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Formation of Ge quantum dots on GaN nanowires by molecular beam epitaxy

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Abstract. Germanium nanocrystals were grown on GaN nanowire sidewalls by molecular beam epitaxy. The transmission electron microscopy measurements revealed the formation of 6–10 nm in size Ge quantum dots, which exhibited diamond cubic crystal structure. Raman spectroscopy indicate that uncapped Ge QDs are stress relaxed compared to ones additionally capped with GaN.

Keywords: nanowire, molecular beam epitaxy, germanium, semiconductors

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Формирование германиевых квантовых точек на поверхности нитевидных нанокристаллов GaN методом молекулярно-пучковой эпитаксии

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Аннотация. В настоящей работе исследованы процессы формирования германия на поверхности GaN нитевидных нанокристаллов при молекулярно-пучковой эпитаксии. Продемонстрирована возможность формирования Ge островков размером 6–10 нм на боковых гранях GaN нитевидных нанокристаллов и создания гетероструктур на их основе. С помощью спектроскопии комбинационного рассеивания показано, что формирование GaN покровного слоя приводит к формированию упругих напряжений в Ge квантовых точках.

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

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Introduction

Germanium based nanomaterials gained large interest because of their interesting optical and electronic properties [1]. Although bulk Ge is an indirect bandgap material, the applying of tensile strain could convert Ge into a direct bandgap semiconductor [2]. It is well known that planar Ge thin films suffer from structural defects. In turn, nanoparticles and quantum dots (QDs) are considerably less sensitive to defects and could hold large strain without plastic relaxation. Such evidences make them very promising for a new class of efficient and tunable optoelectronic devices [3–5]. One of the promising way to obtain tensile-strained Ge QDs is based on the monolithic epitaxial growth on lattices-mismatched substrates. The growth of strained Ge QDs and fabrication of nanocomposite demonstrating efficient photoluminescence have been obtained on Si, GaSb, InAlAs surfaces [6–8].

To obtain more functions and superior properties, recent efforts have focused on using nanowires (NWs) as substrates to produce attractive core/shell structures that combine QDs with NWs. Heterostructured NWs can be realized based on pioneering material combinations, otherwise highly defective in their planar form. Looking at the literature on the QDs growth on NW side-facets, a common works have focused mainly on varying NW dimensions for fixed lattice mismatched systems, such as GaAs/InAs [9], Si/Ge [10–12] or GaAs/Ge [13]. At the same time, exploring other templates could reveal many new and important possibilities for further engineering of III-V/IV NWs.

In this work we looked into the feasibility of using GaN NWs as a substrates for Ge QDs growth. The initial results on Ge QDs formation by molecular beam epitaxy and structural analyses are discussed.

Materials and Methods

Growth experiments were performed using the solid state 21EB200 Riber MBE system additionally equipped with N-plasma source and e-beam evaporator for Ge deposition. The growth of samples was carried out on Si(111) substrates. Prior to growth, wet chemical processing followed with degassing and annealing step at 950 °C were performed to achieve atomically-clean Si(111) 7×7 surface. Afterwards, the temperature was decreased to 840 °C and self-assembled plasma-assisted growth of GaN NWs was carried out. The radio frequency N plasma-source was operated at 400W using a N2 flow of 1 sccm, Ga flow rate was set to 1.7 Å/s. The total NW growth time was equal to 16 hours. The reflection high-energy electron diffraction (RHEED) method was used to control in situ the processes occurring on the substrate surface. According to the RHEED patterns GaN NWs had pure hexagonal crystal structure. After the formation of GaN NWs, the substrate temperature was decreased to 320 °C and the deposition of Ge was performed. The growth rate of Ge was corresponded to 0.2 Å/s. During the Ge deposition RHEED revealed the formation of mixed hexagonal/cubic phases.

