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Preparation and optical properties of Ge and C-induced Ge quantum dots on Si

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Pure Ge epitaxially grown on Si (100) at high temperatures forms typically 100 nm lateral size islands on top of a 3-4 monolayer thick wetting layer. In stacked layers of Ge dots pronounced vertical alignment is observed if the thickness of the Si spacer layers is smaller than about 50 nm. Pregrowth of a small amount of C on Si substrate induces very small 10 nm size Ge quantum dots after deposition of about 2 to 3 monolayers of Ge. Photoluminescence (PL) studies indicate a spatially indirect radiative recombination mechanism with the no-phonon line strongly dominating. Strong confinement shift in the 1-2 nm high and 10 nm lateral size dots results in low activation energies of 30 meV , which causes luminescence quenching above 50 K. For large stacked Ge islands with 13 nm thin Si spacer layers we observe a significantly enhanced Ge dot-related PL signal up to room temperature at 1.55 µm wavelength. This is attributed to a spatially indirect transition between heavy holes confined within the compressively strained Ge dots and two-fold degenerated Δ state electrons in the tensile strained Si between the Ge stacked dots.

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1. Introduction

In comparison with III/V semiconductors Si has superior structural properties and is easiest to process. These among other properties are the reasons why Si became the most important semiconductor material. However, it has an indirect bandgap that makes radiative transitions unlikely. Possibilities of increasing the light emission from Si based structures have been extensively studied due to the technologically important prospect of fabricating truly integrated optoelectronic devices [1]. The ideas that have been tried out include alloy-induced luminescence, incorporation of radiatively active impurities like Er, quantum confinement including zone folding or porous Si and hybrid approaches like direct bandgap III-V compounds mounted or bonded onto Si. So far the relatively expensive hybrid version remains the medium term solution. The main problems with the fully Si embedded concepts are still low quantum efficiency, stability and luminescence quenching at room temperature.

Since Si is an indirect semiconductor, the emission of photons involves phonon assistance for momentum conservation. This is schematically illustrated in Fig. 1.a. Each phonon mode provides a distinct channel for light emission with the transverse optic (TO) modes dominating. The TO-phonon assisted photoluminescence (PL) from Si is 4-5 orders of magnitude lower in intensity as typical phonon-less PL intensities from III-V compounds like GaAs. $Si/Si_{1-x}Ge_x$ and $Si/Si_{1-y}C_y$ quantum wells show a no-phonon (NP) PL peak with comparable intensity as the TO-phonon replicas [2]. This is mainly a consequence of relaxed momentum conservation due to alloy-induced disorder. A further increase of NP PL is expected for extremely small 1-2 nm diameter quantum dots, as predicted by Hybertsen [3]. His work was initiated by earlier reports on bright luminescence from porous Si samples, which involve extremely small size Si crystallites. In this case, electron and hole functions are spread in k-space due to momentum uncertainty, thus, the indirect character of the bulk material is no longer meaningful (see Fig. 1.b). In such extremely small quantum dots momentum conservation is achieved by interface scattering events.

In addition to nanoscopic size, carrier confinement energies significantly larger than kT at room temperature (RT) are required for light emitters. Hole confinement in the $Si/Si_{1-x}Ge_x$ system is achieved for high Ge content $Si_{1-x}Ge_x$ layers or even better in Ge islands.

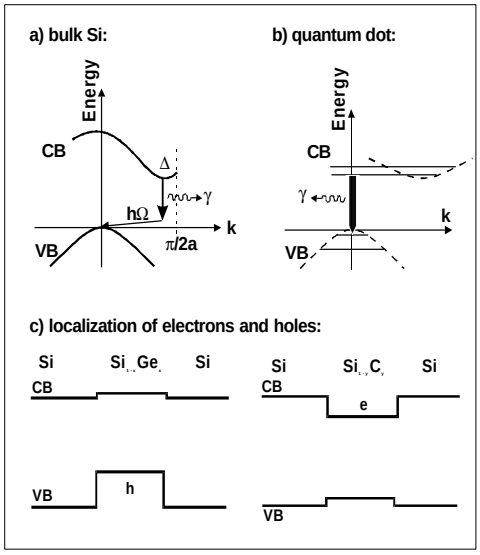

Figure 1. a) Schematic band structure of bulk Si. An optical transition from the Δ minima in the conduction band (CB) to the maximum of the valance band (VB) involves phonon assistance for momentum conservation, which results in low efficiency of optical emission, b) Strong carrier localization within an area of less than 10 nm in quantum dots in Si causes relaxation of the momentum conservation and is thus expected to result in enhanced no-phonon luminescence. c) Localization of holes and electrons in Si can be achieved in compressively strained $Si_{1-x}Ge_x$ and tensile-strained $Si_{1-y}C_y$ layers, respectively.

