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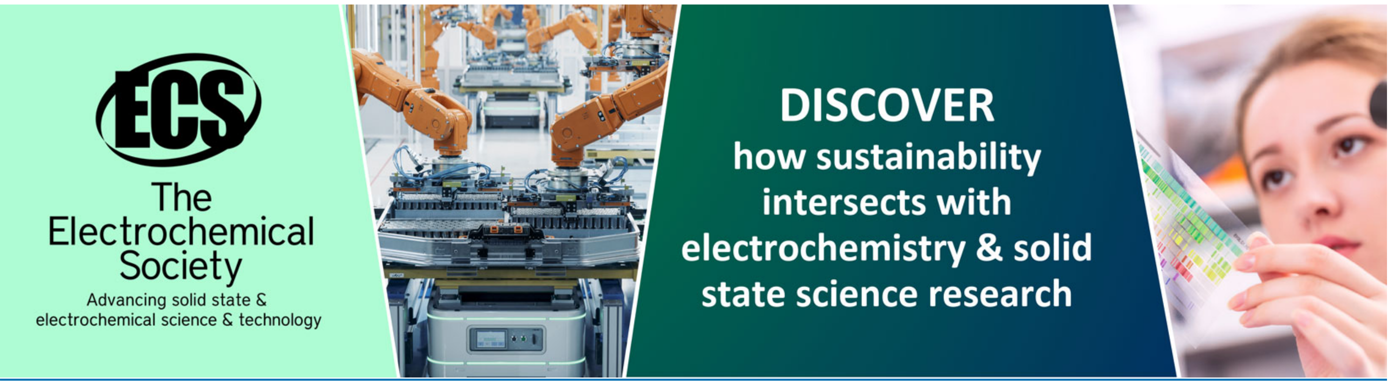

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Luminescence and structural properties of germanium nanocrystals formed by annealing multilayer GeO_x/Al_2O_3 nanostructures

D A Grachev[1], S A Garakhin[1], A V Belolipetsky[2], A V Nezhdanov[1], A V Ershov[1]

[1] Department of Semiconductor Physics and Optoelectronics, Lobachevsky University, Nizhny Novgorod 603950, Russia
[2] Sector of Theory of Optical and Electrical Phenomena in Semiconductors, Ioffe Institute RAS, Saint Petersburg 194021, Russia

E-mail: grachov@phys.unn.ru

Abstract. By Raman scattering, luminescence, and IR-absorption spectroscopy multilayer nanoperiodic structures Ge/Al_2O_3 & GeO_x/Al_2O_3 have been investigated. The samples have been obtained by the physical evaporation; their properties have been varied by changing the layer thicknesses (2–20 nm) and annealing temperature (500–1000 °C). It is found that germanium nanocrystals are formed in the temperature range of 500–800 °C and exhibit intense size-depend photoluminescence at 1.2 eV and 1.8–2.0 eV.

1. Introduction

In recent years there has been a significant growth in interest in the study of germanium nanocrystals (Ge-NCs) in a dielectric, the prospective composite material for LED components and long-term charge storage cells. Compared with silicon nanocrystals (Si-NCs), which are used in the modern microelectronics, Ge-NCs have some important advantages. The process of Ge NC forming is realized at lower temperatures than for Si-NCs that extends the capability of band engineering. Moreover germanium has a low reactivity that improves the stability of the composite [1]. Differences in the band structures of silicon and germanium makes research of systems with Ge-NCs in oxide matrix fundamentally important for better understanding of the quantum size effects in indirect-band-gap materials in general.

One way to obtain Ge-NCs is to anneal nanoperiodic multilayer sandwich structure GeO_x/oxide. This approach is to make possible the control of nanocrystal sizes and their density. The purpose of the study was to form multilayer nanoperiodic samples Ge/Al_2O_3 & $GeO_{x\approx 1}/Al_2O_3$, containing germanium nanocrystals, and to investigate their structural and luminescent properties as well.

2. Preparation of samples and measurements procedure

The nanoperiodic multilayer Ge/Al_2O_3 & GeO_x/Al_2O_3 samples (Figure 1) have been formed on silicon substrates by vacuum physical vapor deposition. As to the Ge/Al_2O_3 structure design, thickness of the Al_2O_3 layers was 5 nm, and the Ge layer thickness was varied between 3 and 7 nm that depended on particular sample. For the GeO_x/Al_2O_3 structure thickness of the Al_2O_3 layers was 8 nm; size of the Ge layers was a value in the range of 2–20 nm. The number of layers was 19. After deposition the

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structures have been divided into chips, which were annealed in nitrogen atmosphere at the temperature from 400 °C to 1000 °C.