The morphological properties of the samples have been studied using scanning electron microscopy (SEM) Zeiss SUPRA 25. The crystal structure of GaN/Ge NWs was investigated in a JEM-2100F TEM (Jeol) equipped with an EDX spectroscope QUANTAX XFlash 6/60 system, Bruker as well as Raman micro-spectroscopy (Horiba LabRam HR-800 with 532 nm excitation laser and ×100 lens with 0.9 numerical aperture). For TEM and Raman analysis, the NWs were transferred onto Cu grids coated with carbon film by gently rubbing the grid against the substrate to break the NWs at the base.

Results and Discussion

Typical array of GaN NWs grown by plasma-assisted MBE growth is presented in Fig. 1. Vertical NWs with 2.2 μm in length were straight, smooth and exhibited sixfold symmetric facets (see Fig. 1, *a*). The diameters of NWs were about 160 nm, while side-facets width corresponded to 80 nm.

Primary, to investigate the Ge growth, 160 nm layer was deposited on the GaN NWs after their formation. As it can be seen in Fig. 1, *b*, it resulted in the formation of rought polycrystalic shells on NWs and bulbs on NW tips. In turn, nanosized Ge QDs decorated the NW sidewalls were found on the samples with lower germanium coverage (about 60 nm). The density of Ge QDs decreased from NW tips to base, which was apparently related to the high density of GaN NWs.

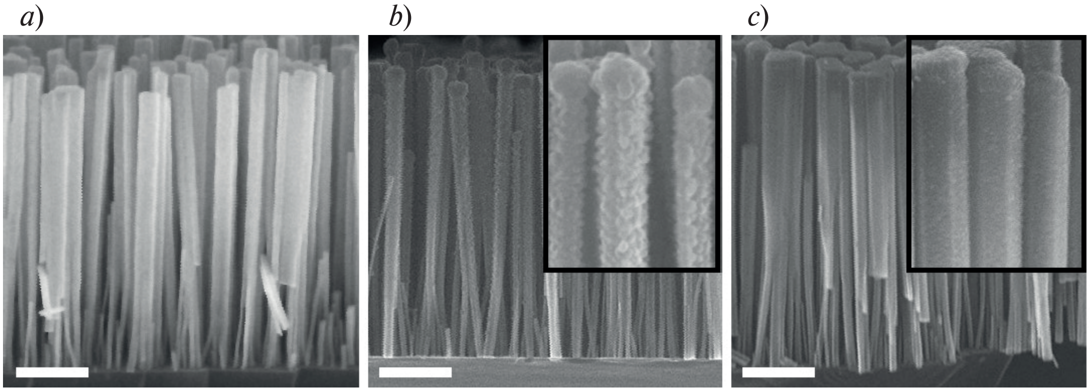

Fig. 1. SEM images of GaN NWs grown on the Si(111) substrates (*a*), GaN/Ge NWs with 1 nm (*b*) and 40 nm (*c*) deposited Ge. The images in the insets illustrate close-up views of NWs. Scale bars correspond to 400 nm

Characterization of GaN-Ge NWs by scanning TEM (STEM) was conducted in high angular annular bright field mode. A low magnification STEM image in the [$1\bar{1}00$] zone axis confirmed the formation of Ge QDs on GaN NW side sidewalls with no overlap between neighbouring dots, as shown in Fig. 2, *a*. Ge QDs exhibited hemispherical shapes with diameter at the base of about 6–10 nm. The high-resolution TEM image shown in the insertion of Fig. 2, *a* indicates that individual Ge dot has a diamond cubic structure unlike the formation of Ge on AlGaAs or GaAs NWs [14]. This finding was verified also by selected area diffraction patterns taken from GaN NW and Ge QD.

Fig. 3 demonstrates Raman spectra of the sample investigated by HRTEM. Raman spectrum contains two peaks with the maximum at 522 cm^{-1} and 302 cm^{-1}. The peak at 522 cm^{-1} is attributed to the well-known A1 (TO) phonon mode of wurtzite GaN [15]. The 302 cm^{-1} peak is assigned to the Ge–Ge mode and it is closely related to relaxed Ge nanocrystals. Thus, it suggest that the Ge QDs are pure. In addition, the line shape of the Ge QDs was observed to be asymmetric. Similar asymmetric line shape has been reported for InAs QDs and other arsenide material systems [16]. A similar asymmetric phonon line shape of Ge QDs is characteristic of Raman spectra of nanocrystalline structures, which can be described by a model of phonon confinement in nanoclusters of inhomogeneous size [17]. Additionally, it was suggested that the stress Ge QDs can be obtained by embedding into the matrix. For this purpose, capping of the samples with Ge QDs by GaN was carried out. Preliminary studying of the samples obtained revealed the downshifting of Ge QDs peak to 297 cm^{-1}.

