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Самоорганізовані метал-напівпровідникові мікро- та наноструктури Au-GaAs для застосування у плазмонній фотовольтаїці

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Self-organized Au-GaAs metal-semiconductor micro- and nanostructures for applications in plasmonic photovoltaics

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Метал-напівпровідникові композитні мікроструктури Au-GaAs були отримані шляхом анізотропного травлення з подальшим фотостимульованим хімічним осадженням благородного металу (Au) на сформовані напівпровідникові квазіґратки. Золото наносилося на структуровану поверхню GaAs у вигляді хаотично розміщених наночастинок металу та/або нанодротів на вершинах пагорбів напівпровідникової мікроструктури. Сформовані структури вивчаються за допомогою скануючої електронної мікроскопії, оптичної спектроскопії та фотоелектричних вимірювань. Створені метал-напівпровідникові мікроструктури Au-GaAs є перспективними для застосування в плазмонній фотовольтаїці, що підтверджується поведінкою спектрів фотолюмінесценції та змінами форми спектрів фотоструму.

Ключові слова: сонячний елемент, арсенід галію, наночастинка, поверхневий плазмон.

Au-GaAs metal-semiconductor composite microstructures have been prepared by an anisotropic etching of n-GaAs (100) wafers doped with Te (10^{16} to 10^{17} cm^{-3}) with subsequent photostimulated chemical deposition of noble metal (Au) on formed semiconductor quasigratings. The microrelief topology of GaAs surface is controlled by the anisotropic etching conditions. Au metal was deposited on the structured GaAs surface as randomly placed nanoparticles of various shape and size and/or nanowires on the top of the hills of formed semiconductor microstructure. As the number of Au nanoparticles increases, they tend to localize on the ledges of the GaAs microrelief forming a system of approximately parallel nanowires. Obtained periodic structures with submicron to microns periods without Au nanoparticles and with deposited nanoparticles have been studied by means of scanning electron microscopy, optical spectroscopy (photoluminescence spectroscopy at room temperature), and photoelectric measurements. The decrease of the relative intensity of main photoluminescence band for samples with Au nanostructures compared to ones without nanoparticles deposition and simultaniously changes of the shape of photocurrent spectra of Au-GaAs microstructures have been observed. Such correlation in behaviour of measured spectra make formed Au-GaA metal-semiconductor microstructures perspective for the application in plasmonic photovoltaics.

Key Words: solar cell, gallium arsenide, nanoparticle, surface plasmon.

Статтю представив д.ф.-м.н. Макарець М.В.

Introduction

In recent decades, silicon solar cells (SCs) are widely used in photovoltaics. Variety of techniques have been developed that allow the most efficient use of silicon to convert solar energy into electricity [1, 2]. At the same time, there are active studies of other semiconductor compounds that may be promising for solar energy, namely InP, CdS, GaAs, CIS-$CuInSe_2$; CIGS- $Cu(In,Ga)Se_2$; CIGSS-$Cu(In,Ga)(Se,S)_2$ [3]. Among these materials, it should be specially mentioned such direct bandgap semiconductor with zinc blende crystal structure as gallium arsenide (GaAs). GaAs is characterised with parameters (bandgap energy, absorption coefficient, resistance to ionizing radiation, reverse saturation current density) that give it a number of advantages not only in comparison with silicon, but also with other above-mentioned compounds [4]. Due to the high cost of material, the GaAs-based SCs are usually made in the form of thin films. At present, the scientists study structures based on A3B5 semiconductors deposited on a silicon substrate that could be perspective for highly efficient solar cells. Moreover, such structures could reduce the cost of multi-junction solar cells.

In the manufacture of effective SCs it is also important to use processing technologies that can improve the characteristics of material. The texturing of the front surface of the SC is a standard treatment aimed on reduction of reflection losses. It also provides the conditions under which the path of light in the element is not perpendicular to the plane of the p-n junction that makes it possible to bring the region of photogeneration of charge carriers closer to the p-n junction, thereby increasing the efficiency of carrier collection, especially in the case of low-energy photons. Moreover, it can provide additional benefits. Combination of surface relief with metal elements (for instant, nanoparticles (NPs)) can stimulate transfer of light energy into excitation of surface plasmons (SP) in NP or surface plasmon-polariton (SPP) in their periodical arrays (nanowires (NWs) on the top of the grooves) for efficient light trapping and increase of absorption in extremely thin layers (Fig. 1) [5, 6].

