Growth-temperature-dependent band alignment in Si/Ge quantum dots from photoluminescence spectroscopy

Mats Larsson, Anders Elfving, Wei-Xin Ni, Göran V. Hansson and Per-Olof Holtz

N.B.: When citing this work, cite the original article.

Original Publication:
http://dx.doi.org/10.1103/PhysRevB.73.195319
Copyright: American Physical Society  
http://www.aps.org/

Postprint available at: Linköping University Electronic Press  
http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-13795
Growth-temperature-dependent band alignment in Si/Ge quantum dots from photoluminescence spectroscopy

M. Larsson,* A. Elfving, W.-X. Ni, G. V. Hansson, and P. O. Holtz

IFM Material Physics, Linköping University, S-581 83 Linköping, Sweden

(Received 4 June 2005; revised manuscript received 11 January 2006; published 22 May 2006)

The present work is a photoluminescence study of Si-embedded Stranski-Krastanov Ge quantum dots. The value of the conduction band offset is a result of the magnitude of the tensile strain in the Si surrounding the compressive strained Ge dot. Due to the increased Si/Ge intermixing and reduced strain in the Si barrier, a reduction of the conduction band offset is observed at increased growth temperatures. The optical properties as derived from photoluminescence spectroscopy are correlated with structural properties obtained as a function of the growth temperature. High growth temperatures result in large Ge dots with low density due to the pronounced surface diffusion and Si/Ge intermixing. As confirmed by photoluminescence, the band gap of the Ge dots increases with increased growth temperature due to the higher degree of Si/Ge intermixing. The band alignment is of type II in these structures, but the occurrence of both spatially indirect and spatially direct transitions are confirmed in temperature-dependent photoluminescence measurements with varied excitation power conditions. An increasing temperature results in a gradual transition from the spatially indirect to the spatially direct recombination in the type-II band lineup, due to higher oscillator strength for the spatially direct transition combined with a higher population factor at higher temperatures.

DOI: 10.1103/PhysRevB.73.195319 PACS number(s): 78.67.He, 68.65.Hb, 73.20.At, 78.55.—m

I. INTRODUCTION

Ge quantum dots (QDs) in Si matrices have attracted a significant interest during the recent years since it is one candidate to realize Si based optoelectronics. An extensive work has been devoted to this field during the years, but there is still a limited knowledge on fundamental properties, such as the band offset.\(^1\) Bulk Si and Ge typically reveal a weak optical emission due to their indirect nature in \(k\) space. However, the optical properties can be improved by making use of low dimensional Si/Ge structures, e.g., QDs. For Ge QDs embedded in Si, alloy disorder and quantum confinement effects relax the \(k\)-conservation conditions enough to increase the probability for phononless absorption or recombination.\(^1\)\(^-\)\(^3\)

Under certain conditions, the growth of the lattice mismatched Si/Ge material system proceeds via the Stranski-Krastanov growth mode,\(^1\)\(^,\)\(^3\)\(^-\)\(^11\) resulting in the production of self-assembled Si/Ge quantum structures compatible with the conventional Si technology.

In the present work, a systematic study of the structural and optical properties for a series of samples, grown at different temperatures, was performed by means of atomic force microscopy (AFM) and photoluminescence (PL) measurements. In the whole range of growth temperatures employed in our study, 430 to 730 °C, we were able to produce dots via the Stranski-Krastanov growth mode. The influence of the growth temperature on the Ge dot size, energy band alignment, band gap, strain, and intermixing of Si into the Ge dots was investigated and discussed. The excitation power and temperature-dependent PL provides the opportunity to discuss and address the origin of different kinds of Ge QD related emissions. By correlating the optical properties with the AFM results, a consistent picture is achieved of the growth-temperature influence on the band gap and energy band lineup, which are determined by the built-in strain and the Si/Ge intermixing during the whole growth sequence. Two different optical recombination paths related to the dots were identified, one spatially indirect across the dot boundary and one spatially direct within the dot. Taking advantage of the observation of these two transitions, it can be concluded that the conduction band offset decreases with increasing growth temperature.

