Mechanism of germanium nanoinclusions formation in a silicon matrix during submonolayer MBE

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Abstract

Si/Ge multilayer structures formed by the embedding of relatively small amounts of germanium (less than the critical thickness for 3D island formation via Stranski-Krastanow growth mode) in a silicon matrix are obtained by submonolayer molecular beam epitaxy. Structural and optical properties of the grown structures are investigated. The formation of relatively small Ge clusters at appropriate growth conditions is observed. Possible growth mechanism responsible for the formation of Ge nanostructures is discussed.

Keywords: Silicon; Germanium; Nanostructures; Submonolayers; MBE

1. Introduction

The strained SiGe/Si system is expected to play an important role in the Si-based opto-and microelectronic integration circuits. It is well known that the Ge/Si system is an example of Stranski-Krastanow growth mode, where 3D islands appear at the surface after exceeding of a certain critical thickness. In the present work, we report on the observation of the nanostructures formed by sub-critical Ge insertions in a Si matrix. For the submonolayers (SML) in other heteroepitaxial systems \[1,2\] is known that the narrow photoluminescence (PL) line leads to the increase of the optical gain. Concerning Si/Ge system, our approach is based on the following assumption: incorporation of a small amounts of Ge into Si may lead to the formation of the ensemble of relatively small islands resulting in a hole localization and exciton formation 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 produced by Ge inclusions in the conduction band. The PL intensity will also increase if multilayer structures are used in which Ge layers are separated by appropriate Si spacers. Due to the relatively small strain energy accumulation in such a system, low density of structural defects is expected. In fact, despite of the total amount of the Ge is lower than the critical thickness of 3D island formation, we show that they, under certain growth conditions, exhibit (quasi) 3D properties when capped with a host material (Si).

2. Experiment

All structures are grown by molecular beam epitaxy (MBE) on Si(1 0 0) substrates using a Riber SIV A 45 set-up. After chemical cleaning by the method described in Ref. [3], the substrates are transferred into the MBE set-up loading chamber. The method of chemical treatment allows us to remove the oxide layer from the silicon surface at 840 °C in the growth chamber by direct radiating heating. In order to grow Ge SMLs we use the SML epitaxy technique, which we have also used to grow the SML insertions in the \(A_2B_5\) and \(A_2B_6\) systems [4,5].

The structures consist of a Si buffer layer of 100 nm, a Ge/Si superlattice (20 pairs) and a Si 20 nm capping layer. The growth rates for Si and Ge are 0.5 and 0.05 Å/s, respectively. The substrate temperature \(T_s\) is set at 650 °C. Ge nominal thickness 0.07 or 0.14 nm is used. Spacer thickness is set at 5 nm. The total pressure during growth is better than \(5 \times 10^{-10}\) Torr. The surface
Fig. 1. TEM plan-view images of samples containing 0.07 nm (a) and 0.14 nm (b) of germanium.

is monitored in situ by reflection high-energy electron diffraction. The PL is excited by an argon laser (\(\lambda = 514.5\) nm, maximal excitation density \(\sim 10\) W/cm\(^2\)), and is detected by a Ge cooled photo-detector. The samples are also investigated by different electron microscopic (TEM) and selected area electron diffraction techniques using a JEM 4010 microscope with acceleration voltage (400 kV) and a CM 20 (200 kV) microscope equipped with a field-emission gun.

3. Results and discussion

As we demonstrated in earlier paper [6], for the substrate temperature \(T_s\) in the interval 600–700 °C and Ge layer thickness less than 1 ML (0.07–0.1 nm) new PL lines appeared. These lines were in the ranges (0.98–1.01), (1.04–1.07) and (1.11–1.13) eV (measured at 15 K) depending on the Ge amount deposited. Higher \(T_s\) led to significant decreasing of PL intensity. The effect observed was explained by the formation of quasi 3D inclusions in the sample with non-integer number of Ge ML [6] at the \(T_s\) less than 700 °C. In the following we describe the possible growth mechanism responsible for the formation of such Ge nanoclusters.

In Fig. 1a and b we present plan-view TEM images of the samples containing with 0.5 and 1 ML of Ge. One can easily see the structural differences. In the first case a high density of small 3D islands is observed (surface density \(\sim 5 \times 10^{11}\) cm\(^{-2}\)), whereas in the second case they are completely not observable. The analysis of cross-section high-resolution images and satellite reflections in electron selected area diffraction pictures shows that the thickness of the 3D islands is approximately 4–7 MLs, while in the sample grown with Ge 1 ML it is almost continuous monolayer. Similar results are obtained for the samples with Ge amount higher than 1 ML in sub-critical thickness range. Corresponding PL spectra of the same samples taken at helium temperatures are presented in Fig. 2. We emphasize that for an integer number of Ge (1 ML) deposited at the same \(T_s\) the intensity of Ge-associated PL lines decrease by at least 20 times integrally in comparison with the case of 0.5 ML of Ge deposited. We propose the following interpretation of the phenomenon.

It is well known from the theory of phase transformation in solids that above some size of (quasi) 3D inclusion they may transfer into the platelets. This size is determined by balance of elastic strain and surface energies. To put it differently, below this critical size the 3D shape of the inclusion is more energetically preferable, whereas above the critical size the platelet is more stable. The deposition of a half ML of Ge firstly results in the formation of relatively small one-atomic layer thick islands on the Si surface because the quantity of material (Ge) is not enough to fill completely the whole surface. After covering by Si these platelets turned out to be imbedded in bulk Si. They will transform into 3D inclusions if their diameter is below the critical size or otherwise will keep their platelet shape. Such is indeed the case (Fig. 1a and b).

To prove this mechanism we have grown a set of the samples with and without growth interruption (GI) after Ge deposition. We expected that during the GI Ge adatoms efficiently migrate on the surface and form larger 2D islands than without GI. If so, the GI case
should be similar to that we observe for full monolayer case. The size of these large islands is already far over the critical size which is why they will keep 2D shape after Si overgrowth. In Fig. 3 we compare PL spectra from the samples containing 0.07 nm Ge deposited at 650 °C one of which (#831A) is subjected to the 120 s GI and the other (#828B) is grown without GI. In fact, we have observed well pronounced PL peaks labeled as Ge–TO and Ge–NP correlated with the formation of 3D islands for the sample with no GI but such features are absent for the GI case. TEM images taken for these samples show very similar structure as presented in Fig. 1a and b: morphological features correspond to the formation of Ge nanoclusters for the sample without GI and otherwise smooth surface. It means that no 3D islands are formed during GI and consequent Si overgrowth due to the formation of the 2D nuclei with the lateral size exceeding the critical one. These results are in agreement with the simple growth model proposed above.

In conclusion, under appropriate MBE growth conditions we observe the formation of Ge nanoclusters having up to 3 nm diameter in a Si matrix. If such nanoclusters are formed and are embedded in silicon, they became optically active. Possible growth mechanism of the formation of these clusters is discussed on the basis of optical and structural data.

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References


