Photoelectric Properties of Nanostuctured Layers

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***Abstract* — The paper is focused to study the photosensitivity modulation in crystalline and nanostructured materials. The photoresistor with modulated photosensitivity on the basis of III-V compounds was elaborated. In the results of investigation the photoresistor characteristics and the physical model to modulate photosensitivity are presented. Nanostructured films were formed by selective photo-assisted electro-chemical etching of the n-GaP and n-InP substrate and were separated from it by wet chemical etching. Researches of photoelectric characteristics of nanostructured films are presented, modeled and discussed. Photoelectric properties of nanostructured layers make it possible to use such structures for the manufacture of optical detectors and switches.**

***Index Terms* — nanostructured layer, photoconductivity, photoresistor, porous film.**

I. INTRODUCTION

Recently semiconductor nanostructures have stimulated much of interests, because they exhibit different physical properties relative to those of bulk crystals. The high surface area, band gap shift, and special characteristics promised the use of semiconductor nanostructures over a wide range, from optoelectronics to chemical and biochemical sensors applications.

One of the most common techniques to fabricate porous structure is the photo-assisted electrochemical etching, which can form various semiconductor nanostructures in a self-assembled fashion, where a high-density array of nanometer- or micrometer-sized pores is formed over a large area on the semiconductor surface.

The semiconductor nanostructures on Si, Ge and various compound semiconductors, such as GaAs, InP, GaP and GaN were obtained by electrochemical etching. Their structural and optical properties, in particular, low reflectance in ultra-violet, visible, and near-infrared ranges by improving the surface morphology of the porous structure allow to suggest that surface-controlled porous structures are promising materials for application to photoelectric-conversion devices such as solar cells and photo detectors [1, 2].

In the present we studied semiconductor nanostructures properties and photodetectors are proposed.

II. MODEL OF CLASSIC PHOTORESISTOR

The photoconductive detector (photoresistor) is a radiation-sensitive resistor. A photon with energy larger than the semiconductor bandgap energy is absorbed within the bulk material by interaction with electrons, creating an electron-hole pair, resulting in the change of the electrical conductivity of the semiconductor. Electrodes are attached to the sample in order to measure the change in conductivity. The applied voltage across the sample is preferred to be constant for high resistance photodetectors, and the signal is detected as a change in current in the bias circuit.

However, for low resistance material, a constant current circuit is usually used, and the signal is detected as a change in voltage across the sample.

The current responsivity of the photodetectors is determined by the quantum efficiency η, which describes how well the detector is coupled to the radiation to be detected, and by the photoelectric gain g, which describes how well the generated electron-hole pairs are used to generate the current response of a photodetector. The quantum efficiency η is usually defined as the number of generated electron-hole pairs per incident photon, and the photoelectric gain g is the number of carriers passing electrical contacts per generated pair. Both values are assumed as constant over the whole device. The spectral current responsivity is equal to

$$R = \frac{\lambda\eta}{hc} qg , \quad (1)$$

where: λ is the wavelength, h is Planck's constant, c is the light velocity, q is the electron charge, and g is the photoelectric current gain.

The classic photoresistor is manufactured by form of a p-type or n-type semiconductor layer with 1-10 μm thickness on a semiconductor substrate. The ohmic contacts formed as a grid have the distance between the strips of the grid less than the diffusion length of minor charge carriers, which is 2-4 μm for holes and 5-10μm for electrons (depending on the doping level of active layer, which variable between $10^{15} – 10^{18}$ cm^{-3}).

A supply voltage is applied to contacts. Without optic flux, a current, named dark current, appears in the active layer under the influence of applied voltage. Dark current decreases the photoresistor detectivity, determined by the noise currents:

$$\overline{i_n^2} = 2q\left(I_{ph} + I_d\right)\Delta f \quad (2)$$

where: I_{ph} – photocurrent, I_d – dark current, Δf – the transparency band of the frequencies.

At illumination of the photoresistor with an optic flux, excess charge carriers generated inside the active layer are separated by the electric field created by the external

source of voltage. Separated charge carriers form a photocurrent proportional to the intensity of the incident optic flux.

