Raman and photoluminescence spectroscopy of SiGe layer evolution on Si(100) induced by dewetting

A. A. Shklyaev,1,2 V. A. Volodin,1,2 M. Stoffel,3 H. Rinnert,3 and M. Vergnat3
1A.V. Rzhanov Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia
2Novosibirsk State University, Novosibirsk 630090, Russia
3Université de Lorraine, Institut Jean Lamour UMR CNRS 7198, B.P. 70239, 54506 Vandœuvre-lès-Nancy Cedex, France

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High temperature annealing of thick (40–100 nm) Ge layers deposited on Si(100) at ~400 °C leads to the formation of continuous films prior to their transformation into porous-like films due to dewetting. The evolution of Si-Ge composition, lattice strain, and surface morphology caused by dewetting is analyzed using scanning electron microscopy, Raman, and photoluminescence (PL) spectroscopies. The Raman data reveal that the transformation from the continuous to porous film proceeds through strong Si-Ge interdiffusion, reducing the Ge content from 60% to about 20%, and changing the stress from compressive to tensile. We expect that Ge atoms migrate into the Si substrate occupying interstitial sites and providing thereby the compensation of the lattice mismatch. Annealing generates only one type of radiative recombination centers in SiGe resulting in a PL peak located at about 0.7 and 0.8 eV for continuous and porous film areas, respectively. Since annealing leads to the propagation of threading dislocations through the SiGe/Si interface, we can tentatively associate the observed PL peak to the well-known dislocation-related D1 band.

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I. INTRODUCTION

Solid-state dewetting is a process that can drastically modify the properties of surface layers. It is widely used for the formation of various metal layer surface morphologies.1–3 The dewetting of SiGe layers was observed recently on both Si(111)4 and Si(100)5,6 substrates. A detailed investigation of the dewetting process would be thus highly desirable both from the scientific and applied viewpoints. SiGe heterostructures are usually grown far from equilibrium, thereby producing strained structures due to the Si-Ge lattice mismatch. The main processes that release the strain under post-growth annealing are Si-Ge interdiffusion and dislocation nucleation.7,8 In the case of dewetting, strain energy minimization additionally occurs through the formation of Si substrate areas that are not covered with SiGe films, thus reducing the size of interface areas between the deposited film and the substrate.9

The dewetting in a Si-Ge system can induce the formation of submicron- and micron-sized SiGe particles on Si substrates,6 which can serve as dielectric particles with a refractive index n > 3. The light scattering on such particles leads to the generation of electrical and magnetic resonances, according to Mie theory, when the relation d ~ λ/n between the particle size (d) and the wavelength of light (λ) is satisfied.10,11 This leads to an essential redistribution of the electromagnetic field around the particles. In addition, the particles can work as lenses for far-field light focusing.12

Due to their properties, the introduction of Si or Ge Mie-resonance particle arrays can improve the performance of photodetectors, light sources, solar cells, and sensors.13 The other result of dewetting is the formation of surface morphologies more complicated than particles, such as nets of ridges, which can substantially enhance the light absorption. Although the dewetting in the Si-Ge system leads to a spontaneous change in the surface morphology, being caused only by the total energy minimization, it can, nevertheless, be controlled. This can occur through the introduction of nucleation centers to form a new surface morphology using patterned substrates.14 The dewetting control can ensure the quasi-random photonic nanostructure formation, for example, similar to those obtained in multistep technological processes using wrinkle lithography.15

The dewetting of a Ge layer deposited on Si substrates occurs at temperatures above 750 °C. It can be realized in two approaches. In one of them, Ge is deposited on Si surfaces straight at the high temperatures. It leads to the formation of different surface morphologies depending on the surface crystallographic orientation. The appearance of structures such as the net of ridges was observed on Si(111),4 whereas compact individual islands were formed on Si(100).16 In the other approach, about 30–100 nm thick Ge layers, initially deposited on Si(100) or Si(111) surfaces at relatively low temperatures (~400 °C), were subsequently annealed at higher temperatures. On Si(111), it leads to the formation of ridge-like structures, and it occurs suddenly on the whole surface.4 On Si(100), a continuous film formation is observed at the initial stage of high temperature annealing, and then, it slowly transforms into a porous film. The transformation occurs through a slow movement of the boundary between the continuous and porous film areas.5 As a result, both continuous and porous film areas can exist simultaneously on a same sample. In this work, we study the changes in the film properties along a line crossing the boundary between continuous and porous regions, using both Raman and photoluminescence...
(PL) spectroscopies. We further discuss the reason for the compressive stress appearance in the Si substrate and the origin of the photoluminescence band formation in Si/Ge heterostructures after high-temperature annealing.

