Sb mediated formation of Ge/Si quantum dots: Growth and properties

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The phenomenon of surfactant (Sb) mediated formation of Ge/Si(100) islands (quantum dots) by means of molecular beam epitaxy is discussed. The limited diffusivity of Si and Ge adatoms caused by the Sb layer leads to a reduction of the size of Ge islands, the increase in the island density, and the sharpening of the interfaces of Ge islands. Thereby, a thin Sb layer is considered to be a powerful tool that provides more freedom in designing Ge quantum dot features. Ge quantum dots, grown via a thin Sb layer and embedded coherently in a Si p–n junction, are revealed to be the origin of the intense photo- and electroluminescence in the spectral range of about 1.5 μm at room temperature.

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1. Introduction

Nowadays the search for an efficient silicon based light emitting source attracts a lot of attention, because the niche of the light emitter device for chip to chip communications is not yet occupied [1]. The low quantum efficiency of radiative recombination in bulk Si, caused by the indirect nature of its band gap, is the difficulty to overcome. While the hybrid III–V technology based on Si is supposed to be most promising, other approaches are investigated as well. In practice, there is a need for artificial centers in a Si matrix. Carriers being trapped there should recombine with a photon faster than non-radiatively in the Si host. In this respect, attention should be paid not only to these centers, but also to the quality of the surrounding Si matrix. These traps can be generated by a thin Ge layer, grown epitaxially on Si (100) substrates, e.g., in the form of quantum dots (QDs). The carrier lifetime in Ge QDs has been found in the range of micro-seconds [2]. A slight modification of the Ge QDs growth by using a thin Sb layer deposited prior to Ge pushes these lifetimes into the sub-microsecond range [3]. Sub-microsecond lifetimes have been found as well in Sb-mediated Ge QD multilayers [4]. These radiative recombination rates in Ge QDs are already shorter than the carrier lifetimes in nominally undoped Si (≥10 μs [5]), which can be obtained, for instance, by molecular beam epitaxy (MBE). Moreover, we have reported recently that Sb mediated Ge QDs are the origin of an intense photoluminescence (PL) at room temperature [6]. The latter means that the traps in the QDs are deep enough to localize carriers even at high (room) temperatures. Despite the fact that bulk Ge has an indirect band gap, the energy band diagram of Ge QDs in Si is modified due to the elastic strain and the quantum confinement effect. However, electrons and holes are still located on the opposite sides of the junction: electrons are located in Si, but holes are located in Ge [7]. Thereby the quality of the QD interface plays an important role as well. In the present study we investigated peculiarities of Sb-mediated Ge QD formation by MBE leading to room temperature electroluminescence (EL) of Si light emitting diodes.

2. Experiments

Since kinetics governs the Ge QDs formation in MBE, the lower the growth temperature, the higher the QD density. However, the quality of the epitaxial film is strongly affected by the growth temperature, i.e. the ability to control the QD array properties is limited. A thin Sb layer has been shown to reduce the Ge adatom mobility leading to the formation of smaller QDs [8, 9]. We utilized and developed this technique further to obtain an array of small Ge QDs on Si (100) substrates at elevated temperatures (≥550 °C).

The growth was performed in the MBE SIVA 45 (Riber) setup. The deposition rates of Si, Ge and Sb were 0.5 Å/s, 0.2 Å/s, and 0.013 monolayers (ML) per second, respectively. The sub-ML Sb film was deposited before the Ge QDs growth. The critical thickness (hS,K) of the Stranski–Krasnov 2D–3D transition was detected in situ by reflection high-energy electron diffraction (RHEED) at an accelerating voltage of 30 kV. The transformation of stripes-to-spots, seen in RHEED patterns during the formation of QDs, was used to define the critical thickness of the Ge film [9]. The in situ Auger electron
3. Results and discussion