Disadvantages of the classic photoresistor are:

- the photocurrent is formed by the minor charge carriers, which reduce the photocurrent value;
- the contact grids occupy more than 50% of the active area. To exclude the optic flux loses, it is necessary to use heterostructures which allow to light up the active layer from the back side of the structure;
- the active layer thickness can't be less than $1/\alpha$, α - the absorption coefficient of the optic radiation. This determines the big values of the dark current, which limits the photoresistor's detectivity.

III. PHOTORESISTOR WITH MODULATED SENSIBILITY

The new photoresistor (Fig. 1,a) is manufactured on basis of the III-V semiconductor compounds, in particular GaP, and consists from a semi-isolator substrate and a p-type or n-type active layer [3]. SnO_2 layer of n^+-type is deposited by the pyrolysis method between the ohmic contacts, which are connected to the supply voltage U_1.

The energetic diagram of heterostructure SnO_2-semiconductor is presented in Fig. 1,b.

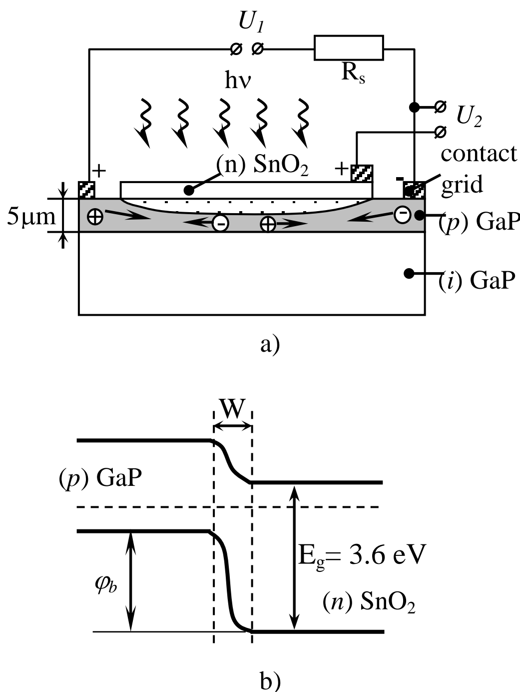


Fig. 1. Structure (a) and energetic diagram (b) of photoresistor without any polarization voltage.

The heterostructure is reverse polarized by the source of voltage U_2. The width of the space charge region W of the heterojunction depends on the height of the potential barrier φ_b, on the reverse polarization voltage value U_2 and on the acceptor (or donor) dopant concentration N_a (N_d) of the active layer, by the relation:

$$W = \left[2\varepsilon_0\varepsilon_s\left(\varphi_b - U_2\right)/qN_d\right]^{\frac{1}{2}} \qquad (3)$$

At the certain value of the polarization voltage U_2 the space charge region extends into the whole thickness of the active layer and blocks channel for the dark current generated by the supply voltage U_1 (Fig. 2,a).

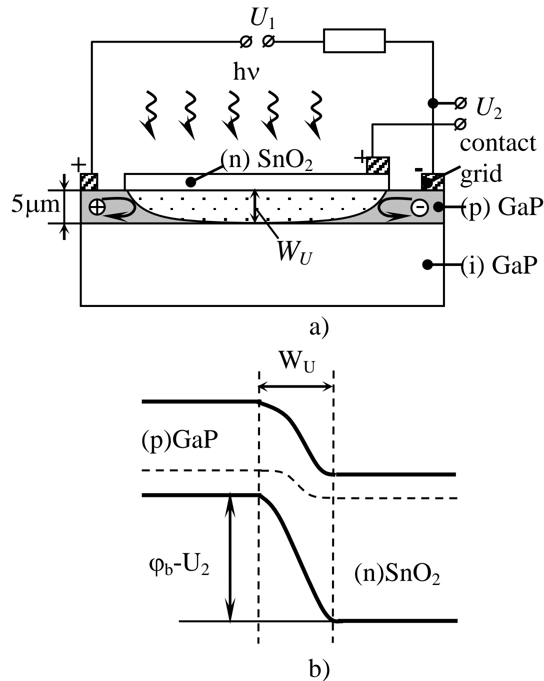


Fig. 2. Structure (a) and energetic diagram (b) of photoresistor at reverse polarization voltage ($U_2 \geq U_{thr}$).

