Thermal Stability of Defect-Enhanced Ge on Si Quantum Dot Luminescence upon Millisecond Flash Lamp Annealing

Lukas Spindlberger,* Slawomir Prucnal, Johannes Aberl, and Moritz Brehm*

The intentional merging of epitaxial Ge on Si(001) quantum dots with optically active defect sites promises low-cost applications such as room temperature (RT) light emitters in Si photonics. Despite recent progress in this field, important benchmarks, for example, the thermal stability of such a combination of low-dimensional nanosystems, as well as the curing of parasitic charge-carrier recombination channels, have been barely investigated thus far. Herein, the structural robustness of defect-enhanced quantum dots (DEQDs) is examined under millisecond flash lamp annealing (FLA), carried out at sample temperatures up to 800 °C. Changes in the optical DEQD properties are investigated using photoluminescence spectroscopy performed in a sample temperature range from 10 to 300 K. It is demonstrated that FLA—in contrast to in situ thermal annealing—leads to only negligible modifications of the electronic band alignment. Moreover, upon proper conditions of FLA, the RT emission intensity of DEQDs is improved by almost 50% with respect to untreated reference samples.

1. Introduction

Thermal annealing is omnipresent in Si-based semiconductor technology,[1–3] including processes like dopant activation and recrystallization of crystal regions affected by ion implantation.[4–6] These are processes with a large thermal budget that impose a natural bottleneck for any new technologies that aim at entering the existing Si technology. This is particularly true when dealing with low-dimensional nanostructure systems such as quantum dots (QDs) for which already slight changes in size and material composition induced by bulk or surface diffusion effects can detrimentally change their designed optical or electronic properties.

In this work, we investigate the influence of millisecond flash lamp annealing (FLA)[7–9] on the optical properties of recently discovered defect-enhanced quantum dots (DEQDs). DEQDs consist of epitaxially grown Ge QDs on Si substrates containing isolated point defects that are intentionally introduced in situ upon low-energy Ge ion implantation.[10–12] These nanostructures exhibit exciting optical properties, i.e., clear signs for optically pumped lasing from DEQDs in photonic resonators,[10,11] and DEQD light emitting diodes operating efficiently at temperatures of 100 °C have been reported recently.[13] Thus, the DEQD system is an imminent candidate as gain material in Si-compatible light sources to be used in the field of Si photonics,[14,15] i.e., for future on- and inter-chip optical data communication as well as sensing in lab-on-a-chip systems that are driven by the power of Si microelectronics.[16] However, the thermal stability of DEQDs was insufficiently investigated so far and is thus the topic of this work. Here, we examine the influence of high-temperature FLA on the optical properties of DEQDs. This was investigated by temperature-dependent photoluminescence (PL) spectroscopy in a very broad temperature range from 10 K to room temperature (RT).

2. Experimental Section

2.1. Sample Fabrication

The defect-enhanced Ge QD samples were grown on Si(001) substrates in a Riber Siva 45 solid-source molecular beam epitaxy (MBE) system. Before the growth, the samples were cleaned ex situ, including a standard Radio Corporation of America cleaning procedure. To remove the natural Si oxide at the sample surface, a dip in diluted hydrofluoric acid (1%) was performed right before loading into the load-lock chamber. After this, the samples were degassed in situ for 20 min at a sample temperature of 720 °C. First, a 50 nm-thick Si buffer layer was deposited at growth temperature (Tg) ramped down from 550 to 500 °C, the Tg for Ge deposition, followed by the growth of Ge QDs formed in the Stranski–Krastanow growth model[17] by depositing...
8.4 Å of Ge at $T_C = 500 \, ^\circ$C and a growth rate of 0.05 Å s$^{-1}$. At this growth temperature, QDs of {105}-faceted and $\approx$2 nm high clusters with Ge concentrations close to 100% evolve on the initially grown Ge-rich wetting layer. During the entire deposition time of Ge, Ge ions with an estimated dose of about $10^4$ μm$^{-2}$ were implanted into the Ge epilayer by applying a bias of −2 kV to the substrate. Applying such low-energy ion implantation using heavy ions like Ge$^+$ result in ion implantation depths of 1–2 nm which was carefully adjusted to the height of the QDs. This ensures that ions can stop within the formed Ge crystal and leads to beneficial optical properties of the QDs. To conclude the growth, a 70 nm thick Si capping layer was deposited at 0.6 Å s$^{-1}$ by ramping $T_C$ from 500 to 570 °C. In total, 15 nominally identical samples were fabricated, whereas 13 were treated by FLA, and two samples were used as reference.