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However, electron localization requires tensile-strained Si layers, which can be realized by epitaxial growth on relaxed $Si_{1-z}Ge_z$ buffer layers. The substitutional incorporation of C into Si opens the possibility to create tensile strained layers directly on Si without the need of strain relaxed SiGe buffer layers [4]. The band offset in a $Si/Si_{1-y}C_y$ quantum well is known to be mainly in the conduction band (CB) [4-6]. PL and electroluminescence (EL) intensities in SiGe quantum well structures [7,8,28] neighboring $Si_{1-x}Ge_x/Si$ quantum wells on relaxed $Si_{1-z}Ge_z$ buffer layers with z<y [9,10] and $Si_{1-x}Ge_x/Si_{1-y}C_y$ quantum wells on Si [11] have been found to exhibit only small confinement energies and thus suffer from temperature quenching. Strong hole confinement is achieved in self assembling SiGe islands prepared by the Stranski Krastanov growth mode. Nominally pure Ge and SiGe dots on Si have been prepared using different epitaxial growth techniques [12-19] and by etching SiGe quantum wells [8]. However, the dot diameters are very difficult to reduce to less than 20 nm. Recently we have suggested a new concept for making extremely small 10 nm lateral size Ge quantum dots by C pre-deposition on Si [20,21]. The pre-grown C introduces nucleation centers for the subsequent formation of Ge islands, which results in the formation of a high density of extremely small dots. In the following, we report transmission electron microscopy (TEM) and PL investigations of 100 nm lateral size Ge islands and 10 nm size C-induced Ge quantum dots in Si. The different recombination pathways are discussed for single and stacked dot layers. The goal is to evaluate different ways of using self assembling quantum structures for Si-based emitters in the wavelength range of 1.3 to 1.55 µm.

The samples were grown by solid source molecular beam epitaxy (MBE). After SiO_2 desorption from the Si substrate in the growth chamber at 900 °C, a 380 nm thick Si buffer was grown while decreasing the substrate temperature T_s from 900 °C to 700 °C or 460 °C. The pure Ge islands were deposited at 700 °C. Growth steps for the C-induced Ge dots were all executed at T_s = 460 °C as follows: 5 s growth interruption (GI), 0.2 ML C deposition, 5 s GI, 2.2 ML Ge (or 2.4 ML Ge for the stacked layers) , 5 s growth interruption, 150 nm Si cap layer. Typical growth rates were 1.00, 0.15, 0.01 Å/s for Si, Ge and C, respectively. PL was excited by a 514 nm Ar^+ laser line with an excitation power of P = 30 mW if not explicitly stated differently. The beam was focused to a sample area of about 2 mm^2.

2. Results and discussion

Figure 2.a shows a cross-sectional TEM micrograph from a layer of C-induced Ge quantum dots prepared by deposition of 0.2 ML C followed by 3 ML Ge. For direct comparison, figure 2.b shows a Ge island formed by deposition of nominally 6 ML pure Ge on Si (100) substrate. The pure Ge islands fully embedded in Si are

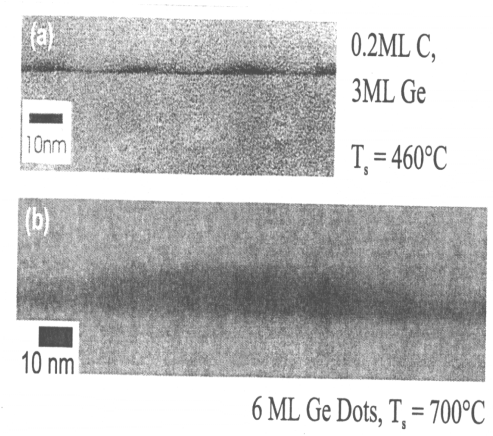

Figure 2. Cross-sectional TEM micrograph from (a) a layer of C-induced Ge quantum dots prepared by deposition of 0.2 ML C followed by 3 ML Ge at a substrate temperature T_s=460°C, and (b) Ge island formed by deposition of 6 ML Ge at T_s=700°C.

about 100 nm wide and 7 nm high, whereas the C-induced Ge dots have only 10 nm diameter and about 2 nm height. Further details about the C-induced Ge dots are described elsewhere [21]. PL spectra of two samples similar to those in figure 2 are shown in figure 3. In this case the C-induced Ge quantum dots have 0.2 ML C and 2.2 ML Ge.

