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Germanium polytypes formation on AlGaAs nanowire surface

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Abstract. Raman spectroscopy was applied to investigate a series of Ge films grown on GaAs and AlGaAs nanowires by molecular beam epitaxy. The formation of both cubic and hexagonal Ge phases was revealed using Raman spectroscopy. DFT calculations of the volumetric energies suggest Ge-16R or Ge-6H hexagonal polytype.

Keywords: nanowire, molecular beam epitaxy, germanium, semiconductors

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Формирование политипов германия на поверхности нитевидных нанокристаллов AlGaAs

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Аннотация. Продемонстрирована возможность формирования кубических и гексагональных политипов германия на поверхности AlGaAs нитевидных нанокристаллов методом молекулярно-пучковой эпитаксии. Впервые измерена диэлектрическая проницаемость гексагонального Ge в зависимости от энергии фотонов.

Ключевые слова: нитевидные нанокристаллы, молекулярно-пучковая эпитаксия, германий, полупроводники

Финансирование: Ростовые эксперименты были проведены при финансовой

поддержке Министерства науки и высшего образования Российской Федерации (гос. задание № 0791-2023-0004). Спектроскопические исследования методом эллипсометрии были выполнены при финансовой поддержке Санкт-Петербургского государственного университета в рамках исследовательского гранта № 94031047. Рамановские спектры были получены при поддержке ресурсного центра СПбГУ «Оптические и лазерные методы исследования вещества». Расчеты методом ТФП были выполнены при финансовой поддержке Санкт-Петербургского государственного университета в рамках исследовательского гранта № 94033852.

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Introduction

During recent years, semiconductor nanowires (NWs) attract great attention due to their unique properties. Nanometer size cross-section and high aspect ratio rise to many interesting physical properties, which are not seen in bulk materials, such as the possibility to exist in different crystal structures [1]. These opens up wide possibilities to form tune optical and electronic properties. For instance, polytypic inclusions in A3B5 NWs can acts as a crystal phase quantum dots [2], the periodic structure composed of alternating WZ/ZB phases showed yield interesting superlattice effects [3–4].

In group IV semiconductors, including silicon and germanium, the formation of polytypic NWs has attracted enormous interest among researchers in recent years [5–8]. Among various germanium polytypes (3C, 5h, 9R, 12R, 2H etc.), hexagonal 2H phase (properly named as lonsdaleite) is of particular interest. Hexagonal 2H Ge has been predicted to have a direct bandgap structure [9]. As a result, efficient light emission from hexagonal Ge and SiGe alloys has recently been achieved [10].

It this work, we investigate molecular beam apitaxy growth and properties of Ge on the surface of pure wurtzite AlGaAs NWs and probing the heterostructured NWs with Raman spectroscopy combined with DFT modelling to investigate Ge polytype formation.

Materials and Methods

The nanostructures were synthesized using a Riber Compact 21 EB200 MBE setup equipped with effusion sources for growing III–V semiconductors and with e-beam source for the evaporation of germanium. Thus, this equipment allowed us to perform germanium deposition directly after the NW formation. We synthesized arrays and $Al_{0.3}Ga_{0.7}As$ NWs on Si(111). The NWs were grown at the substrate temperature of 500 °C using gold drops as a catalyst, which were obtained by deposition of a thin metal film onto a heated substrate. Then we lowered the substrate temperature to 320 °C and conducted the deposition of germanium layer with the equivalent thickness of 150 nm.

After the completion of growth, the samples with NW arrays were cooled to room temperature and unloaded to study the morphological properties by scanning electron microscopy (SEM). The optical properties were studied by Raman spectroscopy. The Raman spectra were recorded in the backscattering mode of measurements with the use of a Witec Alpha 300R microscope at room temperature. For excitation, we used Nd:YAG laser radiation at a doubled frequency; the wavelength was 532 nm.

Results and Discussion

Examination of as-grown AlGaAs NWs by SEM showed that they were straight with tapered tips. The NWs were about 60 nm wide and 2.6 μm long. Ge deposition resulted in a slight (~ 10 nm) increase of their average width and the formation of bulbs on the NW tips. Plan-view

examination revealed a slight rounding of AlGaAs-Ge NWs compared to the initial AlGaAs NWs, which had six-fold symmetry.

The Raman spectre of the uppermost part of the NWs, i.e. where Ge was deposited is shown in Fig. 1, *a*. In addition to the peaks corresponding to GaAs and AlAs, the spectrum has two peaks corresponding to Ge, namely, 200 cm^{-1} and 300 cm^{-1}. The peak at 300 cm^{-1} is characteristic of all Ge polytypes (depending on the symmetry of the polytype, it can split into several peaks and shift slightly). The peak at 200 cm^{-1}, forbidden for the 3C and 2H polytypes, was previously observed in Ge hexagonal phases, which were obtained at high pressures during nanoindentation [11]. This peak is absent at the base of the NW.

