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Tuning the luminescence emission of {105}-faceted Ge QDs superlattice using proton implantation and thermal annealing

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ABSTRACT

We report on the low temperature PL emission of self-assembled Ge/Si(001) hut cluster multilayers grown by molecular beam epitaxy at relatively low temperature. We found that PL spectrum of Ge/Si hut cluster superlattice is slightly blueshifted with respect to the emission of single layer. The dependence of PL spectra on rapid thermal annealing temperature was investigated. We found a hitherto unexpected result, namely a remarkable difference in PL emission thermal behavior between multilayers and single layer. In contrast to single layer case, annealing-enhanced PL intensity is found to be ineffective for multilayer structures. Moreover, an anomalous redshift is observed after annealing below 780 °C. The origin of this redshift is tentatively attributed to a possible enhancement of the tensile strain in Si interlayers during annealing in this range of temperature. Further increase in temperature induces a blueshift in PL emission. Post-annealing induced increase of PL intensity has been found to be less pronounced than in single layer samples. We also show that proton implantation can be used to tune the emission energy of hut cluster superlattice. PL spectra are found to shift upwards depending on ion dose by ~25 to 130 meV after implantation followed by a flash annealing at 750 to 900 °C. The detected blueshift is attributed to radiation defect mediated Si–Ge intermixing.

1. Introduction

The 4% lattice mismatch between Ge and Si drives the self-assembly of Ge islands via the Stranski–Krastanow growth mode [1]. These low-dimensional heterostructures are promising candidates as light emitter compatible with CMOS technology making conceivable the monolithic integration of electronic and optoelectronic devices in the same platform. Under given growth conditions Ge/Si islands have well-defined sizes and shapes. Essentially four forms of islands have been reported: shallow mounds (prepyramids), pyramidal {105}-faceted clusters—the so-called hut clusters, square-based pyramids and large domes with facets in different orientations [2]. In particular, Ge/Si hut clusters have been the subject of intensive studies due to their quantum size and high density. However, most of the investigations have dealt with their structural properties [3].

Although hut clusters present interesting attributes in terms of size and density, only few works were devoted to investigate their optical properties [4–7]. These huts emit a PL signal centered on ~800 meV associated to phononless radiative recombination. The emission energy has been found to be sensitive to Ge coverage, Si capping temperature, and post-growth annealing temperature [4,6]. In a recent report [7], a systematic study was performed to evidence and to single out the contribution of point defects to PL signal of hut clusters grown by chemical vapor deposition (CVD). In fact, the relatively low temperature (generally lower than 530 °C) required for the growth of hut clusters induces highly defective epilayers due to the reduced mobility of adatoms. Therefore, the observed PL of hut clusters may contain defect bands sometimes found near similar energies in dislocated or damaged Ge/Si heterostructures [8,9].

To the best of our knowledge, all reports on PL of hut clusters treat only the case of a single layer of these nanostructures. PL studies of multilayer hut cluster structures are still missing. In this work, we mainly deal with this issue by investigating the PL emission of ultra small Ge/Si islands superlattice grown at relatively low temperature. The dependence of PL spectra on rapid thermal annealing (RTA) temperature has been investigated. In contrast to single layer case, where a systematic blueshift has been observed after annealing, we found that PL evolution as a function of RTA temperature shows two regimes. A redshift of PL spectra is observed after annealing at temperature below 780 °C, whereas annealing above this temperature induces a blueshift. We also studied the effects of proton implantation at different doses on the emission properties of hut clusters superlattice. No significant PL signal is detected immediately after implantation. However, 1 s flash annealing

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above 750 °C has been found to be efficient for PL recovery. Post-implantation annealing induces a blueshift of PL spectra which is slightly sensitive to the implanted dose.