Another possibility is formation of nanosize semiconductor hills on the surface. Due to quantum size effect their energy spectrum is shifted to high energy side, that could result in photocurrent gain in blue spectral region due to reduce of surface recombination losses. It worth noting that not only front surface of the cell can be made relief. Relief

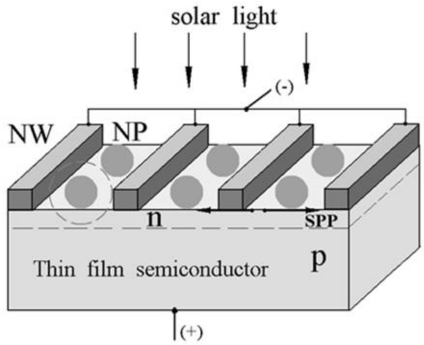


Fig.1. Interaction of light with metal-semiconductor microstructure

rear surface of semiconductor and metal back contact can also scatter transmitted light and support SPP on that interface. Texturing of semiconductor surface can be performed by different methods, for example, anisotropic chemical etching or ultrafast laser treatment [7]. Obtained relief is formed as a result of self-organization and/or interference of the incident laser radiation with surface electromagnetic waves. Its morphology depends on treatment conditions.

Experimental details

The metal-semiconductor composite microstructures have been fabricated on the n-GaAs (100) wafers doped with Te (10^{16} to 10^{17} cm^{-3}). Surface microrelief of the quasigrating type topology has been prepared by the method of wet chemical anisotropic etching in $2HF:2H_2SO_4:1H_2O_2$ during 3 or 5 minutes. Varying the etching conditions (etchant temperature and etching duration) allowed to change the relief depth and mean period of microstructures. The photoinduced chemical deposition of Au from aqueous salt $AuCl_3$ solution has been realized to prepare the nanoparticles of various shape and size located predominantly at the top of microrelief. If amount of deposited Au is large enough its nanoparticles can form the NWs on the top of the grooves of the quasigratings. Au NPs deposited on a flat GaAs surface do not display preferred directions and usually are randomly distributed on the surface.

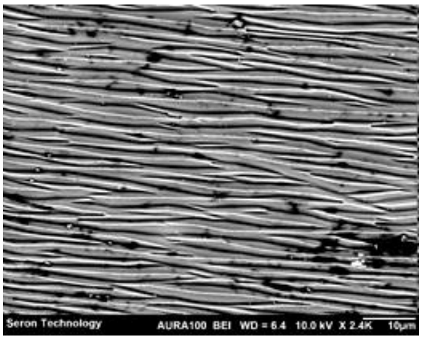
The morphology of treated GaAs surfaces has been analysed using a scanning electron microscope (SEM) AURA 100 (SERON Technology Inc.).

The photoluminescence (PL) spectra have been recorded with the setup based on a single-grating spectrometer MDR-3 under an excitation of Ar+ continuous laser λ_{ex} = 488 nm (E_{ex} =2.54 eV).

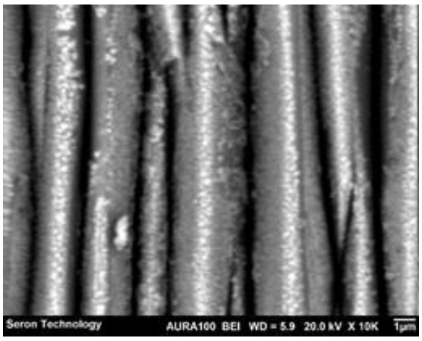
The Keithley SMU (Model 2420) device, which is a measuring source, has been used to measure the current-voltage characteristics.

