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Mechanism of Nanohills Growth in $Si_{1-x}Ge_x$/Si Structure by Laser Radiation

Arturs MEDVID[1,3*], Pavels ONUFRIJEVS[1], Klara LYUTOVICH[2], Michael OEHME[2], Erich KASPER[2], Igor DMITRUK[4], Iryna PUNDYK[4], Ivan S. MANAK[5]

[1]*Riga Technical University, 14 Azenes Str., Riga, LV-1048, Latvia*
[2]*Universitat Stuttgart, Pfaffenwaldring 47, 70569 Stuttgart, Germany*
[3]*Institute of Semiconductor Physics National Academy of Science of Ukraine, 45 Pr.Nauki, 252650, Kyiv-28, Ukraine*
[4]*Kyiv National Taras Shevchenko University, Kyiv-03022, Pr.Acad.Glushko, 2-1, Ukraine*
[5]*Belarusian State University, Prosp. Nezavisimosti, 4, 220030, Minsk, Belarus*

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The study is focused on formation and optical properties of nanostructures induced by laser radiation on the surface of $Si_{1-x}Ge_x$/Si hetero-structures. Formation of self-assembling nanohills induced by irradiation of nanosecond Nd:YAG laser pulses on the $Si_{0.7}Ge_{0.3}$/Si hetero-epitaxial structures is reported. The atomic force microscope (AFM) study of the irradiated surface morphology has shown a start of nanohills formation after laser irradiation of the intensity $I = 7.0\ MW/cm^2$. The giant "blue shift" of photoluminescence (PL) spectra with maximum intensity in region of 700 nm – 800 nm (1.76 eV – 1.54 eV) is explained by the quantum confinement effect (QCE) in the nanohills. The maximum of this PL band slightly shifts to shorter wavelengths with the increase of the intensity of laser pulses used for sample treatment. Appearance of the 300 cm^{-1} Ge-Ge vibration band in Raman scattering (RS) spectra for sample irradiated with $I = 20.0\ MW/cm^2$ is explained by Ge phase formation. Formation of the Ge-rich phase is explained by localization of Ge atoms drifting toward the irradiated surface under the thermal gradient due to strong absorption of laser radiation.

Keywords: laser radiation, nanohills, $Si_{1-x}Ge_x$/Si, photoluminescence, quantum confinement effect.

1. INTRODUCTION

Considerable attention is paid to the semiconductor nanostructures as building blocks of future nanoscale devices for electronics and photonics. Nowadays, nanostructures are the most investigated object in solid-state physics, especially concerning the quantum confinement effect in quantum dots (QD) [1], quantum wires [2] and quantum wells (QW) [3]. In the case of nanosize structures the energy band diagram of a semiconductor is strongly changed leading to crucial change of properties such as electro-conductivity (due to the change of charge carrier concentration and mobility of electrons and holes), optical parameters (absorption coefficient, reflectivity index, radiative recombination efficiency); mechanical and thermal properties.

It is known that in indirect band-gap semiconductors such as Si and Ge radiative electron-hole recombination efficiency is strongly enhanced in nanostructures due to quantum confinement effect (QCE) [4]. Moreover, shift of PL spectrum toward high energy of spectrum, so called "blue shift", has been predicted [4] and observed in Ge [5] and Si [6] single crystals. A new flexible possibility is predicted to change the semiconductor basics parameters into QDs of $Si_{1-x}Ge_x$ solid solution both by change of x and QDs diameter. Increase both content of Ge atoms – x, and diameter of QDs leads to the same effective shift of PL spectrum toward low energy of spectrum, so called "red shift". It has been shown that increase of x from 0.096 to 0.52 leads to shift of maximum position in IR part of PL spectrum toward low energy (0.3 eV) [7]. The same, "red shift" of PL spectrum on 0.7 eV has been observed for nanoparticles with diameter 5 nm – 50 nm and $x = 0.237$ – 0.75 in visible part of spectrum [8]. Authors explain this result by the incorporation of the Ge atoms into Si nanoparticles and associated surface state. Another effect has been observed in [5], for pure Ge crystal where decrease of QDs diameter till 4 nm leads to the "blue shift" of PL spectrum maximum position up to 1.1 eV [5] in comparison with the PL spectrum of bulk crystal. Therefore in this paper we will show that the main role in control of PL spectrum and its intensity is QCE and Ge content has only small influnce.

