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Optical Properties of Germanium Monolayers on Silicon

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Abstract—Photoluminescence and Raman spectra of thin germanium layers grown on silicon at a low temperature (250°C) have been studied. In structures of this kind, in contrast to those grown at high temperatures, luminescence from quantum wells is observed at germanium layer thicknesses exceeding ~9 monolayers (ML). With the development of misfit dislocations, the luminescence lines of quantum wells are shifted to higher energies and transverse optical (TO) phonons involved in the luminescence are confined to a quasi-2D germanium layer. Introduction of an additional relaxed $Si_{0.95}Ge_{0.05}$ layer into the multilayer Ge/Si structure leads to a substantial rise in the intensity and narrowing of the luminescence line associated with quantum dots (to 24 meV), which points to their significant ordering. *© 2001 MAIK "Nauka/Interperiodica".*

INTRODUCTION

Nanostructures consisting of thin germanium layers on silicon have aroused a growing interest because of the prospects for their use in various electronic and optoelectronic devices [1]. In particular, one important application is associated with the generation of direct gap luminescence in these structures for creating (by means of integrated silicon technology) devices emitting light at 1.5 μm, necessary for fiber-optic communication lines. Quasi-direct transitions are possible in nondirect semiconductors in the case of free-carrier localization. Such a localization is observed in covariant Ge/Si and SiGe/Si heterostructures, with electrons commonly localized in the silicon quantum well (QW) and holes, in the germanium QW. Another possible kind of localization is associated with self-organization on the silicon surface under the action of heteroepitaxial stresses to form an ensemble of nanoclusters—quantum dots (QDs). The difference between the crystal lattice parameters of silicon and germanium [1 monolayer (ML) of Ge is ~1.4 Å thick, and 1 ML of Si is ~1.35 Å] results in that pseudomorphic 2D growth continues in the course of heteroepitaxy to a certain critical thickness (h_c) of the germanium film: close to 4 ML, i.e., the wetting layer. With increasing thickness, the stress is relieved via self-consistent growth of dislocation-free germanium clusters on the silicon surface by the Stranski–Krastanow mechanism. First, the so-called hut clusters are formed in the form of tetrahedral pyramids; then, the larger dome clusters. With the thickness increasing further, plastic relaxation of stresses with the formation of dislocations occurs. Owing to the smallness of the clusters, they manifest effects of quantum confinement on the electronic spectrum. It has been noticed that lowering the growth temperature T_s to 200°C makes the nanoclusters smaller, their density higher, and h_c larger [2, 3]. The intensity of quasi-direct-gap luminescence from QDs must increase with a decreasing size and an improving spatial uniformity of the forming nanoclusters. One of the methods of nanocluster ordering is the successive growth of layers with germanium clusters overgrown with silicon layers (vertical self-organization). A photoluminescence spectrum of such structure was reported in [3]. It is known from the literature that the structure of the ensemble of nanoclusters changes substantially in a narrow range of germanium layer thicknesses (approximately up to 15 ML). In [4], this conclusion was confirmed by means of scanning-tunneling and atomic-force microscopies; in [2], this was done by studying the Raman scattering.

SAMPLES AND MEASUREMENT TECHNIQUE

Low-temperature photoluminescence (PL) and Raman spectra were studied at germanium layer thicknesses of up to ~15 ML. Multilayer structures with different thicknesses of Ge and Si layers were grown by molecular-beam epitaxy on *n*- and *p*-type (001)Si substrates (5–20 Ω cm). After a standard substrate cleaning procedure, a buffer layer of silicon was deposited onto the substrate at $T_s \approx 800$°C and then periodic structures consisting of Ge layers and thicker Si layers were grown at lower temperature. In the final stage, the structure was coated with a protective silicon film several hundred angstroms thick. Data on the growth modes of the structures discussed below are presented in the table.