Excessive charge carries generated by the optic flux absorbed inside the active layer GaP are separated by the internal electric field of the GaP-SnO_2 heterojunction. So, only excessive major charge carriers form the photocurrent in the channel. The total photoresistor current consists from the major charge carriers injected by the external voltage source U_1 and the major charge carriers injected by the optic flux (Fig. 3,a). This way, the losses at the charge carriers' recombination inside the active layer's volume are reduced to zero. The distance between the contact grid's strips can be much bigger than the diffusion length of minor charge carriers because the minor charge carriers generated by the optic flux do not determine the photocurrent value. The distance between the contact grid's strips influences on the time of response only, which is equal with the drift time of the excessive major charge carriers inside the electric field formed by the source U_1.

Another major advantage of photoresistor is the possibility to vary channel thickness for current, including it's blocking, by the reverse polarization voltage U_2., (Fig.3,b) The space charge region W extends through the whole active layer thickness at the threshold reverse polarization voltage U_{thr}. Total photoresistor current is equal to zero for $U_2 \geq U_{thr}$, but for $U_2 < U_{thr}$ the total current consists from the dark current I_d, which value depends on channel thickness for current (is function of U_2), and from

the photocurrent I_{ph}, which value is proportional with the intensity of the incident flux.

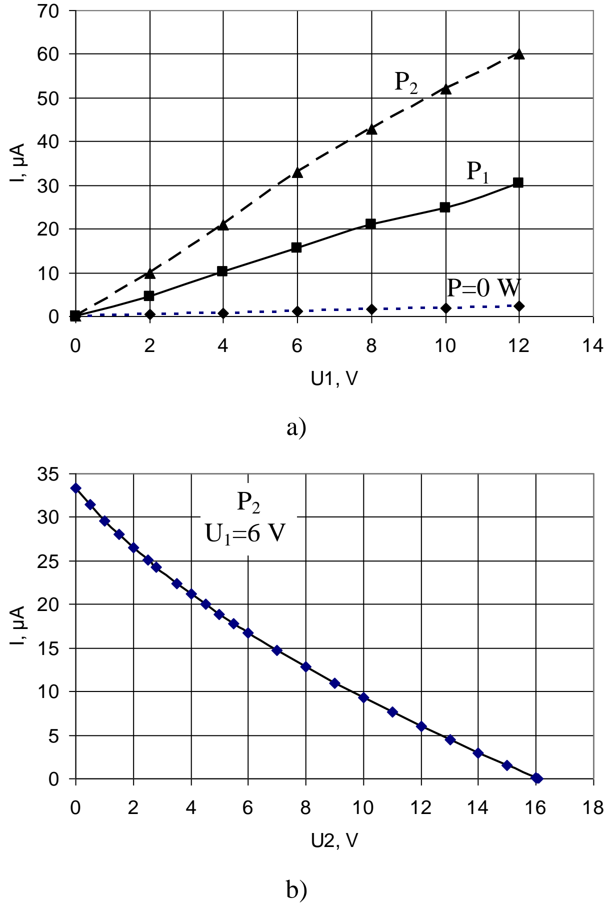


Fig.3. The Current Voltage Characteristics for different illumination at U_2=0 V (a), modulation sensitivity (photocurrent) by the applied voltage U_2 at constant illumination and operating voltage U_1= 6 V (b).

The presented photoresistor as distinct from the classic photoresistor has the following advantages:

1. The photocurrent's value doesn't depend on the recombination processes inside the active layer volume;
2. The dark current can be reduced to minimum by making a thin channel for current;
3. The resistor photosensibility can be modulated by polarization voltage of the GaP-SnO_2 junction.

   This allows to detect selectively the optic signals with different modulating frequencies from a wide packet of signals transmitted by the optic fibers or by other mediums.

The photoreceiver can be successfully used in many fields of functional optoelectronics for receiving, decoding and processing the signals transferred by optic fibers and atmosphere.

IV. MODEL OF SPACE CHARGE MODULATION

Based on the idea of a conductance modulation, we proposed a model to explain the behavior of nanostructured photoconductive detectors.