The pure Ge island sample exposes two pairs of PL lines. It is a TO and NP peak at 0.97 eV and 1.026 eV originating from the 3-4 ML thick Ge wetting layer, respectively. The broadened pair around 0.8 and 0.84 eV originates from the large islands. It should be noticed that the very low energy of 0.84 eV indicates strong hole confinement within the Ge islands, which is due to the large local layer thickness of about 6-7 nm at the island center. Such low energies are not achievable with planar pseudomorphic SiGe layers in Si [28].

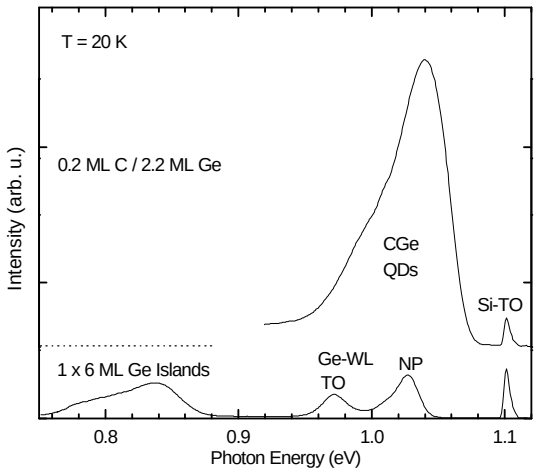

Figure 3. PL spectra from one layer of Ge islands (lower spectrum) and one layer of C-induced Ge quantum dots with 0.2 ML C and 2.16 ML Ge.

The PL spectrum from the 0.2 ML C / 2.2 ML Ge sample is shown in the upper part of figure 3. In this case we observe only one pair of TO and NP PL peaks with the intensive NP peak dominating. We ascribe this to the fact that the height of these quantum dots is only 1-2 nm as show for the 0.2 ML C / 3 ML Ge dots sample in figure 2. The energy shift to higher values as compared to the large Ge islands is also due to the much smaller height of only 1-2 nm in the C-induced Ge dots. A wetting layer luminescence is not observed in this case because it is extremely thin and the dot density is much higher than for large Ge islands [20].

For C-induced Ge dots we assume that electrons confined in the underlying carbon rich layer recombine with heavy hole states localized in the Ge rich upper part of the Ge islands. Gradual variation of the alloy composition and strain across the carbon induced Ge quantum dots is assumed. This band alignment model is deduced from the well known situation in neighboring $Si_{1-x}Ge_x$ / $Si_{1-y}C_y$ quantum wells [22] and a careful PL study of energy and intensity dependence in C-induced Ge dots as a function of the nominally deposited Ge [20,23]. The deposition of a small portion of a monolayer C creates a delta-like $Si_{1-y}C_y$ layer, which is tensile strained. Due to tensile strain the six-fold degeneracy of the CB is lifted and the electrons are in the energetically lower Δ2 valleys. The strain of one C atom is compensated by about 8.2 Ge atoms on Si. That means, we reach strain compensation for about 1.64 ML Ge deposited on 0.2 ML C. Adding more Ge results in pronounced island formation as observed in reflection high energy electron diffraction (RHEED) and *in situ* scanning tunneling microscopy [25]. As already mentioned, confinement of the heavy holes is achieved in the Ge rich upper part of the Ge islands, which reduces the PL energy.

For the large Ge islands electrons in the Si matrix will recombine with strongly localized holes within the Ge islands [24]. The low PL intensity is explained by low electron localization and small overlap of electron and hole wave function.

Figure 4 shows temperature dependent PL and EL intensities for a single layer of 0.2 ML C/2.2 ML Ge dots and a sample with 50 times stacked C-induced Ge dots with 0.2 ML C / 2.4 ML Ge with the Si spacer layers of 9.6 nm thickness. In contrast to pure Ge islands no vertical correlation is observed for stacked C-induced Ge dots, which is explained by the kinetically limited islanding process [25,26]. The activation energies are only 15 meV for the single dot layer and 30 meV for the stacked dots. For the sample with 50 dot layers the PL energy is about 40 meV lower because they have a slightly larger size.The intensity is about seven times higher as compared to the single dot layer at 20 K. The inset of figure 4 indicates the carrier transfer at higher temperatures from the holes in