PL spectra were measured at $T = 2$ K with the use of an MDR-2 monochromator. A semiconductor laser with wavelength $\lambda = 0.66$ μm (quantum energy $h\nu$ = 1.87 eV) served as an excitation source. The maximum radiation power was 70 mW, with the power density incident on a sample equal to 4 W/cm^2. The emission from the samples was recorded using a liquid-nitrogen–cooled germanium *p–i–n* photodiode. For some of the samples, to ensure that light is emitted by the QDs or the wetting layer (and not by the substrate), luminescence spectra were recorded from two sides of a sample. At $\lambda = 0.66$ μm photoexcited carriers are mainly formed in a layer up to several micrometers deep at the illuminated surface. In the case of illumination from the structure side, the photoexcitation region encloses the entire structure and several micrometers of the substrate and, with illumination from the substrate side, only several micrometers of the substrate, the sample thickness being 300 μm and light incident on the back side not reaching the structure. At photocarrier diffusion lengths common for silicon, we observe emission from both the structure and the substrate in the former case and mainly from the substrate in the latter.

Spectra of Raman scattering on optical phonons were measured at room temperature. The excitation was done with argon laser (λ= 0.488 μm), the emitted light was recorded with a U-1000 spectrometer.

RESULTS AND DISCUSSION

The measured PL spectra are presented in Figs. 1–5 for both the structure and the substrate. Emission from QDs appears beginning with germanium layer thicknesses ≥4 ML as a weak broad band QD at $h\nu$ = 0.75–0.85 eV. With the thickness increasing to 6–8 ML, the emission intensity grows and the band narrows. With the germanium thickness increasing further (to >10–15 ML), germanium clusters form a continuous layer and stress relaxation occurs through the formation of misfit dislocations. In this case, the emission again takes the form of a broad weak band with weak dislocation-related lines observed on its background and then completely disappears. The range of the germanium thicknesses within which the emission intensity is the highest varies with the growth temperature and growth rate and depends on whether or not additional SiGe sublayers relieving the internal stress are present. At fixed growth parameters, the emission lines are shifted to longer wavelengths with increasing germanium layer thickness.

The introduction of an additional relaxed SiGe sublayer (sample 9) presumably leads to QD ordering, with the intensity of emission increasing and the emission band narrowing. The full width at half-maximum (FWHM) of the QD emission line in this sample is 24 meV. The lines of emission from QDs should be distinguished from lines associated with dislocations in silicon (D_1 line at 810 meV and D_2 at 870 meV) lying in the same energy range. The following facts testify that it is the QDs that are responsible for the emission from sample 9.

(1) The D_1 and D_2 lines commonly appear in pairs; the FWHM of dislocation lines is ~10 meV. On raising the temperature to 77 K, the intensity of dislocation-related luminescence decreases severalfold. A single luminescence line is observed in sample 9 at

Structure growth mode

Sample 8	Sample 9
Si, 235 Å, 450°C	Si, 235 Å, 450°C
Si, 20 Å, 250°C ×7	Si, 20 Å, 250°C ×6
Ge, 10 Å, 250°C	Ge, 8 Å, 250°C
Si, 100 Å, 450°C	Si, 100 Å, 450°C
	$Si_{0.95}Ge_{0.05}$, 700 Å, 450°C
Si, 1150 Å, 780°C	Annealed at 1050°C after growth
Substrate: *p*-Si, 7.5 Ω cm	Si, 1150 Å, 780°C
	Substrate: *p*-Si, 7.5 Ω cm

Sample 15	Sample 48	Sample 66
Si, 235 Å, 450°C	Si, 300 Å	Si, 400 Å
Si, 20 Å, 250°C ×7	Ge, 13 Å, 300°C	Si, 100 Å ×5
Ge, 13 Å, 250°C	Si, 700 Å	Ge, 12 Å
Si, 100 Å, 450°C	Substrate: *n*-Si, 7.5 Ω cm	Si, 400 Å
Si, 1150 Å, 780°C		Substrate: *n*-Si, 7.5 Ω cm
Substrate: *n*-Si, 4.5 Ω cm		