Results and discussion

Morphology of microrelief formed on the surface of GaAs formed by anisotropic etching is presented in Fig. 2. The formed structure is quasigratings with submicron to microns periods. The relief depth was no more than 0.7 µm. These patterns is characterised by the triangular shape of the grooves. We did not quantify the filling of the structured surface with Au NPs. At this step, we controlled only the significant changes in the GaAs surface morphology. At certain amount, Au NPs localize on the ledges of the microrelief forming a system of approximately parallel NWs (see Fig. 2,b). Mean size of Au NPs aggregates which form NWs is evaluated as about 100 nm.



a)



b)

Fig. 2. SEM images of surface GaAs quasigrating structures (a) and surface Au-GaAs quasigrating structures with Au on the top of the grooves (b)

Photoluminescence (PL) spectra of Au-GaAs quasigrating structure are presented in Fig. 3. The main PL band around 1.4 eV is caused by recombination of free excitons or also localized excitons characteristic for direct bandgap GaAs semiconductor. Observed PL band is rather wide with long high-energy wing. This band is complex. This band shape could indicate the quantum confinement of excitons in GaAs nanostructures or the influence of transitions connected with impurities and defects in oxide layer that is formed during the etching procedure. Moreover, the behaviour of PL spectra of metal-semiconductor composite even at room temperature could be indicative for evaluation of the effectiveness of such microstructure with deposited NPs. The observed decrease of PL intensity for samples with Au nanostructures can be attributed to screening of GaAs with gold or to more efficient separation of carriers. The latter is consistent with increase of photocurrent for this kind of cells.

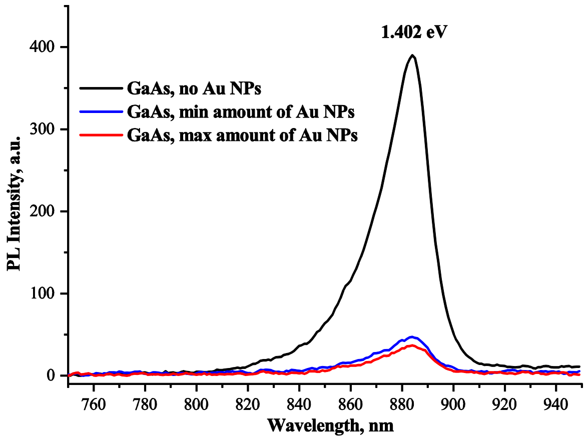


Fig. 3. PL spectra of Au-GaAs structures without and with different amounts of deposited Au NPs, $\lambda_{exc.}$ = 488.0 nm, T= 300 K

Photocurrent spectra of Au-GaAs cells with quasigrating surface topology (Fig. 4) demonstrate substantial increase in blue-green spectral range comparing to Schottki barrier GaAs cells with flat surface. Fine structure of these spectra depends on the amount of deposited gold weather it is present in the form of individual particles or nanowires on the top of the grooves.

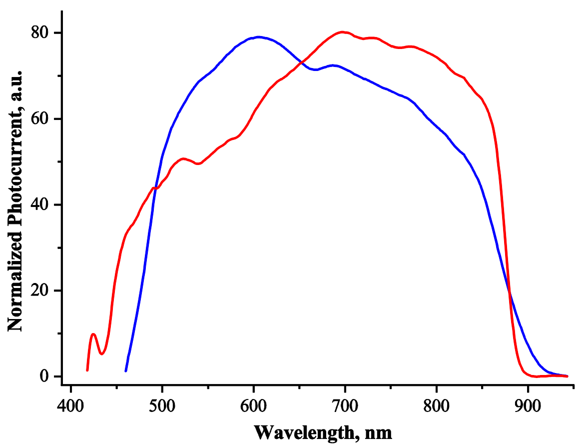


Fig. 4. Spectral dependence of short-circuit photocurrent of Au-GaAs quasigrating structures with different amounts of deposited Au NPs

Conclusions

Our results demonstrate that the deposition of noble metal (Au) nanoparticles on the textured surface of GaAs direct bandgap semiconductor results in the photocurrent enhancement. The microrelief topology of GaAs surface could be controlled by the conditions of chemical anisotropic etching. It was found that the formation of Au nanowires is more beneficial for the purposes of plasmonic photovoltaics. Nano sized metal features on the structured surface of semiconductor provide an increase of the light transformation into the surface plasmons and surface plasmon-polaritons, and consequent increase of photocurrent.

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