We performed modeling of different hexagonal polytypes of Ge based on the density functional theory (DFT). The Vienna ab initio simulation package was used realizing the projector-augmented wave method [12]. In order to improve the accuracy of calculations, the exchange-correlation energy was computed using the SCAN functional [13]. The cutoff energy for the plane waves was set to 420 eV throughout the study. The Monkhorst-Pack grid with the 0.25 1/Å distance between *k*-points was implemented. In this case, the calculations of Ge lattice constants are in the good agreement with the experimental values, for example, 5.650 Å and 5.658 Å for 3C Ge. DFT calculations yield the following results for the energies of different polytypes (the zero level corresponds to cubic Ge-3C): E_{21R} = 3.0 meV/atom, E_{6H} = 5.0 meV/atom, E_{5H} = 6.3 meV/atom, E_{15R} = 8.6 meV/atom, E_{8H} = 8.7 meV/atom, E_{4H} = 8.7 meV/atom, and E_{2H} = 13 meV/atom. Therefore, the two lowest energy polytypes are Ge-21R and Ge-6H. DFT calculations of the Raman spectra for different polytypes showed that Ge-21R and Ge-6H could correspond to the experimental spectrum.

In particular, theoretical Raman spectrum of Ge-21R contains the three highest peaks at 295 cm^{-1}, 250 cm^{-1}, and 200 cm^{-1}. The first and the third peaks agree exactly with the data, while the middle line may not be seen due to a large peak of GaAs. The highest peaks of Ge-6H are calculated at 280 cm^{-1}, 255 cm^{-1}, and 165 cm^{-1}. The correspondence to the data is not as good as for Ge-21R polytype, but still plausible considering the fact that we are dealing with a thin Ge stripe rather than with the bulk crystal. In any case, the contribution of the surface or interface energies and possible size-dependent effects are not taken into account in our DFT calculations and the exact identification of the hexagonal Ge polytype requires further study. Our analysis reveals, however, a principal difference between the peaks at 300 cm^{-1} and 200 cm^{-1}, illustrated in Fig. 1, *a*. The classical peak at ~ 300 cm^{-1} originates from the oscillations of 2.45 Å long Ge-Ge bonds perpendicular to the bonds. The new peak at 200 cm^{-1} originates from the oscillations of Ge atomic rows along the bonds as a whole (Fig. 1, *b*). The energy of such oscillations strongly depends on the polytype and is very close to 200 cm^{-1} for Ge-21R.

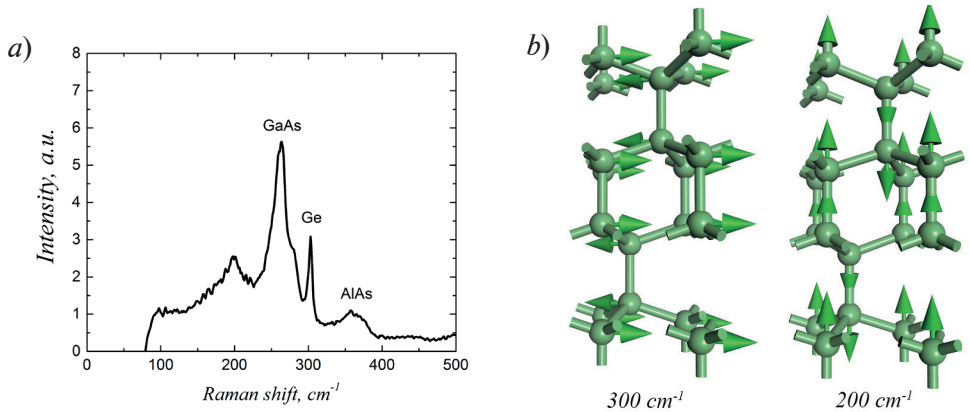

Fig. 1. Raman spectrum from an ensemble of AlGaAs-Ge NWs showing two Ge peaks at 300 cm^{-1} and 200 cm^{-1} (*a*); the latter peak originates from hexagonal Ge. Illustration of the oscillations of Ge atoms corresponding to the Raman peaks at 300 cm^{-1} and 200 cm^{-1} (*b*)

We additionally carried out measurements of the dielectric constants of hexagonal Ge formed on the AlGaAs NWs. The ellipsometric spectra $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ was measured with an automatic rotating-analyzer ellipsometer M-2000D (J.A. Woollam) in the 0.7–6.4 eV range.

Dielectric constants were determined with spline approximation in the framework of a single-layer model [14]. in the range of 1.6–6.4 eV, i.e. where hexagonal germanium is no longer transparent. The real and imaginary parts of dielectric constants for cubic germanium taken from the literature [15] and hexagonal germanium determinated from the experimental data are shown in Fig. 2. The results obtained show a clear difference in dielectric constants for cubic and hexagonal germanium formed on the surface of AlGaAs NWs.

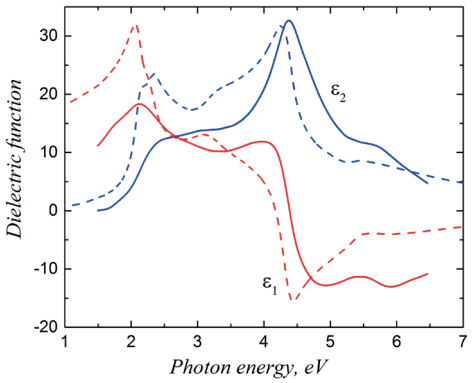

Fig. 2. Dependence of the dielectric constant (real part ε_1 and imaginary part ε_2) of cubic (dotted line) and hexagonal (solid line) germanium on the photon energy

Conclusion

In summary, growth of germanium on wurtzite AlGaAs NWs by MBE was demonstrated. Raman spectroscopy study revealed the formation both cubic and hexagonal Ge phases. DFT calculations of the volumetric energies suggested the formation Ge-16R or Ge-6H hexagonal polytype. Dielectric constant of hexagonal Ge as a function of the photon energy was first measured.

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