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Photodegradation of surface passivated GaAs nanowires

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Abstract. Efficiency of *in situ* AlGaAs and GaP and *ex situ* nitride surface passivation of p^+ GaAs nanowires was studied. The efficiency was estimated by comparing of the photoluminescence intensity of the passivated nanowires with the unpassivated nanowire. The AlGaAs and nitride passivation lead to the increasing of the PL intensity by three orders of magnitude while the GaP passivation increases PL intensity only by one order. Photodegradation of the passivated NWs under intensive laser illumination was observed. AlGaAs, GaP and nitride passivated NWs photodegrade after one-minute exposure under laser power densities of 500, 300 and 30 kW/cm^2, respectively.

1. Introduction

III-V semiconductor nanowires (NWs) are promising building blocks for third generation solar cells [1]. Specially designed nanowire array exhibit better light absorption with less amount of semiconducting material in solar cell with respect to conventional III-V planar solar cell [2]. Moreover, high quality III-V nanowires can be grown on cost effective silicon or even glass substrates [3]. Despite the abovementioned advantageous an efficiency of GaAs NW based solar cells do not exceed 20%. The main reason of this is a high density of surface electronic states reducing lifetimes of the non-equilibrium charge carriers [4]. To improve the efficiency of the NW solar cell, different techniques of a surface passivation where the surface states density decreases are conventionally used [5]. These techniques can be based on *in situ* growth of protecting semiconducting layers (AlGaAs, GaP etc) [6] or *ex situ* chemical sulphide or nitride passivations [7]. Recently, it was observed that under intensive optical pumping a photooxidation process leads to quenching of the photoluminescence from GaAs [8,9] and AlGaAs [10] nanowires. Moreover, in dependence of the ratio between excitation wavelengths and a NW diameter a nonuniform photoetching of the NW can occur leading to formation of the hollow tubes from GaAs NWs [11]. These processes should also affect on passivation layers; however, they are not studied. The aim of this work was to study an efficiency of the different *in situ* and *ex situ* passivation methods on the photoluminescence of the p^+ GaAs NWs and also find a value of the pumping density leading to degradation of the passivation layers.

2. Samples and methods

2.1. Samples

GaAs nanowires were grown by metalorganic vapour phase epitaxy (MOVPE), more growth details can be found here [6]. Length of the NW was of 1 µm and a diameters of ~ 100 nm. Level of the p^+ Zn doping was of ~10^{19} cm^{-3}. After the NW growth, a 10 nm-thick AlGaAs passivation layer or GaP monolayer were radially grown *in situ*. Additionally, an *ex situ* chemical nitride passivation was done in hydrazine sulfide solution. Thus, four type of samples were produced: reference, GaP passivated, AlGaAs passivated and chemically nitrided.

2.2. Methods
The samples were studied by photoluminescence (PL) spectroscopy. The experiments were carried out at room temperature (300 K) using Horiba Jobin Yvon T64000 and LabRAM HR spectrometers equipped with a Linkam THMS600 temperature-controlled microscope stage. The measurements were performed with continuous-wave (cw) excitation using the 532 nm laser line of a Nd: YAG laser. We used a Mitutoyo 100× NIR (NA=0.90) long working-distance objective lens to focus the incident beam into a spot of ~1 µm diameter, which was sufficient to measure the PL signal from a separate nanowire transferred to a Si/SiO_2 substrate.
The experimental procedure of studying photodegradation process was as follows. First, photoluminescence spectrum was measured for the as-received nanowires with power density of 10 kW/cm^2. Then, the nanowires were exposed to successive one-minute laser irradiations with a power density set from a range from 10 to 2000 kW/cm^2. After each laser-light exposure, the PL spectra were measured at a low pumping density of 10 kW/cm^2.

3. Results and discussion
Figure 1 shows PL spectra measured for reference (unpassivated) and passivated NWs at a low pumping density of 10 kW/cm^2. PL spectrum in figure 1(a) exhibit a relatively wide peak with maximum intensity at 1.4 eV. Shift of the peak to the lower energies (with respect E_g=1.42 eV for GaAs at room temperature) and its shape are caused by high p^+ doping and agree with PL spectra measured by other groups for Zn doped p^+ GaAs [12].

