CHAPTER 1

Self-Assembled Germanium Quantum Dots on Silicon and Their Optoelectronic Devices

J. L. Liu,1 S. Tong,2 K. L. Wang2
1Department of Electrical Engineering, University of California at Riverside, Riverside, California 92521, USA
2Device Research Laboratory, Electrical Engineering Department, University of California at Los Angeles, Los Angeles, California 90095, USA

CONTENTS
1. Introduction ....................................... 1
2. Structural Properties of Germanium (Ge) Quantum Dots .......... 2
   2.2. Ge Quantum Dot Superlattice Growth ................. 9
3. Optical Properties of Ge Quantum Dots ..................... 14
   3.1. Interband Properties: Photoluminescence Studies ........ 14
   3.2. Intersubband Properties ............................ 20
4. Ge quantum dot optoelectronic devices ..................... 22
   4.1. Ge Quantum Dot Light Emitting Diodes ............... 22
   4.2. Near-Infrared p-i-n Ge Quantum Dot Photodetectors Operating at 1.31–1.55 μm ......................... 24
   4.3. Mid-Infrared Ge Quantum Dot Photodetectors Operating at 3–5 μm .................................... 26
5. Summary ......................................... 29
References ........................................ 29

1. INTRODUCTION
Since the invention of successful hetero-epitaxial growth techniques, such as molecular beam epitaxy (MBE) and ultra-high vacuum chemical vapor deposition (UHV-CVD), there have been tremendous efforts in Si-based SiGe microelectronics. Individual devices with high performances have been fabricated [1–6]. The effort on the research of Si-based photonic components for 1.3–1.55 μm fiber-optic communications and 3–5 μm telecommunication, however, is much smaller in scale. This is due to the fact that some intrinsic physical properties of Si and/or Ge, in particular the nature indirect bandgap, pose an obstacle to the
Self-Assembled Ge Quantum Dots on Si and Their Optoelectronic Devices

realization of photonic devices [7]. Today, the primary devices in optoelectronic integrated circuit (OEIC) technology are still based on III-V semiconductors like AlGaAs/GaAs and InGaAsP/InP.

The main goal of investigating Si-based photonics is to integrate optic and electronic devices on a Si substrate by using low-cost and well-developed Si VLSI technology. Such an integrated circuit will have greater performance and functionality than those of separated optical and electrical circuits. A simple Si-based OEIC chip consists of electronic devices, such as heterojunction bipolar transistors and modulation-doped field effect transistors, interconnects, such as optical switches, waveguides, and photodetectors, and optical devices, such as laser diodes and optical amplifiers with heterogeneous integration of epitaxial growth of InAs light sources on Si [8]. Former research work has shown that infrared light (\(\lambda > 1.2 \, \mu m\)) can be waveguided, emitted, modulated and switched in Si, and the technology of the fabrication of low-loss waveguide has been super based on Si on insulator (SOI) substrates or epitaxial Si [9]. The challenge in the Si-based OEIC technology still exists in the fabrication of room temperature Si-based light sources and fast photodetectors with low noises in the spectral region of 1.3 and 1.55 \(\mu m\).

Mid- and far-infrared detectors which detect lights in the region of 3–5 \(\mu m\) and 8–12 \(\mu m\) have applications in pollution monitoring, thermography, and telecommunication. Previously, quantum well infrared photodetectors were developed using intersubband transitions between confined states for those applications [10, 11]. A major limitation of such devices is the weakness of normal incidence absorption because of the selection rules. Quantum dots have an intrinsic capability of normal incidence detection because the confinement potential is three-dimensional. Theoretical calculations also predicted a reduced dark current and higher electric gain in quantum dot system compared with quantum well photodetectors [12].

Towards the goal of fabricating Si-based efficient light sources and fast detectors, self-assembled Ge quantum dots grown on Si by MBE and CVD were considered as one of potential materials of choice. The size of the Ge dots (40–80 nm in base diameter and 3–10 nm in height) is on the order of the electron wavelength and thus the discrete energy levels are formed. The ability to form the energy-quantized islands without any artificial masking and patterning (by self-assembly) and their compatibility with the current Si technology provide a great deal of potentials for the fabrication of novel devices on Si, such as lasers and photodetectors.

The self-assembled dots are known to form during epitaxial growth in the Stranski-Krastanov growth mode, which was first investigated by Stranski and Krastanov six decades ago [13]. After that, a great deal of effort has been attempted in order to increase the critical thickness and to form smooth thin films in heterostructure growth. The critical thickness is only several atomic monolayers for pure Ge growth on Si (100) [14], beyond which islands form and/or dislocations generate. For almost five decades, people were keeping on discarding those samples and it was not until the formation of coherent self-assembled Ge dots in the early 1990s [15, 16], people started to realize that these quasi-zero dimensional structure may have potential applications in optoelectronics. Since then, there have been thousands of papers published which related to self-assembled semiconductor quantum dots.

This review paper mainly deals with the research on the growth of Ge quantum dots on Si (100) and their optoelectronic properties. The paper is organized as follows: First, we will report the growth of single-layered and multi-layered quantum dots and their corresponding mechanisms. Then, we describe the results of near-infrared properties of Ge quantum dots by photoluminescence studies, followed by mid-infrared properties of boron-doped Ge quantum dot superlattices. In the end, optoelectronic devices based on Ge quantum dots are reported.

2. STRUCTURAL PROPERTIES OF GERMANIUM (Ge) QUANTUM DOTS

2.1. Single-Layered Ge Quantum Dots on Planar Si

The dot formation via the Stranski-Krastanov mode, begins with layer-by-layer growth followed by island formation. The key driving force for the dot formation is the 4.16\% mismatch between the Si and Ge lattice constants. At the beginning of the growth of Ge on Si, misfit
Self-Assembled Germanium Quantum Dots on Si and Their Optoelectronic Devices

Figure 1. Epitaxy of Ge on Si process. The Ge film growth begins with the 2D growth mode. When the film exceeds its critical thickness of several monolayers, the Ge islands are formed. A bi-modal distribution, i.e., the coexistence of pyramids and domes is typical for the deposited Ge thickness smaller than 20 Å, beyond which the Ge islands coalesce to form a 2D film with dislocations and rough surface.

strain is built up and fully accommodated. Once the Ge film thickness exceeds its critical thickness of a few monolayers, the strain starts to relax by forming small pyramidal islands, and the film becomes rough. Those small islands may evolve to large domes after continuing Ge deposition. When Ge deposition exceeds 20 Å or so, misfit dislocations and threading dislocations form to relieve the additional strain arising from the accumulation of the film thickness [17]. A schematic illustrating this process is shown in Fig. 1.

In this section, we present some results of Ge quantum dot growth by MBE. Throughout this paper, Si (100) substrate is assumed. Figure 2(a) presents a typical AFM image of self-assembled Ge dots. The nominal Ge thickness is 16 Å. The growth temperature is 550 °C. One can clearly see that there are two kinds of Ge dots. The smaller dots are square-based pyramids with four \{105\} facets, and the larger dots are multi-faceted domes (shown in Fig. 2(b)).

The strain-related dot formation can be cross-checked by the incorporation of the impurities or dopants into dots. Figure 3 shows AFM images of three samples. The growth conditions are the growth temperature of 550 °C, the growth rate of 0.2 Å/s, and the Ge deposition thickness of 15 Å, except that Fig. 3(a) is for non-doped, Fig. 3(b) is for B-doped, and Fig. 3(c) is for Sb-doped. The doping density was $5 \times 10^{18}$ cm$^{-3}$ in both cases. The difference of the dot size distributions is apparent. In non-doped case, most of the dots are domes while some of them are square-based pyramids with the base orientation along [100] and [010] directions. The dot density is estimated to be about $8 \times 10^{9}$ cm$^{-2}$. The average diameter of the dot base is around 64 nm and the height is about 12 nm for this particular case. For the B-doped sample, the dot density around $4 \times 10^{9}$ cm$^{-2}$ is lower than that without doping. The typical dot size is 72 nm in base diameter and 11 nm in height, i.e., larger base and lower height than that of the non-doped sample. For the Sb-doped sample, the dots become smaller and much denser with an areal density of around $5 \times 10^{10}$ cm$^{-2}$. The change of the dot morphology and the density can be explained by the well-known growth

![Figure 2](image-url) (a) 2D AFM image of typical bi-modal Ge dots including square-based pyramids and multi-faceted domes; (b) 3D AFM images of a pyramid (top) and a dome (bottom).
Self-Assembled Ge Quantum Dots on Si and Their Optoelectronic Devices

Figure 3. AFM images of (a) non-doped, (b) B-doped, and (c) Sb-doped Ge quantum dot sample. All three samples contain 15 Å Ge deposition at 550°C. The difference in dot density is evident.

mechanism of Ge islands on Si. In the B-doped case, a flattening effect, i.e., somewhat larger base and smaller height compared with that of undoped dots, is observed. This is due to the smaller atomic size of boron compared with Si and Ge. The incorporation of boron in Ge compensates the compressive strain in Ge and reduces mismatch, leading to the increase of the critical thickness of the growth mode changeover [18]. This explains the density reduction of Ge islands in doped case. To relieve the reduced strain in doped Ge, the Ge dots change to smaller-curvature, or flattened dots. It should be noted that a completely different result was obtained for formation of Ge dots when boron was pre-deposited [19, 20]. In the latter case, higher-density, smaller Ge dots were obtained. In these cases, the driving mechanism of Ge dot formation was not by B in Ge but by B on Si. This result is similar to the case of the carbon pre-deposition [21]. Since the atomic size of B is small compared to that of Si, B atom is likely to cause atomic-scale rough surface, i.e., step instability, resulting in a high-density preferential sites for Ge dot growth.