From application point of view in optoelectronics, the investigation of light-emitting diodes based on $Si_{1-x}Ge_x$ structure has been of much interest due to the possibility to change the radiation wavelength in near infrared region of spectrum (~1.5 μm) by varying the concentration of solid solution components [4]. This structure is in good compatibility with Si technology.

Therefore this study is focused on formation of optical properties of nanostructures induced by laser radiation on the surface of $Si_{1-x}Ge_x$/Si hetero-structures.

2. EXPERIMENTAL

Crystal $Si_{1-x}Ge_x$ alloys were grown on Si(100) wafers by Molecular Beam Epitaxy (MBE). $Si_{1-x}Ge_x$ films were grown by MBE on top of a 150 nm thick Si buffer layer on Si. Schematically cross-section of the $Si_{1-x}Ge_x$/Si hetero-epitaxial structure is shown in Fig. 1.

Alloys containing 30 % Ge were used in the experiments. The surface of a $Si_{1-x}Ge_x$/Si structure was irradiated by 15 ns pulses of a Nd:YAG laser (wavelength 1064 nm, power 1 MW). The spot of laser beam of 3 mm diameter

*Corresponding author. Tel.: +371-7089445; fax.: +371-7089074.
E-mail address: *medvids@latnet.lv* (A. Medvids)

was moved by 20 μm steps over the sample surface. The experiments were performed in ambient atmosphere at pressure 1atm, at room temperature ($T = 20$ °C) and 80 % humidity. The structural and optical characteristics of Ge nanostructures were studied by atomic force microscope (AFM), photoluminescence (PL), excited by 488 nm radiation of Ar ion laser and Raman scattering (RS), excited by 514.5 nm radiation of an Ar ion laser.

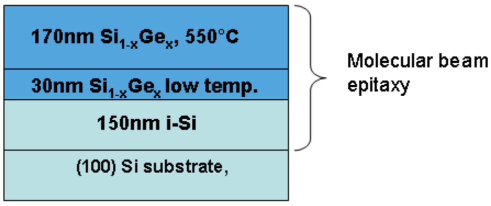

Fig. 1. Cross-section of the $Si_{1-x}Ge_x$/Si hetero-epitaxial structures grown by MBE

3. RESULTS

The three-dimensional image of surface morphology of $Si_{0.7}Ge_{0.3}$/Si hetero-epitaxial structure recorded by AFM measurements after irradiation by the Nd:YAG laser at intensities of 7.0 MW/cm^2 (a) and 20.0 MW/cm^2 (b) is shown in Fig. 2. In Fig. 2, a, the nanohills of the average height of 11 nm formed by laser radiation at the intensity of 7.0 MW/cm^2 are seen. Similar nanohills of the average height of 27 nm seen in Fig. 2, b, have been obtained by irradiation intensity of 20 MW/cm^2. Due to higher irradiation intensity they are more compact in diameter and higher.

The two-dimensional images of surfaces morphology of the same spots as in Fig. 2, a and b, are shown in Fig. 2, c and d.

PL spectra of the $Si_{1-x}Ge_x$/Si hetero-epitaxial structures with the maxima at 1.60 eV – 1.72 eV obtained after laser irradiation at intensities of 2.0 MW/cm^2, 7.0 MW/cm^2 and 20.0 MW/cm^2 are shown in Fig. 3. The spectra are unique and unusual for the material, because, depending on Ge concentration, the band gap of SiGe is between 0.67 eV and 1.12 eV [7]. As seen from Fig. 3, the $Si_{1-x}Ge_x$ structure emits light in the visible range of spectrum and the intensity of PL increases with the intensity of irradiation.

