Optical and structural properties of Ge submonolayer nano-inclusions in a Si matrix grown by molecular beam epitaxy

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Abstract
The optical and structural properties of the Ge submonolayer nano-inclusions in a Si matrix grown by molecular beam epitaxy are investigated. It is shown that at relatively high growth temperatures >600 °C new features appear in the photoluminescence spectra. It is found that these features correspond to formation of the germanium nano-inclusions in a silicon matrix.

1. Introduction
Nowadays, silicon is the base material in the microelectronics market but it is hardly applicable in optoelectronics due to its indirect bandgap nature. Nevertheless, the integration on the same wafer of the well-developed silicon microelectronics technology with optical devices is one of the most actual tasks attracting significant efforts. Several approaches have been proposed to fabricate silicon-based light-emission (SBL) devices using porous silicon [1], Ge/Si and GeSi/Si quantum dots (QDs), rare-earth doping of silicon [2], insertion of InAs nano-inclusions in a Si matrix [3], etc. Despite progress in this area, these approaches have had no practical use until now. This fact has encouraged us to find other ways of obtaining SBL. In this paper we propose to insert a Ge submonolayer (SML) in a Si matrix and to investigate the optical properties of these heterostructures.

Our approach is based on the following assumption: Ge SMLs in Si may lead to the formation of the ensemble of relatively small islands (with lateral sizes less than the hole Bohr radius). This can result in a partial lifting of the selection rule for radiative recombination and exciton formation (which may be stable up to room temperature) via electron and localized-hole interaction. This situation is possible if the Coulomb attraction energy is high enough to localize electrons near the potential barrier which is produced by Ge SML inclusions in the conduction band. In the case of relatively large sizes of QDs or large widths of quantum wells, this barrier may also lead to spatial separation of the electrons and holes [4]. Furthermore, for the SML in other heteroepitaxial systems [5, 6] the narrow photoluminescence (PL) line leads to the increase of the absorption (gain). The PL intensity will increase if multiple vertical stacking of the layers is used with Ge SMLs separated by Si spacers. Due to relatively small strain accumulation in such a system, it is expected that there will be a low probability of dislocations and formation of structural defects.

2. Experiment
All structures are grown by molecular beam epitaxy (MBE) using a Riber SIVA 45 set-up on Si(100) n-type substrates (conductivity 3 Ω cm). The substrates are five inches in diameter, manufactured by OKMETIC. After chemical preparation by the method described in [7] the substrates are transferred into the MBE set-up loading chamber. This method of preparation allows us to remove the oxide layer from the silicon surface at 840 °C in the growth chamber by direct radiating heating. During the growth process the rotation of the samples is used, and the temperature field inhomogeneity across the surface is about ~5%. In order to grow Ge SMLs we use the SML epitaxy technique, which we have also used to grow the SML insertions in the A3B5 and A2B6 systems [8–10].
The structures consist of a Si 1000 Å buffer layer, a Ge(0.7–1.3 Å)/Si(44 Å) superlattice (20 pairs) and a silicon 200 Å capping layer. The growth rates for Si and Ge are 0.5 and 0.05 Å s\(^{-1}\), respectively. The growth rate is controlled by two mass spectrometers with feedback which are set to 28 (Si) and 74 (Ge) masses. The substrate temperatures are varied from 600–750 °C. The total pressure during growth is better than 5 x 10\(^{-9}\) Torr. The surface is monitored in situ by reflection high-energy electron diffraction (RHEED).

The PL is excited by an Ar\(^+\) laser (\(\lambda = 514.5\) nm, maximal excitation density \(~500\) W cm\(^{-2}\)), and is detected by a Ge-cooled photo-diode. During the growth process, the RHEED patterns show behaviour independent of the growth temperature in comparison with the initial surface reconstruction (2 x 2). Thus, even on the upper layers of the superlattice the surface remains atomically smooth and the three-dimensional (3D) structural formation due to strain relaxation does not occur.

The samples were investigated by different electron microscopic techniques and selected area electron diffraction (SAED).

3. Results and discussion

As was shown in [7], a new set of PL lines appears if the structure with SML Ge inclusions (the structure consisting of 99 pairs of 0.7 Å Ge SMLs separated with 35 Å Si spacers) is grown at a relatively high temperature (>750 °C).

These PL lines exist both at high and low levels of excitation density and correspond to emission from excitons localized at germanium islands in the SML superlattice. We have found that such lines (denoted in following as SL lines) are present in PL spectra in the growth temperature range 600 °C < \(T < 800\) °C (due to effective silicon and germanium intermixing and the formation of the solid solution at a high temperature). The increase in the growth temperature leads to a narrowing of the SL PL line. A maximal PL intensity from SL is observed for the substrate temperature 650 °C during the growth of the active region under similar growth conditions.