2. Experimental details

Ge/Si hut clusters superlattice structures were grown by solid-source molecular beam epitaxy (MBE) on Si(001) wafers that were chemically cleaned using modified Shiraki's method [10], introduced to MBE chamber, and deoxidized at 900 °C. 20 periods of 6 ML (monolayers) of Ge layers separated by 15 nm Si layers were deposited at 520 °C. Ge clusters are grown at rate of 0.04 ML/s using ^{70}Ge-rich source. An atomic force microscopy image of a reference structure is shown in Fig. 1(a). We note that the lateral size of the grown islands is about 20–50 nm, the height is about 1–2 nm, and the cluster density is in the order of 10^{11} cm^{-2}. Cross section electron transmission microscopy image of the grown superlattice shows that Ge/Si hut clusters are not vertically correlated (Fig. 1(b)). One series of superlattice samples was than implanted by hydrogen. Ion implantation was performed at room temperature at four different doses ranging from 1×10^{13} to 5×10^{14} ion/cm^2. The energy of the ions is 20 keV which places hydrogen and damage peaks over hut cluster region as shown in Fig. 1(b) displaying the implantation profiles as calculated using SRIM code [11]. To minimize the channeling effect, the implantation is carried out at 7° off <100> direction. As-grown and implanted samples were subject to RTA at temperature in the range of 730–900 °C. Low temperature (2 K) PL measurements were carried out using a Fourier transform spectrometer under the excitation of a 514.5 nm line of an Ar$^+$ laser. The excitation power was kept at 150 mW. The PL signal was collected with a liquid nitrogen cooled InSb photodetector.

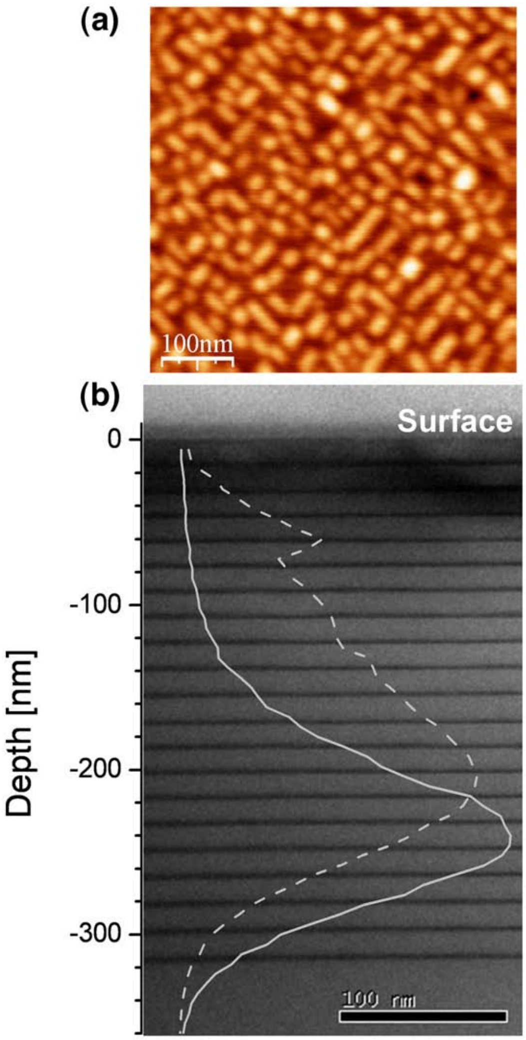

Fig. 1. (a) Atomic force microscopy image of Ge/Si hut clusters grown after deposition of 6 ML for Ge at 520 °C; (b) Cross section transmission electron microscopy image of 20 periods of 6 ML Ge/Si hut cluster layers separated by 15 nm Si layers. Gray lines show the calculated implanted hydrogen ions at 20 keV (solid line) and implantation damage (dashed line) profiles.

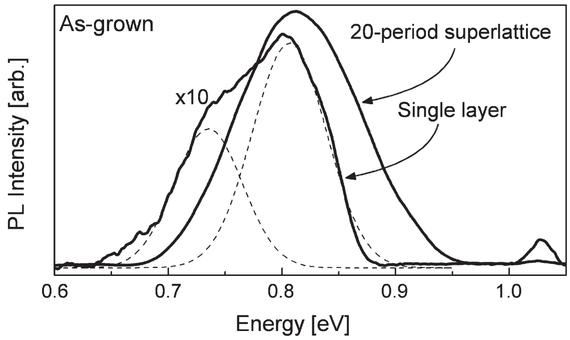

Fig. 2. 2 K PL spectra of Ge/Si hut cluster single layer and 20 periods superlattice.

