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# EFFECT OF SULPHUR ATOMS ON SURFACE CURRENT IN GAAS P-N JUNCTIONS

Sulphur atoms passivation of GaAs surface and its influence on *I-V* characteristics of forward and reverse currents, photocurrent spectrum, and sensitivity of GaAs p-n structures as gas sensors were studied. The passivation reduces the excess forward current and reverse current in p-n junctions, enhances the photosensitivity in the spectral region of strong absorption, substantially increases the sensitivity to ammonia vapors. All these effects are explained, taking into account lowering of the surface states density as a result of sulphur atoms deposition.

## 1. INTRODUCTION

Gas sensors on p-n junctions [1, 2] have some advantages in comparison with these, based on oxide polycrystalline films [3] and Shottky diodes [4, 5]. P-n junctions on wide-band semiconductors have high potential barriers for current carriers, which results in low background currents. Sensors on p-n junctions [1, 2] have crystal structure, high sensitivity at room temperature, selectivity to the gas components, and can be manufactured in microelectronic technology. The ammonia sensitivity of these sensors is due to forming of a surface conducting channel in the electric field induced by the ammonia ions adsorbed on the surface of the natural oxide layer [`1, 2]. The surface current induced by adsorption of $NH_3$ molecules in p-n structures on GaAs linearly depends on the applied voltage (at low biases) and on the ammonia partial pressure (in some range depending on device parameters).

The threshold $NH_3$ partial pressure of a sensor on p-n junction depends on the surface states density in the semiconductor [6]. The results of calculations [6] predict rise of the sensitivity to low concentrations of a donor gas when the surface states density in the p-n junction is diminished. The surface states density in GaAs can be lowered by sulphur atoms deposition from some solutions [7].

The purpose of this work is a study of the influence of sulphur atoms on surface currents in GaAs p-n junctions, as well as on their parameters as ammonia vapors sensors. Effect of sulphur-atoms passivation on I-V characteristics of forward and reverse currents, photocurrent spectrum, and gas sensitivity of GaAs p-n structures was studied.

## 2. EXPERIMENT

*I-V* measurements were carried out on GaAs p-n junctions with the structure described in previous works [1, 2]. The effect of saturated ammonia vapors over water solutions of several $NH_3$ concentrations was studied on stationary *I-V* characteristics, as well as on kinetics of surface current in p-n junctions.

The sulphur atoms deposition (passivation) was carried out by a treatment of different durations in 30% water solutions of $Na_2S \cdot H_2O$.

*I-V* characteristic of the forward current in a typical p-n structure is presented as curve 1 in Fig. 1. Over the current range between 1μA and 1ma the *I—V* curve can be described with the expression

$$I(V) = I_0 \exp(qV/nkT), \qquad (1)$$

where $I_0$ is a constant; $q$ is the electron charge; $V$ denotes bias voltage; $k$ is the Boltzmann constant; $T$ is temperature; $n \approx 2$ is the ideality constant. Such *I-V* curves can be ascribed to recombination on deep levels in p-n junction and (or) at the surface [8]. And the corresponding current is known as a recombination current.

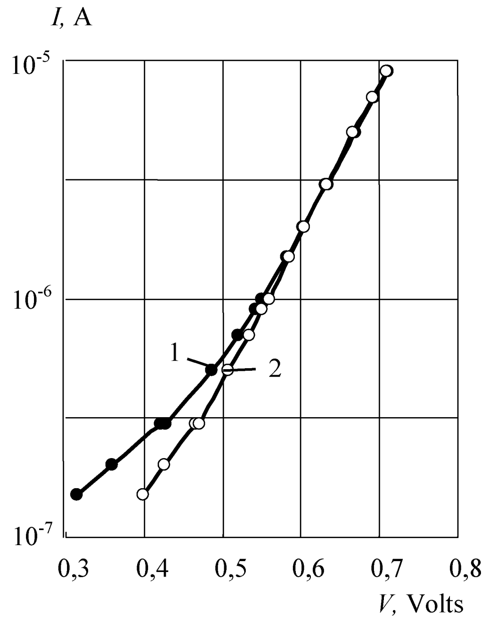


Fig. 1. Forward branches of *I-V* characteristics of a p-n structure: 1 — initial; 2 — after passivation during 20s

At lower biases curve 1 has a section of an excess current, which has an ideality constant $n > 2$ and corresponds to the phonon-assisted tunnel recombination at deep centers [8]. This recombination is located at the p-n junction non-homogeneities, which cause local increase of the electric field [8].