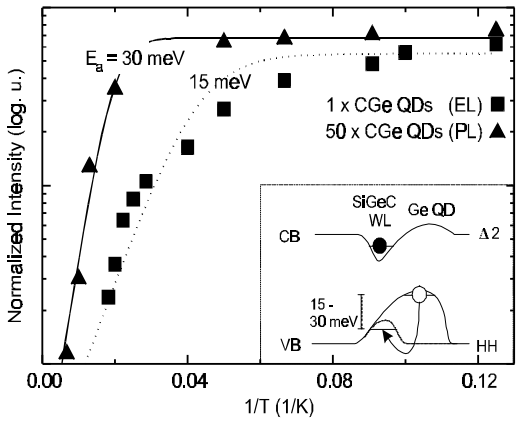

Figure 4. Temperature dependent PL and EL intensity for a single layer of 0.2ML C / 2.2 ML Ge dots and a sample with 50 times stacked C-induced Ge dots with 0.2ML C / 2.4 ML Ge. The activation energy is only 15 and 30 meV, respectively. The inset indicates the carrier transfer at higher temperatures from the holes in the dots to the wetting layer. The intensity is strongly decreasing above 50 K due to the extremely small size of the dots. Consequently, even so we get very strong NP PL for the C-induced quantum dots at low temperature we still have the problem of low activation energy which makes these structures difficult to apply in emitting devices at RT. The energy difference to the SiGeC wetting layer and the Si barrier material may be too low to realize 1.3 µm devices based on this concept.

the dots to the SiGeC wetting layer. The intensity is strongly decreasing a bove 50 K due to the extremely small size of. For Si-based RT emitters one clearly needs maximum confinement for both types of charge carriers. As mentioned above, the best hole confinement is achieved with large Ge islands since the band offset for pseudomorphic SiGe on Si is almost completely in the VB. In the ideal case of pure Ge fully strained on Si one expects more than 700 meV band offset in the VB. The Ge island related PL signal is about 300 meV below the Si bandgap as shown in figure 3. This reduction is mainly due to Si alloying into the islands and confinement shift. There is also an influence from the fact, that the Ge island is not fully strained. Some strain is also transferred into the surrounding Si matrix as indicated by finite element calculations [29].

Obviously, it would be preferable to have a combination of self assembling Ge islands with tensile strained Si close to the center of the Ge islands, which provides electron localization and overlap of the electron and hole wave functions. This situation can be realized in vertically aligned densely stacked Ge islands.Figure 5 shows a cross-sectional TEM micrograph of a sample with 5 layers of stacked nominally 6.5 ML Ge islands and a nominal Si spacer thickness of 13 nm. Finite element calculations for this sample structures [23] demonstrate that the compressive strain within the vertically aligned

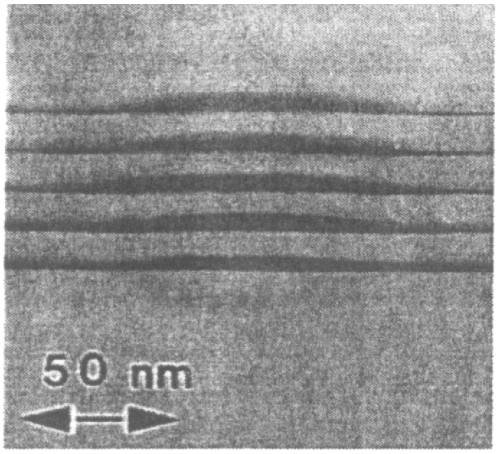

Figure 5. Cross-sectional TEM micrograph from five times stacked 6.5ML Ge islands with Si spacer thickness of 13nm.

dots decreases and compared to single Ge dot samples more strain is transferred into the surrounding Si matrix. It is obvious that the thin Si layers between the Ge islands will be under considerable lateral extension as the Ge islands reduce their compressive strain. This is illustrated by arrows in the upper part of figure 6. The lateral extension of the thin Si layer between the Ge is about 0.5% to 1 % for the sample shown in figure 5. The measured thickness of the Si spacer layers across the central line of the vertically aligned Ge islands is about 5-7 nm. A 0.5 to 1 % in-plane extension of the Si spacer layer at this position introduces a band offset in the order of 100 meV for the Δ2 minima. This effect is schematically indicated in figure 6b. It also illustrates the optical transitions in such densely stacked Ge islands from the 2-fold degenerated Δ states (Δ2) in the CB to the heavy holes (hh) states confined within the compressively strained Ge islands.