2.2. Defect-Enhanced Quantum Dots

When the Ge ion with a given energy of $\approx$2 keV hits a Ge QD, it leads to a locally amorphized zone of about 1–2 nm depth in the Ge crystal lattice. The implantation of an excess heavy ion into an already perfect crystal lattice naturally leads to the formation of a crystal defect structure, at least as long as it ensures that the defect can not migrate to the sample surface. This is ensured by the employed growth conditions of the Ge epilayer and the Si capping layer. However, the thermal budget during the sample and Si capping layer growth is large enough ($T_C = 500 \, ^\circ$C), such that the initially amorphized zone recrystallizes to an atom configuration with minimum formation energy. From density functional theory calculations, it was found that such a minimum energy configuration would be a Ge–Ge split-[110] self-interstitial surrounded by a slightly distorted Ge crystal lattice. This interstitial defect leads to electron states at the Γ-point within the QD. Thus, despite the type-II band alignment in the Ge/Si system, electrons recombine directly with the holes confined in the Ge QD after tunnelling into the electron states at the defect site. Because tunnelling is temperature independent and holes are strongly confined by the large band offsets of Si and Ge of $\approx$300 meV, these DEQDs maintain their optical light emission properties up to RT and beyond. In addition to being used as gain material in optically pumped lasers, DEQDs possess especially high potential concerning electrically pumped semiconductor devices, as the active material is integrated into a single-crystalline Si matrix of excellent crystalline quality that is easily doped as p- and n-type. This was evidenced by the recent report on DEQD-LEDs working efficiently up to 100 °C.

2.3. Photoluminescence Spectroscopy

For the PL measurements, the samples were excited using a diode laser operating at 442 nm with a laser power of 1.6 mW and a spot diameter of about 2 μm. A microscope objective with a numerical aperture of 0.7 was used for both laser focusing and collection of the PL signal. The laser was filtered from the signal by a longpass filter with a cut-on wavelength of 850 nm. The PL response was coupled into a multimode fiber, dispersed by a grating spectrometer, and recorded by an InGaAs line detector cooled with liquid nitrogen. The detector cut-off at about 1580 nm does not detrimentally influence the peak positions of the DEQD PL spectra as demonstrated by Spindlberger et al. For the temperature-dependent PL measurements, the samples were mounted into a continuous flow cryostat cooled with liquid He. The laser spot size was kept constant during the temperature sweep from 10 to 300 K to ensure consistent excitation power density of about 50 kW cm$^{-2}$ and collection efficiency throughout the measurement.

2.4. Flash Lamp Annealing

Like rapid thermal annealing (RTA) or laser annealing (LA), FLA is a thermal annealing technique. These three annealing techniques cover significantly different time scales. On the one hand, the annealing times for RTA are limited to the range of 1–100 s, caused by the fundamental limits of halogen lamps, whereas LA covers annealing times from the millisecond range down to the nanosecond regime. On the other hand, FLA using Xe lamps is operated in the time range from 100 μs to about 100 ms. These different time scales directly affect the temperature distribution across the samples. Both RTA and FLA are methods for which whole wafers can be processed, which is not the case for LA for which the substrate is heated only locally. But in contrast to RTA for which the whole wafer is brought to a desired temperature, during the FLA process the annealed side of the sample is significantly hotter than the back side. Therefore, FLA is an important technology, e.g., for the fabrication of ultra-shallow junctions in advanced CMOS devices because the transient-enhanced dopant diffusion can be inhibited due to the significantly shorter annealing times as compared with RTA. Moreover, the FLA tool is equipped with a preheating system composed of halogen lamps. The applied preheating, prior to the flash, reduces the thermal stress created in the wafer during the millisecond range FLA. The short annealing times in FLA are appealing when dealing with DEQDs, as one seeks to only locally enhance lattice recrystallization while inhibiting SiGe intermixing and defect migration caused by long annealing times.