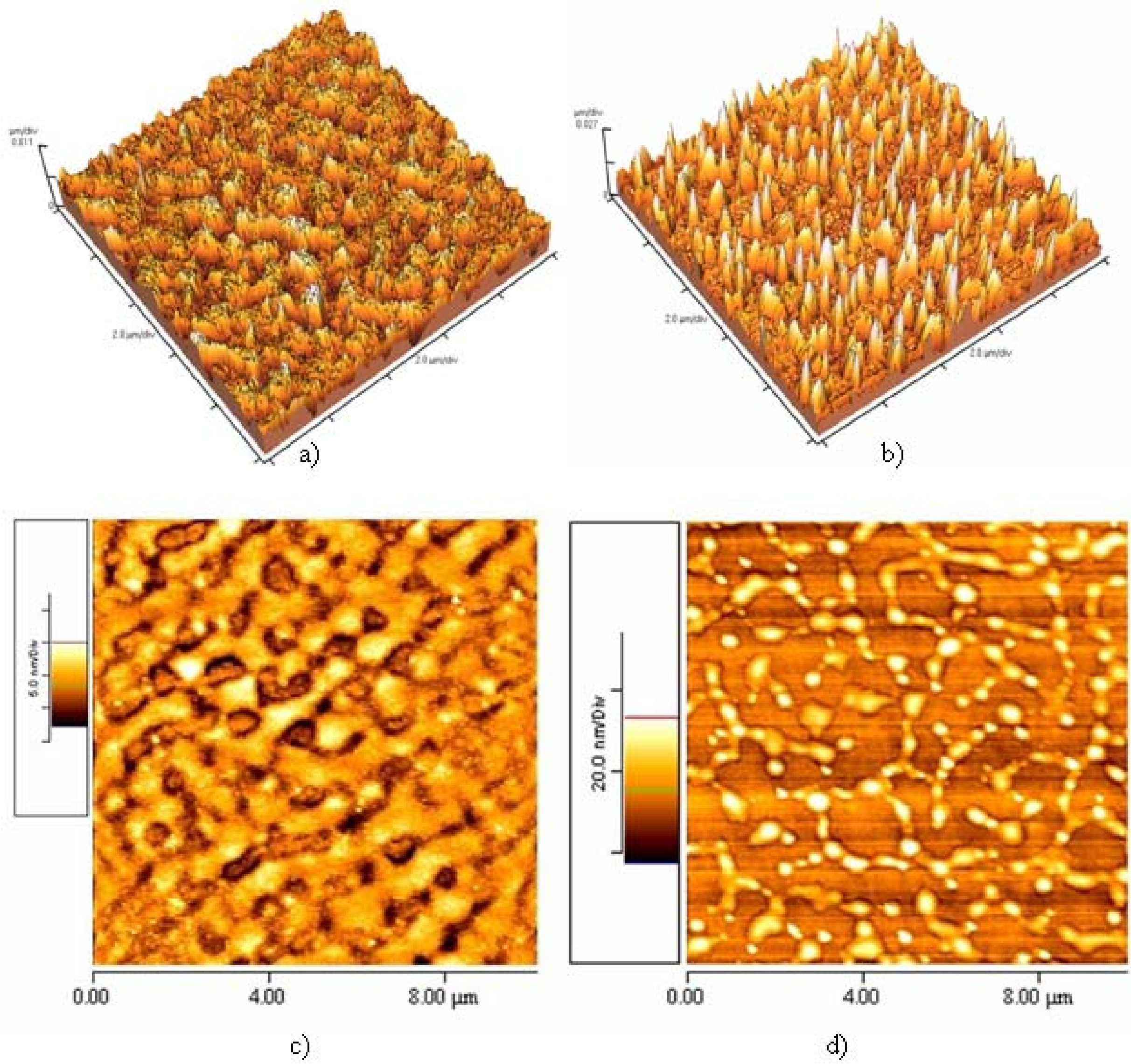

Fig. 2. Three-dimensional AFM images of $Si_{0.7}Ge_{0.3}$/Si surfaces irradiated by the Nd:YAG laser at intensity 7 MW/cm^2 (a) and 20 MW/cm^2 (b) and two-dimensional images of surface morphology of the same spots of structure at intensities: 7.0 MW/cm^2 (c) and 20.0 MW/cm^2 (d)