II. EXPERIMENTAL DETAILS

The growth experiments were carried out in an ultrahigh-vacuum chamber with a base pressure of about $1 \times 10^{-10}$ Torr. A $10 \times 2 \times 0.3$ mm$^3$ sample was cut from an $n$-type Si(100) wafer with a miscut angle of $<10^\circ$ and a resistivity of $5-20 \Omega$ cm. Clean Si surfaces were prepared by flash direct-current heating at 1250–1270 °C. A Knudsen cell with a BN crucible was used for the Ge deposition at a rate up to 1.0 nm/min. The Ge growth on Si(100) surfaces was performed in situ at 850 °C. The sample temperature was measured using an IMPAC IGA 12 pyrometer. After the removal of samples from the growth chamber, their morphology was analyzed by scanning electron microscopy (SEM) using a Pioneer microscope manufactured by Raith. The chemical composition of the surface layers was measured using the energy-dispersive X-ray spectroscopy (EDX) of SEM SU8220 made by Hitachi. To obtain a better spatial resolution in EDX measurements of chemical compositions along a certain line along a sample cleavage, the incident e-beam energy was reduced to 4 keV. The use of samples with sharp Si/Ge interfaces showed that this gives 95% changes in the chemical composition within the 50 nm length across the interface.

The Raman spectra were measured at room temperature in the backscattering geometry using a T64000 Horiba Jobin Yvon spectrometer with the excitation by an Ar$^+$ laser with the wavelength of 514.5 nm. The PL was excited by a laser diode emitting at 488 nm and detected by a multichannel InGaAs based detector, which can detect light up to 2100 nm (i.e., 0.6 eV). The laser beam, focused on the sample surface, was about 1.3 mm in diameter, and its power varied between 0.5 and 50 mW. A cryostat with a temperature stability $\pm0.5$ K was used for the low-temperature PL study. PL measurements were performed for sample temperatures in the range from 10 to 150 K. A detailed description of the experimental setup is given elsewhere.

III. SURFACE MORPHOLOGY AND Si-Ge COMPOSITION

The surface morphology of the Ge layers grown on Si(100) at 400 °C strongly depends on the deposited Ge amount. For Ge thicknesses larger than 30 nm, the morphology is composed of continuous ridges that are formed as a result of the coalescence of large dome-like islands. After 60 nm Ge deposition, the surface morphology still exhibits uncovered Si(100) areas. Such surface morphologies are thermally unstable due to the lattice strain between the areas with deposited Ge and the underlying Si(100) substrate. Annealing of 60 nm thick Ge films at temperatures as high as 850 °C leads to the formation of two areas with different surface morphologies, the sizes of which depend on the annealing time and the temperature. During the first few minutes, the annealing causes a reduction of the surface roughness leading to an almost continuous film, as shown in Fig. 1(a). A further annealing initiates the transformation of the continuous film into a porous-like film [Fig. 1(b)]. The transformation occurs slowly starting preferentially at surface defects and sample edges. As a result, two different surface morphologies (flat and porous) can coexist on the sample surface. Moreover, the cross-sectional SEM images [see the insets of Figs. 1(a) and 1(b)] show that the interface between the Ge film and the Si substrate remains sharp for both surface morphologies. In the inset to Fig. 1(b), one can recognize that the pores are extending into the Si substrate, well below the interface between the Ge film and the Si(001) substrate.

We then perform the cross-sectional measurements of the Si-Ge composition using EDX. The composition profiles were measured along a line crossing the interface between the substrate and the grown films. The obtained results are presented in Figs. 2(a) and 2(b) for the continuous film and in Figs. 2(c) and 2(d) for the porous film. For the continuous film [Figs. 2(a) and 2(b)], the Si-Ge composition does not vary abruptly across the interface. Instead, the interface is strongly interdiffused having a width of about 10–30 nm. Our measurements further show that the continuous film is alloyed with an average Si content of about 50%. After the continuous film transformation into the porous one [Figs. 2(c) and 2(d)], the compositional changes are less pronounced across the interface.

