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RHEED studies of nucleation of Ge islands on Si(001) and optical properties of ultra-small Ge quantum dots

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Abstract

The initial stages of Ge growth on the Si(001)-(2 × 1) surface have been studied by using a RHEED pattern zero-streak profile analysis technique. Thicknesses for {105} and {113} facets formation, corresponding to the nucleation of coherent 'hut'-clusters and dislocated 'dome' three-dimensional (3D) islands respectively, were determined in a growth temperature range of about 200–600°C. Multilayer structures containing ultra-small Ge quantum dots (QDs) with a plane size of about 10 nm and a height of 1.5 nm have been studied by photoluminescence (PL). PL bands assigned to QDs show an intensity comparable to data in the literature, but a band width five times smaller.

Keywords: Germanium; Silicon; Self-organization; Quantum dot

1. Introduction

Self-organization of Ge quantum dots has attracted considerable attention in recent years due to an old hope of creating high efficiency GeSi-based optoelectronic devices. Many authors reported intense photoluminescence (PL) in the 0.7–0.9 eV range of Si-capped self-assembled GeSi three-dimensional (3D) islands (i.e. QDs) [1–5]. Such QDs are formed during the Stranski–Krastanov film growth of highly mismatched materials. The morphological transformation of Ge films on Si(001) surface is passed through two stages. 3D Ge islands are formed above some critical thickness of about 4–6 monolayers (MLs) [6,7]. These first generation islands (the so-called 'hut'-clusters) are always shaped as perfect tetrahedral pyramids with side orientation of {105}-type. There are no misfit dislocations in the 'hut'-clusters, and the strain relaxation in them proceeds due to the partial elastic deformation. Much bigger relaxed 3D islands with misfit dislocations are formed at a later stage of Ge film growth. These are the so-called 'dome'- or macro-islands with the main side orientation of {113}-type. 'Hut'-clusters are preferred for the design of a heterostructure with the self-organized QDs due to smaller sizes and the absence of defects (misfit dislocations). The temperature of the silicon substrate is among the main factor determining the size and surface density of both 'hut'- and 'dome'-islands because of the temperature dependence of the Ge adatoms diffusion length. Recent papers in the field of Ge QDs-assisted photoluminescence reported the growth of structures comprising Ge QDs at 550–750°C, the in-plane size of the 3D islands being 100–200 nm [1–5]. On the other hand, our measurements of the hole tunnel current through a Ge island layer, each of which was sandwiched between two Si barriers, demonstrated the formation of Ge 'huts' with in-plane size 12-20nm at 300-400°C [8–13]. 'Hut'-clusters of the same size were observed by TEM [9,11] and STM [7] in the Ge films grown at the same temperature. Moreover, resonance RAMAN spectroscopic studies showed Ge QDs size of ca. 7 nm after 6–10 ML film growth at 200°C [14]. QDs smaller by an order of magnitude could reveal rather different properties than the large ones.

Systematic data on the structure of Ge 3D-island films grown at low temperatures (bellow 300–400°C) are rare and limited in the literature. The knowledge on the thickness of both 'huts' and 'domes' formation and the in situ control of the growth of QDs containing heterostructures is of impor-

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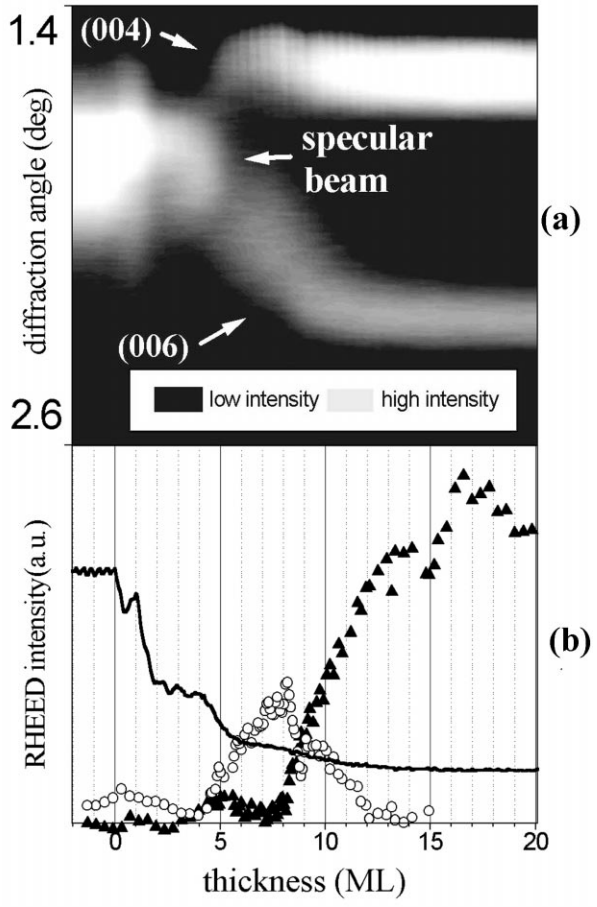