For the Sb-doped sample, on the contrary, the incorporation of larger-atomic-size Sb in Ge increases mismatch between Ge and Si, leading to the reduction of the critical thickness. In order to relieve the larger strain in this case, the curvature of dots becomes larger compared to the non-doped case, leading to high-density and small dots. For Sb pre-deposition, similar dot change, i.e., smaller size with higher density, was observed [22], and the reason is similar to that of the B pre-deposition case described in the above. For another n-type dopant P in Ge, a contrary result to the Sb case was evidenced, i.e., an overall increase in size and nonuniformity of the dots [23], which can be again explained by strain-related dot formation mechanism as a result of the smaller-atomic-size P incorporation in Ge. On the whole, the doping experiments described in the above reveals a self-consistent dot formation mechanism.

The observed bi-model distribution of Ge dots is a typical experimental result for Ge dot growth on Si (100) [24]. However, it takes several years to understand the bi-model distribution formation mechanism. Shchukin et al. [25] proposed a thermodynamic model that there are minima in the free energy of self-assembled dot ensembles, resulting in a stable Boltzman size distribution. This model was proved by the scanning tunneling microscopy measurements of the dot size distribution [26]. On the other hand, Ross et al. [27] studied the evolution of self-assembled Ge dots by real-time low energy electron microscopy and found that the size of large dots increased at the expense of small dots and concluded that it was a kinetic process driven by an Ostwald ripening effect. Kamin's et al. [28] has also quantitatively studied the formation of the bi-model distribution of Ge dots and conducted annealing experiments to distinguish the stages of the two mechanisms, i.e., Ostwald ripening and equilibrium distribution. They found that dot evolution was impeded with increasing annealing time at 550 and 600°C and it would finally reach an equilibrium distribution.

To better understand the dot evolution process, we have performed the areal density of dots as a function of post-growth holding time, which is the time interval between the stopping the deposition and the reduction of the temperature. Figure 4 illustrates the result of this study. The dot density decreases nearly exponentially at the beginning and the dot change slows down with increased holding time, in consistent with Kamin's annealing study.
Figure 4. Areal dot density versus the holding time for dot samples grown at the growth temperature of 575 °C. The solid line is a simple exponential decay fitting, showing that the time constant is 2.3 minutes.

[29]. This suggests that at the beginning, the density decreases with holding time, which is due to the dominance of Ostwald ripening, and after about 5 minutes, the dot density reaches a final stable density, suggesting there is a kinetically limited mechanism.

Bi-modal distribution was an overwhelming morphology, however, other kinds of dots could also be observed. For example, with a relative thick Ge coverage, superdomes were observed [30]. In another situation, i.e., for a prolonged growth at high temperature, such as 700 °C, larger pyramidal dots with flat top (or truncated pyramids) were observed [31]. The size distribution of the dots was then referred as to a tri-modal (or multi-modal) distribution. In our studies, we found the Ge deposition rate effect on the formation of the super-dome dots. Figure 5 shows an AFM image of a sample grown at the Ge deposition rate of 0.5 Å/second. Ge thickness was 1.5 nm. The growth temperature was 540 °C and the post-holding time was 2 minutes. Besides the round-shaped domes and the square-based

Figure 5. AFM image of a Ge quantum dot sample grown at 540° C on Si (100). The nominal Ge thickness is 15 Å. The growth rate is 0.5 Å/second. In addition to normal domes and pyramids, some super-size islands (super-domes) are present.
Self-Assembled Ge Quantum Dots on Si and Their Optoelectronic Devices

Pyramids, superdomes are evident. These superdomes are in reality the combination of several smaller dots. The formation of the superdomes suggests that the diffusion of Ge atoms on the surface to other sites is a kinetically limited process.

The bi-modal or multi-modal distributions of dots in Ge/Si(100) system are, in reality, not desirable. A narrow distribution or high uniformity is essential for many potential applications. The uniformity of the dots has been found to depend critically on the growth parameters, such as growth temperature, growth rates, Ge deposited coverage, post-growth holding time, and substrate orientation type. For example, Ross et al. [32] observed a narrow size distribution on planar Si (100) substrates by prolonging the growth time after nucleation. Jin et al. [33, 34] observed the formation of a mono-modal distribution of Ge dots on Si mesas formed with selective epitaxial growth. Here, we show the studies of the growth temperature influence on the formation of the self-assembled Ge dots while the other growth parameters were kept fixed for comparison. All of the samples had a Si buffer of 100 nm and 16Å Ge was deposited on top at the temperature between 500 and 700°C with a deposition rate of about 0.1 Å/seconds. The post-holding time was about 2 minutes.

Figure 6(a) shows a two-dimensional AFM image of the highly uniform self-assembled Ge dots on Si (100) substrate at a growth temperature of 600°C. Figure 6(b) is its three-dimensional view. The dots are all dome-shaped with the base size and height of about 70 nm and 15 nm, respectively. The areal density of the dots is about $5 \times 10^{10}$ cm$^{-2}$ and the height deviation of the dots is about ±3%. The formation of the highly uniform distribution of the Ge dots at 600°C is believed to attribute to the enhanced diffusion at a higher growth temperature [35].

Figure 7 shows the AFM images of the self-assembled Ge dots at various temperatures from 500 to 700°C. For growth below 500°C, the dot formation is kinetically suppressed [36] and elongated islands are frequently seen [37]. At the growth temperature of 550°C (Fig. 7(b)), one can clearly see two kinds of Ge dots, pyramids and domes, which are of a typical bi-modal distribution. At the lower temperature of 500°C (Fig. 7(a)), the pyramids are dominant. As the growth temperature increases up to 600°C (Fig. 7(c)), the number of pyramids decreases and finally disappears, and all the dots are dome-shaped and the size distribution becomes narrower, leading to a mono-modal distribution. As the temperature increases further to 650°C and 700°C (Fig. 7(d) and 7(e), respectively), the size of the domes becomes larger and the pyramids re-appear. Moreover, these pyramids at higher temperatures are larger than those at lower temperatures. Besides the pyramids and domes, very small pyramids, whose height is in the range of 2–4 nm, appear. They might be the precursors of the larger dots [38].

Figure 6. (a) 2D AFM image of the uniform self-assembled Ge dots on a planar Si (100) substrate at the growth temperature of 600°C. The Ge thickness is 1.6 nm. The base size and the height of the dots are about 70 nm and 15 nm, respectively, and the best standard deviation of the dot height is about ±3%. (b) The corresponding 3D AFM image.
Figure 7. 2D AFM images of the Ge dots on planar Si (100) substrates with various growth temperatures. (a) \(T_g = 500\,^\circ\text{C}\), (b) \(T_g = 550\,^\circ\text{C}\), (c) \(T_g = 600\,^\circ\text{C}\), (d) \(T_g = 650\,^\circ\text{C}\), and (e) \(T_g = 700\,^\circ\text{C}\). The scale for the top three images is 0.8 \(\mu\text{m} \times 0.8 \mu\text{m}\) and 2 \(\mu\text{m} \times 2 \mu\text{m}\) for the bottom two images.