The top view (and cross-sectional view in the insets) of the continuous SiGe film area (a) and of the porous SiGe film area (b). The white arrows in the insets show the position of the interface.
interface, the Ge content reaches only 20%. It should be noted that the latter value was measured for an area located far from the boundary between the continuous and porous films, contrary to that used for the Raman spectroscopy measurement described below.

IV. RAMAN SPECTROSCOPY CHARACTERIZATION

The Raman spectra of a 60 nm thick Ge film deposited onto Si(001) at 400 °C prior to (spectrum 1) and after the annealing at 850 °C for 1 h are shown in Fig. 3. Spectrum 2 was measured on a continuous film area, while spectrum 3 was measured on a porous film area. Spectrum 1 is characterized by two main peaks at 301.6 and 520.6 cm⁻¹, which can be associated with the Raman peaks of bulk crystalline Ge and Si, respectively. The growth temperature of 400 °C is too low to initiate the Si-Ge intermixing, i.e., the possible Raman peak shifts can be produced by the strain due to the Si-Ge lattice mismatch rather than by the Si-Ge intermixing. The weak peak at 390 cm⁻¹, which is associated with the Si-Ge vibration mode, probably originates from the Si/Ge interface. However, the Si-Si-related vibration band being observed at 520.5–520.6 cm⁻¹ indicates that the Si in the open areas of the Si substrate, which are located between the ridges of the deposited Ge films, is unstrained, since this band position is typical of unstrained Si. As for the peak from the Ge-Ge vibration band, its intensity and spectral position are predominantly determined by the top part of the deposited Ge layer, since the penetration depth is about 19 nm for the laser beam with the 514.5 nm wavelength. The Ge-Ge vibration band is observed at 301.6 cm⁻¹, which is close to its known position for unstrained Ge (~301.3 cm⁻¹).

Significant changes in the Raman spectra were observed after the sample annealing at 850 °C. In particular, the intensity of the Ge-Si vibration mode located between 350 cm⁻¹ and 450 cm⁻¹ strongly increases for both the continuous and the porous film areas (spectra 2 and 3 in Fig. 3). This indicates that a strong Si-Ge intermixing takes place during the annealing and, thus, it confirms the EDX results shown in Fig. 2(b).

To highlight the changes in the continuous film during its transformation into the porous film, a set of the Raman spectra were measured at 11 points along a line crossing the boundary between the continuous and the porous film areas [Fig. 4(a)]. The Ge-Ge and Ge-Si mode intensity significantly decreased, while the Si-Si mode intensity increased as a function of the distance across the boundary [Fig. 4(b)]. This behavior is expected, since the pores are protruding into the Si substrate [Fig. 1(b)], leading to Si areas which are not covered with SiGe layers. It should be noted that, despite the very short penetration depth of the laser beam for Ge, it is about 760 nm for Si. The continuous SiGe film obtained after annealing at 850 °C has a Ge content of ~0.55 [Fig. 2(b)]. This clarifies the possibility of the Si substrate-related peak observation in the Raman spectra for the continuous layers.

The dependencies presented in Fig. 4 show that the main changes in the surface layer composition occur within a width of about 100 µm. After the formation of the porous film area, slower changes continue to occur under annealing. In particular, the decrease in the intensity of the Si-Si mode, related to the substrate, is observed [Fig. 4(b)]. This indicates that the annealing causes a slow reduction of the pore sizes and that the surface morphology gradually becomes smooth. Smoothing is accompanied by the Si-Ge intermixing as
shown by the evolution of the Ge-Ge Raman peak position [Fig. 4(c)].