A schematic sketch of the FLA system used in these experiments is shown in Figure 1. The sample was mounted on a quartz holder inside the process chamber, which was flooded with $N_2$ to inhibit sample oxidation. For the experiments conducted in this work, three different flash lamp pulse durations...
(3, 6, and 20 ms) were performed without a preliminary heating step. The FLA voltages were carefully chosen in a way that the highest voltage of each FLA pulse duration set (3 ms: 4.35 kV; 6 ms: 3.6 kV; 20 ms: 3.8 kV) corresponds to a temperature on the sample’s surface of about 800 °C. Moreover, a decrease in the FLA voltage by about 200 V induced a change in the temperature at the sample’s surface by about 100 °C. Thus for each of the three pulse duration sets in the FLA experiments, surface temperatures ranging from 500 to 800 °C were achieved.

3. Results and Discussion

The integrated RT PL intensities ($I_{PL}$) of the three sample sets with FLA pulse durations of 3, 6, and 20 ms are plotted in Figure 2 for different FLA voltages, which correspond to different effective applied energy densities. Black squares depict $I_{PL}$ of the samples before the FLA treatment. Evidently, even though the samples were nominally grown in the same way, changes in the PL yield are observed. Thus, it is necessary to compare the influence of FLA on the PL emission (red circles) with the PL response recorded before FLA for the same sample (black squares).

Notably, the samples treated with 3 ms FLA pulses show the highest relative PL intensity increase of up to a maximum of almost 50% at RT, independently of the applied energy density as evaluated in the range from 45.8 to 60 J cm$^{-2}$. For the longer pulse duration times, the benefits of FLA become less clear. For 6 ms FLA and 20 ms FLA, a slight PL intensity improvement (<36% and <20%, respectively) is observed for lower energy densities, while for higher energy densities the PL response from DEQDs can be even slightly reduced. In general, the RT PL intensity benefits from FLA are more pronounced for lower thermal budgets, i.e., for shorter FLA pulses and lower energy densities.

In Figure 3a, the spectrum of the sample with the highest RT PL increase (3 ms, 60 J cm$^{-2}$, 4.35 kV) is plotted before (black) and after (red) FLA. Notably, and in strong contrast to in situ annealing of DEQDs reported in previous works,[12] the spectral shape at RT is not altered by FLA which can be attributed to a lack of structural change of the light emitter itself.

In Figure 3b, PL spectra recorded at sample temperatures $T_{PL}$ of 10 K are shown. In contrast to the results obtained at RT (Figure 3a), at $T_{PL} = 10$ K, no significant difference between the untreated reference (cyan) and the flash lamp annealed sample (blue) can be observed (Figure 3b). In Figure 3c,d PL spectra recorded at RT and 10 K are depicted originating from samples before and after FLA treatment at a longer FLA pulse (20 ms, 80 J cm$^{-2}$, 3.4 kV). No distinct shift of the emission wavelength is observable even after the application of a 20 ms FLA pulse. We tentatively attribute the PL enhancement at RT to the curing of thermally activated nonradiative recombination channels in the DEQD samples. To support this claim, we performed temperature-dependent PL measurements on a reference sample and a sample treated with FLA (3 ms, 60 J cm$^{-2}$, 4.35 kV). In Figure 4, the integrated PL intensities ($I_{PL}$) investigated for a $T_{PL}$ range from 10 to 300 K are plotted over the reciprocal temperature on a double-logarithmic scale. Both samples show a distinct plateau in $I_{PL}(T)$ between 170 and 250 K which is, however, more pronounced for the reference sample that did not undergo FLA treatment. The analysis of the origin of the plateau in $I_{PL}(T)$ (Figure 4) is still a matter of ongoing investigations. Here, we tentatively ascribe its existence to the capture and thermally activated release of charge carriers trapped at localized states in the Si matrix induced by imperfect ion implantation conditions.[22]