Figure 8 plots the number ratio of the pyramids to the domes versus the growth temperature. It is interesting to note a nearly symmetric behavior with the center temperature at 600\,°C. As the temperature increases from 500\,°C, the ratio of the bi-modal dots reduces and reaches a minimal value at about 600\,°C, and then increases again beyond this temperature. The optimum growth temperature for the formation of the mono-modal distribution of the Ge dots occurs at 600\,°C and is attributed to the enhanced diffusion kinetics at higher growth temperature [39]. Specifically, the dot size increases as the temperature increases due to diffusion, leading to the accommodation of larger strain in the dots, especially, at the dot edges. The large edge strain suppresses the further increase of dot size, leading to the self-limited size [40, 41], i.e., mono-modal distribution. On the other hand, the intermixing may occur and becomes pronounced as the temperature increases beyond 650\,°C [42], which results in the modification of the interface strain distribution, and thus leads to the re-occurrence of bi-modal dots. Due to the intermixing of Si with Ge, the wetting layer is no longer a pure Ge layer, but a SiGe-like layer, and then the lattice mismatch becomes smaller than 4.16\%, and the strain energy is thus reduced leading to the larger pyramids at higher temperatures (as shown in Fig. 7(d),(e)) [43]. Meanwhile, the relaxation of the strain at the
edges will cause dislocations, which exaggerate the intermixing by lowering the intermixing barrier. However, at lower temperatures (≤550°C), the diffusion is limited and impedes the formation of uniform dots.

For better understanding of the temperature effect on the dot density, we measured the areal dot density including pyramids and domes, but excluding the small precursors at high temperatures, which is only a very small portion of the total Ge amount. Figure 9 gives the areal density of the dots versus growth temperature. As the temperature increases, the areal density monotonously decreases. The nucleation density presumably only depends on the surface diffusion if we neglect the surface defects, steps and other external nucleation centers. This assumption is reasonable since the samples were cut from the identical wafer and treated with the same processes. The relation between diffusion length \( L_d \) and temperature \( T \) can be expressed as

\[
L_d^2 = \frac{D}{S} \tau = \frac{D_0}{S} \cdot \exp\left(-\frac{E_a}{kT}\right),
\]

where \( D \) is diffusion coefficient, \( E_a \) is activation barrier, \( \tau \) is diffusion time, and \( D_0 \) is a prefactor constant. From the relation, \( L_d \) is expected to increase with the increase of temperature.

In order to clarify the dependence of dot density on temperature, we calculated the values of the average dot spacing (or called the characteristic length) \( L_c \) based on our experimental results, which was defined as the inverse of the square root of the areal density \( (L_c = 1/\sqrt{\sigma}) \). Figure 10 plots the Arrhenius relation of the average dot spacing \( L_c \) versus the growth temperature. It is found that a discontinuity of \( L_c \) occurs at a temperature of 600°C with two slightly different slopes, corresponding to the activation energies of 0.88 eV and 0.91 eV.
self-assembled germanium quantum dots on Si and their optoelectronic devices

Figure 11. Bright-field cross-sectional TEM image of a ten-period Ge quantum dot superlattice sample. The nominal thickness is 1.5 and 20 nm for Ge and Si, respectively. Vertical correlated dots are evident.

and 0.91 eV, respectively. These suggest that diffusion is not the only driving force for determining the dot density at higher temperatures. (If the diffusion is the only driving force, \( L_c \) will show a continuous increase with temperature.) Intermixing of Si with Ge taken place at the temperature of above 600°C [44, 45] is responsible for the observed discontinuity. The change of activation energy also indicates the change of the mechanism from enhanced diffusion at lower temperatures to the intermixing of Si with Ge at higher temperatures investigated [46].

In summary, single-layered self-assembled Ge quantum dots were formed by Stranski-Krastanov mode. The morphology of Ge quantum dots is directly related to growth conditions. Uniform mono-modal quantum dots can be obtained by properly controlling these growth conditions.

2.2. Ge Quantum Dot Superlattice Growth

For many practical applications, multi-layered Ge quantum dots are important. An interesting feature observed in the multi-layered dot structures was that the dots in the upper layers tended to grow on top of the buried ones or there was a vertical correlation [47-52]. Figure 11 shows a typical cross-sectional TEM image of a sample with 1.2-nm-Ge thick Ge quantum dot superlattice separated by 10-nm-Si spacers. Ge quantum dots appeared as dark features in the TEM image are observed on top of two-dimensional Ge wetting layers, indicating Stranski-Krastanov growth mode. The density of the dots is determined to be \(3 \times 10^9 \text{ cm}^{-2} \) and the average dimension of the dots is 11.9 nm in height and 110 nm in base diameter. It should be noted that as expected, these dots are vertically correlated.

Vertical ordering of islands in multilayers was also observed in InAs/GaAs systems [53, 54]. For SiGe/Si (100) system, it has been shown by AFM that islands undergo a transition from a broad size distribution in a single SiGe layer to intraplanar size equalization in a SiGe/Si multi-layered structure [55]. A model based on elastic continuum theory was proposed and established that the origin of the vertical correlation of the islands in successive layers is attributed to preferential nucleation due to an inhomogeneous strain field induced by buried dots [56]. In this model, the authors calculated the surface strain using continuum elasticity theory [57]. The quantum dots embedded are treated as spherical inclusions in an isotropic elastic matrix, and are assumed to be small relative to their lateral and vertical separation. It was found that an island buried at a depth \(L\) (Si spacer layer thickness) and lateral position \(x = 0\) leads to surface strain \(\varepsilon\) at lateral position \(x\), where:

\[
\varepsilon(x) = C(x^2 + L^2)^{-3/2} \left[ 1 - 3 \frac{L^2}{(x^2 + L^2)} \right]
\]

The coefficient \(C\) is proportional to the volume of the buried island and to the misfit. The island nucleation at the surface occurs at each local minimum in misfit strain. An interesting result by this model is that, for successive layers, the island size and spacing becomes progressively more uniform. Regardless of the initial condition, after many layers the lateral island spacing is about \(3.5L\). It should be noted that this model is only valid when no dislocations are involved. When more layers are grown and the total thickness exceeds
its effective critical thickness, the quantum dot morphology will be different from the results predicted by this model, as will be shown in the following.

The strain-related vertical correlation is obviously related to spacer layer thickness. Therefore, the change of Si spacer layer thickness has an influence on the distribution of the misfit strain at the surface and the degree of vertical correlation. On the basis of TEM measurements, Rahmati et al. [58] investigated multi-layered dot structures grown by LPCVD and found that the strain field from the buried islands is too weak to induce vertical correlation when the Si spacer layer thickness is greater than 100 nm. This number drops to 70 nm in multi-layered structures grown by solid source MBE [59]. Kienzle et al. [60] also found small Si interlayer thickness leads to a high degree of island position alignment but causes rapid coarsening of the islands, i.e., the increase of the average island size with increasing the number of deposited layers. The reason of coarsening was related to the decrease of the Ge wetting layer thickness in the upper layers of a multi-layered structure [61]. Such an evolution of the Ge wetting layer thickness arises from an accumulation of elastic strain in the Si spacer layers induced by the lower Ge layers. The increasing non-uniformity of dots in different layers due to coarsening effect is a limitation for many applications. In order to minimize the coarsening effect, Thanh et al. [62] grew narrow-size distributed quantum dot superlattices by continuously decreasing Ge coverage in upper layers.

To the best of our knowledge, however, the coarsening effect only occurs in the first several periods and is not evident afterwards. Figure 12(a) shows a 22-period multi-layered dot structure. The nominal Si and Ge thickness is 20 nm and 1.5 nm, respectively. The sample was grown at 600°C. The coarsening for the vertically correlated dots is clearly observed for the first 6–7 dot layers. After that, the dots show no significant change in size. Figure 12(b) is the AFM image of the 22nd dot layer. High-uniform dots are observed. The strain distribution on the Si spacer surface in the successive layers becomes more and more uniform as the increase of the period. The strain distribution as a function of the number of layers shows exponential relationship, which can be derived from Eq. (??) and also shown in the reference [63], leading to the rapid elimination of the coarsening effect.

Though coarsening effect is minimized with many periods, more layers of superlattice lead to strain relaxation. The critical thickness of heteroepitaxial SiGe alloy on Si was widely studied and may be seen in the reference [64]. Due to the different lattice constant between epitaxial SiGe and substrate Si, the strain is built in the film, which is fully strained until reaches its critical thickness, beyond which the dislocations are formed to relieve accumulated strain. The critical thickness of SiGe/Si quantum well superlattice on Si was found to be similar to SiGe alloy on Si with the equivalent Ge content obtained by considering the nominal thickness of SiGe and Si [65, 66].