The air-semiconductor barrier is the same for a metal-semiconductor one with a high density of surface bound states for electrons. These surface states, lying inside the bandgap and close to E_F, produce E_F pinning effect. The surface charge density is related to the surface band-bending, φ_b, and the space charge region width is given by the surface charge density and the doping level by

$$W_{dark} \approx \left(\frac{2\varepsilon_0\varepsilon_s}{qN_d}\varphi_b\right)^{1/2} \quad (4)$$

When the sample is illuminated by radiation, the photogenerated carriers are swept by the space charge region. A photovoltage U_{ph} is developed across the sample.

The width of the space charge region W_{ph} decreased by equation

$$W_{ph} = \left[\frac{2\varepsilon_0\varepsilon_s}{qN_d}(\varphi_b - U_{ph})\right]^{1/2}, \quad (5)$$

where:

$$U_{ph} = \frac{kT}{q}\ln\left(\frac{I_{ph}}{I_0}+1\right), \quad (6)$$

here I_{ph} is function of the incident light flux power P_{opt}.

In this way the conductive volume inside the photoconductor, rather than the carrier density in 'dark' volume, is actually increased because of the reduction of the space charge region width. Many studies [4, 5] have shown that this spatial modulation effect surpasses any carrier density increase effect.

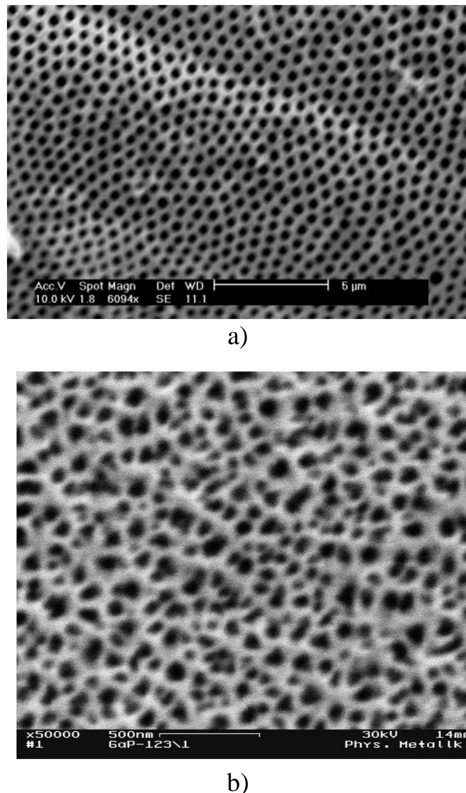
This effect is especially pronounced in the porous structures, where the area of the air-semiconductor surface is large and significantly changes the structure and properties of the material. This is confirmed by our research photoconductivity of porous films.

Persistent photoconductivity is a light induced change in the free carrier concentration which persists after the illumination is removed. This effect has been found in many compound semiconductors and can be due to a variety of reasons. It is commonly accepted that the persistent photoconductivity is related the existence of defect states or traps, which are bistable between a shallow and a deep energy state. One such defect is the DX center, which forms when shallow donors undergo a large lattice relaxation and convert into deep donors [5]. Under illumination, these deep donors are able to be converted back into metastable shallow donor states. The barrier, developed due to the difference in lattice relaxation between the two states, prevents recapture of the electrons into the stable deep donor state, thus giving rise to persistent photoconductivity. There are also many other physical models proposed to explain the origin for persistent photoconductivity for different semiconductors.

V. PHOTOELECTRIC PROPERTIES OF NANOSTRUCTURED FILMS

We studied electro- and photoconductivity processes in porous InP and GaP films. As semiconductor materials for the nanostructures fabrication, n-type InP and GaP wafers were used. Epitaxial layers with a thickness of 10 μm were grown on n^+InP (001) substrates by standard metal-organic vapor-phase epitaxy with silicon doping of 1×10^{17} cm^{-3}; n-GaP layers with majority charge carrier concentration $3 \cdot 10^{17}$ cm^{-3} were grown on n-GaP substrates.

The porous structures were formed in the n-type epitaxial layers by using a standard cell with three electrodes, namely, an InP electrode as a working electrode, a platinum counter electrode, and a saturated calomel electrode as a reference. Anodic bias was applied to the semiconductor electrode to obtain high-density porous structures. The surface of porous structures on the basis of InP and GaP are shown in Fig. 3(a, b), respectively. Porous InP and GaP films were formed by selective chemical etching and separated from monocrystal substrate.



a)

b)

Fig. 3. Top view SEM images of the InP (a) and GaP (b) porous structures.