For the set of samples investigated in this work we have found that the integral intensity ratio between the SL–TO and Si–TO lines is very sensitive to excitation density. In figure 1(a) PL spectra taken at different excitation densities for the sample with 20 layers of 1 ML of Ge separated by 44 Å Si spacers are shown; the growth temperature for the active region is 750 °C. There is steady increase of the integral intensity ratio of Si–TO/SL–TO lines with the increase of excitation density, but even at very high excitation levels the integral intensity ratios of these lines are comparable. At low excitation levels the SL–TO line dominates the spectra. The full width at half maximum is about 15 meV. The SL–TO line shifts towards long wavelengths with the increase of the excitation density.

In figure 1(b) PL spectra for the same sample taken at different temperatures and a constant excitation density of \(~500\) W cm\(^{-2}\) are shown. There is a significant decrease of the SL–TO intensity line with the observation of the temperature increase, which is accompanied by a blueshift. In contrast, a large redshift in comparison with the shift of band PL was observed, for example, in the InAs/GaAs heteroepitaxial system [11]. This was explained by both bandgap shifting and the evaporation of carriers from small QDs having lower localization energy. In our case the observed phenomena cannot be explained in the framework of this simple model. Possibly it occurs due to the occupation of excited states on the islands with the increase in temperature or due to the redistribution of carriers between islands of different sizes.

The SL–TO line exhibits a shift towards long wavelengths with the increase of Ge in each layer of the SL. In figure 2 PL spectra for the samples with 0.7, 1.0 and 1.3 Å of Ge in each layer of the SL are shown. This shift can be explained by the increase of the lateral size of the Ge islands. However, if the height of the Ge nano-islands becomes larger than the respective hole Bohr radius, then holes delocalize in a direction perpendicular to the growth direction and the efficiency of the corresponding lines in the PL spectra can decrease.

The cross-section images of the grown structures taken in a diffraction contrast mode at relatively low resolution are shown in figure 3. The periodicity in the [001] growth direction is 4.4 nm in both cases. It should be noted that the images...
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1.00 1.05 1.10 1.15

PL intensity, arb. un.

Ar laser 15 K

1.069 eV

Ge (0.7Å) / Si(44Å) x 20

1.064 eV

Ge (1Å) / Si(44Å) x 20

1.060 eV

Ge (1.3Å) / Si(44Å) x 20

Figure 2. Effect of the influence of the amount of Ge in each layer on the PL peak position.

Figure 3. Cross section diffraction contrast images of specimens with 0.5 ML Ge (a) and 1 ML Ge (b). The periodicity of the structures in the [001] growth direction are equal to 4.4 nm in both cases.

Figure 4. Line scans in the [001] growth direction of the zero beam spot in the diffraction patterns from multilayer structures A (a) and B (b). In the case of sample B the number of satellites n is twice as large as that in sample A.

of both structures A and B look almost identical under these imaging conditions. However the diffraction patterns show a distinct difference (figures 4(a) and (b)). In the diffraction pattern from the superlattice formed by 0.5 ML Ge layers (specimen A) the number of Fourier harmonic n is twice less than in the case of 1 ML one (specimen B). This means that the thickness of the incorporated Ge layers in the second case is practically one or/and two monoatomic layers while in the first case it amounts to several monolayers. Compositional non-uniformities of different contrast and very high density are clearly resolved in the plane-view transmission electron microscopy (TEM) image (figure 5(a)) of the SML sample, as opposite to the smooth TEM image of the 1 ML structure.

The single monolayers of Ge are clearly seen in the high-resolution cross section image (figure 6(a)) taken from the very thin crystal region (t ≈ 20–30 nm) where the kinematical approximation still works well enough. According to this approximation $x = (k - 1)/(f_{Ge}/f_{Si} - 1)$, where $f_{Ge}$ and $f_{Si}$ are the atomic scattering amplitudes for Ge and Si respectively, and $k = ΔI_{Ge}/ΔI_{Si} = (I_{Ge,max} - I_{Ge,min})/(I_{Si,max} - I_{Si,min})$. This gives $x = 0.9 ± 0.1$ which indicates that these monolayers are practically pure Ge in the case of sample A, the compositional fluctuations are observed in the Ge SMLs (figure 4(a)). The thickness of these fluctuations in the [001] growth direction is about 0.8 nm which agrees quite well with the diffraction data in figure 4(a). Besides, in the plane-view images of sample A one can observe larger compositional inhomogeneities ($N = 1.7 × 10^{10} \text{ cm}^{-2}$) which look like very small QDs; these are completely absent in sample B (figures 5(a) and (b)). The diameter and thickness of these QDs estimated in the cross section high-resolution transmission electron microscopy (HRTEM) image (figure 7) are 7 and 3.5 nm, respectively. The PL spectra from specimens A and B
are shown in figures 1 and 2. Sample B with 1 Ge ML shows a rather uniform distribution of Ge in the layer plane. There is almost no appearance of intermixing in the perpendicular direction. This is a strong indication of the morphological stability of a one monolayer structure.

In conclusion, we have investigated the optical and structural properties of the Ge SML nano-inclusions in a Si matrix. We have shown that, under certain growth conditions, new lines appear in the PL spectra. These lines correspond to the formation of the Ge nano-islands with sizes less than the respective hole Bohr radius. If their sizes are higher, there are no such PL lines. The investigated system may be considered as one possible way of creating SBLE devices.

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References