Curve 2 in Fig. 1 was measured after p-n junction passivation during 20s. It is evident that passivation does not affect the recombination current (at $I$ > 1μA) and remarkably lowers the excess current. This means that passivation during 20s reduces the surface states density only in surface non-homogeneities, which are responsible for the excess current.

Fig. 2 depicts the reverse branches of the *I—V* characteristic of the same sample, obtained before (curve 1) and after passivation (curve 2). It is seen that sulphur atoms deposition substantially reduces the reverse current in a GaAs p-n junction. This indicates that the reverse current is due to the same surface non-homogeneities in the studied p-n junctions as the excess forward current.

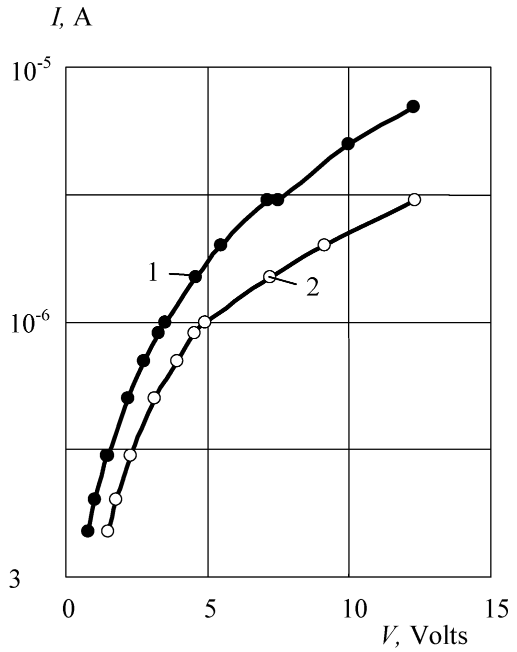


Fig. 2. Reverse branches of *I-V* characteristics of a p-n structure: 1 — initial; 2 — after passivation during 20s

Curve 1 in Fig. 3 depicts the photocurrent spectrum in one of the studied samples. The photocurrent strongly falls off at the photons energies $h\nu > E_g$, where the electron-hole pares are generated in a thin layer at the surface. It indicates that the lifetime (and the effective diffusion coefficient) of current carriers at the surface is much lower at the surface, than in the bulk. Curve 2 in Fig. 3, measured after 20s passivation, practically coincides with curve 1, which means that this treatment does practically not change the surface recombination velocity and consequently, does not lower the deep states density on much of the GaAs surface. It is in an agreement with the fact that the 20s-passivation does not lower the recombination current component.

Curve 3 in Fig. 3, measured after passivation for 60s, has a high-energy shoulder, which argues that this treatment is sufficient for a substantial reducing of the surface recombination states density.

Fig. 4 illustrates the effect of the sulphur passivation on the sensitivity of GaAs p-n junctions as gas sensors. Curves 1 and 2 are measured in air and in ammonia vapors at a $NH_3$ partial pressure of 4000 Pa, respectively. The curves practically coincide, which means that the surface current in this p-n junction is not sensitive to ammonia vapors. Curve 3 is obtained on the same sample in ammonia vapors at a $NH_3$ partial pressure of 200 Pa (20 times lower, than curve 2) after passivation for 20s. It is seen that placing the passivated p-n junction in ammonia vapors strongly increases the forward excess current. Similarly behaves the reverse current. It indicates that sulphur-atoms passivation essentially enhances the sensitivity of GaAs p-n junctions as ammonia sensors.

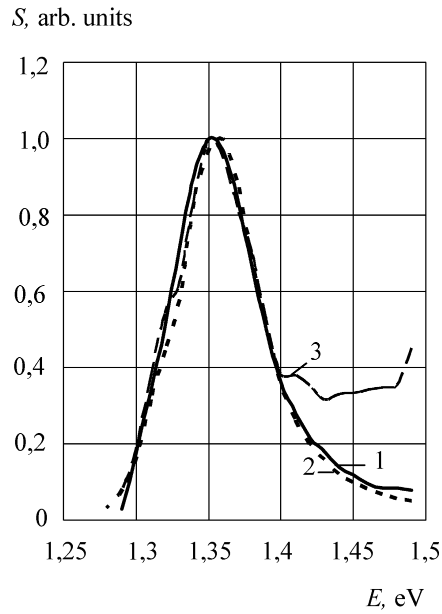


Fig. 3. Photocurrent spectra of a p-n structure: 1 — initial; 2 — after passivation during 40s ; 3 — after 60s