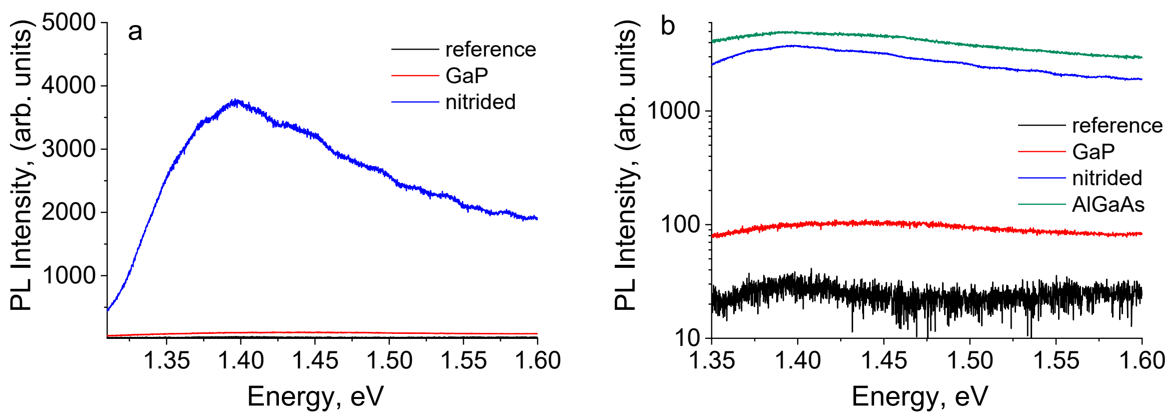

Figure 1. Photoluminescence spectra measured for unpassivated GaAs NW (black curve), GaP passivated (red curve), nitride (blue curve) and AlGaAs passivated (green curve) plotted in (a) linear scale and (b) logarithmic scale.

To estimate efficiency of passivation techniques on PL intensity PL spectra are presented in logarithmic scale in figure 1 (b). Since the passivation decreases surface states density which act as non-radiative recombination centers a PL intensity should increase. The lower the surface states density the higher will be the PL intensity. From figure 1 (b) it follows that the AlGaAs passivation is the most effective and increases the PL intensity by almost three orders of magnitude. The nitride chemical passivation is slightly less effective, while the GaP passivation increases the PL intensity only by one order of magnitude.

Study of the NW photodegradation reveals that AlGaAs passivation is the most stable and the photoluminescence quenches after minute exposure of the NW under laser irradiation with a power density of 500 kW/cm^2. GaP passivation degrades after one-minute exposure with a power density of 300 kW/cm^2. The least stable passivation was the nitride passivation which degrades after 30 kW/cm^2. For the explanation, it is worthy to note that both GaP and nitride passivation layers were only monolayer thick. The nitride passivation is less stable due to high crystal lattice mismatch between GaAs and GaN. Strained GaN layer under laser excitation and corresponding heating degrades faster than less strained GaP and AlGaAs layers. The importance of the heating effect is also confirmed by the experiment where NWs were transferred on the transmission electron microscopy lacey carbon grid. NWs had only few contact points with the grid and degrades under one order lower power density with respect to NWs transferred on the Si/SiO_2 substrate [9].

4. Conclusions

Thus, by measuring of the photoluminescence intensity an efficiency of *in situ* AlGaAs and GaP and *ex situ* nitride surface passivations of p$^+$ GaAs nanowires was studied. The AlGaAs and nitride passivation lead to the increasing of the PL intensity by three orders of magnitude while the GaP passivation increases PL intensity only by one order with respect to the PL intensity from unpassivated nanowire. Increasing of the PL intensity was due to the decreasing of the surface electronic states in passivated NWs.

The effective AlGaAs and nitride passivations show different level of stability under intensive laser illumination. AlGaAs layer with thickness of 10 nm degrades after one-minute exposure under laser power densities of 500 kW/cm^2, while nitride monolayer degrades after only 30 kW/cm^2. Such low stability of the nitride layer is due mechanical strains formed by high crystal lattice mismatch between GaAs and GaN. Obtained results are important for the design of the nanowire based solar cells.

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