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Ge/Si self-assembled quantum dots grown on Si(001) in an industrial high-pressure chemical vapor deposition reactor

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We report on the structural and optical properties of Ge/Si self-assembled quantum dots epitaxially grown on Si(001). The Ge islands are grown in an *industrial* 200 mm single-wafer chemical vapor deposition reactor. The surface density of the Ge islands is as much as $2\times10^{10}\,\mathrm{cm}^{-2}$. The islands exhibit a maximum photoluminescence at 1.55 μm wavelength. The photoluminescence energy is correlated to the three-dimensional quantum confinement energy and to the size and geometry of the clusters, as observed by cross-section transmission electron microscopy. *© 1999 American Institute of Physics.* [S0021-8979(99)00713-6]

I. INTRODUCTION

Semiconductor quantum dots are a subject of intense research in the field of micro- and optoelectronics. One of the most motivating challenges is the realization of Si-based nanostructures like Ge/Si which are compatible with Si-based electronic processing. This research is at the frontier of two trends: (i) the reduction of device sizes down to a few tens of nanometers; such downscaling has constituted the driving force in the microelectronics industry; and (ii) the study of fundamental properties and quantum confinement in nanostructures.[1] To date, different growth techniques have been successfully investigated to elaborate Si-based quantum dots. One of the most popular is the so-called self-assembled growth technique which eliminates the need for sophisticated processing techniques. This growth method relies on a strain-driven mechanism between lattice-mismatched semiconductors.[2] It leads to the spontaneous formation of nanostructures which nucleate in order to relieve the strain accumulated in a compressively strained wetting layer. Using this Stranski–Krastanow growth mode, the formation of self-assembled Ge/Si dots has been demonstrated by different deposition methods, including molecular beam epitaxy,[3] low-pressure chemical vapor deposition,[4] or ultrahigh-vacuum chemical vapor deposition.[5]

The future monolithic integration of self-assembled quantum dots for micro- or optoelectronics applications will, however, only be achieved if the formation of the nanostructures can be performed in an industrial reactor and environment. Indeed, reproducible, and low-time consuming deposits must be obtained, from wafer to wafer and batch to batch. The challenge of compatibility with an industrial environment dictates that the growth is not necessarily performed in an ultrahigh-vacuum growth reactor and that the formation of nanostructures is not significantly affected by the residual vacuum or by different processes like thermal and cleaning processes. A first report on the formation of Ge/Si self-assembled quantum dots in a conventional epitaxial reactor has been previously published.[6] In this article, the authors described the influence of the growth parameters on the formation of Ge dots in a chemical vapor deposition chamber operated either at 10 Torr or atmospheric pressure. However, no optical properties or direct demonstration of quantum confinement in these nanostructures have been reported.

In this article, we show that the growth of high optical quality self-assembled quantum dots on Si(001) can be achieved in an equivalent industrial reactor. The surface density of quantum dots, as observed by plan-view transmission electron microscopy, is large ($2\times10^{10}\,\mathrm{cm}^{-2}$). The quantum dots have a typical base size of 50 nm and height of 4 nm. The self-assembled quantum dots exhibit photoluminescence which is maximum at 1.55 μm wavelength. The observation of the photoluminescence is a signature of the crystalline quality of the nanostructures, as illustrated by the absence of predominant nonradiative pathways. We finally show that the photoluminescence energy can be correlated to the quantum confinement energy in the small three-dimensional islands.

II. GROWTH CONDITIONS

The samples were grown in a single wafer ASM Epsilon 2000 chemical vapor deposition epitaxial reactor. The heating of 200 mm Si(001) wafers was achieved with quartz–halogen lamps. The reactor was equipped with silane and germane reactor gases. The epitaxial growth was performed under hydrogen carrier flow. Deposition pressures could range from 20 Torr to atmospheric pressure. A detailed description of the reactor can be found in Ref. 7.

