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Temperature evolution of GaP nanowires photoelectronic properties

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Abstract. This work is devoted to study photoelectric properties of GaP nanowires (NWs) modified by carbon nanodots (CDs). Photoelectric properties of samples were studied by electrochemical impedance spectroscopy (EIS) over a wide frequency range. Impedance spectra were shown in Nyquist plot in dark conditions and under ultraviolet (UV) illumination allowed to evaluate changes of active resistance of the NWs before and after modification with the CDs, in terms of resistance response. Temperature evolution of GaP NWs impedance spectra in the range from 25 to 205 °C before and after the modification was studied also in dark and UV conditions. The largest response reached 25% and was detected at room temperature in modified NWs. Heating of the samples lead to decreasing of response down to 25% with modified NWs, whereas for GaP the response did not exceed 13%. The result is interesting for processing of photosensitive detectors working in room temperature.

Keywords: nanowires, GaP, carbon nanodots, electrochemical impedance spectroscopy

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Температурная эволюция фотоэлектронных свойств нитевидных нанокристаллов фосфида галлия

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Аннотация. Данная работа направлена на изучение фоторезистивных свойств нитевидных нанокристаллов фосфида галлия, а также путей их модификации углеродными наноточками (УТ). Свойства изучались в терминах спектроскопии электрохимического импеданса в широком диапазоне частот (100 Hz–500 kHz). Наибольшее изменение сопротивления при засветке ультрафиолетовым светом по сравнению с темновыми условиями показывают модифицированные УТ нитевидные нанокристаллы GaP при 25 °C. Таким образом, эта работа может быть интересна при создании фотодетектора, работающего при комнатной температуре.

Ключевые слова: нитевидные нанокристаллы, углеродные точки, спектроскопия электрохимического импеданса, фотодетектор

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Introduction

Gallium phosphide (GaP) is a semiconductor material that is widely used in photonics, nanooptics and nanoelectronics. GaP and other III-V nanowires (NWs) can be obtained by molecular beam epitaxy (MBE) [1], chemical-vapor deposition (CVD) [2] and via another techniques [3]. GaP NWs exhibit peculiar optical properties. The latter allowed to develop optical cavities [4], waveguides [5] and light emitting devices [6]. GaP is not widely used as a material for photodetectors due to its wide bandgap (2.27eV) making it transparent in the visible range. Here we propose surface modification of GaP NWs allowing to tailor their optical properties. Heterostructured compositions based on GaP nanowires and organic photoabsorbing agents can be effectively used for the development of new generation photodetector devices. This work is aimed at studying the evolution of photoresistive properties of GaP NWs decorated with carbon dots (CDs) at different temperature conditions.

Materials and Methods

GaP NWs were grown on (111) Si substrate by molecular beam epitaxy (MBE) using a Veeco GEN III epitaxy machine. Morphology of NWs was investigated by scanning electron microscopy using Zeiss Supra25 (Carl Zeiss, Germany) at 5 kV accelerating voltage. NWs were separated from the substrate by ultrasonication (50 kHz, 30 seconds) in 120 μl of deionized water. CDs synthesized via hydrothermal method [7] were used to decorate the NWs. The CDs solution was shared between the two tubes. To decorate the NWs, 2 μl of CDs solution was added into one of tubes and shacked in a spin mixer. A few drops of each solution were applied onto the substrate with interdigitated gold contacts (DropSens Co. Ltd., Spain). Contact strip width/gap was 10 μm. Substrates were dried for 24 hours at room temperature. Overall three samples were fabricated: the first covered with pristine NWs, the second one with NWs decorated with the CDs and the third one covered with CDs.

Optical images of the samples were taken using Zeiss LSM 710, Carl Zeiss MicroImaging GmbH confocal microscope (Jena, Germany). 405 nm laser light illumination was used, collected light was filtered by 387–415 nm or 439–634 nm filters.