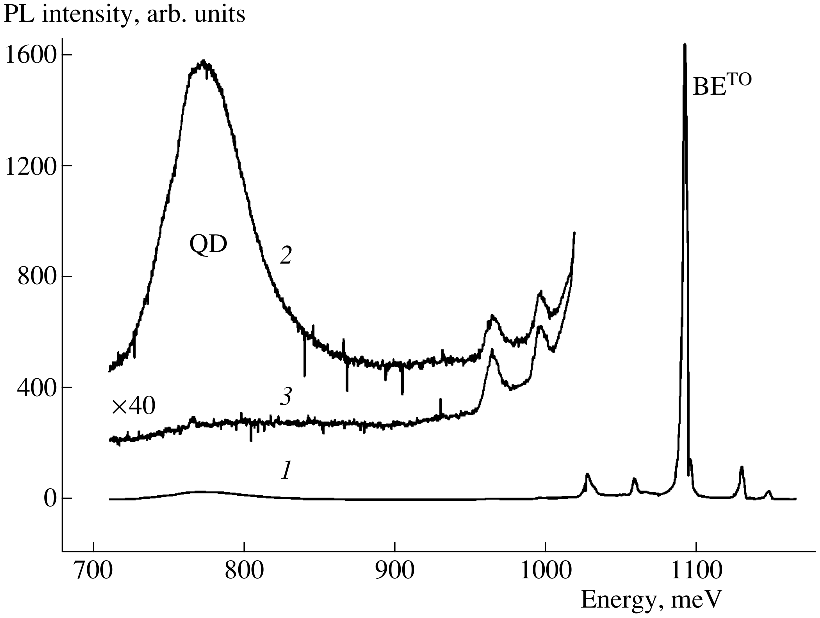

Fig. 1. (*1*) PL spectrum of sample 8 at $T = 2$ K and (*2*) part of the spectrum of the structure and (*3*) substrate at a higher amplification. QD is luminescence from QDs, BE^{TO} is the luminescence line of bound exciton with emission of a TO phonon.

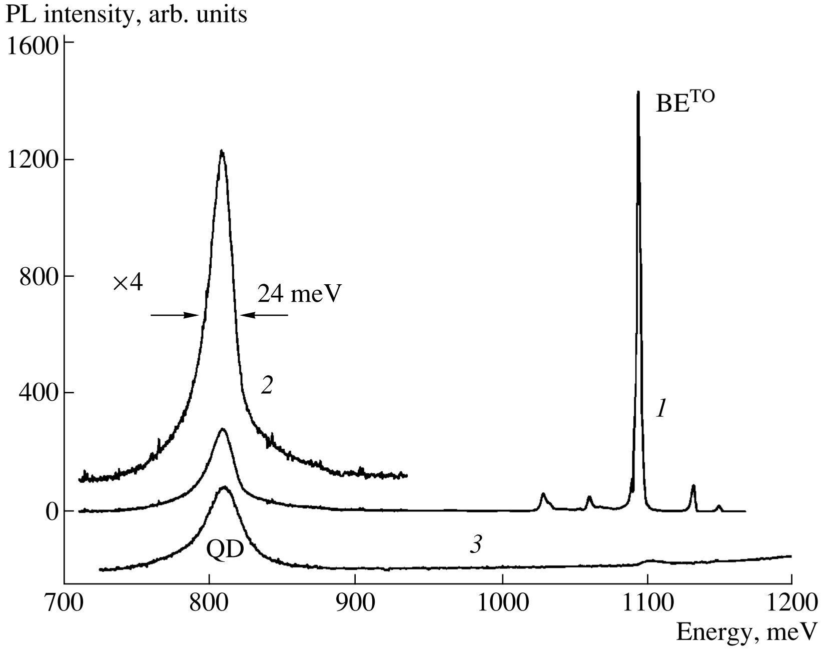

Fig. 2. PL spectrum of sample 9 with additional SiGe sublayer at T = (*1*, *2*) 2 and (*3*) 77 K.