![Figure 12. (a) TEM image of 22-period Ge quantum dot superlattice. The coarsening effect is evident for the first 6–7 bilayers, after which it is not evident at all. (b) The top surface shows uniform Ge quantum dots.](image-url)
In the quantum dot superlattice system, the situation becomes somehow complex. After Ge exceeds its critical thickness of several monolayers, the rest of Ge deposited relaxes by forming quantum dots. To understand critical thickness for quantum dot superlattice, similar to quantum well superlattice, the equivalent Ge content should be determined. In this case, a question is whether Ge wetting layer thickness or nominal deposited thickness should be taken into account. In order to clarify this, TEM investigations were performed. Figure 13 shows cross-sectional TEM images of the four samples. These samples were grown at 540°C with the Ge and Si nominal thickness of 1.5 nm and 20 nm in each period, respectively. The difference was the superlattice period. These are 10-period, 20-period, 35-period, and 50-period sample. Coherent vertical-correlated Ge dots were observed for the 10, 20, and 35-period samples. For the 50-period sample, however, high-density dislocations were generated when the film reached the 25th period. The dislocations then penetrated to the rest of layers on top. The equivalent Ge content by taking into account nominal Ge thickness was 7% in the samples. The total thickness of the first 25 periods was approximately 0.5 μm. From both theoretical and experimental results of the critical thickness of SiGe alloy and SiGe/Si superlattice on Si [67–69], SiGe alloy with 7% Ge is more possible to fully relax at

![Figure 13. Cross-sectional TEM images of (a) 10, (b) 20, (c) 35, and, (d) 50-period Si(20 nm)/Ge(1.5 nm) superlattice samples. Vertically correlated dots are observed for 10, 20, and 35-period samples. For the 50-period sample, dots are still vertically correlated but the high-density dislocations are evident.](image-url)
0.5 \mu m and generate high-density dislocations, while SiGe alloy with 2.9% Ge (taking the wetting layer thickness of about 0.6 nm into account only) is still fully strained or at most partially relaxed. Therefore, we believe that the nominal Ge thickness rather than wetting layer thickness only contributes on the strain accumulation and determines the film critical thickness, even though misfit strain in each layer is partially relaxed by the formation of the dots. It should be noted that no threading dislocations were observed in the cross-sectional TEM image for 35-period sample as high-resolution TEM characterization could not catch any threading dislocation with the density less than $10^7 \text{ cm}^{-2}$. Therefore these samples with 20 or 35 periods are only at most partially relaxed. This is confirmed by PL studies as it shows indeed dislocation related luminescence peaks in these samples in the following section.

To see a clearer picture of the strain distribution and the evolution of the dot morphology, these samples were characterized by AFM. Again, these samples were grown at 540°C and consisted of 100 nm Si buffer followed by superlattices with Si(20 nm)/Ge(1.5 nm) in each period. These samples have 1, 2, 5, 10, 20, 35, and 50 periods, respectively. Figure 14 shows the AFM images of the top surfaces of the Ge quantum dot superlattice samples with different periods of 2, 5, 10, 20, 35, and 50. The increasing uniformity as the increase of the period (less than 35 periods) is clearly observed. Moreover, the surface under the dot layer for samples with the period less than 35 is reasonably flat while for 50-period sample, the surface under the dot layer shows clearly circular holes, which are induced by the threading dislocations.

Figure 15 shows 2D and its corresponding 3D AFM images of magnified local area near some dislocation-induced pits on the surface of the 50-period sample, respectively. A circular hole with Ge dots arranged at its edge is clearly observed in the center of the images. It should be noted that there are also elongated holes on the surface due to the piles-up effect from more than one threading dislocation. By counting the pits on the surface, the density is around $10^8 \text{ cm}^{-2}$, which is similar to threading dislocation density characterized in previous TEM measurements. The Ge atoms deposited near to these holes preferably diffuse to form dots at their edges as shown in these images. This phenomenon is similar to the formation
Figure 15. (a) 2D and 3D AFM images of magnified area of the 50-period sample, respectively. A circular hole in the center and an elongated hole due to the effect from more than one dislocation were observed with dots nucleated at their edges.

of SiGe islands at the edge of the rectangular-shaped pits induced by embedded carbon [70]. At the edge of each of dislocation-induced holes, the convex curvature of the Si lattice results in a larger local Si lattice constant, therefore reducing the mismatch between Si and Ge and providing an energetically favorable site for Ge nucleation [71]. The dots near to these holes tend to nucleate at the edge.

Figure 16 shows the quantum dot density and root-mean-square dot height relative to average dot height (non-uniformity) as a function of the number of bilayers. The density of the sample with only one Ge layer is estimated to be $8 \times 10^9$ cm$^{-2}$. The density decreases dramatically as the period increases and saturates to about $2 \times 10^9$ cm$^{-2}$ when the number of periods reaches 20. After 35 periods, the density increases slightly, indicating a change in the growth mode or the generation of threading dislocations, which provide additional sites for nucleation of the Ge dots. The solid circle symbols are experimental root-mean-square variation of dot height relative to average height $\Delta H/\langle H \rangle$ for different samples. The selection of height rather than base or volume of the dots to represent the size uniformity

Figure 16. Ge quantum dot density and root-mean-square height relative to average height as a function of the period for Si(20 nm)/Ge(1.5 nm) superlattices. The density decreases dramatically as the period increases and saturates to about $2 \times 10^9$ cm$^{-2}$ when the period reaches 20. After 35 periods, the density increases slightly. For the dot height characterization, the increasing uniformity with the superlattice period less than 35 is observed. After 35 periods, the uniformity becomes worse. The trend of the data for both density and height of the dots suggests the change of the growth mode or the generation of threading dislocations in the thick samples.
of the dots is due to the non-trivial determination of real base value of a dot associated with the AFM tip effect. The increasing uniformity with the superlattice period less than 35 is evident, which is a result of the increasing uniformity of misfit strain distribution at the upper layers predicted by elastic continuum model, where no defects and dislocations were assumed [72]. It should be noted that in the 20 and 35-period samples, there are already a few dislocations due to partial strain relaxation, but the effect of the small amount of dislocations is not enough to degrade the uniformity until after 35 periods, the uniformity becomes worse, indicative of the generation of very high-density threading dislocations, as observed in AFM and TEM measurements.

In summary, vertical correlation is observed and analyzed in our Ge quantum dot superlattices. Coarsening effect was observed and minimized when more periods were introduced. Even more periods of superlattice lead to the strain relaxation of the film. The dot morphology such as uniformity and density change after the strain is relaxed by forming dislocations.

3. OPTICAL PROPERTIES OF Ge QUANTUM DOTS

3.1. Interband Properties: Photoluminescence Studies

The understanding of interband optical properties is important for near-infrared optoelectronic applications. Figure 17 shows low-temperature photoluminescence (PL) spectrum at 4.2 K for a typical dot sample, which consists of 10-period Ge dot/Si (20 nm) superlattices. Peaks at 1.153, 1.132, 1.095, 1.061, and 1.027 eV are presumably originated from Si and they correspond to non-phonon (NP) replica, transverse acoustic (TA), transverse optical (TO), 2TA+TO, and TO+O peaks, respectively. The broad peak with a peak energy at 0.963 eV is associated with the Ge wetting layers. The peak at 0.771 eV is from the Ge quantum dots. The inset shows the possible mechanism for the NP peak arising from the Ge quantum dots. The Ge/Si quantum dot system has been shown to have a type-II band alignment. The radiative recombination occurs between electrons in the Si layers and holes confined in the Ge dots, giving rise to the Ge quantum dot peak in the PL spectrum. To the 1st order estimation, the energy of the ground state is mainly determined by the height of the dots. The lateral sizes of our dots are more than 110 nm and they provide features similar to 2D films.

The type-II band alignment of the Ge/Si quantum dot system is assessed from the power dependence of quantum dot NP peak. The power-dependent PL measurements have been widely used to study the band alignment of the GeSi quantum dots [73–75], SiGe/Si quantum well [76,77], and III–V heterostructures [78]. For type-II band alignment as in the Ge/Si system, a dipole layer forms due to the fact that the holes are confined in the GeSi layer while electrons are confined outside. Then a band bending occurs at the interfaces due to the Hartree potential. At higher excitation power levels, additional electrons
and holes are induced, resulting in a higher Hartree potential, which increases the energy separation of the electron and hole states and results in the blueshift of the PL band [79].