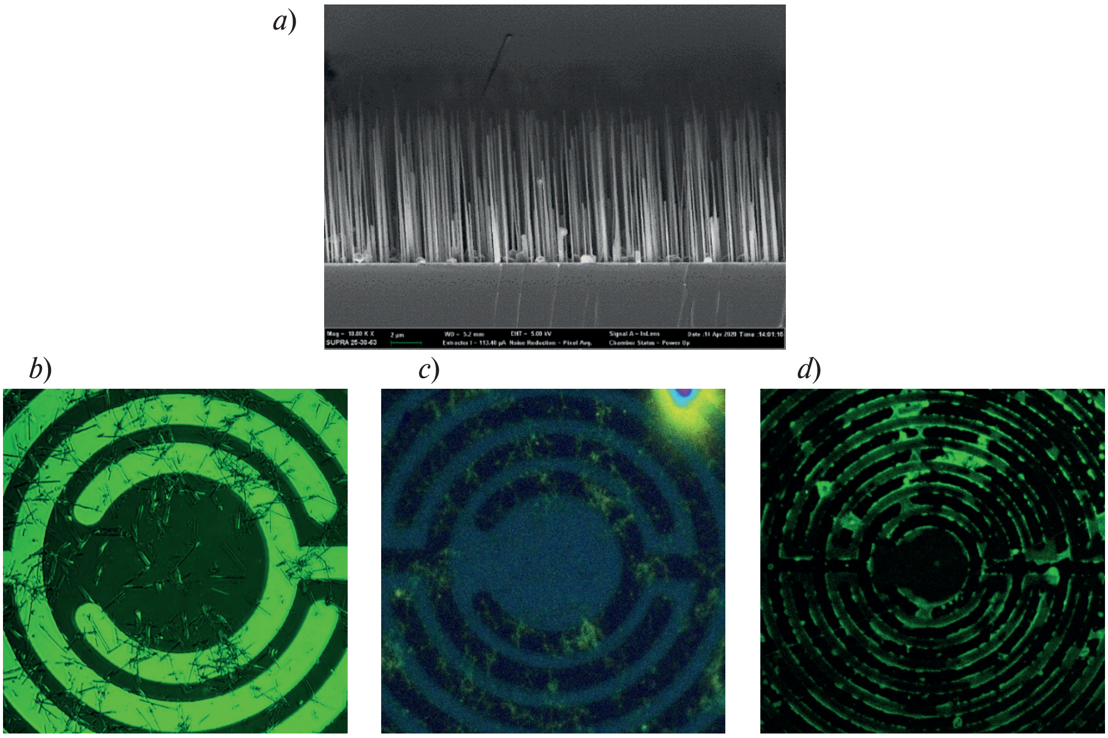

Fig. 1. SEM image of GaP NWs (*a*), bright field confocal microscopy image of GaP NWs on substrate with interdigitated contacts at 10 μm pitch (*b*), confocal microscopy image of GaP NWs covered with CDs with colors close to real (*c*), confocal microscopy image of CDs with colors close to real (*d*)

Study of the photoelectric properties of the obtained samples were carried out with the use of a Z500P impedance meter (Elins, Russia) in dark conditions and under ultraviolet (UV) diode illumination with optical power of 1200 mW. For all the samples the experiments were carried out at 25, 105, 155 and 205 °C to study the temperature effects. The impedance spectroscopy was employed at 100 mV bias in the 100 Hz–500 kHz frequency range, allowing for analysis of various electronic processes that may occur upon the UV exposure. Further analysis was made by plotting results in Nyquist coordinates [3].

Results and Discussion

The shape of the synthesized NWs is shown in Fig. 1, *a*. They are approximately 20 μm long and about 250 nm thick. Fig. 1, *b* shows the confocal image of GaP NWs on the substrate with interdigital gold contacts. A 405 nm laser, a 387–415 nm filter and a Fluar 20x/0.75 lens were used. Evidently, the light reflected from the gold contacts and places where the light is reflected in GaP NWs. These places are seen well because of high refractive index of GaP (about 4). When the filter is changed to 439–634 nm the image of this sample turns dark. Fig. 1, *c* shows the sample with modified GaP NWs under the 405 nm laser illumination. Here a 439–634 nm filter and an EC Epiplan-Apochromat 50x/0.95 lens are used. The optical image is taken in lambda-mode, i.e., each point of the sample was consecutively illuminated and excited photoluminescence was recorded. Pumping light is removed by filter from the reflected beam and bright spot in the image appears due to CD luminescence. Colors in Fig. 1, *b* are close to the real ones. It is clearly seen that GaP NWs covered with CDs are distributed all over the contact surface and some of them are able to provide electric connection between the pads. The image in Fig 1, *d* is also taken under 405 nm laser illumination and signal collected through 439–634 nm filter in lambda mode. It demonstrates that CDs are filling the space between the contacts but almost no CDs could be seen on the pads.

To study photoelectric properties of the samples, electro-chemical impedance spectra were measured and plotted in Nyquist coordinates (see Fig. 2, *a*–*c*). Impedance spectra of pristine GaP NWs sample taken at 25, 105, 155 and 205 °C in the dark and under UV illumination are shown in Fig. 2, *a*. Fig. 2, *b* shows spectra of sample with decorated NWs