The Raman data allow us to obtain the Si-Ge composition and strain evolution caused by the continuous film transformation into the porous one. We will use linear approximations between the Raman peak shifts from one side and Ge content \( x \) and strain \( \varepsilon \) from the other side. Our analysis showed that reasonable results can be obtained using the following parameters in the linear approximation:\(^{21,23}\)

\[
\begin{align*}
x_{\text{SS}} &= 520.6 - 70x - 830\varepsilon, \quad (1a) \\
x_{\text{SG}} &= 400.5 + 12x - 575\varepsilon, \quad (1b) \\
x_{\text{GG}} &= 282.2 + 19.4x - 385\varepsilon, \quad (1c)
\end{align*}
\]

where \( x_{\text{SS}} \), \( x_{\text{SG}} \), and \( x_{\text{GG}} \) are the Raman peak positions of the Si-Si, Si-Ge, and Ge-Ge vibration modes. The parameters in Eq. (1) are similar to those derived in Refs. 19, 21, and 23–25 with the corrected positions of the Si-Si and Ge-Ge peaks of bulk Si and Ge measured using our equipment. Equations (1a) and (1c) provide good approximations for a wide range of \( x \) values, whereas the linear approximation for \( x_{\text{SG}} \) is generally used for \( 0 < x < 0.5 \). From Eqs. (1a) and (1b), and from Eqs. (1b) and (1c), the following expressions for \( x \) can be derived:

\[
\begin{align*}
x_{\text{SSGG}} &= \frac{1.44 \times (x_{\text{GG}} - 400.5) - (x_{\text{SS}} - 520.6)}{87.3}, \quad (2a) \\
x_{\text{SGGG}} &= \frac{1.49 \times (x_{\text{GG}} - 282.2) - (x_{\text{SG}} - 400.5)}{16.9}, \quad (2b)
\end{align*}
\]

respectively. The values of \( x \), calculated from the experimental data using Eqs. (2a) and (2b), as a function of the distance across the boundary between the continuous and porous films are shown in Fig. 5(a). Assuming that the EDX spectroscopy data are correct, Eq. (2a) better describes the \( x \) values for \( x > 0.5 \). In the range \( x < 0.5 \), both Eqs. (2a) and (2b) give similar results. The obtained \( x \) value for the porous film area decreases during the porous film formation and its annealing. It eventually reaches 0.2 after a longer annealing, which is consistent with the Ge content determined in the porous area far from the boundary using EDX spectroscopy.

The \( \varepsilon \) values can be obtained using the calculated \( x \) values and Eq. (1a) written in the form

\[
\varepsilon = \frac{520.6 - x_{\text{SS}} - 70x_{\text{SSGG}}}{830}.
\]

According to Eq. (3), the obtained strain is positive (corresponding to a compressive stress) in the continuous film area. However, the strain becomes negative (corresponding to a tensile stress) in the porous film area [Fig. 5(b)]. The Ge films grown on Si substrates at temperatures close to 500 °C normally undergo the compressive stress due to the lattice mismatch between Si and Ge. Our results show that the continuous film remains compressive even after the annealing at
At such high temperatures, both Si-Ge intermixing and dislocation nucleation at the interface reduce the strain to a minimum value. The following film cooling to room temperature can lead to the appearance of a tensile strain, since Ge has a bigger thermal expansion coefficient than Si. This can happen when the effect of thermal expansion is greater than the remaining compressive stress caused by the lattice mismatch. This can occur in the case of the porous film formation leading to the appearance of the tensile stress. A similar effect was observed by Zhao et al. after annealing at 680 °C for 10 min of an initially weakly strained Ge film on Si.

The Si-Si vibration band related to the substrate down-shifts by about Δω ≈ 0.2 cm⁻¹ when the probing area moves along the continuous film to the boundary with the porous film. This shift may be caused by the lattice strain. Using the relation

$$
\varepsilon_S = \frac{-(\omega_{SS} - 520.6)}{830}
$$

derived from Eq. (1a) with x = 0, we obtain a compressive stress in the Si substrate below the continuous film. This is quite unusual, since the continuous film is also compressive. The Si-Si Raman peak position is up-shifted when the measurement is performed in the porous film area. This leads to the appearance of a tensile stress in the upper part of the Si substrate. In the case of the porous film, the main contribution in the Raman peak originates from the bare Si areas located in the pores, since the probing laser beam penetration depth is limited. This means that the Si-Si peak, related to the substrate, characterizes the status of Si located only in pores. The Si in pores can be tensely strained when lying under a compressive SiGe film. Indeed, calculations have shown that if Si, lying under a Ge island, is tensely strained, then Si, lying behind the island edge, is compressively strained. Thus, for both continuous and porous films, the Si substrate areas are probably compressively strained when located under the SiGe film areas, as schematically illustrated in Fig. 7.