For photoconductivity measurements, samples were cut into 15 mm × 5 mm pieces. The porous GaP films have a thickness **d** = 10 μm. The pore average diameter was from 80 to 400 nm for different samples and distance between them was of about 100 nm. The nanostructured sample was attached to the sapphire substrate during the formation of ohmic contacts on the basis of Ag paste with annealing. To avoid white light on photoconductivity, samples were kept in the dark at ~ 300 K for more than 24 h before each measurement.

Model of nanostructured film and measurement setup is presented in Fig.4.

Dark current-voltage characteristic has shown lack of current in the porous film to voltage > 300 V. It is possible because space charge regions of air-semiconductor potential barrier, localized around pores with width W_o, determined by equation (4), are overlapping and close current channels.

The potential barrier φ_b and width of the space charge region W_o can be modified by external factors, the most essential is optical radiation.

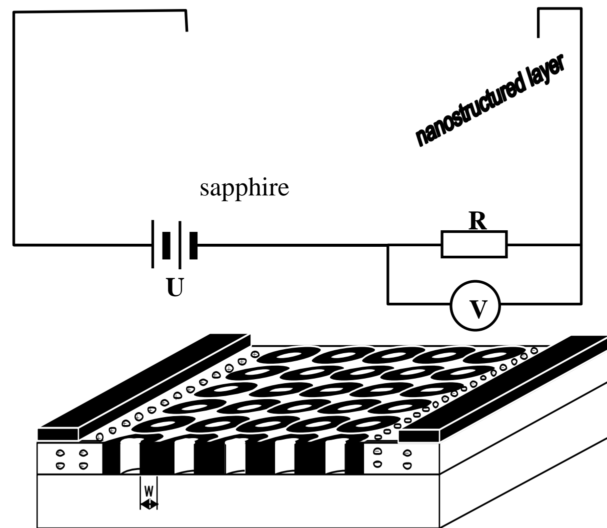


Fig.4. Experimental setup and structure model showing the air-semiconductor space charge region width around the pores.

The absorbed optical radiation generates minority charge carriers, which are separated by potential barrier φ_b. The width of the space charge region W_{ph} decreased by equation (5). So, the width of the space charge region around pores decreases with the increase of incident light flux power. The flow of current between space charge regions around the pores appears for some values of the incident light power, as shown in Fig.5. At the same time, the supply voltage is redistributed lengthways of channels according to channel resistance and potential barrier φ_b has vanished. Further, the porous GaP films behave as a classic resistor.

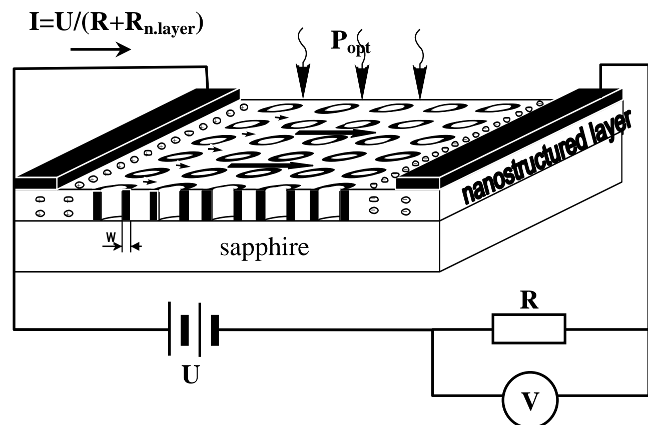


Fig.5. Schematic illustration of the space charge region width around the pores at the illumination.

Fig.6 shows current-voltage characteristics of porous n-GaP film for various light conditions: dark current (1), incident light flux power P_o=2.5 mW/cm^2 (2), P_o=0.05 mW/cm^2 (3). The curve 3 shows that the opening process of conducting channels can be controlled by light flux intensity and supply voltage.