The Δ2 CB states are at k_x and $k_y = 0$. The electrons are strongly localized along growth direction z because the Si spacer layer is only about 5-7 nm along the center line of the Ge islands (A-Á in figure 6a). This causes relaxation of k conservation for k_z and, consequently, enhanced optical no-phonon transitions can be expected even without strong carrier confinement in all three directions. Figure 7 shows the measured PL intensity at room temperature for the 5 times stacked 6.5 ML Ge islands in Si shown in figure 5. The intense peak at exactly 1.55 µm wavelength originates from the Ge islands. The temperature dependent PL intensity is shown in the insert. The calculated activation energy is 181 meV, which is about the same as the energy difference between the PL from Ge island and the wetting layer, as shown in figure 3 for the single layer and in ref. [23] for the stacked sample. The measurement shown in figure 7 is a first promising result. We expect significant space for improvement of optimized structures, especially with the Ge island size and Si spacer layers tuned thinner

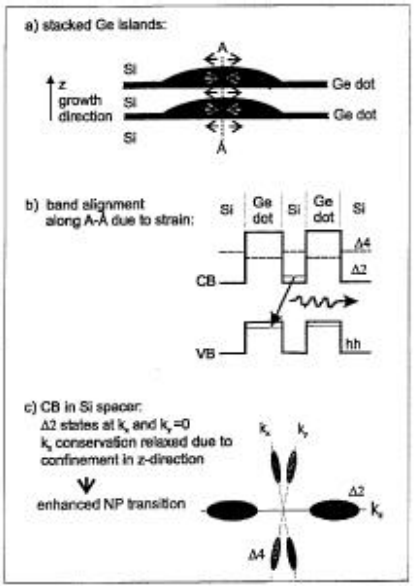

Figure 6. Schematic illustration of the optical transitions in densely stacked Ge islands:
(a) Compressive and tensile strain within the Ge islands and the Si spacer layers between the islands, respectively. (b) Band alignment along the line A-Á indicated in a). Optical transitions are expected from the 2-fold degenerated Δ states (Δ2) in the conduction band to the heavy holes (hh) states confined in the compressively strained Ge dots. (c) The Δ2 CB states are at k_x and k_y = 0. The electrons are strongly localized along growth direction z because the Si spacer layer is only about 5-7 nm thick between the Ge islands. This causes relaxation of k conservation for k_z and as a consequence enhanced optical no-phonon transitions can be expected.

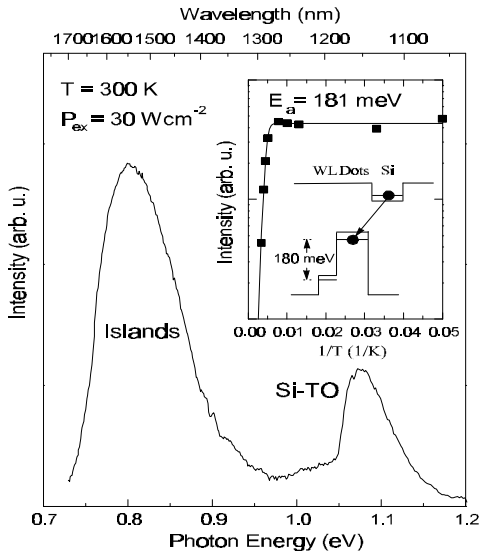

Figure 7. PL intensity at room temperature for the 5 times stacked 6.5 ML Ge islands in Si shown in figure 5. The peak at 1.55µm originates for the Ge islands. The insert shows temperature dependent PL with the activation energy determined as 181 meV.

for larger momentum uncertainty in k_z – direction and improved overlap of the electron and hole wave functions.

3. Conclusions

Pure Ge epitaxially grown on Si (100) at high temperatures forms typically 100 nm lateral size islands on top of a 3-4 monolayer thick wetting layer. In stacked layers of Ge dots pronounced vertical alignment is observed if the thickness of the Si spacer layers is smaller than about 50 nm [27].

Pregrowth of a small amount of C on Si substrate induces very small Ge quantum dots with a lateral size of 10 nm and a height of 1-2 nm after deposition of about 2 to 3 monolayers Ge. PL studies indicate a spatially indirect radiative recombination mechanism between electrons in the C-rich SiGeC wetting layer and holes localized in the Ge dots, with the no-phonon line strongly dominating.

Strong confinement shift in these extremely small quantum dots results in low activation energies of only about 30 meV, which causes luminescence quenching above 50 K. Thus, the application of these quantum dot structures for room temperature emitters will be difficult. For the large stacked Ge dots with extremely thin Si spacer layers we observe a significantly enhanced Ge dot related PL signal up to room temperature at 1.55 µm wavelength. This is attributed to spatially indirect transitions between heavy hole states confined within the compressively strained Ge dots and Δ2 state electrons in the tensile strained Si between the stacked Ge islands.

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