Fig. 1 shows the dependence of the critical thickness of the Ge film on the Sb amount deposited to the surface ($\theta_{Sb}$, bottom and left axes). The plot of the adsorbed Sb ($\theta$) is given as well in Fig. 1 (bottom and right axes). The $\theta$-dependence (open circles), obtained by in situ Auger spectroscopy, obeys well the $\theta(\theta_{Sb}) = 1 - \exp(-\theta_{Sb})$ law (dashed line). The latter equation is a solution to the adsorption rate equation at the Si surface, keeping in mind that the limit of the adsorbed Sb at elevated substrate temperatures approaches 1 ML [10]. The dependence of the critical thickness of Ge (open squares) on the deposited Sb has a pronounced minimum at about 2 ML of Sb. Therefore, two regions can be distinguished on the plot and analyzed separately. The first region (where $\theta_{Sb} \leq 2$ ML) is characterized by a slight decrease in $h_{crit}$, In this region the critical thickness $h_{crit}(\theta)$ can be fitted well by the inverse empirical dependence: $h_{crit}(\theta) = 1/(\theta + \alpha) \pm \beta$ (the curve is marked as "enhanced mode"). Here $\beta$ is the $h_{crit}(\theta)$ minimum, and $(1/\alpha + \beta)$ is given by the critical thickness of Ge without any Sb. In the second region, the critical thickness $h_{crit}(\theta)$ is proportional to the adsorbed Sb amount ($\theta$) (the curve is marked as "inhibited mode"). To explain this phenomenon we propose the following model. If the Sb coverage is low ($\theta \approx 0$), then Sb atoms serve as additional centers for the nucleation of Ge islands. Thus, their formation proceeds faster and the critical thickness decreases. If the Sb coverage is close to the limit ($\theta = 1$), the diffusion of Ge ad-atoms is reduced [11], and Ge atoms cannot reach the Ge islands. Thereby, the nucleation rate decreases, accompanied by the increase in the critical thickness. It is worth to notice that the modification of the wetting layer thickness has been already mentioned in the case of hydrogen mediated Ge island growth by means of ultra high vacuum chemical vapor deposition [12].

Fig. 2a and b shows examples of Ge island arrays grown without Sb (Fig. 2a) and with Sb (Fig. 2b). The nominal thickness of deposited Ge was the same for both cases, namely, 1.0 nm. The growth temperature was 600 °C. The amount of the Sb attached to the surface in the second case was $\theta = 1$ ML. The Sb-free Ge island array consists of dome-shaped and pyramid-shaped islands. The sizes of pyramid-shaped islands are about 40–50 nm at the basis and 5–7 nm in height. The sizes of dome-shaped islands are about 50–60 nm at the basis and 12–13 nm in height. The overall density of the islands is $8 \times 10^{10}$ cm$^{-2}$ in this case. The density of the islands grown with Sb amounts to $2 \times 10^{11}$ cm$^{-2}$. The sizes of Ge islands are about 10–15 nm at the base and 1.5–2.0 nm in height. These islands are much smaller than those grown without Sb. The effect of size reduction of Ge islands with increasing Sb amount at the surface has the same origin as the decrease in the island size with decreasing growth temperature [13]. The latter can be illustrated by considering the dependence of the density of Ge islands on $\theta$ at 550 and 600 °C. This is shown in Fig. 2b. Two regions of low ($\theta \approx 0$) and high ($\theta \approx 1$) Sb amounts could be distinguished. In the low Sb coverage range the density of the Ge islands increases. It is explained by the increase in the number of nucleation centers provided by the Sb atoms. In the high Sb coverage range the density of Ge islands saturates (at 600 °C) or even drops down (550 °C). We attribute the saturation of Ge island density to the saturation of the adsorbed Sb, which takes place at $\theta_{Sb} > 2$ ML. The drop in the island density at 550 °C might be related to the increase in the critical layer thickness ($h_{crit}$) to a value, higher than the thickness of the deposited Ge. It should be mentioned that the island density, achieved with Sb at elevated temperature (600 °C, $N_{Ge,Sb} = 2 \times 10^{11}$ cm$^{-2}$), is at least one order of magnitude lower than that observed in the case of Sb-free Ge islands.
magnitude higher than the island density achieved without Sb ($N_{\text{Ge, noSb}} \approx 8 \times 10^{12} \text{ cm}^{-2}$).