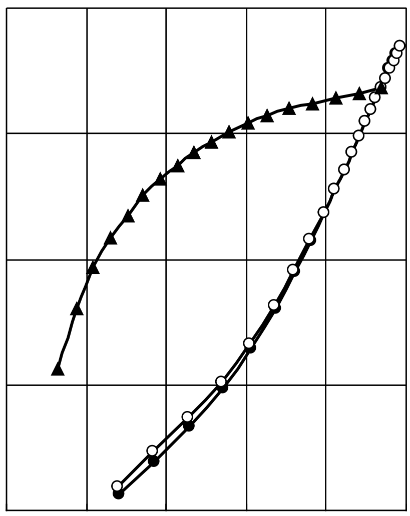

Fig. 4. Forward branches of *I-V* characteristics of a p-n structure: 1 — in air; 2 — at ammonia partial pressure 4000 Pa; 3 — after passivation, at ammonia pressure 200 Pa

## 3. DISCUSSION

One of mostly interesting questions, which appear in the light of presented experimental results, is why the low-duration (20s) sulphur passivation substantially reduces the excess current (at $I < 1\mu A$) and does not affect the recombination current (at $I > 1\mu A$). For an explanation of this phenomenon one must take into account some features of these two currents. The recombination current passes at much of the surface and is proportional to the surface recombination velocity, which linearly depends on the surface states density. Therefore low decrease in the surface states density only slightly lowers the recombination current. At the other hand, the excess current is located at the non-homogeneities, where the surface depletion layer is thinner than in the average and the electric field is stronger. Ideality coefficient of $I-V$ characteristic of the excess current $n>2$, which is due to the dependence of the surface recombination center cross section on the field.

The cross section of surface states for current carriers capture, due to phonon-assisted tunneling [8], can be expressed as

$$C_t = C_{t0} \exp\left[\frac{(q\hbar E_m)^2}{24 m_t (kT)^3}\right], \qquad (2)$$

where $C_{t0}$ is a constant; $E_m$ is the maximum electric field on the surface; $m_t$ is the effective mass of the tunneling carrier. In turn, $E_m$ linearly depends on the local surface states density. Therefore the surface centers capture cross section (and the excess current) is predicted by this model to exponentially grow with the local surface states density. This effect must be observed in electric fields of the order of $10^5$ V/cm.

Thus, the excess current in GaAs p-n junctions is much more sensitive to the change in the surface states, caused by sulphur atoms deposition, than the recombination current, which agrees with a prediction of model calculations [8].

A substantial decrease in the reverse current in p-n junctions, due to sulphur-atoms passivation as illustrated in Fig. 2, can be explained, taking into account that reverse current is located at the same non-homogeneities as the forward excess current.

The results of photocurrent measurements presented in Fig. 3 can be explained taking into account that the light was directed along the p-n junction, and the photons were directed on the lateral surface. In the case

$$\alpha d < 1, \qquad (3)$$

where $\alpha$ is the absorption coefficient; $d$ is the p-n structure width, for the photocurrent can be written

$$I_{ph} \sim (1 - r)\alpha d L_b \Phi, \qquad (4)$$

where $r$ is the reflectivity; $L_b$ is the bulk minority-carriers diffusion length; $\Phi$ is the photon flux. If the inequalities are valid

$$1/\mathrm{d} < \alpha < 1/L_b, \qquad (5)$$

the photocurrent is proportional to $L_b$ as

$$I_{ph} \sim (1 - r) L_b \Phi, \qquad (6)$$

And in the case of

$$\alpha < 1/L_b \qquad (7)$$

the photocurrent is proportional to the effective surface diffusion length $L_s$ *as*

$$I_{ph} \sim (1 - r) L_s \Phi, \qquad (8)$$

where

$$L_s = \sqrt{D_s w_s / S}, \qquad (9)$$

$D_s$ is the surface diffusion coefficient for minority carriers; $w_s$ is the effective thickness of the surface layer where the carriers are located; $S$ is surface recombination velocity.

From the photocurrent spectrum, by using (6) and (8), we obtain

$$I^m_{ph} / I^M_{ph} \approx L_s / L_b, \qquad (10)$$

where $I^M_{ph}$ and $I^m_{ph}$ are the photocurrent values in the spectral maximum and at $h\nu > E_g$, respectively.