The formation, shape, and bidimensional density of the Ge/Si self-assembled quantum dots depend on a number of

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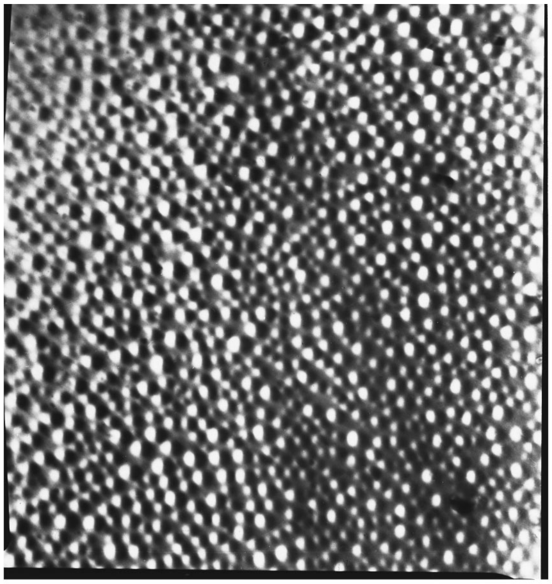

FIG. 1. Transmission electron microscopy plan-view image of the Ge/Si self-assembled quantum dots. The figure width is 1.34 μm.

parameters including the deposition time, the gas pressure, and the growth temperature. The influence of these different parameters have been separately investigated. In the present experiments, a single layer of Ge was grown at 650 °C at a pressure of 20 Torr. The Ge quantum dots were capped with silicon in order to observe the photoluminescence of the three-dimensional islands.

III. TRANSMISSION ELECTRON MICROSCOPY

Figure 1 shows a plan-view transmission electron microscopy image of the sample surface. The sample consisted of one single Ge layer capped with silicon. For imaging, the sample was tilted in order to be in the two-beam (220) diffraction condition. In this condition of dark-field imaging, the strain contrast around the islands is observed and manifests itself as a black and white contrast. Figure 1 shows a large density of islands with a narrow spacing (25–50 nm) separating their centers. The bidimensional density of islands is estimated to be $1.7\times 10^{10}\ \mathrm{cm}^{-2}$.

Figure 2 shows a cross-section bright field image of the capped Ge layer. The imaging was done in three-beam-symmetrical Bragg conditions between the (004) and $(00\bar{4})$ directions. In these conditions, the image and the contrast reveal the differences in composition between the layers but not the strain field contrast. In Fig. 2, the regions of dark contrast are associated with Ge-rich regions while the regions of bright contrast represent the Si-rich layers. The micrograph of Fig. 2 shows several islands which lie on top of a thin (1–1.2 nm thick) wetting layer. The base length of the largest island corresponds to the base length measured in Fig. 1. The analysis of the plan-view images in different orientations [two-beam (220) and (400) diffraction condition] did not reveal any lateral facets. The islands have rather a cone shape and the island images of Fig. 2 represent cone sections along the (110) direction. The angle measured from the (001) direction is around 9°. It is worth noticing that the cone shape of the islands was observed after silicon overgrowth. A careful look at the composition contrast in Fig. 2 shows several distinctive features: (i) in the case of the wetting layer, the contrast at the first Ge/Si interface between the Ge layer and the Si substrate is abrupt, whereas it is less pronounced at the second Ge/Si interface between the Ge and the Si capping layer; (ii) a similar trend is also observed on top of the three-dimensional islands. These observations are indicative of a probable segregation of Ge which occurs on a few monolayers. The segregation explains that the effective thickness of the wetting layer is around 1 nm. This segregation effect might not be very important for the large quantum dots (6 nm height) since it occurs on a small fraction of the quantum dot height. However the segregation is expected to exhibit pronounced effects on the confinement energy for islands with a height around 1 or 2 nm since it strongly modifies the confinement volume. This point will be discussed in Sec. IV. The aspect ratio of the islands (height/base diameter) is relatively weak ≈0.08, as already reported for small Ge islands grown by low-pressure chemical vapor deposition.[8]