In a study performed by Dashiell et al.,\(^12\) structures including small Ge hut clusters were subjected to rapid thermal annealing, which resulted in a transformation of the dot layer to a two-dimensional (2D) layer. The PL from that 2D layer shows a doublet peak, originating from the electronic transition combined with the TO phonon replica. However, the high growth temperatures used in our study gives rise to large three-dimensional islands, which also results in a doublet peak in the PL spectra but with different characteristics and identified as the spatially direct and indirect transitions.

II. EXPERIMENTAL DETAILS

A series of samples was grown by solid-source molecular beam epitaxy (MBE) at growth temperatures ranging from 430 to 730 °C, where eight Ge monolayers were deposited on Si(100). The Ge QDs were formed from this Ge layer via the Stranski-Krastanov growth mode and then capped with a 140 nm Si capping layer. The growth temperature for the upper part of the Si capping layer was 600 °C in order to avoid point defects. The growth rates used during the process were 1.04 Å/s for Si and 0.13 Å/s for Ge. In order to analyze the structural properties by AFM, a second dot layer was grown on top and left uncapped. The thick Si spacer layer implies that there is reduced strain-induced correlation between the two dot layers. For the samples that were used for optical spectroscopy, the upper uncapped layer was removed,
by reactive ion etching, not to influence the optical measurements. A Ge QD sample grown at 700 °C was employed for temperature and excitation power dependent PL measurements. PL measurements were performed in a He-flow cryostat with the 514 nm line of an Ar-ion laser as the excitation source. A standard lock-in technique together with a double-grating monochromator and a liquid nitrogen cooled Ge detector was used to analyze the PL signal. Even though there will be a significant interdiffusion of Si into the Ge dots during the growth and the dots are composed of a Si$_{1-x}$Ge$_x$ alloy we will in the following refer to them as Ge dots.

III. RESULTS AND DISCUSSION

A. Type-II band alignment and Si/Ge intermixing

In a Si$_{1-x}$Ge$_x$ alloy, the band gap is a function of the composition as well as the strain in the material. Furthermore, the energy band alignment at the interface between two differently composed Si$_{1-x}$Ge$_x$ layers is sensitive to the strain present in each layer. Van de Walle and Martin have performed band gap and band alignment calculations for Si/Ge interfaces, including calculations on Si$_{1-x}$Ge$_x$ alloys matched to either Si or Ge substrates. Their results can be used to estimate energy band discontinuities in the strained Si/Ge material system. However, the situation is quite complex for the case of Ge QDs. Interdiffusion of Si will bend the energy bands which results in a blueshift of the spatially indirect transition, i.e., $E_{A} < E_{B}$. The energy of the spatially direct transition is practically unaffected by the increased carrier density.

B. AFM analysis

Representative AFM images are shown in Fig. 2 from samples grown at three different growth temperatures, 480, 580, and 730 °C. As for the samples grown at 430 and 530 °C, the sample grown at 480 °C is dominated by so-called “huts,” small elongated dots with a high density [Fig. 2(a)]. The lateral dimension is about 30 nm, and the height is around 2 nm, while the dot density is $1.4 \times 10^{11}$ cm$^{-2}$. A small fraction, less than 5% of the dots are significantly larger as exemplified in Fig. 2(a). A higher growth temperature results in an increase of the average dot dimension, but also a change of the dot shape. Dome-shaped dots dominate the sample grown at 580 °C and the average diameter is 65 nm and the height is about 11 nm [Fig. 2(b)]. The increase of the average dot size is accompanied by a decrease of the density, e.g., for the sample grown at 580 °C, the density was reduced to $7 \times 10^9$ cm$^{-2}$. The samples grown at temperatures of 580 and 630 °C show a homogeneous size distribution and practically all dots (>90%) are dome shaped. At even higher growth temperatures, a bimodal size and shape distribution is introduced. As illustrated by the AFM image of the sample grown at 730 °C [Fig. 2(c)], pyramids and domes coexist.
This disappearance and reappearance of pyramidal shaped dots as the growth temperature is increased has previously been observed by Jin et al.6 The dome-shaped dots are the largest and exhibit an average diameter of 250 nm and a height of approximately 45 nm, while the pyramidal-shaped dots are slightly smaller with a base length of 200 nm and a height of about 20 nm. The total dot density at this growth temperature is about $4 \times 10^{11}$ cm$^{-2}$.