Raman spectra have been carried out in the range of 400–600 cm^{-1}. IR-transmission spectra in the range of 400–1400 cm^{-1} have been obtained. The photoluminescence (PL) spectra have been measured at room temperature in the wavelength range of 580–1100 nm (Nd:YAG laser: 5.29 mW, 532 nm).

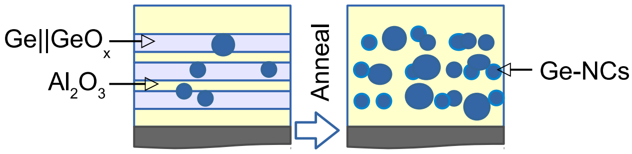

Figure 1. Schematic representation of the GeO_x/Al_2O_3 nanostructure modification.

3. Experimental results and discussion

Figure 2 shows the typical Raman spectra of the Ge/Al_2O_3 nanostructures. Prior to annealing germanium is amorphous, since there is a band of 260–280 cm^{-1} [2,3]. When the temperature is over 600 °C the sharp peak of 299 cm-1 appears for the reason that germanium crystallizes. As to the luminescence spectra (Figure 3), annealing at 600 °C gives rise to intense PL-band in the range of 1.6–2.0 eV, peak position of which is about 1.9 eV. It can be inferred from papers [4,5] that origin of the band should be associated with nothing but crystalline germanium phase.

Maximum volume fraction of a crystalline germanium phase corresponding to the higher scattering peak is observed at the temperature of 800 °C. In this case, the PL counter plot (Figure 3) shows two luminescence bands at 1.2 eV and 1.8–2.0 eV. The first may be also associated with Ge-NCs, but of smaller size [2,6,7]. That small particle formation seems to be caused by the oxidation process, which confirms the second luminescence band of the oxygen-deficient centers in GeO_2 [2]. At the temperatures above 900 °C germanium metal phase on the Raman spectra as well as Ge-NCS luminescence bands are not observed. We attribute this to total oxidation of germanium and formation of a volatile compound of germanium monoxide [1].

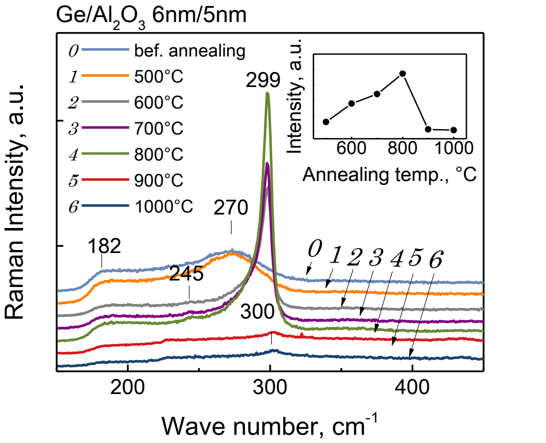

Figure 2. Raman spectra of the Ge/Al_2O_3 nanostructure (3 nm/ 5 nm bilayer) annealed in the temperature range of 500-1000 °C.

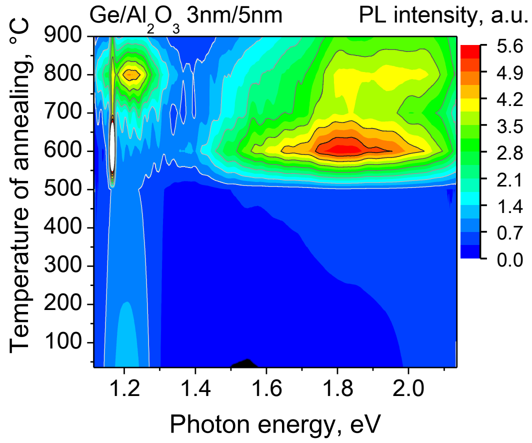

Figure 3. PL counterplot of the Ge/Al_2O_3 nanostructure (3 nm/ 5 nm bilayer) annealed in the temperature range of 500-1000 °C.

The non-annealed structures also exhibit slight luminescence at 1.2 eV. This may indicate that the deposited amorphous germanium layers are inhomogeneous. Presumably, the structures before annealing are consisted of small amount of Ge-NCs, that volume concentration is not enough for detecting by the Raman spectrometer.

As far as the thin GeO_x/Al_2O_3 system is concerned, it is observed the similar problem of the Raman spectra interpretation. The maximum intensity of the 1.2 eV PL peak corresponds to the annealing temperature of 500 °C, but in this case the sharp of the Raman curve (Figure 4) doesn't have the features peculiar to the crystalline phase, there is a domed peak instead. According to the Raman spectra crystallization of germanium starts at 600 °C. It is quite possible that effect stems from extremely small sizes of the Ge NCs, 3 nm.