Fig. 1. (a). Zero-streak RHEED profile intensity variations during Ge films growth at 350°C. (b) Dependence on Ge film thickness during growth at 350°C of the specular beam intensity (solid line) and (004) bulk spot intensity from {105} (open circles) and {113} (solid triangles) facets.

tance for synthesis of QD structures. For this reason, the present work was aimed at reflection high energy diffraction (RHEED) studies of the morphological transformations of germanium-on-silicon layers during MBE growth and the growth of GeSi-heterostructures with ultra-small (less than 10 nm) QDs for PL experiments.

2. Experimental details

In situ RHEED experiments and growth of QDs containing heterostructures have been done in 'KATUN-S' and 'RIBER-Siva32' MBE installations (in the Institute of Semiconductor Physics, Novosibirsk, and in the Center for Condensed Matter Sciences, Taipei, respectively). Each MBE installation was equipped with two electron beam evaporators for germanium and silicon. Si(001) wafers of 2.5–3 inches diameter were used as substrates. The growth process was controlled by using the RHEED technique (20 keV). Diffraction patterns and intensity variations at separate points and along the given profiles were recorded by using a computer-aided system 'PHOTON-4'. The Ge and Si growth rates were controlled by using quartz thickness monitors.

3. In situ RHEED of Ge islands nucleation on Si(001) surface

The initial stages of germanium growth on the Si(001)-(2×1) surface were studied by detecting intensity profile variations along the (00) streak in the [110] azimuth. An example of such a measurement for 20 ML Ge deposition at 350°C is shown in Fig. 1. Each vertical line represents the RHEED intensity profile at the Ge film thickness shown on x-axis. The recording interval for one intensity profile was 0.5 s. RHEED intensity profiles for three characteristic film thicknesses are shown at the Fig. 2. At the onset of Ge growth, one intensity maximum is observed at the diffraction angle $2.00 \pm 0.05°$ (Fig. 2a) with respect to the incident electron beam. It corresponds to the specular beam reflection during the initial 2D growth of Ge film. RHEED oscillations were measured in this thickness range to calibrate the Ge growth rate (Fig. 1b, solid line). Each oscillation period corresponds to filling one monolayer (ML) of $a/4$ (0.14 nm) thickness. Bulk spots (004) and (006) appears at the film above 4–5 ML at 1.61 ± 0.02 and $2.3 \pm 0.1°$, respectively (Fig. 2b). After the Ge film reached about 8 ML thickness, the spots were replaced by 1.66 ± 0.02 and $2.54 \pm 0.03°$, respectively, and the (006) reflection became much sharper (Fig. 2c). Earlier, we attributed such an unusual behavior of the bulk spots to the consecutive nucleation of 'hut'- and