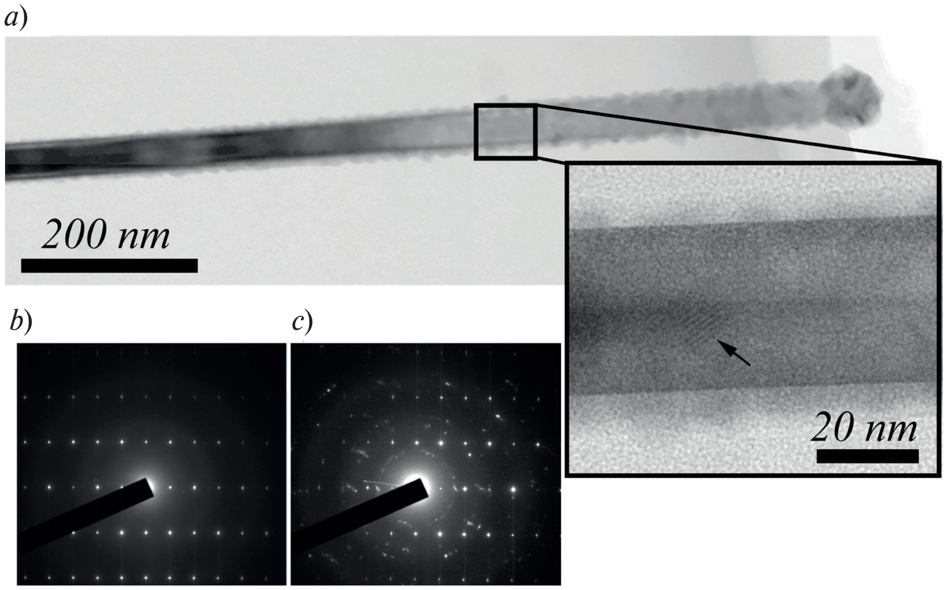

Fig. 2. Low magnification scanning TEM images of GaN/Ge NW and HR TEM image GaN/Ge NW acquired in the $[11\bar{2}0]$ zone axis in the insertion. Diffraction pattern of pure hexagonal GaN NWs (*b*) and of Ge QD from the area pointed by arrow (*c*)

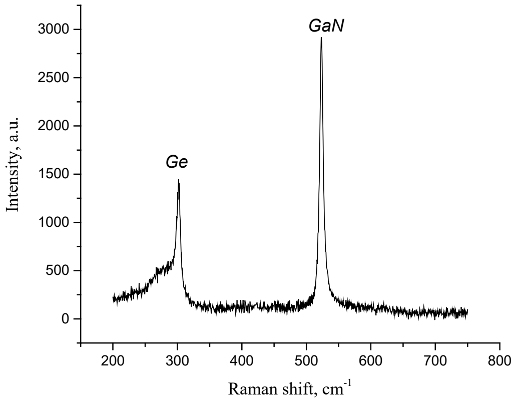

Fig. 3. Survey Raman spectra of GaN/Ge NW heterostructure

Conclusion

In summary, this study demonstrated the growth of 3D epitaxial Ge QDs around GaN nanowires. Cross-sectional TEM verified the surface faceting of the GaN core nanowires as well as the Ge quantum dots. Raman spectroscopy revealed the asymmetric line shape of Ge QDs, which could be caused by the inhomogeneous sizes of the QDs as well as the phonon confinement. The Raman results also indicate strain relaxation in uncapped Ge QDs, as well as strain shifting in Ge QDs additionally capped with GaN.

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