Notwithstanding that further growth of the annealing temperature leads to drastic decrease in the volume fraction of germanium (Figure 4) and its PL intensity (Figure 5), the 1.2 eV band appears in the second time when the temperature reaches 800 °C, as to the Ge/Al_2O_3 system (Figure 3). The phenomenon is assumed to be caused by rising diffusivity.

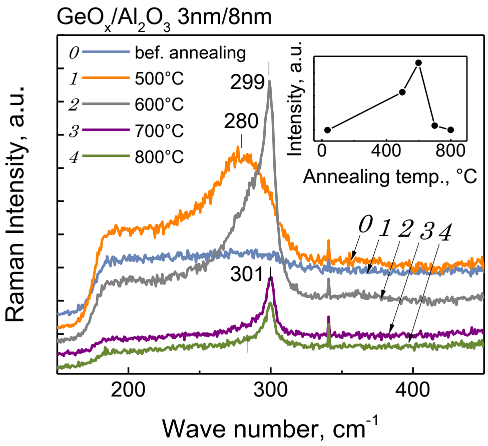

Figure 4. Raman spectra of the GeO_x/Al_2O_3 nanostructure (3 nm/ 8 nm bilayer) annealed in the temperature range of 500-1000 °C.

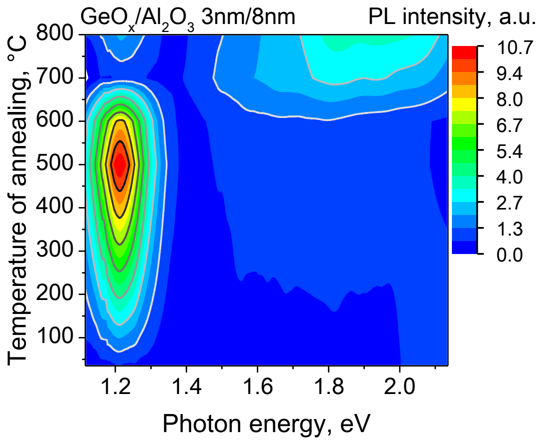

Figure 5. PL counterplot of the GeO_x/Al_2O_3 nanostructure (3 nm/ 8 nm bilayer) annealed in the temperature range of 500-1000 °C.

Figures 6 shows FTIR spectra of the GeO_x/Al_2O_3 systems where thickness of the GeO_x layers is more than 6 nm. For the non-annealed sample weak-intensity bending band of GeO_x (780 cm^{-1}) is observed [8]. After temperature treatment of 500 °C band at 800 cm^{-1}, GeO_2 characteristic [2], clearly appears. This confirms the fact [9] that the process of splitting GeO_x into the Ge and GeO_2 occurs at a temperature not more than 500 °C.

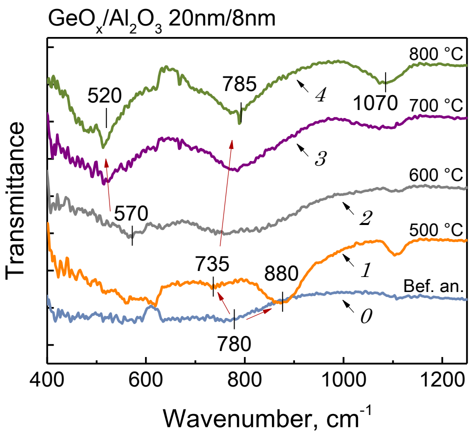

Figure 6. FTIR spectra of the GeO_x/Al_2O_3 nanostructure (20 nm/ 8 nm bilayer) annealed in the temperature range of 500-1000 °C.

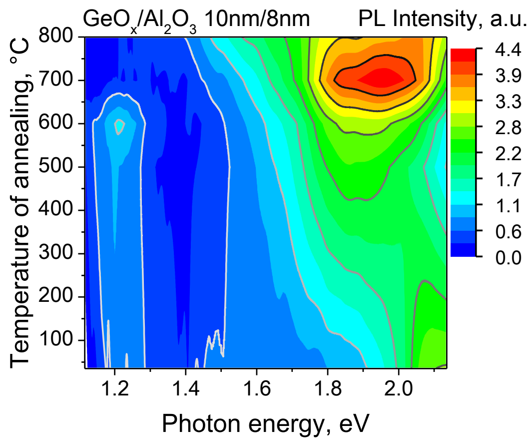

Figure 7. PL counterplot of the GeO_x/Al_2O_3 nanostructure (10 nm/ 8 nm bilayer) annealed in the temperature range of 500-1000 °C.