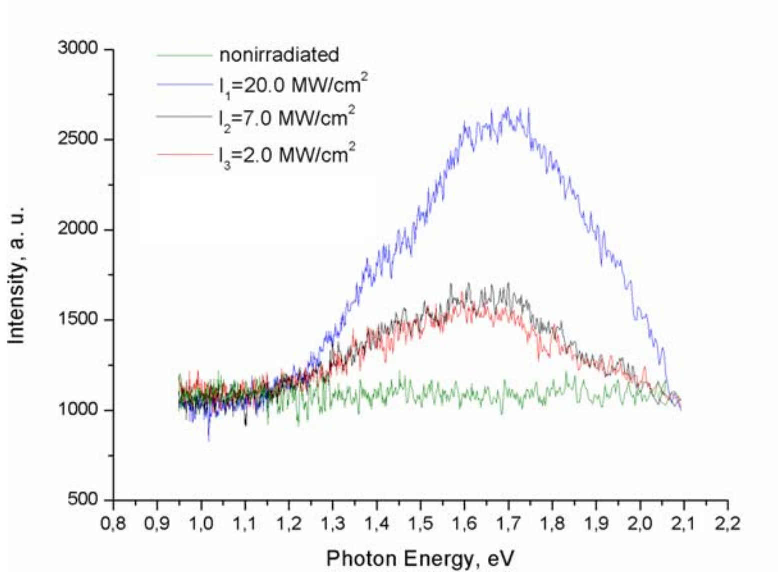

Fig. 3. PL spectra of the $Si_{0.7}Ge_{0.3}$/Si hetero-epitaxial structures before and after irradiation by Nd:YAG laser radiation at intensities 2.0 MW/cm^2, 7.0 MW/cm^2, and 20.0 MW/cm^2 (color online)

The Raman scattering spectra of $Si_{1-x}Ge_x$/Si hetero-epitaxial structures both non-irradiated and laser irradiated surfaces of the crystal at intensities of 2.0 MW/cm^2, 7.0 MW/cm^2 and 20.0 MW/cm^2 are shown in Fig. 4.

4. DISCUSSIONS

After irradiation of the $Si_{1-x}Ge_x$/Si hetero-epitaxial structure by the laser at intensity of 7.0 MW/cm^2 the surface structure begins to look as spots on un-wetting material, for example, it looks like water spots on a glass, Fig. 2, c. It means that laser radiation induces segregation of Ge phases at the irradiated surface of the material. This conclusion is in agreement with data from paper [14] where it was shown that Ge phase starts formation at 50 % concentration of Ge atoms in SiGe solid solution. According to the thermo-gradient effect [11], it is supposed that laser radiation initiates the drift of Ge atoms toward the irradiated surface of the hetero-epitaxial structure. The maximum of the PL band at 1.70 eV is explained by the quantum confinement effects [12]. Position of the observed PL peak compared with the bulk material shows a significant "blue shift". The maxima of PL spectra of the $Si_{1-x}Ge_x$/Si hetero-epitaxial structure slightly shift to higher energy when the laser intensity increases from 2.0 MW/cm^2 to 20.0 MW/cm^2, which is consistent with the quantum confinement effects too. Our suggestions, concerning to the Ge phase formation, are supported by the Raman spectra. After laser irradiation at the intensity of 20.0 MW/cm^2 a Raman band at 300 cm^{-1} appears in the spectrum. This band is attributed to the Ge-Ge vibration and is explained by formation of a new Ge phase [14] in the $Si_{1-x}Ge_x$/Si hetero-epitaxial structure. The estimate of the concentration of Ge atoms in the nanohills by the formula (1) from paper [13] gives 42 % and 31 % at $I_3 = 20.0$ MW/cm^2 and $I_2 = 7.0$ MW/cm^2 respectively, at $B = 3.2$.