809 meV, having nearly the same intensity at 2 and 77 K (Fig. 2).

(2) In samples with the germanium thickness of ~10 ML in which stress relaxation does occur with the formation of dislocations, their emission is very weak or not observable at all (Fig. 3, structure no. 15).

Raman spectra allow a conclusion as to the extent of relaxation of strained germanium layers on silicon. Such spectra are presented for samples 8, 9, and 15 in Fig. 6. The spectrum of sample 8 shows lines at 520 cm^{-1} (optical phonon in silicon), 420 cm^{-1} (vibrations of Si–Ge bonds), and 316 cm^{-1} (optical phonon in strained germanium). Since the frequency of an optical phonon linearly depends on the strain, then, as shown in [2], a line at 300 cm^{-1} corresponding to optical phonons in bulk germanium appears upon the relaxation of stress at dislocations. For sample 9, the line at 300 cm^{-1} is much weaker than that at 316 cm^{-1}; i.e., the

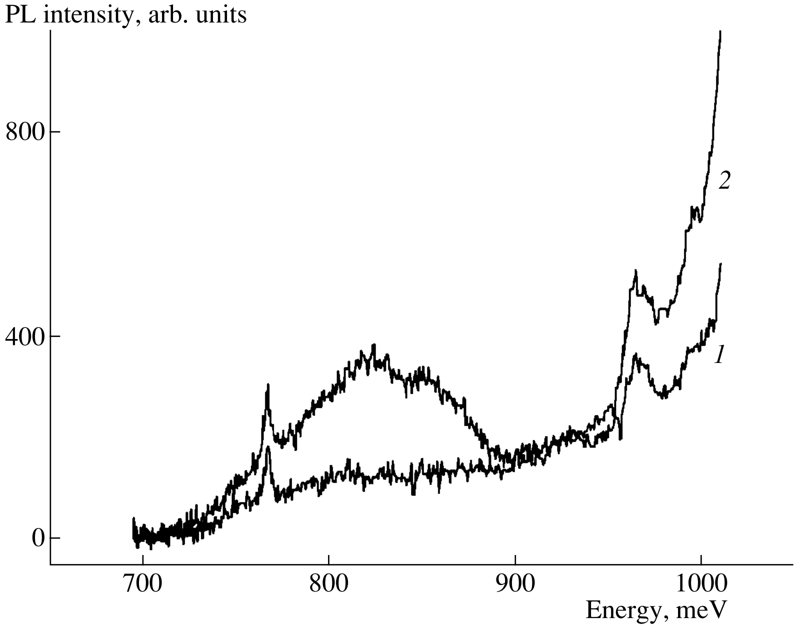

Fig. 3. PL spectra of sample 15 at $T = 2$ K: (*1*) structure and (*2*) substrate.