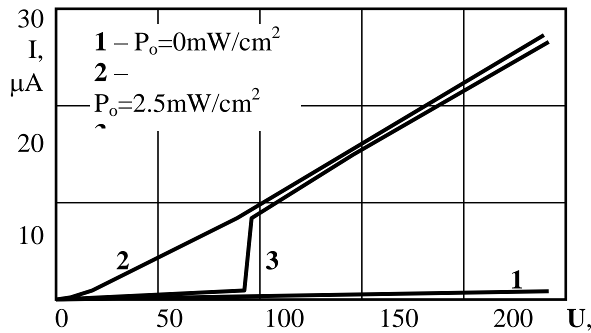


Fig.6. The current-voltage characteristics of porous n-GaP film for various light conditions: dark current (1), incident light flux power P_o=2.5 mW/cm^2 (2), P_o=0.05 mW/cm^2 (3).

We studied influence of supply voltage on the threshold of incident light flux power to open nanostructure for current. Fig.7 shows the dependence of current in porous n-GaP film of incident light flux power for various supply voltages. As can be seen from the measured characteristics with increasing applied voltage decreases the threshold optical power required to open a channel for the flow of current through the nanostructured layer.

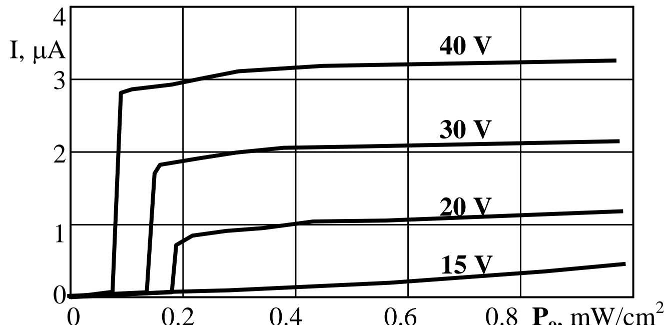


Fig.7. Current dependences of incident light flux power for various supply voltages.

In nanostructured samples, the photocurrent exhibits optical quenching, when the optical irradiance is varied. This is due to the effect of persistent photoconductivity and the time necessary for photogenerated charge annihilation. So, samples were kept in the dark at room temperature ~ 300 K for more than 24 h before each measurement to to eliminate the influence of previous illumination.

The spectral characteristics of the photoresponse study show that the photoelectric effect is observed strictly for wavelengths less red border. Photocurrent is formed only by non-equilibrium charge carriers photogenerated by photons with energy more than the band-gap of gallium phosphide and value of supply voltage doesn't influence on threshold current. The photoresponse spectra for various supply voltages are presented in Fig.8.

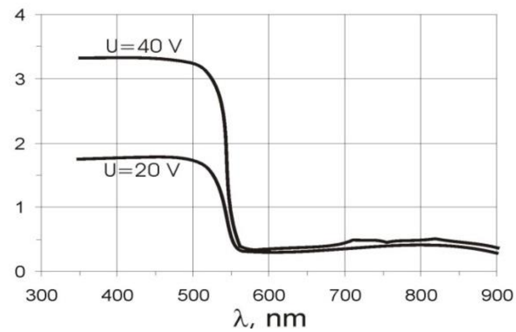


Fig.8. The photoresponse spectra for various supply voltages.

CONCLUSION

The presented photoresistor has new properties and advantages: the photocurrent's value doesn't depend on the recombination processes inside the active layer volume; the dark current can be reduced to minimum by making a thin channel for current; the resistor photosensibility can be modulated by polarization voltage. This allows to detect selectively the optic signals with different modulating frequencies from a wide packet of signals transmitted by the optic fibers or by other mediums.

The special photoconductivity properties of nanostructured layer are manifested in the fact that the operating current isn't formed by separation of photogenerated minority charge carriers. The photogenerated minority charge carriers contribute only to conducting channels formation between pores. Operating current is formed by majority carriers injected from external power supply and vanish in incident flux absence, because without the divided photogenerated charge carriers the width of the space charge region W_{dark} is described by the equation (4) increases and blocks channels of current flow through the nanostructured film. In this case, the life time and span length of minority carriers do not determinate the output current of detector. This is the main advantage of the detector on the basis of nanostructured semiconductor films.

The investigations show that semiconductor films with nanodimension structure can be used for photosensor or optical switch fabrication.

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