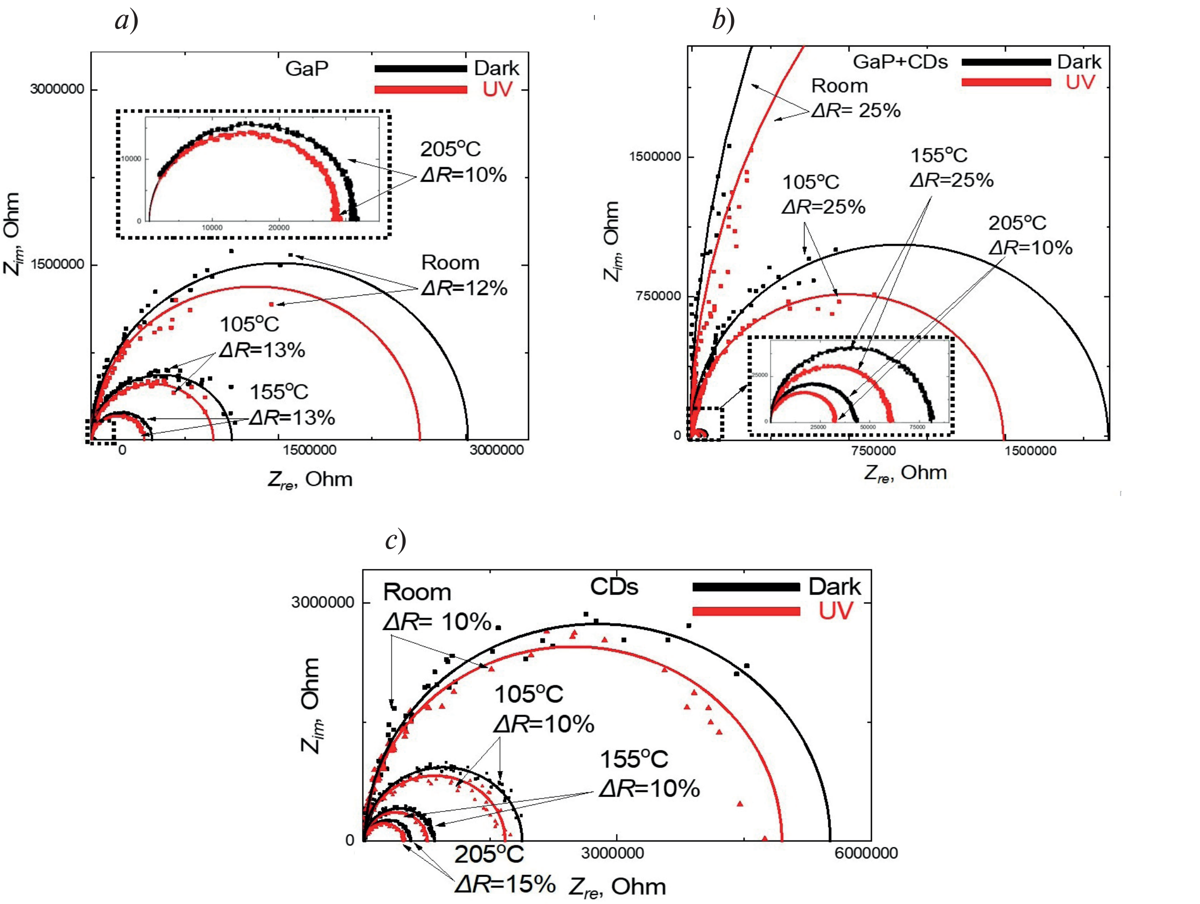

Fig. 2. Impedance spectroscopy of pristine GaP NWs (*a*), modified GaP NWs (*b*) and CDs on substrate with interdigital contacts (*c*)

taken in the same conditions is shown, Fig. 2, *c* shows spectra corresponding to CD-covered substrate. Impedance is a complex number or vector rotating in the complex polar ohmic plane: $Z = Z_{Re} - iZ_{Im}$. In Nyquist coordinates, the real part of impedance (Z_{Re}) is plotted on the x-axis, while the frequency-dependent imaginary part (Z_{Im}) is plotted on the *y*-axis. Each point on the impedance spectrum corresponds to a specific frequency of the measurement voltage, and the angle of inclination of the line connecting the origin of the coordinates with each point describes the phase of the measurement voltage. The projection of the spectrum on the x-axis indicates the active resistance of the sensor (R) under UV and dark conditions. The response of the samples in terms of ΔR was estimated using a simple expression $(R_{dark} - R_{UV})/R_{dark} \cdot 100\%$. For every sample, it is shown that its resistance decreases when the temperature increases. Furthermore, in every experiment the resistance in the dark was higher than under the UV light.

The difference in resistance for every sample at various temperatures is presented in Table. As shown in Table 1, for sample with pristine GaP NWs, the largest difference in the resistance between dark and light conditions is between 105–155 °C (13%), the lowest effect of illumination is at 205 °C (10%). Overall, the change of that difference is only about 3%. Thus, temperature has small influence on the electronic processes that takes place. On the other hand, substrate with CDs exhibits the highest response difference: 15% at high temperature (205 °C), whereas for the temperature range from 25 to 155 °C, the difference is about 10%. Resistance of the sample with modified GaP NWs drops with temperature rising, the highest response is obtained at 25 °C, the lowest at 205 °C. From all the experiments, the largest difference is for modified NWs at room temperature. Thus, it was found out that modification by CDs increased the photoabsorption. The highest impact was obtained at room temperature.

Table

UV-reaction of samples at different temperatures

Sample	Temperature, °C	Response, %
GaP	room	12
	105	13
	155	13
	205	10
CDs	room	10
	105	10
	155	10
	205	15
GaP+CDs	room	25
	105	25
	155	25
	205	10

Conclusion

Thus, in this work properties of GaP NWs and GaP NWs covered with CDs were studied. Modification by Carbon nanodots leads to a 4-fold increase in response compared to dark conditions, but with increasing temperature the difference decreases. The difference is vanished when the temperature rich 205 °C. So modified GaP NWs can be used for creating photodetectors working in room temperature.

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