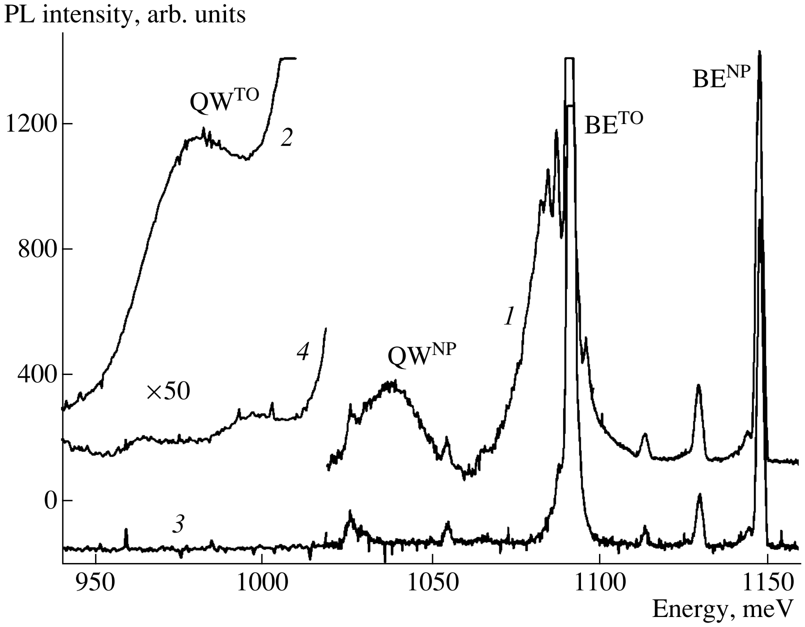

Fig. 4. (*1, 2*) PL spectrum of the single QW in sample 48 (13 Å Ge) compared with (*3, 4*) the emission spectrum of the substrate at $T = 2$ K. QW^{NP}and QW^{TO} are QW luminescence lines—zero-phonon and with emission of TO phonon, respectively. BE^{NP} and BE^{TO} are the corresponding lines for bound exciton.

dislocation density in this sample is relatively low. The line at 300 cm^{-1} is presumably associated with the relaxed SiGe sublayer.

It has been shown that in Si/Ge/Si structures grown at T_s = 700°C, the luminescence from a QW (i.e. strained wetting layer) and that from QDs are competing processes [5]. At small germanium thicknesses, the emission from QWs predominates. With the formation of QDs, the emission from wells becomes weaker and the emission from dots grows in intensity. Germanium layers in the samples under study were obtained at low temperatures T_s = 250–300°C. The diffusion length of adsorbed atoms is low at low temperatures; therefore, hut clusters responsible for the emission from QDs are formed simultaneously with the growth of the wetting layer, beginning with the zero thickness. For this rea-

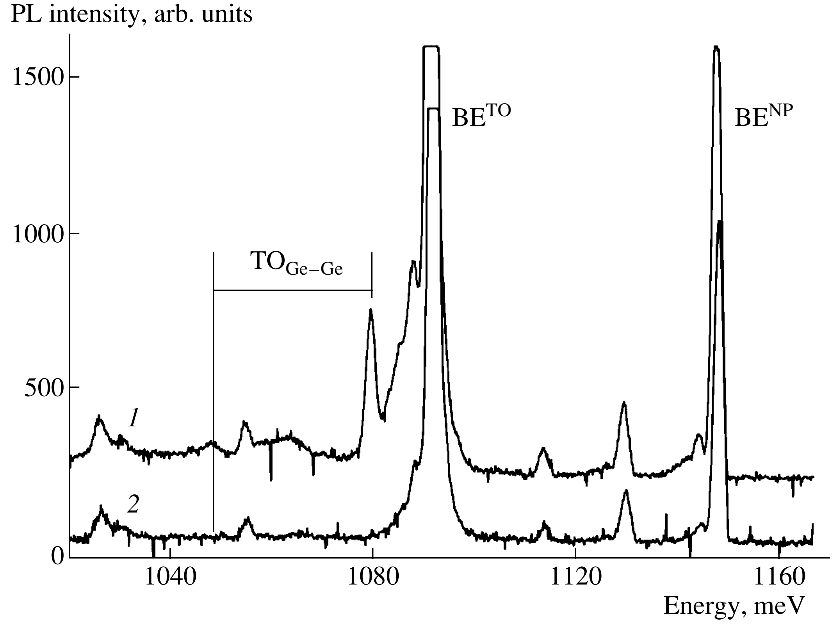

Fig. 5. PL of QW sample 66 at $T = 2$ K: (*1*) structure and (*2*) substrate. BE^{NP} and BE^{TO} are luminescence lines of bound exciton—zero-phonon and with emission of TO phonon, respectively.