$$\frac{I_{GeGe}}{I_{SiGe}} \approx B\frac{x}{2(1-x)} \quad . \qquad (1)$$

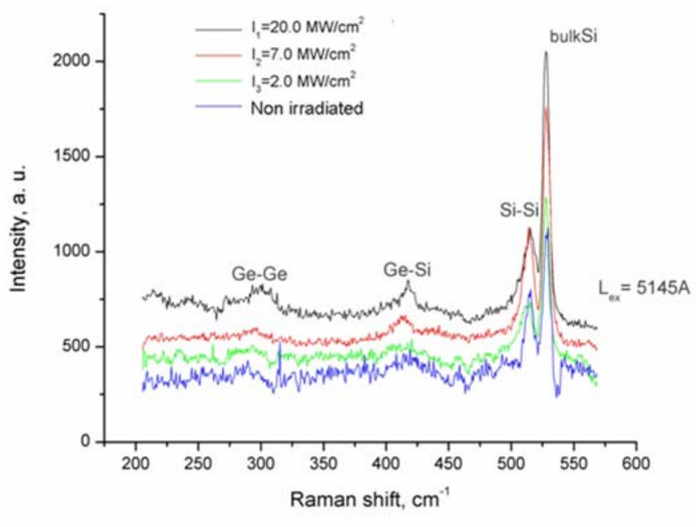

Fig. 4. Micro-Raman spectra of the $Si_{1-x}Ge_x$/Si hetero-epitaxial structures: non-irradiated (blue) and laser irradiated (green, red and black) surfaces of the crystal (color online)

There is proposed to use modified formula (2) from paper [12] for determination of concentration x in the nanohills of $Si_{1-x}Ge_x$/Si hetero-epitaxial structure formed by laser radiation using PL spectra.

$$E_g = E^0{}_g + \frac{(\pi\hbar)^2}{2d^2}\left[x_{Ge}\left(\frac{1}{m_e^{*Ge}} + \frac{1}{m_h^{*Ge}}\right) + (1-x)_{Si}\left(\frac{1}{m_e^{*Si}} + \frac{1}{m_h^{*Si}}\right)\right]. \quad (2)$$

Determination of x for diameter of nanodot $d = 4.2$ nm on the top of nanohill from AFM measurements and band gap from maximums of PL spectra at $E_{g1} = 1.74$ eV, $E_{g2} = 1.69$ eV and $E_{g3} = 1.60$ eV, and $E^0_g = 0.95$ eV for 30 % of Ge in Si [10] were used. In this way, Ge concentration in the nanohills are $x_1 = 34$ %, $x_2 = 55$ % and $x_3 = 66$ %, respectively, where E^0_g is band gap of bulk material, $m_{e,h}^{*Ge,*Si}$ are the electron and hole effective mass for Ge and Si, respectively. In this preliminary analysis we used the same value of d. The exact measurements are the objects of later investigations.

The last formula (2) gives data of value of x higher than from Raman scattering spectra. This discrepancy in value of x we explain by difference of sources of light in the PL and Raman scattering spectra. So, the PL spectrum is created by top of nanohills, where diameter of the quantum dot is less than 4.2 nm, but Raman scattering spectrum is created by the whole irradiated spot of the sample. Therefore in the first case, the mean concentration of the Ge atoms is more than in the second case. We suppose that concentration of the Ge atoms at the plane is less than in the top of nanohills. The Ge-Ge LO phonon band gives an evidence of our suggestion.

The following model is proposed for explanation of dynamics of nanostructures formation.

Irradiation of the $Si_{1-x}Ge_x$/Si hetero-epitaxial structure by Nd:YAG laser initiates a drift of initially uniformly distributed Ge atoms to the irradiated surface due to the gradient of temperature – the thermogradient effect [11]. The process has a positive feedback: after every laser pulse, the gradient of temperature increases due to the increase of the concentration of Ge atoms at the irradiated surface. A new Ge phase starts to form when the concentration of Ge atoms reaches more than 50 % [14]. At the end of the process Ge atoms are localized at the surface of Si like a buried thin film. The self-assembly of a nanostructure on the irradiated surface takes place due to the Stranski-Krastanov' mode of nanostructure growth.

5. CONCLUSIONS

1. Formation of nanohills by laser irradiation of the $Si_{0.7}Ge_{0.3}$/Si hetero-epitaxial structure is shown to be possible.

2. Photoluminescence spectra of the $Si_{1-x}Ge_x$/Si hetero-epitaxial structure with nanohills are explained by the quantum confinement effect.

3. Formation of a new phase of crystalline Ge nanohills is found on the surface of $Si_{0.7}Ge_{0.3}$/Si hetero-epitaxial structures after laser irradiation at intensities exceeding I = 2 MW/cm^2.

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