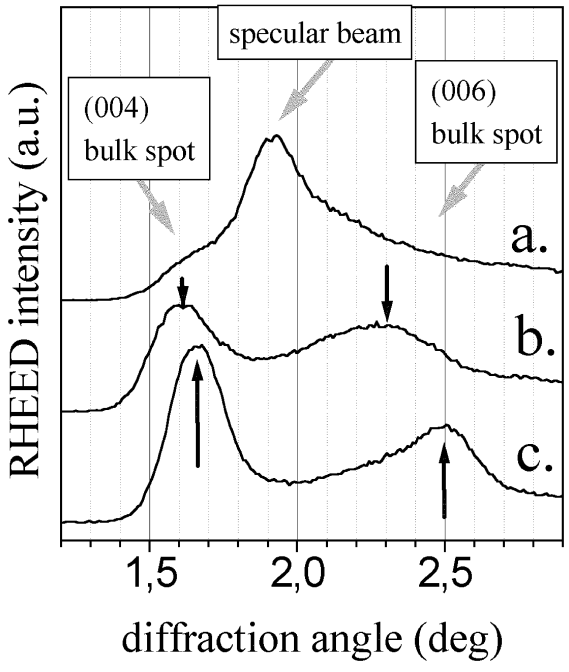

Fig. 2. Zero-streak RHEED intensity profiles at 2 (a), 7 (b) and 10 ML Ge film thickness during MBE growth at 350°C. Vertical arrows show bulk spot positions at the corresponding film thickness.

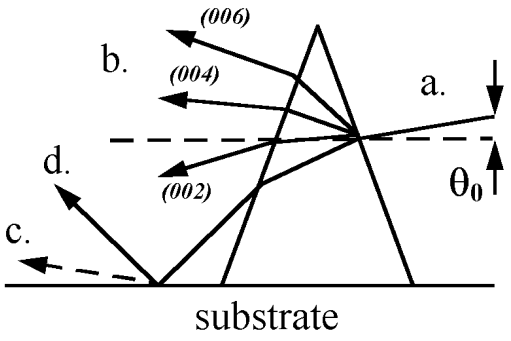

Fig. 3. Schematic presentation of electron diffraction and refraction in 3D-islands (refraction coefficient $n = 1.00033$ in Ge for 20 keV electrons [15]): (a) incident electron beam; (b) bulk diffraction beams; (c) original specular beam; (d) one time refracted specular beam.

'dome'-clusters [11], although the nature of this phenomenon was not clearly understood.

Considering possible reasons for the considerable shift of the bulk spot allowed us to conclude that their different angle positions is due to electron beam refraction in 3D Ge islands similar to the refraction of a light beam in a glass prism. The refraction process is shown schematically in Fig. 3. Electrons with energy 20 keV refract in Ge with coefficient $n = 1.00033$ [15]. The estimation was based on Snell's law ($n_0 \mathrm{Sin}\ \theta_0 = n_1\ \mathrm{Sin}\ \theta_1$). Even such a low refraction was shown to be sufficient for a decrease in the bulk spot diffraction angles by about 0.12 and 0.08° for {105} and {113} facets, respectively, due to their different angles (11 and 18° in [110] azimuth, respectively) to the (001) surface. Thus, the difference between the angles of 0.04° agrees well with the experimental difference of $0.05 \pm 0.02°$ for (004) reflection. The discrepancy for the (006) bulk spot can be accounted for by its much more intricate nature at the 'huts' occurrence. Apart from the bulk reflection, this spot includes one time refracted specular beam (2.44° from Snell's law estimation – see Fig.3) and Kikuchi-lines. The inelastic electron scattering into Kikuchi-lines is much stronger in the 'huts' than in the 'domes' due to the elastic deformation of its crystal lattice and the smaller size of the former. Besides, the (006) bulk reflection in the 'huts' area is a complicated interplay of many different electron reflections, and for that reason we used the (004) bulk reflection only for further analysis.

The different angle position of the (004) spot after the nucleation of the 'hut'- and 'dome'-clusters allowed us to separate the contributions of both {105} and {113} facets to the bulk diffraction spot intensity. The analysis included the approximation of each intensity profile by three separate Gaussian peaks at the fixed angle positions equal to 2.0, 1.61 and 1.66°. Of these three angles, the first one corresponds to the specular beam, and the others to the (004) bulk reflection from {105} and {113} facets, respectively. Dependencies of intensities of the last two reflections on the film thickness are shown in Fig. 1b. The bulk spot corresponding to the {105} facet appeared at 3.3 ± 0.3 ML. Its intensity increases up to the appearance of {113}-related reflection at 7.9 ± 0.2 ML and then starts decreasing. A similar analysis was performed for the intensity profile variations obtained at different temperatures. The result is summarized in the phase diagram in Fig. 4. The thickness at which {105} and {113} facets formation starts (open symbols in Fig. 4) coincides well with the nucleation of 'huts' and 'domes', respectively, reported by Tomitori [7] (solid symbols in Fig. 4) for the temperature range of 300–500°C. However, our data show the existence of the 'hut'-clusters at temperatures below to 200°C.