The activation energies describing the thermal PL intensity quenching for temperature below and above this plateau were extracted using Arrhenius fits

$$I_{PL}(T) = I_0 \cdot \frac{1}{1 + A \cdot e^{\frac{-E}{kT}}}$$  

The resulting two activation energies for the reference sample are $E_{A1}(\text{Ref}) = (285 \pm 26.5)$ meV and $E_{A2}(\text{Ref}) = (11.2 \pm 0.3)$ meV for the quenching of $I_{PL}(T)$ at high and low temperatures, respectively. The corresponding activation energies for the FLA-treated sample are found to be $E_{A1}(\text{FLA}) = (317 \pm 30.6)$ meV and...
$E_{A2}^{\text{FLA}} = (7.7 \pm 1.2) \text{ meV}$ for the high- and low-temperature quenching, respectively. The smaller activation energies $E_{A2}$ can be ascribed to exciton binding energies in the system, whereas the higher $E_{A1}$ of $\approx 300 \text{ meV}$ was, in previous works, attributed to the thermally induced escape of holes from the deep QD potentials that are induced by the large valence band offsets of the Ge/Si hetero interface.\[10\]

As the spectral shape of the PL emission does not change if the FLA treatment is applied (Figure 3), we conclude that the increase in $I_{\text{PL}}$ at RT induced by the FLA treatment is not based on an alteration of the emitter properties, e.g., changes in the microstructure of the defects or intermixing of the Ge QD crystal with the surrounding Si matrix material.\[12\] The emission enhancement is, therefore, likely caused by the thermal curing of residual defects in the Si matrix below the DEQDs, possibly originating from imperfect implantation conditions caused by implantation through the only $\approx 4$ monolayer-thin Ge wetting layer between two adjacent QDs.\[22\] A reduction in such nonradiative recombination centers will lead to an increased fraction of charge carriers contributing to radiative recombinations and thus to a higher

Figure 3. a) RT PL spectra before (black) and after (red) a 3 ms FLA pulse with an energy density of $60 \text{ J cm}^{-2}$ resulting in a peak surface temperature of about $800 \text{ °C}$. b) Low-temperature PL spectra of the very same samples before and after the FLA treatment recorded at a temperature $T_{\text{PL}}$ of 10 K. c) RT PL spectra before (black) and after (red) a 20 ms FLA pulse with an energy density of $80 \text{ J cm}^{-2}$ resulting in a peak surface temperature of about $600 \text{ °C}$. d) Low-temperature PL spectrum of the sample after the FLA treatment reported in (c) measured at a temperature $T_{\text{PL}}$ of 10 K.

Figure 4. Temperature-dependent PL measurements of an FLA-treated sample (red circles) and an untreated reference (black open squares) on a double-logarithmic scale. The activation energies for thermal PL quenching are extracted using Arrhenius fits (solid and dashed lines).
pumping efficiency of the light emitters. The low-temperature PL measurements in Figure 3 and 4 suggest that carriers at nonradiative recombination centers cannot be thermally detrapped at temperatures below \( \approx 35 \) K. With increasing \( T_{\text{PL}} \), the PL intensity of FLA-treated DEQDs increases as compared with the untreated reference DEQDs, leading to \( \approx 30 \) meV higher activation energies for thermal quenching and a clearly improved PL yield stability with increasing \( T_{\text{PL}} \). As a universal approach to cure possible remaining nonradiative defects in the Si matrix that are caused by imperfect ion implantation conditions, we will consider for future works supplementary hydrogen passivation techniques that can be paired with the FLA method presented in this work.

4. Summary

The main conclusion of this work is that we were able to demonstrate that DEQDs can withstand high temperatures of up to \( 800 \) °C, occurring during FLA processes. We show that FLA—in contrast to in situ thermal annealing\([12]\)—leads to only negligible modifications of the electronic band alignment. What is more, for accurately chosen FLA treatment parameters, the optical emission yield can be amplified by almost 50% as compared with untreated reference samples. We envision that an adaptation of the ion implantation voltage to the corresponding actual film thickness during growth or a delayed implantation that starts only after QD formation will allow us in the future to further boost light emission from DEQDs.

The FLA-treated samples presented here exhibit an improved stability of the PL emission intensity over a temperature range from 10 to 300 K which we attribute to the reduction of nonradiative recombination centers in the Si matrix. Overall, these results show that DEQDs can in principle be implemented into hybrid integrated circuits where high-temperature steps are necessary for the fabrication process.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

flash lamp annealing, germanium, photoluminescence, quantum dots

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