Polarized Raman spectroscopy of GaP nanowires under 5% elastic strain

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Abstract. Optical properties of highly-strained gallium phosphide nanowires were investigated via polarized Raman spectroscopy. 5% elastic strain was created in individual nanowire lying on nickel substrate by the means of atomic force microscopy. Micro-Raman mapping along the nanowire cross section in parallel and perpendicular polarization was carried out. Strain-induced effects on transverse optical mode position and shape were analyzed. The pronounced splitting of the mode due to high level of strain was observed. It was found that in parallel polarization the mode shape is sensitive to the position of the pumping spot which can be attributed to enhanced light-nanowire coupling effects.

INTRODUCTION

Semiconductor nanowires (NWs) are prospective building blocks for next generation nanoscale electronic devices [1]. Due to high surface-to-volume ratio and surface strain relaxation, NWs can withstand large elastic strains (up to 15%) [2]. Such strains can significantly modify semiconductor properties due to the changes in symmetry and energy structure. Therefore, strain engineering, i.e. utilizing mechanical stress for NW-based device performance improvement, is of interest. Successful tuning or enhancement of NW optical and transport properties was recently shown in numerous papers. Thus, red shift of photoluminescence of ZnO [3] and GaAs [4] NWs under applied tension was reported. Also, the enhancement of carrier mobility in Si NWs up to 5 times was achieved under 2% strain [5]. Recently we utilized elastic strain for the enhancement of InGaAs NW conductivity [6] and GaAs NW solar cell efficiency [7]. Here we investigate stress-induced changes in Raman spectra of the bent GaP NWs. GaP NWs are prospective for nanophotonics as they demonstrate effective wave-guiding properties, exhibit one of the broadest transparency range, high values of the nonlinear refractive index and good thermal conductivity. Raman spectroscopy is conventionally used for strain analysis in semiconductors. Recently, some strain-induced effects in the Raman spectra of GaP NWs with 3.5% strain were revealed and explained [8, 9]. Higher strain level allows better understanding of strain-induced phenomena. In a logical continuation of the preceding works, here we provide data on the Raman spectra of the NWs with 5% strain.

RESULTS AND DISCUSSION

GaP NWs were grown in self-catalytic vapour-liquid-solid regime on (111) Si using solid-source molecular beam epitaxy, the main details about the growth process may be found elsewhere [10]. NW average length exceeded 25 µm (see SEM image on figure 1a). For subsequent study NWs were dispersed on nickel substrate by mechanical rubbing (see figure 1b). Figure 1c shows polarized Raman study of a straight NW. Optical measurements were carried out using Horiba LabRam HR 800 confocal Raman microscope equipped with 532 nm laser and aberration-corrected

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FIGURE 1. SEM image of studied GaP nanowire array (a) on the growth substrate, (b) on nickel substrate. ×100 objective with 0.9 N.A. and optical resolution 280 nm. First, we conducted Raman study of a straight NW in two polarization geometries: $\bar{z}(xx)z$ (parallel) and $\bar{z}(yy)z$ (perpendicular) according to Porto’s notation [11]). Pronounced transverse optical (TO), surface optical (SO) and longitudinal optical (LO) modes appear at 366, 395 and 402 cm$^{-1}$ respectively. Raman selection rules are not fully masked by antenna effect as NW diameter (around 120 nm) is large enough. Full width on half maximum (FWHM) of TO mode doesn’t exceed 4 cm$^{-1}$.

Then, individual NWs were bent using atomic force microscope probe as a nanomanipulator. Due to the great NW length, the elastic energy was balanced with van der Waals forces between NW and the substrate. AFM topography of the bent NW is shown in figure 2a. The strain level can be estimated from the topography using the following expression: $\varepsilon = r/R$, where $\varepsilon$ is elastic strain, $r$ is the NW radius and $R$ is the NW curvature radius. In our case, $r=60$ nm and $R=1200$ nm giving $\varepsilon=5\%$. According to the latest study, Young modulus of zinc blende GaP NW is approximately 150 GPa [12] so the obtained strain level corresponds to 7.5 GPa stress which is much higher than the fracture toughness of bulk GaP single crystals (0.6 - 0.8 GPa) [13]. One-dimensional micro-Raman profilling along the cross section of the bent NW with the step size 90 nm in both polarizations was carried out (see figure 2b). The results for parallel and perpendicular polarizations are shown in figure 2c and d respectively. Y coordinate of the maps corresponds to the pumping spot coordinate. It can be seen, that in case of parallel polarization, the spectrum shape changes with this coordinate. On the contrary, in case of perpendicular polarization, the shape is constant. This is illustrated with figure 2e and f which show certain spectra from the maps. Spectra 1 correspond to the pumping spot coordinate near the tensed NW side. In case of spectra 2, the pumping spot is located at the center of NW cross section, and the impact from tensed and compressed regions is equal. Spectra 3 correspond to the case when the pumping spot is located near the compressed side.

The results are different as compared to the similar study that was recently carried out for bent GaP NW on glass.
FIGURE 2. (a) AFM topography of the bent nanowire, (b) Scheme of Raman profiling, (c) Raman profile of the bent nanowire in parallel polarization, (d) Raman profile of the bent nanowire in perpendicular polarization, (e) The Raman spectra from figure 2c, (f) The Raman spectra from figure 2d.

[9] which showed only nonlinear broadening and linear shift of TO mode. According to deformation potential theory, tension and compression induce red and blue shift of the TO mode respectively [14]. Thus, bending deformation should lead to the uniform broadening. However, when the substrate material is changed to nickel, the broadening is masked due to substrate-induced effects. The uniform broadening only appears when the pumping coordinate is at the center of the NW cross section in parallel polarization (spectrum 2 in figure 2e). In other cases, the mode splitting is observed: TO mode splits into two components with maximums at 350 and 378 cm$^{-1}$. The spectra obtained in
perpendicular polarization were found not to be sensitive to the coordinate of pumping spot though showing a mode splitting. LO mode also undergoes strain-induced broadening and splitting in both polarizations, but its accurate analysis is hindered by the proximity to the SO mode. The obtained effects highlight the enhanced Raman signal from NW sides which may be connected with light-nanowire coupling effects leading to a specific field distribution inside the NW.

**CONCLUSION**

To conclude, we provided polarization-dependent Raman study of individual GaP nanowire under 5% elastic strain corresponding to 7.5 GPa stress. The studied NWs were lying on a nickel substrate. Strain-induced non-uniform broadening and splitting of TO and LO modes were observed. In perpendicular polarization, the spectrum shape is independent from pumping coordinate, the TO mode is split into two components with the maximums at 350 and 378 cm$^{-1}$. In parallel polarization, the TO mode is either split or not depending on the pumping coordinate. The results are different from previous studies and cannot be fully explained with deformation potential theory. The impact from local highly-strained NW regions is found to be more pronounced, which we attribute to substrate-induced effects. The comprehensive theoretical study of this phenomena needs to be done.

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