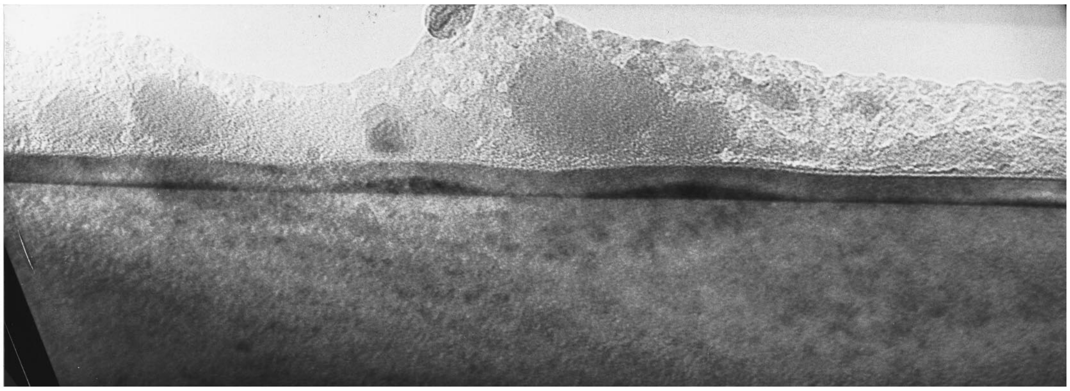

FIG. 2. Cross-section electron microscopy image of the Ge/Si self-assembled quantum dots. The figure width is 390 nm.

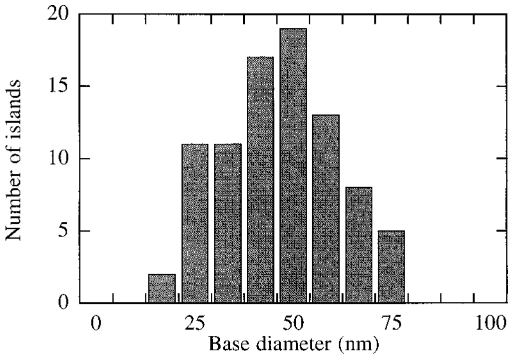

FIG. 3. Island distribution as a function of quantum dot base diameter.

Figure 3 shows the size distribution of the three-dimensional islands as a function of the base diameter. A monosize island distribution is observed with an average base diameter around 50 nm and a full width at half maximum of ±15 nm. It is worth noticing that few islands have a very small base length (20 nm or less) and a height less than 2 nm. The small dimensions involved in the small clusters are expected to lead to a strong quantum confinement of the carriers.

IV. PHOTOLUMINESCENCE

Photoluminescence experiments were performed at low temperature (4.2 K) using an argon ion laser as the excitation source. The photoluminescence is detected with a liquid-nitrogen-cooled Ge photodiode. A typical photoluminescence spectrum of the capped Ge layer is presented in Fig. 4. The spectrum consists of two separate parts: (i) the Si photoluminescence with the characteristic no-phonon and phonon assisted replica [transverse acoustical (TA), transverse optical (TO), TO+zone center phonon TO+O_Γ); (ii) and a radiative recombination band which is maximum at 0.8 eV. The low-energy band is unambiguously attributed to the self-assembled Ge quantum dots. This radiative band disappears when the thickness of deposited Ge is below the onset of three-dimensional island nucleation. Its shape and energy position is modified for larger deposition times which correspond to the coarsening of the islands. The broadening of the quantum dot photoluminescence (70 meV full width at half maximum) is attributed to the size dispersion of the islands. We did not observe the photoluminescence associated with the two-dimensional wetting layer. This feature can be explained by the high areal density of dots in the present sample and the efficient trapping of the carriers by the quantum dots. Note that the intensity of the quantum dot photoluminescence is lower than the photoluminescence intensity of the Si layer. However, the quantum dot photoluminescence only stems from a single Ge layer (2–3 nm average thickness), whereas the Si photoluminescence is integrated over the 1 μm penetration depth of the argon laser. Moreover, the Ge layer lies very close to the surface as observed in Fig. 2. Nonradiative surface recombination of the carriers is, in this case, a limiting factor for the optical efficiency.

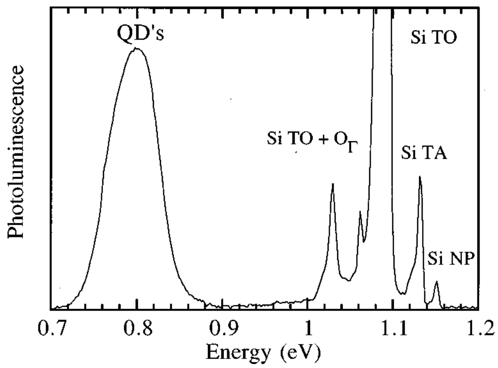

FIG. 4. Photoluminescence spectrum of the single Ge layer, as observed in Fig. 2. The quantum dot (QD) photoluminescence is maximum at around 0.8 eV. The high-energy photoluminescence peaks are associated with the silicon layer.