The appearance of a compressive stress after high-temperature annealing in the Si substrate, when being located under a SiGe film, is suggested to have the following origin. The Ge atom diffusion into the Si substrate predominantly occurs via interstitial lattice sites. The Ge atom introduction in the interstitial sites of the Si substrate can produce a compressive stress among neighboring Si atoms. In this case, a substantially lower Ge content is required to ensure the lattice mismatch compensation than in case of the Ge atoms located at the lattice sites. This is consistent with the formation of rather sharp Si/SiGe interfaces, which indicates, in particular, that the interdiffusion predominantly occurs by means of Si diffusion from the substrate into the SiGe film, whereas an essentially smaller amount of Ge atoms penetrates the Si substrate.

V. PL PROPERTIES

The low temperature PL spectra measured on both continuous and porous film areas are shown in Fig. 8. A rather
Si$_{0.8}$Ge$_{0.2}$ alloys. The complex PL peak shape of the porous cated Si containing only the D1 line. 37,38,40,41 The similarity PL spectra shown in Fig. 8(a) are similar to those of dislo-
area, and it reaches a maximum at 0.7 eV [Fig.8(a)]. This peak is distant from
in the films with the nominal Si 0.4Ge0.6 composition.39 The
peaks, (D1-D2, in particular) if the crystal defects are intro-
absorption becomes essential and leads to the excitation
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The porous area formation leads to a decrease of the PL intensity and to an increase in the power exponent $m$ of the PL intensity dependence on the pump power (see inset of Fig. 8). These changes can be associated with an increase in the surface recombination rate, which causes a decrease in the free carrier concentration. Consequently, the PL intensity decreases, as observed in Fig. 8(b), and the exponent $m$ of the PL intensity dependence on the pump power increases. The PL intensity of the continuous and porous films was measured as a function of the sample temperature for the constant excitation power of 30 mW. The obtained temperature behavior (not shown here) was similar to that of the dislocation-related PL from Si caused by thermal quenching.45,46 The PL from the SiGe films almost quenches for temperatures higher than 150 K.

Dislocated Si exhibits several dislocation-related PL peaks, (D1-D2, in particular) if the crystal defects are intro-
duced in Si using mechanical treatment37,38 or electron,
as well as ion\textsuperscript{49} beam irradiations. However, if the dislocations appear as a result of thermal treatment of SiGe structures, this leads to the predominant formation of only one PL peak at about 0.8 eV\textsuperscript{40,41} This peak is associated with the D1 dislocation-related band in Si. The PL results obtained here for the porous SiGe film area also show the formation of the dislocation-related D1 band, which appears in the Si substrate, as well as in the Si\textsubscript{0.8}Ge\textsubscript{0.2} porous film area. The fact that only one dislocation-related peak dominates in the PL spectra of SiGe layers, initiated by high-temperature annealing, is likely to be a common feature of the Si/Ge heterostructures. This suggests that the corresponding deep energy levels in Si and SiGe can be the result of the presence of Ge atoms in the interstitial lattice sites near the threading dislocations. This is in agreement with a compressive stress in the Si substrate, which may be due to the Ge atoms located in the interstitial lattice sites in Si.

VI. CONCLUSION

We have shown that the annealing of SiGe films at 850 °C leads to a gradual displacement of the boundary between continuous and porous film areas. The width of the boundary is about 100 μm. Both EDX and Raman spectroscopy data showed that the boundary displacement is accompanied by a decrease in the Ge content from about 60% to 20% when moving from the continuous to the porous film area. This is further accompanied by a change in the stress from a compressive in the continuous film area to a tensile in the porous film area. For the Si substrate, instead of the tensile stress, which should be expected due to the Si-Ge lattice mismatch, the annealing at 850 °C results in the appearance of a compressive stress. It is suggested that this occurs due to the Ge atom occupancy of the interstitial lattice sites in the Si substrate.

The PL with the photon energies \(\sim 0.3\) eV smaller than the SiGe bandgap is observed for both continuous and porous film areas. This PL can be associated with deep energy levels in SiGe caused by the crystal defects, such as threading dislocations. The PL spectra indicate that the presence of Ge in Si, as well as in SiGe, after annealing produces preferably only one type of radiative recombination centers, such as the D1 dislocation-related PL band. In agreement with the previous suggestion, these centers can be associated with the Ge atoms located at interstitial lattice sites near dislocation cores.

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