An analysis of curves 1 an 2 in Fig. 3 by using (10) yields $L_s/L_b \approx 0.06$ before passivation and $L_s/L_b \approx 0.3$ after the treatment.

The effect of passivation on the ammonia-sensitivity of p-n structures can be interpreted by using the model [6], schematically depicted in fig 5.

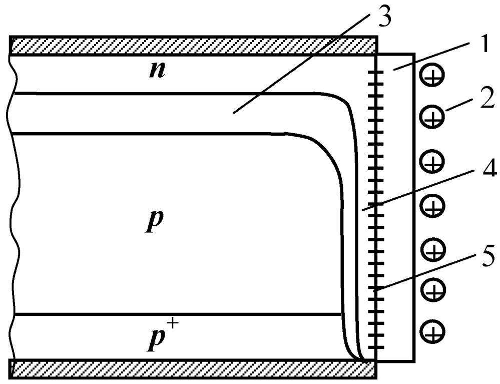


Fig. 5. Schematic of the p-n structure in $NH_3$ vapors: 1 – oxide layer; 2 – ions; 3 – depletion layer; 4 – conducting channel; 5 – surface states

Ionized molecules of $NH_3$ are placed on the external side of the natural oxide layer. The electric field of ions bends down c- and v- bands in the crystal. If a conducting surface channel is formed, as is depicted in Fig. 5, the n-layer surrounds the p-region at the perimeter and shorts the p-n junction.

The electric field at the semiconductor surface is given by

$$E = e/(\varepsilon\varepsilon_0)(Q_s + \Delta Q_s), \qquad (11)$$

where $\varepsilon_0$ and $\varepsilon$ is the permittivity of vacuum and of the semiconductor, respectively; $\Delta Q_S$ is the surface density of the adsorbed ions charge. The density of the charge on surface states was calculated as

$$Q_s = eN_s(p - n)/(p + n + 2n_c), \qquad (12)$$

where $N_S$ is the surface density of these states; *p, n* are the electrons and holes concentrations at the surface; $n_i$ is the intrinsic carriers concentration. In $NH_3$ vapors, the charge on surface states is negative, and the conducting channel is formed only in the case of the inequality

$$N_i > N_s. \qquad (13)$$

The absence of the ammonia-sensitivity of the initial samples, as seen comparing curves 1 and 3 in Fig. 4, can be explained, taking into account that the surface states density is very high, and the inequality (13) cannot be satisfied at $NH_3$ concentrations used. A high sensitivity, that arises after passivation, as seen comparing curves 1 and 3 in Fig. 4, is the result of the reduction of the surface states density due to the treatment.

## 4. CONCLUSIONS

Sulphur atoms deposition (sulphur passivation) substantially reduces forward and reverse currents in GaAs p-n junctions, increases the photocurrent in the spectral region of $h\nu > E$. The passivation also enhances the sensitivity of GaAs p-n structures as ammonia sensors.

These effects are due to lowering the surface states density as a result of such treatment. Mostly sensitive to the passivation is the excess current, which passes thru non-homogeneities, where the depletion layer is thinned and phonon-assisted tunnel recombination occurs.

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**ВПЛИВ АТОМІВ СІРКИ НА ПОВЕРХНЕВИЙ СТРУМ У P-N ПЕРЕХОДАХ НА ОСНОВІ GAAS**

Досліджено пасивацію поверхні GaAs атомами сірки та її вплив на ВАХ прямого і зворотного струмів, спектр фотоструму і чутливість p-n переходів на основі GaAs як газових сенсорів. Пасивація зменшує надлишковий прямий струм та зворотний струм у p-n переходах, підвищує фоточутливість у спектральній області сильного поглинання, суттєво збільшує чутливість до парів аміаку. Всі ці явища пояснюються зменшенням щільності поверхневих станів у результаті нанесення на поверхню атомів сірки.

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**ВЛИЯНИЕ АТОМОВ СЕРЫ НА ПОВЕРХНОСТНЫЙ ТОК В P-N ПЕРЕХОДАХ НА ОСНОВЕ GAAS**

Исследованы пассивация поверхности GaAs атомами серы и ее влияние на ВАХ прямого и обратного токов, спектр фототока и чувствительность p-n переходов на основе GaAs как газовых сенсоров. Пассивация уменьшает избыточный прямой ток и обратный ток в p-n переходах, повышает фоточувствительность в спектральной области сильного поглощения, существенно повышает чувствительность к парам аммиака. Все эти явления объясняются уменьшением плотности поверхностных состояний в результате нанесения на поверхность атомов серы.