3. Results and discussion

For comparison, Fig. 2 displays PL spectra recorded immediately after the growth for Ge/Si hut cluster single layer and multilayers structures. PL signal recorded for Ge/Si hut cluster single layer shows an asymmetric band around 650–850 meV consistent with the earlier observations [4,6]. This band can be deconvoluted in two Gaussian peaks centered at ~735 meV and ~807 meV. Low-energy asymmetry of PL spectrum has been previously reported for CVD grown Ge/Si hut cluster single layer [7]. However, in that work, the low energy shoulder has been observed around ~776 meV and attributed to point defects incorporation in silicon

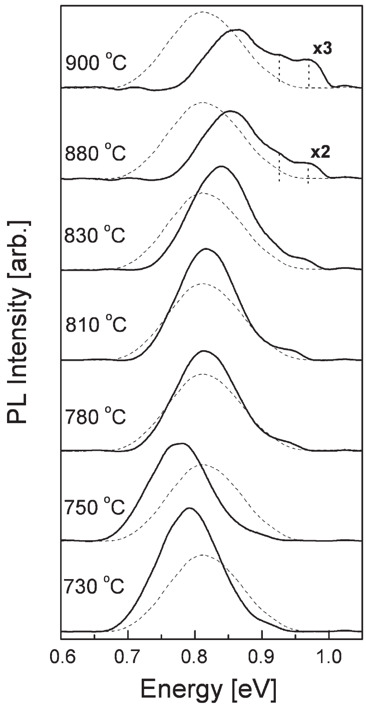

Fig. 3. 2 K PL spectra of Ge/Si hut cluster multilayers after 1 s RTA at temperature ranging from 730 to 900 °C. As a reference, the as-grown PL signal is included as dashed lines.

epilayers during the growth. It has been shown that this low energy shoulder disappears after flash annealing at temperature around 750 to 850 °C. In the other hand, PL emission detected from superlattice shows a well-defined Gaussian band at 812 meV and having a ~106 meV full width at the half maximum. The low energy shoulder is not detected.

Fig. 3 displays the 2 K PL spectra of Ge/Si hut cluster superlattice after 1 s post-growth RTA at different temperatures. Spectra of the as-grown sample are shown as a reference (dashed lines). A slight increase of the Ge-related PL intensity, compared to the as-grown intensity, is observed after annealing at temperature below 830 °C. A more pronounced enhancement has been found for a single layer of hut clusters annealed under the same conditions (not shown) or annealed for longer duration at relatively lower temperature [5]. This increase in PL intensity after post-growth annealing is attributed to reduction of point defects density [12,13]. Intriguingly, thermal evolution of the emission energy shows a quit different behaviour compared to single layer sample in which a systematic blueshift is observed by increasing annealing temperature. Indeed, in multilayer structure the annealing below 780 °C induces a redshift in PL spectra with a maximum of ~32 meV at 750 °C. It is well known that an increase in Ge content or a decrease in Ge/Si cluster size may induce a redshift in PL spectra of Ge/Si nanostructures. Obviously, this cannot explain our observations since the post-growth annealing induces a decrease in Ge content due to Si–Ge intermixing which is always associated with an increase in Ge/Si island size. Alternatively, a possible enhancement by annealing at this range of temperature of the tensile strain in Si interlayers may explain the observed redshift [14]. This tensile strain was evidenced by our Raman analysis (not shown), however, the presumed enhancement is below Raman sensitivity. Above 780 °C, the emission energy shifts up and simultaneously high energy shoulders appear in PL spectra. In the temperature range of 780–830 °C only one shoulder can be distinguished at ~100 meV from hut cluster PL peak. At 880 and 900 °C a second peak emerges at relatively lower energy compared to low temperature shoulder. The two shoulders are separated in energy by ~55 meV indicating a quantum-well-like PL signature generally observed as the 3D confinement potential becomes smeared out [4,13]. This splitting of PL spectrum is also detected for relatively long annealing durations (15 to 60 s) at 800 °C (not shown).

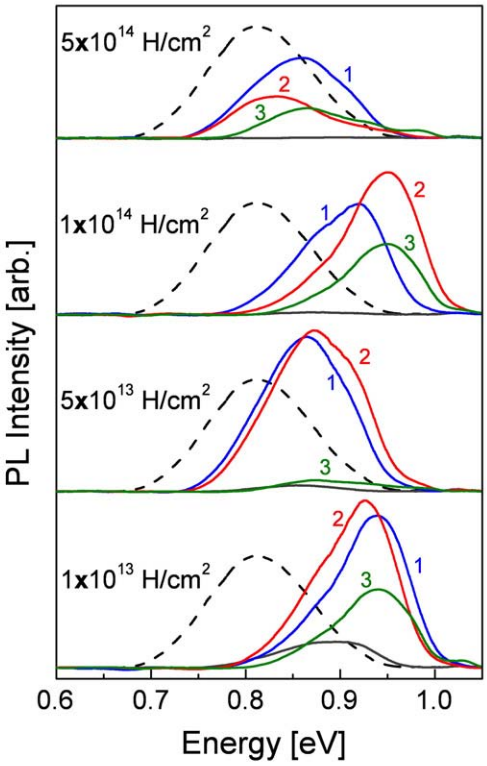

Fig. 4. H-implanted Ge/Si hut cluster superlattice PL spectra collected at 2 K for: as-implanted (gray lines), post-implantation annealed for 1 s at 750 °C (1), at 800 °C (2), and at 900 °C (3). As a reference, the as-grown PL signal is included as dashed lines.