Raman spectroscopic studies support the formation of 'hut'-clusters at low temperatures. The peak at 316 cm^{-1} in the Raman spectra corresponds to fully strained germanium in 'huts' (Fig. 5). Its intensity is amplified due to the strong localization of charge carriers in Ge QDs [14]. The peak resonance dependence gave the estimated QDs size of ca. 7–10nm for Ge films grown at 200–250°C. The peak at 316 cm^{-1} was observed only for Ge films of the 5–10 ML thickness range (dashed area in Fig. 4). Its intensity decreased quickly after 10–12 ML and a peak at 305 cm^{-1} corresponding to relaxed Ge appeared [14].

4. Photoluminescence in ultra-small Ge quantum dots

Multilayer structures comprising six layers of Ge were grown at a low temperature to study photoluminescence properties of ultra-small QDs. Ge layers are separated from one another by 25 nm Si layers. The PL measurements were performed at 4.2 K, using an Ar laser at a wavelength of 514.5 nm. The measurements were performed using a liquid nitrogen-cooled Ge detector. Fig. 6a shows the spec-

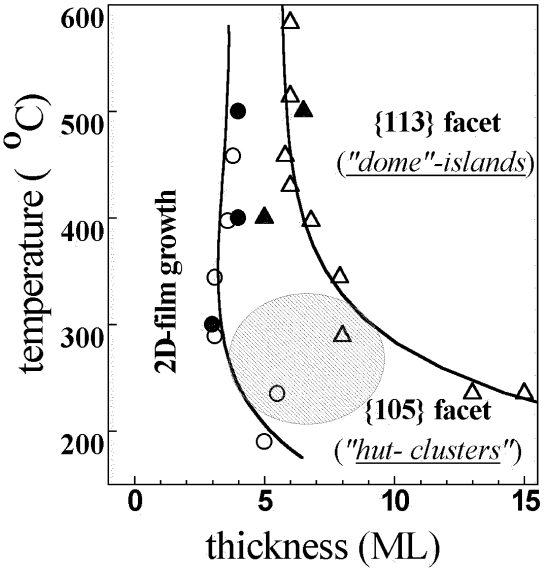

Fig. 4. Phase diagram comprising three regions of Ge film growth: two-dimensional growth and {105}- and {113}-facet formation thickness ('hut'- and 'dome' 3D islands nucleation, respectively). The 'hut'-assisted RAMAN peak 316 cm^{-1} (see Fig. 5) is observed in dashed area.

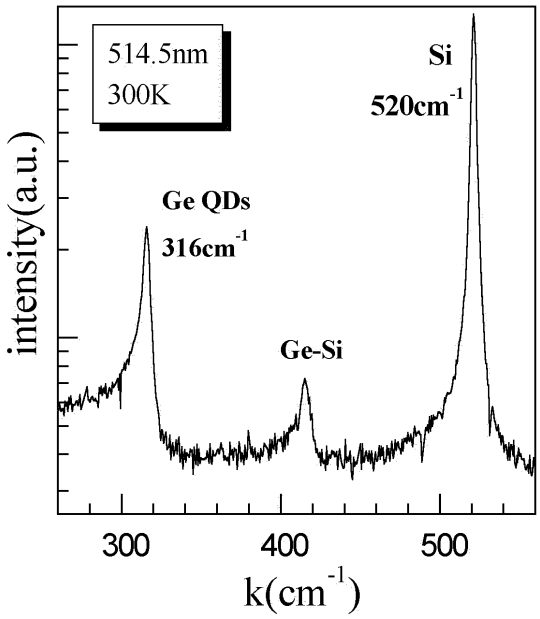

Fig. 5. RAMAN spectra of a 6-fold stack of 8 ML Ge quantum dots separated by 25 nm Si. The Ge films were grown at 250°C.