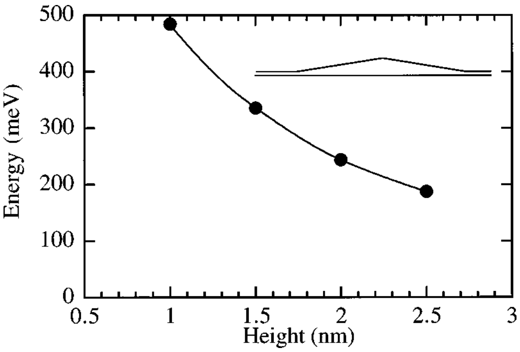

FIG. 5. Energy level calculation of the hole ground state in Ge island as a function of the dot height. The inset shows the quantum dot geometry (square-base pyramids) chosen for the calculation. The aspect ratio (height/base) is 0.05.

Similar photoluminescence bands have already been reported in the literature for self-assembled dots grown either by molecular beam epitaxy or chemical vapor deposition.[3,9] However it has, to our knowledge, never been reported in the case of Ge/Si self-assembled quantum dots epitaxially grown in an industrial reactor. Two remarkable features of the photoluminescence are of importance: (i) it is maximum at 1.55 μm which corresponds to the optimum wavelength for telecommunication technology; (ii) the low-energy position of the photoluminescence is associated with a large effective barrier height for the confined holes (≈300 meV). The larger barrier height limits the thermal quenching of the photoluminescence which therefore can be observed up to room temperature.[10]

V. DISCUSSION

The understanding of the energy position of the photoluminescence in Ge/Si self-assembled quantum dots is a critical point. Band alignment between Ge and Si is of type II,[11] which means that the radiative recombination occurs between the electrons in the Si barrier layer and the holes confined in the Ge islands. In the valence band, the discontinuity between Ge and Si is around 700 meV,[11] which implies that the quantum confinement should be large in the islands in order to observe photoluminescence at around 0.8 eV. In order to clarify this point, we performed a numerical calculation to estimate the hole confinement energy in the Ge islands. This calculation is derived from a three-dimensional numerical solution of the Schrödinger equation in the effective-mass framework which has been successfully applied to InAs/GaAs self-assembled quantum dots.[12] For the valence band of Ge, only the heavy hole band was considered. The effective mass is decoupled between the z growth axis and the in-plane component, $m_z = 0.21 m_0$ and $m_{x,y} = 0.07 m_0$, where m_0 is the free-electron mass. The study of the influence of the band mixing in the valence band on the confinement energy is beyond the scope of this article. In the calculation we did not take into account the influence of Ge segregation. This segregation would nevertheless lead to an increase of the photoluminescence energy.[13] Figure 5 shows the confinement energy of the ground hole state in square base pyramids as a function of the quantum dot height. In this calculation an aspect ratio (height/base length) ≈ 0.05 was chosen. The geometry of the island slightly differs from the experimental one. The calculations represent, however, a good first order approximation. As seen, the confinement energy can be very large in small clusters. The main contribution to the confinement energy stems from the confinement along the z direction, since it represents the smallest dimension. For a 2 nm height quantum dot, a 350 meV confinement energy is predicted for the hole ground state. This large confinement energy corresponds to an interband photoluminescence energy around 0.8 eV. As reported in Fig. 3, the small dots of the distribution have a height which is around 2 nm, or even less if we account for the segregation. The energy position of the photoluminescence is therefore found in agreement with the calculated one which accounts for the quantum confinement in small Ge islands.

VI. CONCLUSION

In conclusion, Ge/Si self-assembled quantum dots have been grown in a chemical vapor deposition reactor. Near-infrared photoluminescence associated with the quantum dots has been observed, thus demonstrating the high optical quality of the layers. The energy position of the photoluminescence has been correlated to the hole quantum confinement energy in the small Ge islands. This work demonstrates that results similar to those obtained for Ge/Si quantum dots grown by molecular beam epitaxy or low-pressure chemical vapor deposition can also be obtained in an industrial chemical vapor deposition reactor, thus extending the range of these industrial machines to more advanced research and development applications.

ACKNOWLEDGMENT

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