In Table I, a summary of the average dot sizes and densities as a function of the growth temperature is presented. It is found that the total volume of the QDs, as estimated from AFM measurements, exceeds the volume of the deposited Ge material for growth temperatures above 500 °C, an observation that confirms the proposed Si/Ge intermixing during the growth. The continuous increase of the dot dimensions as well as the total volume is then a result of both an increased surface diffusion length of the Ge adatoms and an increased Si/Ge intermixing in the dots at increased growth temperatures, causing a reduced strain factor. Several samples have also been analyzed by high-resolution transmission electron microscopy and the results will be published elsewhere.18 In agreement with earlier studies, we find that the shape of the dots is changed by the overgrowth of a capping layer.19 However, it is expected that the concentration of dots will remain unaffected by the capping.

<table>
<thead>
<tr>
<th>Growth temp. (°C)</th>
<th>Density (cm$^{-2}$)</th>
<th>Diameter (nm)</th>
<th>Height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>$1.5 \times 10^{11}$</td>
<td>20–25</td>
<td>≈2</td>
</tr>
<tr>
<td>480</td>
<td>$1.4 \times 10^{11}$</td>
<td>≈30</td>
<td>≈2</td>
</tr>
<tr>
<td>530</td>
<td>$4 \times 10^{10}$</td>
<td>50–60</td>
<td>2–2.5</td>
</tr>
<tr>
<td>580</td>
<td>$7 \times 10^{9}$</td>
<td>60–70</td>
<td>≈11</td>
</tr>
<tr>
<td>630</td>
<td>$5 \times 10^{9}$</td>
<td>70–80</td>
<td>≈15</td>
</tr>
<tr>
<td>680</td>
<td>$2 \times 10^{9}$</td>
<td>140–150</td>
<td>15–20</td>
</tr>
<tr>
<td>730</td>
<td>$4 \times 10^{8}$</td>
<td>200–250</td>
<td>20–45</td>
</tr>
</tbody>
</table>

This disappearance and reappearance of pyramidal shaped dots as the growth temperature is increased has previously been observed by Jin et al.6 The dome-shaped dots are the largest and exhibit an average diameter of 250 nm and a height of approximately 45 nm, while the pyramidal-shaped dots are slightly smaller with a base length of 200 nm and a height of about 20 nm. The total dot density at this growth temperature is about $4 \times 10^{11}$ cm$^{-2}$.

In Table I, a summary of the average dot sizes and densities as a function of the growth temperature is presented. It is found that the total volume of the QDs, as estimated from AFM measurements, exceeds the volume of the deposited Ge material for growth temperatures above 500 °C, an observation that confirms the proposed Si/Ge intermixing during the growth. The continuous increase of the dot dimensions as well as the total volume is then a result of both an increased surface diffusion length of the Ge adatoms and an increased Si/Ge intermixing in the dots at increased growth temperatures, causing a reduced strain factor. Several samples have also been analyzed by high-resolution transmission electron microscopy and the results will be published elsewhere.18 In agreement with earlier studies, we find that the shape of the dots is changed by the overgrowth of a capping layer.19 However, it is expected that the concentration of dots will remain unaffected by the capping.