Figure 18(a) shows a set of PL spectra measured at 4.5 K with different excitation power levels for the same sample (shown in Fig. 7). Apart from the Si peaks, each spectrum consists of two separate peaks at around 0.77 eV and 0.96 eV, which are characteristic of the Ge dots and the Ge wetting layers, respectively. Figure 18(b) is a plot of the excitation power dependence of PL peak energies and integrated PL intensity of the Ge quantum dots. The quantum dot NP peak indeed shows a blue shift of 9 meV with increasing excitation power from 30 to 200 mW. Figure 19 shows the schematic of the band structure change at different excitation powers. It should be noted, however, that in the case of type-I band alignment, band filling at a higher excitation power could only lead to a small blue shift of the PL peak of usually at most 2 meV [80]. The present substantially large blue shift of the PL band with the increase of excitation power indicates a type-II band alignment for the present Ge dot system.

Type-II band alignment can also be understood from the power dependence of the integrated quantum dot PL peak intensity as shown in Fig. 18(b). The dependence can be calculated based on the formula $I = P^m$ [81], where $I$ represents the normalized PL intensity and $P$ is the normalized excitation power. The coefficient $m$ decreases somewhat as the excitation power increases. For power levels greater than 150 mW, the $m$ is determined to be 0.73. This phenomenon is the typical saturation effect for the type-II band alignment.

Figure 18. (a) PL spectra of the Ge quantum dot superlattice sample (shown in Fig. 11) measured at 4.5 K with different excitation power levels, and (b) Peak energy and integrated PL intensity as a function of excitation power.

Figure 19. Schematic of band diagram of Ge quantum dot superlattice at different excitation power. Type-II band alignment was resolved.
In the type-II interface, the indirect excitons are first localized in the interface, and then recombine. There are high-density interface states in the “rough” interface arising from the formation of the quantum dots. At lower excitation power levels, all electrons and holes generated are captured by the interface states to form excitons, and there are still some interface states unoccupied. When the excitation power increases, more electron and holes are generated and occupy all interface states, which rapidly saturate, leading to the decrease of the sublinear coefficient $m$.

Next, we discuss the size dependence of PL spectra. Figure 20 shows PL spectra of three Ge dot superlattice samples with different Ge dot sizes. Each of sample contains 10-period Si (20 nm)/Ge bilayers. AFM measurements show that the dot heights are 11.9 nm, 14 nm, and 16 nm, while the dot base diameters are 110 nm, 122 nm, and 122 nm with nominal Ge of 12, 15, and 18 Å, respectively, for the three samples. As the dot height increases from 11.9 nm to 16 nm, the NP peak of the quantum dots shifts 28 meV to the low energy side along with a decrease in integrated peak intensity. The latter facts further support the argument in favor of the type-II band alignment for the Si/Ge dot system. In a type-II structure, the holes and electrons are separated in the Ge and Si, respectively. As the dot size decreases, the hole wave function penetrates more into the Si layer; likewise, the electron wave also penetrates into the Ge dot. The overlap of these wave functions becomes more significant, leading to a larger oscillation strength. Figure 21 shows the mechanism for the dot peak energy shift. The shift is mainly due to the fact that the quantized ground state energy decreases as the size increases.

It is worthwhile to note that interdiffusion (forming SiGe dots) and strain may also be responsible for determining the quantum dot PL energy, in addition to size confinement [82]. The strain distribution in and around the dots and their dependence on growth conditions are difficult to be characterized. The degree of the Si/Ge interdiffusion, however, can be precisely controlled by annealing. Figure 22 shows PL spectra of as-grown and annealed samples measured at 4.5 K. The as-grown sample contains of 100 nm Si buffer layers followed by ten layers of dots separated by Si spacer layers grown at the temperature of 575°C. The thicknesses of the Ge and the Si spacer layer are 1.6 and 40 nm, respectively. The annealing experiments were done for 5 minutes for different pieces of the same sample by varying temperature between 650°C and 900°C using rapid thermal annealing (RTA) in a nitrogen gas ambient. In the PL spectrum of the as-grown sample, apart from the Si peaks, each spectrum has two separate components which are characteristics of the wetting layers and the GeSi dots, respectively. The broad PL peak of the dots could be deconvoluted into two Gaussian line-shaped peaks and are attributed to the NP transition and TO replica (NP$_{\text{dot}}$ and TO$_{\text{dot}}$). After thermal annealing, the PL peaks shifted to higher energies due to the Ge/Si interdiffusion and the broad dots PL peaks evolved into two well separated peaks. For
the sample annealed at 900°C, the PL from the wetting layer becomes invisible and only PL peaks from the dots and the Si substrate are seen. TEM measurements showed for the as-grown sample, the average base and the height of the dots are 80 and 14 nm, respectively. After annealing, due to the Ge/Si interdiffusion, the average base and the height of the dots increase to 100 and 30 nm, respectively. This suggests that the quantum confinement effect is small in both as-grown and annealed cases and the increase of the peak energy is mainly due to the Si/Ge interdiffusion. Figure 23 shows a schematic band diagram regarding to the annealing effects. The band gap of the dots increases as stronger interdiffusion is anticipated in the samples annealed at higher temperature. Accordingly, the hole ground state is farther away from the conduction band edge.

PL studies may be used to infer oscillation strength of the quantum dot NP peak at various temperatures. Figure 24(a) shows PL spectra of the 12 nm high Ge quantum dot sample (the same as that in Fig. 11) at different temperatures. The excitation power is kept at 30 W/cm² during the measurements. The luminescence arising from the wetting layers disappears around 40 K. In contrast, the PL signal related to Ge dots persists up to 260 K. Figure 24(b) shows the integrated intensity and peak position of the dot PL peak as a function of temperature.
function of temperature. The integrated intensity at 260 K is only reduced by a factor of 10 as compared to low temperature spectrum at 20 K. We can explain this temperature dependence from the formula $I(T) = I(0)/(1 + A(T) \exp(-E_a/kT))$, where $I$ is intensity, $T$ is temperature, $A(T)$ is the coefficient, $E_a$ is an activation energy, and $k$ is Boltzmann's constant. To the first-order approximation, the temperature dependence of $A(T)$ may be neglected with respect to the strong temperature dependence of $\exp(-E_a/kT)$. For very low temperatures (compared with the exciton binding energy), the quenching of the PL intensity is due to thermalization of excitons. The quenching of the dot PL at higher temperatures is mainly attributed to the thermionic emission of holes from the Ge dots to the Si barrier. The slope of the Arrhenius plot at higher measurement temperature gives the thermal activation energy $E_a$, which is related to the depth of the dot confining potential [83]. In the GeSi dot/Si system, since the conduction band offset of the GeSi on Si is small, this activation energy at higher temperatures mainly reflects the valence band offset between the dots and the Si matrix. For the intermediate temperatures, the PL behavior is complicated because of the influence of the former two mechanisms [84]. From Fig. 24b, the trend of the PL intensity indeed shows two regions with different slopes for the two temperature regions. The activation energy at the higher temperatures is fitted to be 210 meV, the barrier for holes emitting from the ground state of dots to Si.

Figure 23. Schematic of the interdiffusion effect on the band alignment of Ge quantum dot superlattice.

Figure 24. (a) Temperature-dependent PL spectra of the quantum dot superlattice sample with dot height of 12 nm (JL210). The quantum dot peak persists up to over the temperature of 260 K. (b) Integrated intensity and PL peak energy of the dots as a function of temperature.
The dot PL energy exhibits a slight redshift of 10 meV when the temperature increases from 20 to 260 K. Assume there is no change of the band with the temperature, this shift can be due to different sizes of dots. Smaller dots have shallower confinement levels. As the temperature increases, the thermionic emission of the holes occurs first to yield PL. For the larger dots, in which the carriers are more deeply confined, the PL occurs at higher temperature [85].

Figure 25 shows the PL results of a series of samples where the period is the only variable. The growth temperature is at 540°C for all of the samples. Each period consists of Si (20 nm)/Ge(1.5 nm). The detailed structural properties can be also seen in the previous section where we discussed the critical thickness of the Ge quantum dot superlattices. The effect of the period on the quantum dot peak is obvious. Figure 25(b) shows the quantitative summary of the quantum dot peak energy as a function of the number of period. As the period increases to about 10, the peak energy decreases and after that the peak energy increases. This is because before 10 periods, the coarsening effects play an important role and the average dot size increases and therefore the dot peak shows a red shift. After 10 periods, the dots do not show significant change in size. The increase of the peak energy as the increase of the period is due to the strain relaxation of the dots. This could be seen from the spectra that starting from 20-period sample, dislocation related peak D2 at around 0.86 eV shows up. The thicker the superlattice, the more strain relaxation, and therefore the ground state of the quantum dots is adjusted further, leading to the blue shift of the

![Figure 25](image-url)
quantum dot peak. The integrated PL intensity of the quantum dot peak increases as the increase of the period to 35 periods, after that it suddenly decreases. This is another strong evidence of the appearance of threading dislocations as a result of the total strain relaxation.