Besides the GeO_2 band, at 735 cm^{-1} it is observed light absorption by GeO_x molecules, $x < 1$. As the temperature increases the position of the band shifts from 735 to 785 cm^{-1} indicating the growth of

x [2], likewise the 550 cm^{-1} stretching GeO_x band occurs [10]. That points to the strong process of germanium oxidation for temperatures of 600–800 °C. These data are in good agreement with the PL spectra (Figure 7) in particular with the 1.8–2.0 eV GeO_x band. In particular GeO emits at 1.6eV, and GeO_2 mentioned above in region of 1.8-2.0 eV.

In discussing the PL spectra of the thick-layer systems, we have to note that the temperature of the 1.2 eV band observing is 600 °C which agrees well with the Raman data (Figure 4). We can conclude that the most suitable temperature to form small Ge-NCs is between 500 °C and 600 °C.

Apart from the 1.2 eV band, in the Figure 7 there is an intensive band at 1.9 eV [5], which is also observed for the Ge/Al_2O_3 system (Figure 3). As it is detected only for the thick-layer structures, we associate it with large Ge-NCs, since GeO_x layers contain enough Ge-fraction to obtain large quantum dots. Presumably their size is about of 4–20 nm [4].

As evidence of whether the band was caused by Ge-NCs luminescence, it was shown how the peak position and its intensity depend on the thickness of the germanium-rich layers (Figure 8). The photon energy decreases with increasing layer size. In the case of the GeO_x/Al_2O_3 systems the 1.9 eV band intensity has maximum when thickness of the GeO_x layers is approximately 10 nm. It should be noted that in Figure 8, as well as in Figure 9, the abscissa shows a value of the thickness of the germanium-rich layers. This value differs from the size of the Ge-NCs. Thus, due to diffusion the average diameter of the Ge-NCs is large than the Ge layer thicknesses [3] and is smaller than the GeO_x layer thicknesses.

As to the 1.2 eV band we have not observed the quantum size effect (Figure 9). It could be explained by prolonged time of annealing (1 hour), during which the nanocrystals are taking thermodynamic equilibrium size about 3 nm [11]. We would like to mention the fact that the intensity of the 1.2 eV band increases exponentially with a decrease in the size of the Ge-NCs [12].

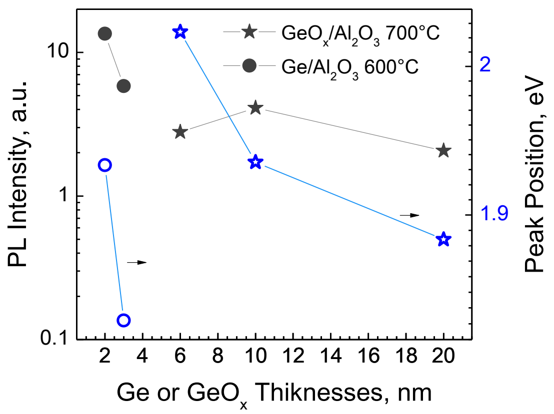

Figure 8. The 1.9–2.0eV L peak properties.

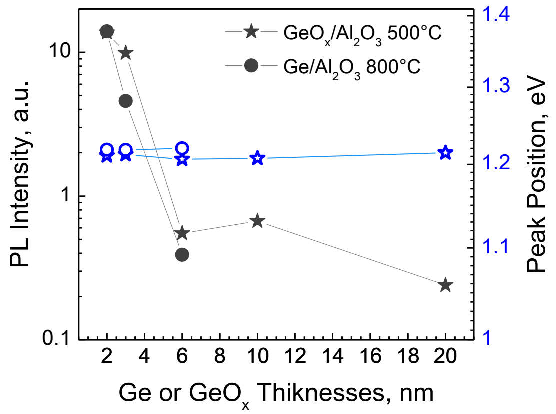

Figure 9. The 1.2eV PL peak properties.

4. Summary

Annealing the Ge/Al_2O_3 nanoperiodic multilayer structures at temperature of 800 °C as far as the GeO_x/Al_2O_3 of 500–600 °C leads to the formation of 3 nm Ge-NCs that exhibit intense 1.2 eV photoluminescence. In case of annealing at 600–700 °C it is observed size-depended 1.8-2.0 eV band for both systems. We associate it with luminescence of large germanium nanocrystals, sizes of which are about 4-20 nm.

Acknowledgments
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