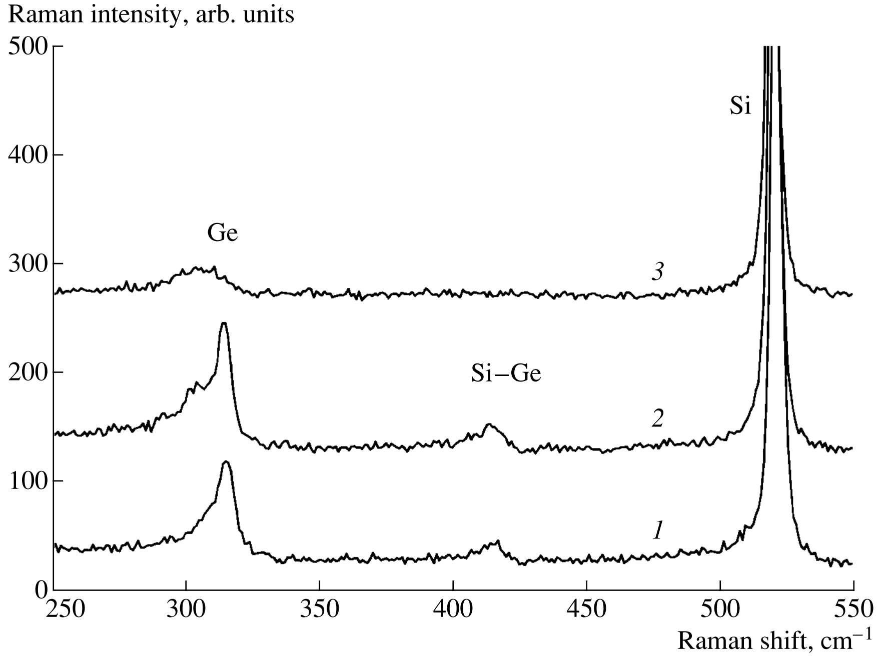

Fig. 6. Raman spectra. Samples: (*1*) 8, (*2*) 9, and (*3*) 15.

son, no emission from QWs was observed at thicknesses ≤8 ML, this emission being suppressed by that of nanoclusters. The emission from QWs was observed at thicknesses ≥9 ML, when separate clusters start to disappear, merging into a continuous layer with misfit dislocations developed. The PL spectra of samples of this kind (nos. 48 and 66) are presented in Figs 4 and 5. A zero-phonon line QW^{NP} is observed in sample 48 at 1039 meV. Phonon replicas are observed at 982 meV—luminescence occurs with the emission of a TO phonon in silicon, $TO_{Si–Si}$ phonon (59 meV). In the spectrum of sample 66, the zero-phonon line is observed at 1080 meV, with a phonon replica (1048 meV) spaced away by approximately the energy of TO phonon in germanium, $\mathrm{TO}_{\mathrm{Ge-Ge}}$ phonon. The shift of the zero-phonon line to higher energies is presumably due to a decrease in the offset of valence band edges of germanium and silicon, which is caused by the partial strain relaxation on misfit dislocations. The Raman spectrum of this sample is similar to that of sample 15, which indicates the presence of a relaxed Ge layer. The spectrum of this sample shows, in contrast to that of sample 48, a strong dislocation-related emission at 700–900 meV on sample excitation both from the side of the structure and from the opposite (substrate) side. Presumably, the strain relaxation on thin Ge is initiated by the high initial density of dislocations in the substrate.

CONCLUSION

Thus, it has been shown that a strong change in the PL spectra, resulting from competition of two kinds of emission (from QDs and QWs), is observed up to germanium thicknesses of ~15 ML in Ge/Si structures grown at low temperature (200–300°C). In contrast to structures grown at high temperatures (600–700°C), in which the luminescence from QWs predominates at thicknesses ≤4 ML, in the structures under study this kind of luminescence is observed at thicknesses ≥9 ML. With the development of misfit dislocations, the lines of luminescence from QWs are shifted to higher energies. It is noteworthy that in this case TO phonons involved in luminescence are confined to the quasi-2D layer of germanium.

It is also shown that introduction of an additional relaxed SiGe sublayer into a multilayer Ge/Si structure makes the intensity of emission from QDs much higher and the emission line narrower.

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