In summary, PL was used to characterize Ge quantum dot superlattices. Type-II band structures were proved by using excitation power dependence experiment and dot size, measurement temperature, and interdiffusion dependent experiments were studied. The PL on thicker superlattice showed dislocation-related peaks.

3.2. Intersubband Properties

Intersubband properties of Ge quantum dots are of interest for mid-infrared detector applications. In our experiments, samples were characterized by Fourier transform infrared spectroscopy (FTIR). Waveguide structures of 10 mm × 5 mm in size were prepared with polished backsides and polished 45° facets in order to enhance the absorption. A beam condenser was used to focus the infrared beam onto the waveguide. An infrared polarizer was placed in the path of the infrared beam to probe the polarization dependence of the absorption process. A Si substrate waveguide with the same dimensions was used as the reference.

Figure 26 shows the infrared absorption spectra from two samples [86]. Both samples were grown at 600 °C and they consisted of 20-period bi-layers with Si spacer layers and uniformly B-doped Ge layers. The doping density was $5 \times 10^{18}$ cm$^{-3}$. The Ge coverages were effectively 10 Å and 5 Å, respectively. No dots but “wetting layers” were present in the 5-Å-Ge sample. The average dot size in the 10-Å-Ge dot superlattice sample was determined to be about 40 Å in height, and 420 Å in base diameter. The waveguide structure used in the experiment is depicted in the inset of Fig. 26. An absorption peak is seen at around 2000 cm$^{-1}$ (5 μm) for the quantum dot sample while there is no absorption peak for the sample with wetting layers only, suggesting that the 5-μm peak came from the transitions related to the intersubband from the quantum dots. The full widths at half maximum (FWHM) of the absorption peak at 5 μm about 100 meV, and is considerably larger than the intersubband peak width observed in InGaAs/GaAs quantum dot superlattice (~13 meV) [87]. The size nonuniformity of quantum dots is a possible factor. Another reason may be that the nonparabolicity of the hole bands can play an important role in the broadening of the absorption peaks as in the quantum well case [88–90]. Both samples have peaks near 1100 cm$^{-1}$, which are mainly due to the strong infrared absorption by SiO$_2$ and water bands in the spectral range of interest.

Because Raman scattering has related selection rules as FTIR, Raman spectroscopy was also performed to investigate intersubband transitions [91]. Figure 27 shows the polarization-dependent Raman spectra of the dot sample. In the experiment, the incident laser light is focused on the cleaved edge side of the sample. The polarization of the incident and scattered light is parallel to the growth direction (z) or perpendicular to the growth direction.

![Figure 27. Polarization dependence of Raman spectra of the same dot sample characterized in Fig. 26. The peaks at about 1500 cm$^{-1}$ and 1850 cm$^{-1}$ are the second Si optical phonon and the inter-sub-level transition in the Ge dots, respectively.](image-url)
(y). In the polarized spectrum $\langle x(z, z) \rangle$, a peak at about 950 cm$^{-1}$ is attributed to the second-order Si optical phonon mode. One peak at about 1850 cm$^{-1}$ with a FWHM of 100 meV is related to the inter-sub-levels within the valence band of the Ge dots. The considerably large FWHM arises from the size non-uniformity of the quantum dots and the non-parabolicity of the hole bands. Compared with the absorption peak at about 2000 cm$^{-1}$ by FTIR, this peak occurs at about 150 cm$^{-1}$ lower energy, which is due to the depolarization effect [92–94].

In the depolarized spectrum $\langle x(z, y) \rangle$, there are no clear observable phonon peaks in the investigated range because the Si optical phonons in this case are forbidden in principle [95]. The absence of an intersubband transition in the spectrum is due to the fact that the Raman tensor is zero in this configuration according to the selection rules [96, 97].

The observed intersubband transitions in the Ge dots can be compared with the calculated subband energies. Here, we assume a Ge dot is a simple infinite-barrier box, and do not consider exciton-like and depolarization effects. The allowed energies in the dot are simply:

$$E_{n, k, l} = \frac{\hbar^2}{2m^*} \left( \frac{k_x^2}{L_x^2} + \frac{k_y^2}{L_y^2} + \frac{k_z^2}{L_z^2} \right), \quad n, k, l = 1, 2, 3, \ldots,$$

where $m^*$ is Ge hole effective mass. The effective masses used for calculation are $0.30m_0$ and $0.044m_0$ for the heavy and light holes, respectively. $L_x$ and $L_y$ are base dimensions while $L_z$ is the height of the dots. For the dot sample, the first two terms of the equation are omitted because $L_x$ and $L_y$ (42 nm) are much larger than $L_z$ (4 nm). The calculated results show that there are two heavy hole bound states at 78 and 311 meV. The light hole bound states are near the top of the Si barrier potential due to the small effective mass and small dot size, and are not occupied. The energy separation between the first two heavy hole states is 233 meV, which is close to the measured peak energy of 247 meV (5 μm peak). It seems that the observed absorption peak of 5 μm is due to the transitions between the first two heavy hole bound states. Nevertheless, the absorption could also arise from an intraband transition between the dot ground state to the continuum since the line shape was asymmetric, characteristic of a bound-to-continuum transition. In addition, other effects such as valence band mixing, depolarization, and exciton-like shifts may also make precise energy assignment difficult.

The normal incidence detection of intersubband transition for dots is of interest. The polarization-dependent FTIR data of the dot superlattice sample are shown in Fig. 28(a). The waveguide structure with the polarization angle definition is depicted inset. Here, for the 0° polarization angle, there was a 50% component polarized along the growth direction of the structure, while the 90° polarization angle was defined as being parallel to the plane of the layers. The absorption of the Ge quantum dots exhibited a maximum at the 0° polarization angle, which is also the direction of the largest confinement in the dots. The absorption strength decreases as the polarization angle increases. Figure 28(b) illustrates the polarization angle dependence of the absorption spectra of the dots at 5 μm in solid sym-

![Figure 28](image-url)
Self-Assembled Ge Quantum Dots on Si and Their Optoelectronic Devices

The solid line is a typical \( \cos^2 \theta \) polarization dependence for a quantum well grown on Si (100) substrates, in agreement with the well-known feature of intersubband transitions. It can be seen that the trend of the absorption strength as a function of the polarization angle behaves like the quantum-well-like feature. The similar result of the quantum-well-like polarization dependence was reported for the n-doped InAs/GaAs quantum dot system [98] and modulation boron-doped Ge quantum dot system [99]. This is due to the fact that multiple quantum dots are usually flattened in the sandwiched spacer layers [100]. These dots have relatively large base dimensions even though the height is very small, and thus the confinement is strong along the growth direction but weak in the lateral directions. In addition, the dots are in reality alloy-like structures as a result of high-growth temperatures. Thus, the polarization dependence of the intersubband peaks in these dots is similar to that in the quantum wells.

In summary, FTIR and Raman scattering were used to study the intersubband transitions in the Ge dots. Mid-infrared absorption was indeed observed in the dots.

4. Ge QUANTUM DOT OPTOELECTRONIC DEVICES

In the previous sections, we have focused on the growth and optoelectronic properties of self-assembled Ge quantum dots. In what follows, we will show results of several optoelectronic devices based on Ge quantum dots.

4.1. Ge Quantum Dot Light Emitting Diodes

As pointed out previously, the development of optical networks based on wavelength division multiplexing is stimulating the research for low-cost optical components, such as photodetectors and light emitting sources, operating in the near infrared spectral range around the 1.3–1.55 \( \mu m \). One possibility for significant cost reduction is to monolithically integrate these optical components on the same Si chip.