C. Photoluminescence

Low temperature PL spectra of six samples grown at different substrate temperatures are shown in Fig. 3. The emission below 0.9 eV is due to Ge dot transitions, while the luminescence at higher energies are contributions from the wetting layer (WL) and typical phonon assisted emissions in bulk Si. The WL emission consists of a no-phonon (NP) transition and transverse optical (TO) phonon replica, which resemble the emission from SiGe/Si quantum wells.20 The series of spectra in Fig. 3 shows that an increased growth temperature from 430 to 580 °C results in a continuous blueshift of the Ge dot related emission. As shown by the AFM study, the Ge dots become larger with increased growth temperature. Accordingly, a blueshift due to increased confinement of the carriers is not expected. Since the sizes of the Ge dots are relatively large, quantum confinement effects are weak and the size change does not significantly influence the emission energy. The resolution of the macro-PL measurements performed is furthermore not sufficient to observe any dependence of the optical characteristics on the shape of the dots. An enhanced intermixing of Si into the Ge dot at increased growth temperature is ascribed to be the main reason for the blueshift since the fraction of Si in the Ge dots determines the band gap, the VB and CB offsets, and hence the emission energy. For the samples grown at temperatures lower than 580 °C, the dot density is sufficiently high to capture most of the carriers from the WL,
resulting in a WL related emission below the detection limit in our PL measurements. An increased growth temperature, from 580 to 730 °C, results in a reduction of the Ge dot emission intensity while the emission energy remains around 0.84 eV.

The emission spectra of samples with different kinds of dot shapes show similar emission properties as samples with a homogeneous dot shape, as observed when comparing the spectra of the sample grown at 630 °C (domes) and the sample grown at 730 °C (pyramids and domes). As demonstrated by AFM, the Ge dot density continues to decrease with increased growth temperature from 580 to 730 °C (Table I), which accordingly results in a considerable increase of the WL area per dot. The reduction of the Ge dot related emission intensity, accompanied by an increase of the WL emission intensity, is thus a consequence of the lowered dot density (Fig. 3). Furthermore, it is well established that the high strain in large islands relaxes via formation of misfit dislocations. The dislocations may act as nonradiative recombination centers, which results in further reduced Ge dot related PL with increasing growth temperature from 580 to 730 °C.

As discussed above, the AFM measurements clearly show that there is an increase of the average dot size accompanied by a decrease of the dot density at increased growth temperatures. It is claimed that due to the increased surface diffusion at elevated growth temperatures, the adatoms have the possibility to diffuse and attach to an existing island, which is more energetically favorable than to nucleate a new island. Signatures of Ostvald ripening have also been observed where some islands grow larger at the expense of other islands in order to minimize the total surface energy of the system, also resulting in large islands with low density.

The increased surface diffusion at high growth temperatures is expected to cause a thinner WL due to the enhanced transfer of material from the strained WL to the partially relaxed Ge islands. This expected thinning of the WL is consistent with the experimental observed strong blueshift of the WL emission with increased growth temperature. The upshift of the transition energy is hence partly due to narrowing of the WL, and consequently increased quantum confinement, and partly due to increased Si/Ge intermixing. The absence of any further blueshift of the Ge dot related emission at growth temperatures above 580 °C shows that the emission energy of large dots is not as sensitive to intermixing as the transition energy for small dots. Intermixing during capping occurs at the dot boundary and is consequently affecting large dots less than small dots. Furthermore, since the intermixing is a composition and strain-driven process, the diffusion of Si into the Ge dot is expected to be less pronounced as the concentration gradient decreases at elevated growth temperatures. The result is however a smeared out energy band offset between the barrier and the dot.