In Fig. 4, we show the 2 K PL spectra of H-implanted Ge/Si hut superlattice at different doses before and after 1 s RTA at 750, 800 and 950 °C. Expectedly, no significant PL signal is detected immediately for as-implanted samples due to nonradiative defects which sharply reduce the carrier lifetime. Note that at the lowest dose a weak PL signal is detected. This can be explained by the non-uniformity of implantation damage which shows a depth distribution with low defect concentration in the top and bottom of Ge/Si hut cluster superlattice as can be seen in SRIM calculated profiles (Fig. 1(b)). In the addition to this weak intensity detected, PL spectrum is shifted upwards by ~80 meV compared to unimplanted sample. This blueshift is attributed to ion implantation induced Si–Ge intermixing. Further increase in the implantation dose induces a high level of damage which blocks the radiative transition in hut cluster multilayers.

Interestingly, and independently on the ion dose, PL recovery is observed after 1 s flash annealing at 750 °C with a blueshift of the emission energy. As mentioned above, the detected blueshift is attributed to implantation damage mediated intermixing in Ge/Si hut clusters. The PL recovery is more important at the lowest doses 1×10^{13} and 5×10^{13} H/cm^2 with an enhancement of the intensity compared to the as-grown superlattice. This increase in PL intensity could result from annealing induced defect recombination or hydrogen passivation of the nonradiative trapping centers. Similar observations have been reported for InAs/InP quantum dots [15,16]. By increasing RTA temperature to 800 °C PL signals shows different behaviours as a function of the implanted dose. At 1×10^{13} and 5×10^{14} H/cm^2 a slight redshift is detected, whereas PL emission is shifted up for 5×10^{13} and 1×10^{14} H/cm^2. PL intensity diminishes at the highest dose with respect to as- grown spectrum while at the same time an enhancement is recorded for other three doses (more pronounced for 1×10^{14} H/cm^2). Finally, PL emission is significantly reduced for all doses after RTA at 900 °C.

From Figs. 3 and 4, we note that the redshift detected in PL spectra of unimplanted samples after annealing below 780 °C is no more observed in H-implanted spectra. The blueshift is more pronounced for H-implanted samples at 1×10^{13} and 1×10^{14} H/cm^2. While the blueshift of PL spectra of unimplanted samples becomes important by increasing RTA temperature, the peak position of PL emission from H-implanted superlattice is not very sensitive to annealing temperature. In other hand, the evolution of the integrated intensity seems to be qualitatively the same for unimplanted and implanted multilayers. Contrarily to InAs/InP quantum dots where an important increase in PL emission has been reported [15,16], no significant enhancement is observed in PL emission of H-implanted Ge/Si hut cluster multilayers. Note that the lowest PL intensity is recorded for the sample implanted at the highest dose (5×10^{14} H/cm^2). This is mainly due to the high damage level induced at high implantation dose and 1 s annealing seems to be too short to allow an excellent recovery of PL. One intriguing aspect of these measurements is the evolution after annealing of PL emission energy as a function of the implanted dose. One may expect that by increasing the implanted dose the defect mediated intermixing becomes more important leading to a blueshift of PL signal. However, we found that the extent of the blueshift does not increase but oscillates as a function of the implantation dose. The origin of these observations is still unclear.

4. Conclusion

In summary, we have studied the low temperature PL emission of Ge/Si hut cluster multilayer structures. Immediately after the growth, PL signal of hut cluster superlattice is a well-defined Gaussian in contrast to signal layer PL emission characterized by a low energy asymmetry. The emission energy shows two different regimes as a function of RTA temperature. A redshift is observed following the annealing below 780 °C. This redshift has been tentatively attributed to an enhancement of the tensile strain in Si interlayers after annealing at this temperature range. Above 780 °C PL emission is shifted up due to Si–Ge intermixing. By using proton implantation we demonstrate that PL emission energy can be tuned due to defect mediated intermixing. However, no significant enhancement in PL intensity is observed after implantation and RTA. We attribute this fact to the short annealing time used (~1 s) which may limit the PL recovery.

Acknowledgments

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