 at. % [88]. The HRTEM images revealed that the particles crystallized after heating since lattice fringes were observed.
Figure 7.2. HAADF-STEM and HRTEM images of the Ge-Sn nanoclusters embedded in silica shown in Figure 7.1 after 185 MeV Au\textsuperscript{7+} irradiation. The HAADF-STEM images (a and b) reveal that upon irradiation, most of the nanoclusters form nanorods oriented in the direction of the ion beam. The lack of lattice fringes observed in the HRTEM images (c and d) suggests that the particles are amorphous after irradiation.
Figure 7.3. HAADF-STEM and HRTEM images of the irradiated Ge-Sn sample shown in Figure 7.2 after in-situ TEM heating from room temperature to 500 °C inside. HAADF-STEM images (a and b) suggest that the orientation and morphology of the particles does not change after heating. However, the internal structure appears to form alternating Ge-rich and Sn-rich regions. Lattice fringes are observed in the HRTEM images (c and d) indicating that the particles have crystallized.
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