D. Temperature and excitation power dependence of PL.

Figures 4(a) and 4(b) show the temperature dependence for the dot-related emission for two samples, grown at 480 and 630 °C, respectively. An important feature of the Ge dot related emission is the fact that it consists of two energy bands. Furthermore, common for both samples is that they exhibit redistribution from the low energy emission band to the high energy emission band with increasing temperature. However, compared to the sample grown at 630 °C, the sample grown at 480 °C requires higher temperatures to ex-
hhibit the luminescence intensity transfer from the low energy band to the high energy band. At temperatures of 10–20 K, the two bands are of equal intensity for the sample grown at 630 °C while the low energy band dominates the spectra of the sample grown at 480 °C. As will be discussed below, the energy difference between the two emission bands in each sample decreases with increasing growth temperature. Furthermore, the two emission bands show not only different temperature dependence but also different excitation power dependence. These observations seem to exclude the possibility that the low energy emission band is related to a phonon replica of the high energy band. Since the appearance of two Ge dot-related bands has often been assigned to a no-phonon and an associated phonon replica, it is very important to clarify the origin of the two contributions. Wan et al.\textsuperscript{21} observed two emission bands at 0.8–0.85 eV in MBE grown samples in accordance with our results, while Huang et al.\textsuperscript{22} observed emission bands at 0.86 and 0.92 eV, in chemical vapor deposition (CVD) grown samples. Huang et al. attributed the origin of the emission to be NP transition and TO-phonon replica, which is not in consistence with our interpretation.

Low temperature (2 K) Ge dot related emission spectra, under varied excitation power conditions, of a sample grown at 700 °C are shown in Fig. 5(a). A significant blueshift of the QD emission is observed as the excitation power is increased from 3 to 100 mW. Since the energy band lineup is of type II, the dominating optical transition at low temperatures is the spatially indirect transition across the interface. Carriers are trapped in the notch potential at the Si/Ge interface on each side of the dot. The electrostatic potential of the spatially separated electrons and holes will bend the energy bands,\textsuperscript{2,16} as illustrated in Fig. 1(b). At increased carrier concentration, the Si CB bending will shift the electron levels to higher energies due to increased confinement in the notch potential. State filling and redistribution of carriers into smaller dots could also cause a blueshift of the emission but are expected to be of minor importance, since our experi-
creases the probability for the electrons to populate the higher energy level inside the Ge dot, which opens the possibility for the spatially direct transition. When the electron is inside the Ge dot, the overlap of the electron and hole wave functions is evidently increased since the electron and hole are located in the same volume. This fact is supported by Penn et al.\textsuperscript{15} who calculated much higher oscillator strength for the spatially direct transition compared with the spatially indirect transition. Consequently, efficient PL emission could be observed from the spatially direct transition despite the fact that there is a quite small fraction of electrons that are thermally excited into the dot. As seen in Fig. 6, the intensity of the high-energy peak increases with increasing temperature. This observation is in striking contradistinction to a possible interpretation of the doublet peak to be related to the electronic transition and TO-phonon replica,\textsuperscript{22} since a phonon replica on the Stokes side is expected to be almost independent on temperature. The slight temperature dependence should even be reversed, i.e., an increasing intensity of the Stokes replica with increasing temperature.

Since the PL measurements establish the picture of two optically active transitions of different origin, one spatially direct and one spatially indirect, the temperature-dependent PL measurements allow studies of the CB band offset induced by strain in the Si/Ge QD system. The difference in the temperature dependence between the samples grown at 480 and 630 °C [see Figs. 4(a) and 4(b)] implies a change of the band alignment with varying growth temperature. Since the high energy band is related to the spatially direct transition, the energy position is consequently expected to be independent of the CB offset, but primarily determined by the dot composition and strain. Furthermore, the low energy emission band is related to the spatially indirect transition across the dot boundary and is in addition to the size of the band gap sensitive to the depth of the notch potential in the Si. Accordingly, the energy difference between the spatially indirect and direct emission bands is essentially determined by the CB offset (neglecting confinement effects in the notch potential).