As a matter of fact, several routes have been investigated in the recent years to integrate an optical emitter operating in the region between 1.3–1.55 \( \mu m \) on Si. Room-temperature electroluminescence (EL) of erbium-doped silicon light emitting diodes were reported by several groups [101, 102]. Erbium-based emitters take advantage of the intra-4f shell transitions resonant at 1.54 \( \mu m \). Room temperature electroluminescence resonant up to 1.35 \( \mu m \) was also observed with Si/Ge/Si\(_{1-x}\)Ge\(_x\) quantum well diodes [103]. The study of such short-period superlattices was motivated by the possibility to achieve a quasi-direct band-gap semiconductor by zone-folding. The most serious problem for EL applications for the above-mentioned approaches is the low luminescence efficiency, especially at room temperature. Localization or confinement of electron-hole pairs is one way to increase the efficiency because of the prevention of nonradiative recombination at impurities or defects outside the localizing structures. Self-assembled Ge quantum dots embedded in Si have type-II band alignment structure as shown in the previous PL studies. This suggests that Ge quantum dot in Si may be a better way to achieve higher efficiency at room temperature because of the three-dimensional confinement of electrons and holes in Si and Ge, respectively and extremely long lifetime of the excitons (up to \( 10^{-3} \) seconds) in the indirect band structures of Si and Ge. Indeed, increased luminescence efficiency was observed for self-assembled Ge quantum dots in Si compared with smooth SiGe quantum well layers [104–106]. In this subsection, we show EL studies of our self-assembled Ge quantum dot light emitting diodes.

The structure of light emitting diodes is a pin design, which consists of an intrinsic tensile Ge quantum dot superlattice sandwiched with an n-type Si layer and a p-type Si layer on an n-doped (100) Si wafer with a resistivity of 14–22 \( \Omega \) cm. The growth temperature was kept at 550°C. The sample structure can be described as follows. After an 100 nm undoped Si buffer layer, a 300 nm \( n^+ \) Si layer was grown with an Sb doping concentration of \( 1-2 \times 10^{18} \) cm\(^{-3} \), followed by a 50 nm intrinsic Si. Then 10 layers of Ge dots were grown under the Stranski-Krastanov mode by deposition of 8 monolayers Ge with 20 nm undoped Si barrier layers. A 100 nm undoped Si space layer was followed, and a 100 nm \( p^+ \) Si contact layer was then deposited with a \( B \) doping concentration of \( 5 \times 10^{18} \) cm\(^{-3} \). Mesas were defined.
Self-Assembled Germanium Quantum Dots on Si and Their Optoelectronic Devices

Figure 29. Current–voltage characteristics of the Ge dot p-i-n diode at room temperature. The breakdown voltage is 7 V. The inset is a semi-log plot, showing clearly a dark current of $3 \times 10^{-5}$ A/cm$^2$ at −1 V.

by optical lithography and dry etching with CF$_4$/O$_2$ or wet etching with TMAH. The mesa size is $150 \times 300 \mu$m$^2$. A 220 nm SiO$_2$ isolation layer was deposited by PECVD. An Al/Ti layer was deposited for contact. The wafer was cut and the chips were packaged to TO-5 holders.

An HP4142 instrument was used for dark current measurement. Figure 29 shows the current-voltage characteristics of a typical diode at room temperature. A low dark current of $3 \times 10^{-5}$ A/cm$^2$ at −1 V was obtained and the breakdown voltage was 7 V at room temperature. This was similar to the results of obtained by Splett, where Si/Ge strained layer superlattices were used instead [107]. However, both were much higher than the ideal dark current of pure Si diodes, which was due to an additional generation process in Ge.

The EL was excited with square electrical pulses at low frequency with a 1:1 duty cycle. EL spectra were measured with a liquid-nitrogen cooled Ge photodiode. Figure 30(a) shows EL spectra measured at 77 K as a function of the current density. The peak at around 1.1 μm is NP-Si peak, while the peak at about 1.33 μm is due to the EL from the quantum dots, which may consist of two peaks of NP and TO-assisted. The broad peak at around 1.48 μm may be due to radiative intraband transition [108]. Figure 30(b) shows EL results at room temperature. It shows clearly that the EL peak of 1.33 μm from the quantum dots at room temperature. The results demonstrate the feasible application of Ge quantum dots for low-cost optical emitters integrated on Si and operated at the telecommunication wavelengths.

In summary, we have achieved Ge quantum dot light emitting diodes. The wavelength of the emitting light lay in the region of 1.3–1.55 μm.

Figure 30. Electroluminescence spectra at different biases measured at (a) 77 K and (b) 300 K. Electroluminescence from quantum dots are observed at around 1.3 μm.
4.2. Near-Infrared p-i-n Ge Quantum Dot Photodetectors Operating at 1.31–1.55 μm

The pin diodes fabricated for EL can be used for photo-detection, i.e., as photodetector devices. Photocurrent (PC) measurement was performed using a normal-incidence configuration at both room temperature and 77 K. A tungsten lamp was used as the light source. The light passes through a 34-cm monochrometer and cast normally onto the diode. An 850 nm low-pass filter was placed in front of the device. The photocurrent signal was amplified by a CMOS micropower operational amplifier. For short circuit (0 bias) photocurrent, the signal was directly output to a Keithley digital multimeter. For biased photocurrent, a lock-in amplifier was used before outputting to the digital multimeter. The data were collected by a computer.

The PC data at room temperature for the same diode used for EL in the above section and a Si photodiode at normal incidence with a tungsten lamp as the light source are shown in Fig. 31. There was no bias applied. The quantum dot sample has two peaks. One is related to Si absorption at low wavelength, ranging from 850 nm to 1250 nm and the other at higher wavelength is related to Ge dots. The photoresponse range of Si photodiode extends to 1.15 μm, corresponding to the Si bandgap. The main peak of the quantum dot sample extends to 1.25 μm, which is 100 nm longer than that of Si photodiode. This may be due to the absorption effect of the inter-diffused wetting layers [109].

Figure 32(a) shows PC spectra of the quantum dot pin photodiode at both room temperature and 77 K with the Ge dot peak magnified. The peak shifts from 1.4 μm to 1.32 μm when the temperature decrease from room temperature to 77 K. The FWHM also shrinks from 95 to 70 meV and the photoresponse intensity shows a clear decrease. Figure 32(b) illustrates a possible mechanism to explain the observed photoresponse for the diode. As discussed in the previous section, Ge dots embedded in Si have a type-II band alignment. For the PL process, the excited holes nearby will drift to the Ge dots very rapidly, and electrons will drift away from dots. Thus, the recombination responsible for the observed PL peaks occurs at the Si/Ge interface. On the other hand, for the PC process, when the photon energy is low, it only happens at the Si/Ge interface region; when the energy is high enough, both the interface and inside the dots will absorb the light. The electron-hole pairs then contribute to conduction current via thermionic emission. From the above picture, it is clear that the peak response is the sum of the Ge dot bandgap and the separation of the valence band edge of Ge dot and the ground state in dots (ground state energy). It is not difficult to understand the shift of the photoresponse at different measurement temperature assuming there is non-uniform dot size distribution present in the intrinsic part of the diode.

The dependence of the photoresponse spectrum on applied reverse bias at room temperature is shown in Fig. 33. As the bias increases, the photoresponse increases but the shape
Figure 32. (a) Short circuit photocurrent spectra of the Ge dot detector at room temperature and 77 K. At room temperature, the response covers the range from 1.3 to 1.52 μm with a maximum detection at 1.4 μm. The peak shifts to 1.32 μm at 77 K, and (b) Schematic drawing of the band diagram of the structure vertically crossing the dots at no bias.

of the curve remains almost unchanged. There is no clear shift in cutoff wavelength shift (less than 10 nm). The quantum confined Stark effect is weak due to the low applied voltage on the devices. The high measurement temperature may also obscure the quantum confined Stark effect. Similar results were also observed in SiGe quantum wells and superlattices [110]. The external efficiency at the peak wavelength of 1.4 μm is 8% at 2.5 V estimated from the excitation power of 360 nW. This efficiency is comparable to that of the Si/Ge strained layer superlattice grown by MBE at 1.3 μm under a waveguide coupling mode reported by Splett et al. [111] (12%).

Figure 34 shows PC spectra of three samples at room temperature. These samples contain nominal Ge thicknesses of 12, 15, and 18 Å in each period, respectively. Other structural parameters are kept the same. The data were taken in the photovoltaic mode. All the samples show a photoresponse peak at the region of between 1.3 and 1.55 μm. It also shows that as the Ge nominal growth thickness increase, the photoresponse peak shifts slightly to longer wavelength. This is due to the fact that Ge dot height increases with increasing nominal growth thickness, and this in turn reduces the ground state energy of holes in the dots. However, the shift is small. It is important to note that the dots are not pure Ge. From a separate grading incidence x-ray diffraction measurement [112], the average Ge content of the dot is about 55%. A 0.88 eV fundamental gap can be extracted for this content according to Reiger and Vogl’s therotical work [113]. The result is in agreement with our PC result.
which shows the peak response of around 0.88 eV. The cutoff transition energy is, however, 0.83 eV, i.e., 50 meV lower. The possible reason for this difference is the presence of the conduction band offset, which has a negative contribution to the transition energy.