An essential step in the process of QD formation is embedding them in the host. At the conditions of MBE, the latter means that the Stranski–Krastanov islands will be overgrown with the matrix material. During the overgrowth, Ge islands often modify their shape and composition [14]. However, surfactant atoms (Sb) change the situation drastically. Recently, we have demonstrated that the presence of Sb at the growing interface during capping of Ge islands leads to the conservation of their shape [11]. The latter has two reasons. The first reason is the reduction in the surface diffusivity of Si adatoms caused by Sb. The second reason is the reduction in the Ge segregation caused by Sb. Therefore, a dense array of Ge QDs with a high Ge concentration is expected, if Sb is deposited prior to the formation of Ge islands. These Ge QDs are shown in Fig. 3a. The dark layer with some variations in the thickness is seen in the TEM cross-section image. The size of Ge QDs measured from this image is less than 20 nm (basis) and about 2.5 nm (height). These values are rather close to those ones obtained by AFM measurements. At lower magnification (Fig. 3b), these islands are seen as two dimensional dark layers of Ge in a light gray Si matrix. Fig. 3b shows the inner part of the Si p–n junction consisting of 10 layers of Sb-mediated Ge QDs. It should be mentioned that the critical layer thickness and the size of the QDs have to be changed with the number of Ge layers due to the strain produced by the underlying Ge QD layers [15]. However, our RHEED observations did not reveal the decrease in the wetting layer thickness in the subsequent Ge layers, numbers 2 to 10. The TEM investigations did not reveal a modification in the QD size in upper Ge layers as well. We believe that this is due to the benefits of the Ge island formation which is more affected by the surfactant than by the strain field caused by underlying Ge layers.

The structure with 10 Ge layers was grown on a p± Si(100) substrate starting with a 200 nm thick Si:B doped buffer layer. Subsequently, 10 layers of Sb-mediated Ge QDs were grown at a substrate temperature of 600 °C. The nominal thickness of each Ge layer was 1.1 nm. The amount of Sb, deposited to the surface prior to the first Ge layer, was 2.1 ML. The undoped Si spacers between the Ge layers were 10 nm thick. Finally, a 200 nm thick Si:Sb n+ cap layer was deposited to provide good ohmic contacts for the EL measurements. It is essential that the strain produced by the Sb-mediated Ge islands is not released by the formation of dislocations. Therefore, Ge QDs are coherently strained. The strong Sb segregation effect taking place during the growth is the cause for the absence of Sb near the Ge QD layers. The latter has been confirmed by secondary ion mass spectrometry (SIMS) having a Sb detection limit of about $2 \times 10^{15} \text{ cm}^{-2}$. Note that the growth procedure of the Si:Sb n+ top contact layer was different.

Fig. 4 shows PL and EL spectra of a sample with 10 QD layers (Fig. 3b). This sample exhibited PL and EL at room temperature at a wavelength of about 1.5 μm related to Sb-mediated Ge QDs. The shift between the PL and EL peaks is caused by the different excitation power densities applied. The higher excitation density leads to a blue shift in the QD-related peak position due to the filling of excited states of the QDs or/and due to the contribution of QDs having smaller sizes. We believe that there are several reasons for the intense room temperature luminescence in the case of Sb-mediated Ge QD. Firstly, the MBE growth at elevated temperatures ($\geq 550 ^\circ \text{C}$) leads to the formation of high quality silicon having longer carrier lifetimes. Secondly, defect free QDs do not allow the formation of additional recombination channels, like misfit dislocations or other defects. Thirdly, the conservation of Ge inside the QDs leads to a higher localisation potential for holes, as well as to a higher strain, and therefore, to a higher localisation potential for electrons at the QD interfaces. Fourthly, the sharp interfaces of Ge QDs lead to a lower separation of electrons and holes, located at the QD interface. The resulting strong overlap of the wave functions leads to a larger probability of radiative recombination.

We conclude that Sb-mediated Ge QDs in the Si host are promising candidates serving as an active region of Si based light emitting devices for the Si photonics.

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References