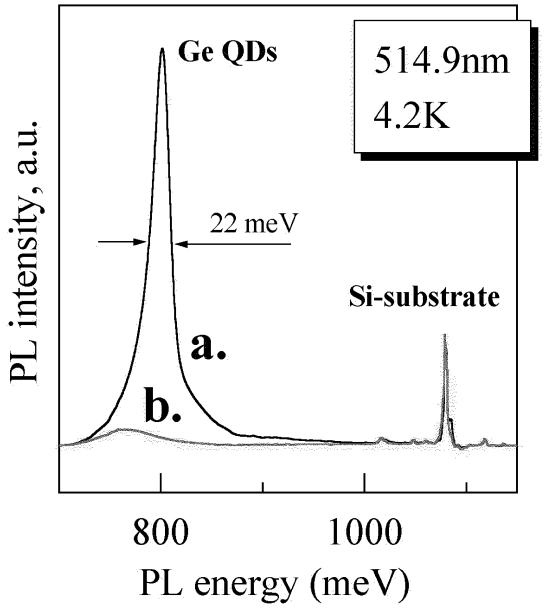

Fig. 6. PL spectra of a 6-fold stack of 8 (a) and 10ML (b) Ge quantum dots separated by 25 nm Si. The Ge films were grown at 250°C.

tra of a sample grown at 250°C with the 8 ML Ge film. The average size of bases of 'hut'-clusters (about 10 nm) was estimated using earlier data [9–14]. The peak at 1.1 eV appeared due to the phonon-assisted band edge luminescence in the Si substrate. The dominant feature in the spectra is the luminescence band centered around 0.8 eV, which originates from the QDs. This feature does not appear for Ge layers of 6 ML thickness and disappears again at 10 ML (Fig. 6b). The main parameters of the spectra shown in Fig. 6a are summarized in the Table 1 and are compared with data in the literature [1–3] for similar structures containing about ten times larger QDs. The fourth column shows the intensity ratios of the QDs ('huts') PL peak to the Si-substrate peak normalized by the number of Ge layers N.

At first sight, it seems surprising to find the QDs PL peak at the same (or even lower) energy in our samples where the 'huts' are almost ten times smaller than for other workers. But, as was mentioned in [16], the main contribution to the confinement energy stems from the confinement along the z-direction in big QDs, since it represents the smallest dimension. This means that 2D-confinement takes place in structures grown at high temperature, while in our samples we observe zero-dimensional confinement in x–y-directions. In our spectra, as we noted above, the QDs PL band is about five times narrower. This is evidence of much better homogeneity in the sizes of ultra-small 'hut'-clusters. The energy barrier for nucleation of new {105} planes, which form 'hut'-clusters, depends more strongly on size for smaller 'huts' than for bigger ones [17]. This fact leads to a strong self-limitation of 'huts' growth and, as a consequence, to a much narrower size distribution of QDs at a low Ge film growth temperature.

5. Conclusions

The thickness for the nucleation of both Ge 'hut'- and 'dome' three-dimensional Ge islands on silicon has been obtained by using RHEED intensity profile analysis in a wide growth temperature range (200–600°C). Multilayer structures containing ultra-small Ge quantum dots with size less than 10 nm in the growth plane and with height less than 1.5 nm have been studied for the first time by photoluminescence. The PL spectra originating in the QDs

Table 1
Author please provide table caption

Reference	Growth method, T_g (°C)	QDs size/height (nm)	QDs/Si PL peaks ratio (N)	QDs PL peak position, width (meV)
[1]	UHV-CVD, 550	6/80	1/10 (10)	820, 80
[2]	MBE, 620	8/100	4/5 (5)	830, 120
[3]	GS-MBE, 750	20/150	1/1 (1)	840, 150
Present work	MBE, 250	1.5/10	1/1 (6)	800, 22

are comparable in intensity, but have five times smaller width than those reported for about ten times larger QDs.

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