It is important to be able to tune the photoresponse peak wavelength to the important optical communication window of 1.55 μm. However from the above result, it is difficult to attain this spectral window by simply changing the dot size. The Ge content in the dots needs to be increased. Growth at lower substrate temperature is one way to increase the Ge content in dots. In order to get a clear picture of this, we did simple calculations and compare with experimental data. The calculations were performed with a quantum dot exhibiting a homogeneous core composition surrounded by Si. The height of the dots for each sample is assumed to be the same as 10 nm. The base diameter is large and induces no quantum effects. The bandgap of the dots and the valence band offsets were taken assuming tetragonally strained SiGe on Si. [114]. The heavy hole effective mass along the z-growth axis was taken as a linear interpolation between the mass of Si (0.29m₀) and Ge (0.206m₀) [115, 116].

The ground state in the dots is estimated from the finite quantum well model. The peak response is simply equal to the sum of the band gap of the dots and the ground state energy of the dots. It should be noted that this single band calculation is only intended to explain qualitatively the experimental features. A more detailed description of the valence states should be obtained in the framework of a multiband $k \cdot p$ calculation. Figure 35 shows the peak energy of the response as a function of the Ge content in dots. The solid line is the calculated result and the triangles are the experimental data shown in Fig. 34 and in [117, 118]. The experimental Ge compositions were obtained by Raman scattering. The experimental data fall into the trend of calculation line, which also predicts that the growth of the dots at the temperature of about 400°C may lead to the peak response of 1.55 μm.

In summary, we have successfully developed Si-based photodetector with embedded Ge quantum dots. The photoresponse wavelength covers 1.3–1.52 μm. High external efficiency of 8% at 1.4 μm was obtained. The active dot layer greatly enhances the absorption. The results indicate that Ge dot materials are potentially applicable for 1.3–1.55 μm fiber-optic communications.

4.3. Mid-Infrared Ge Quantum Dot Photodetectors Operating at 3–5 μm

Since the first observation of the intersubband transition in the Ge quantum dots [119], progress has been made on the fabrication of the Ge quantum dot mid-infrared photodetectors [120–128]. The operation principle of quantum dot photodetectors is similar to that of quantum well intersubband photodetectors. The detector is a photoconductor with an active region, which consists of doped semiconductor quantum dots. Under infrared excitation carriers are photoexcited via intraband absorption and give rise to a photocurrent.
One advantage of using quantum dots instead of quantum wells relies on an expected larger photoconductive gain associated with a reduced capture probability. Another advantage of the quantum dot photodetector is related to the nonvanishing normal incidence absorption, which is extremely important for mid-infrared applications. In this section, experimental results on the quantum dot mid-infrared photodetectors are shown.

The Mid-infrared diode structure was grown on a double-side-polished Si (100) wafer with boron doping as high as $1 \times 10^{19} \text{ cm}^{-3}$. The growth temperature was kept at 540°C during the growth. The active region consists of 20 periods boron-doped Ge quantum dot layers separated by 20 nm Si barriers. The doping for Ge layer is about $6 \times 10^{18} \text{ cm}^{-3}$. The active region was embedded between two $P^+$ Si layer (300 nm) with a Si (100 nm) intrinsic spacer in each side. Mesa-type photodetectors were processed by standard photolithography. Al was used for ohmic contacts. The photocurrent was measured in the normal incident condition with a monochromator and lock-in amplifier. Unpolarized light from a glow bar source was chopped at a frequency of 2000 Hz and on the front side of the detector after passing through a monochromator. A series resistor was used to convert the photocurrent signal to a voltage signal, which was measured using an amplifier and a lock-in amplifier. To reduce the signal to noise ratio, the photoresponse was measured at the low temperature of about 50 K in a cryogenic system.

Figure 36 shows $I-V$ characteristic of the sample at two temperatures of 77 K and 300 K. It shows an exponential increase with increasing applied bias voltage at moderate biases. This agrees with the theoretical analysis of Ryzhii et al. [129]. At 77 K, the forward current density at 1 V is 6.4 mA/cm². The total dark current is consisted of three parts, sequential resonant tunneling, thermionic emission, and phonon assisted tunneling [130]. Thermionic hole emission from QDs is considered to be the major source for the dark current at these temperatures. The unsymmetrical appearance of the $I-V$ curves is due to the growth induced unsymmetrical properties of the dot region, such as the wetting layer and the dot shape. The dark currents, however, are high even at the temperature of 77 K, probably due to the generation of misfit dislocations in the structure because of the thick superlattice. Similar relaxation for a 20-period sample with the same structure was shown in previous PL studies, which supports this assumption.

Normal incidence photocurrent spectra of the sample taken at about 50 K are shown in Fig. 37(a) for bias voltages between 0.4 V to 3 V. Figure 37(b) summarizes the integrated photocurrent intensity as a function of the bias. As the bias increases, the intensity increases as a result of more efficient collection of the photo-generated carriers by the electrodes at higher biases before recombination. The peak maximum is observed at around 2.5 μm at
around 0.4 V, which correspond to 450 meV transition from the ground state of the dots and the continuum state. With the increasing bias a redshift of the photocurrent maximum is observed. A possible explanation may be change of the carrier concentration in the dots due to applied bias. At higher bias, more holes are injected from the contacts and occupy the excited levels in the quantum dots. Because of this, the self-consistent Hartree potential will shift all quantum levels including ground state to higher energy. The similar situation has been observed from the previous excitation power dependent PL in the quantum dot superlattices. In this case, both band filling effect and band bending effect at higher bias reduce the transition energy from the ground state to the continuum state, leading to the redshift of the peak.

To move the photoresponse to the more interesting 3–5 $\mu$m range, one sample was annealed at 900 °C for 10 min. The response spectra at different temperatures were shown in Fig. 38. The photoresponse ranges from 2.4 to 4.6 $\mu$m, covers almost all the interesting range. The peak response is at 3.5 $\mu$m. This shows that annealing is an effective method to tune the photoresponse range of quantum dots samples. This result also shows that with increasing the temperature, the response intensity decreases. With increasing temperature, the bound holes can be excited out of QD states through thermal emission. The emission reduces the number of bound carriers that can be photoexcited, thus reduces the photoresponsivity. Another reason may come from the increasing phonon density, which can reduce the excited carrier lifetime or the by increased scattering, thus reduces the optical gain. The dips in the spectra are due to the atmospheric absorption or the grating response. The shift of the response wavelength is an effect of the interdiffusion of Si and Ge during the annealing process.

![Figure 36](image1.png)

**Figure 36.** $I-V$ characteristics of a p-i-p Ge quantum dot detector at 77 K and 300 K respectively.

![Figure 37](image2.png)

**Figure 37.** (a) Photoresponse of a p-i-p quantum dot diode at three different bias. The measurement temperature is at 50 K. (b) Integrated peak intensity as a function of bias.
Figure 38. Photoresponse of the 900 °C and 10 min annealed sample at different temperatures.

In summary, as-grown Ge quantum dot pip photodetector samples have normal-incident response range from 2.2 µm to 3.2 µm. Annealing can tune the response to longer wavelength range, i.e., 2.5 µm – 4.8 µm for 900 °C 5 min annealed samples. The response is due to the intersubband transitions of the holes in the self-assembled Ge dots.

5. SUMMARY

We have studied the growth and optoelectronic properties of self-assembled Ge quantum dots. The morphology of dots were relate to growth rate, growth temperature, deposited coverage, post-growth holding time, and doping. High-uniform dots were grown on Si (100) at 600 °C. Strain-related phenomena, such as coarsening of dots and critical thickness of the multi-layered Ge dot system have been discussed. PL studies show Ge/Si quantum dot system has type-II band alignment structure and luminescence in the region of 1.3–1.55 µm. From FTIR and Raman scattering studies, Ge/Si quantum dot system shows strong absorption around 5 µm, which is due to the hole intraband transitions. Device structures consisting of Ge quantum dots are shown to have potential applications in near-infrared fiber-optic communication and mid-infrared photo-detection.

ACKNOWLEDGMENT

This work was supported by the Center for Nanoscience Innovation for Defense (CNID).

REFERENCES

13. I. N. Stramski and Von L. Krastanov, Schriftenberichte der Akademie der Wissenschaften in Wien, Abteilung IIb 146, 797 (1939).