A large CB offset gives rise to a strong luminescence from the spatially indirect transition, i.e., the low energy emission band, as for the sample grown at 480 °C [Fig. 4(a)]. In this case, the spatially direct transition requires quite high temperatures to be visible because of the high potential barrier for the electrons to get into the Ge dot. With a reduced CB offset, a lower temperature is required to populate the dot with electrons and the direct transition is considerably stronger, as for the sample grown at 630 °C [Fig. 4(b)]. As discussed above, high growth temperatures give rise to a large intermixing of Si into the Ge dots. As a result of the high degree of intermixing, a lower lattice mismatch between the dot and the barrier is expected. Hence, the tensile strain in the surrounding Si will be reduced with increasing growth temperature, which in turn results in a lower CB offset. Consequently, for the sample grown at 630 °C, the strain in the Si above and underneath the dot is lower which results in a less downshifted Δ(2) valley in the Si and hence a smaller CB offset, in comparison to the sample grown at 480 °C.

The influence of the growth temperature on the recombination energies for the spatially indirect and direct transitions is shown in Fig. 7(a). Due to the continuous change in the energy band lineup, the spatially indirect transitions blue-shifts 60 meV with increasing growth temperature from 430 to 580 °C. Moreover, the energy difference between the spatially indirect and spatially direct transitions, which reflects the CB offset, continuously decreases from approximately 52 to 34 meV as the growth temperature increases from 480 to 630 °C, as shown in Fig. 7(b). Although the difference in peak positions does not directly correspond to the CB offset, our experimental data are consistent with finite element calculations of the band edge alignment in Si/SiGe quantum dots with a CB offset Δ(4)Ge−Δ(2)Si=50 meV.\textsuperscript{13}

As discussed above, emission energies of large dots are not as sensitive to the growth temperature as small dots and the separation between the spatially indirect and direct transitions is practically constant at growth temperatures above 630 °C. However, intermixing of Si and Ge is expected to result in a smeared out band offset. The potential barrier for the electron is then not as abrupt as for lower growth temperatures and the probability for the spatially indirect transition decreases. With increased growth temperature, the high energy emission band consequently gains in intensity in comparison with the low energy band, as shown by the PL spectra for the samples grown at 580, 630, and 730 °C in Fig. 3.

IV. CONCLUSIONS

In the present study, we have focused on the influence of the growth temperature on the correlated structural and optical properties of Si/Ge quantum dots. Due to increased surface diffusion and Si/Ge interdiffusion, the Ge dot density is reduced and the average size of the Ge dots increases with increasing growth temperature. The degree of Si intermixing in the Ge dot determines the band gap, resulting in a blue-
shift of the Ge dot related emission with increased growth temperature up to 580 °C. Above that temperature, the dot emission intensity is reduced due to the decreased density of the dots, the increased smearing of the type-II band offset, and an increased number of misfit dislocations in larger dots. Simultaneously, the WL emissions gain in strength due to the increase in WL area per dot and they are blueshifted due to decreased thickness and increased Si fraction as the growth temperature is increased.

The temperature- and intensity-dependent PL measurements show that there are two different recombination processes related to the Ge QDs. Since the energy band alignment is of type II, the Ge dot related emission is either spatially indirect or direct. Due to the difference in oscillator strength, an increase of the measurement temperature results in a redistribution of the emission from the spatially indirect band to the spatially direct band. The PL dependence on the excitation power shows a blueshift of the spatially indirect transition energy with increasing excitation power density, due to the band bending at the Si/Ge interface at high carrier densities.

The spatially indirect transition dominates the low temperature PL spectrum of the sample grown at the lowest growth temperatures, while the spatially direct transition is observed at temperatures above 2 K and at high excitation conditions. The separation between the two emission bands is observed to decrease with increasing growth temperature. In fact, the high energy emission band related to the spatially direct transition gains in strength with increasing growth temperature, due to a decreasing potential barrier for the electrons. The intermixing of Si into the Ge dots changes the strain in the surrounding Si and accordingly the CB offset. As a result, a reduction of the energy difference between the spatially direct and spatially indirect transition from approximately 52 to 34 meV is observed as the growth temperature was increased from 480 to 630 °C.

ACKNOWLEDGMENTS

This work has been supported by the Swedish Foundation for Strategic Research (SSF) within the NANOPTO project and by the Swedish Research Council (VR).