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NEGATIVE SENSITIVITY OF SILICON *p—n* JUNCTIONS AS GAS SENSORS

The influence of ammonia vapors on *I—V* characteristics of the forward and reverse currents in silicon *p—n* junctions with different doping levels was studied. Some samples had anomalous high forward and reverse currents. They had negative sensitivity to ammonia vapors. The forward and reverse currents decreased with increasing ammonia partial pressure in the ambient atmosphere. This effect is explained under an assumption that some ionized acceptor centers are present on the *n*-region surface and form a surface conductive channel, which shorts the *p—n* junction. Adsorption of ammonia molecules, which are donors in Si, compensates the surface acceptors and diminish the conductivity of the channel.

1. INTRODUCTION

P—n junctions as gas sensors [1, 2] have some advantages in comparison with oxide polycrystalline films [3] and Schottky diodes [4]. *P—n* junctions on wide-band semiconductors have high potential barriers for charge carriers, which results in low background currents. *P—n* junctions on III—V semiconductors exhibit high sensitivity and selectivity to the gas components [5, 6]. The advantage of silicon *p—n* junctions as gas sensors is that they are compatible with silicon amplifying elements. Characteristics of silicon *p—n* junctions as gas sensors were studied in previous works [7—9].

The sensitivity of studied *p—n* structures to donor vapors such as ammonium was explained with the field effect. In the electric field of adsorbed positive ions a surface conductive channel is formed, which sorts the *p—n* junction [5—9]. It results in an increase of the forward and reverse currents in a *p—n* junction in presence of a donor gas.

The purpose of this work is a comparative study of the influence of ammonia vapors on stationary *I—V* characteristics of silicon *p—n* junctions with different surface currents.

2. EXPERIMENT

The measurements were carried out on silicon *p—n* junctions with different gradients of the doping concentrations. The *n* regions were doped with phosphorus and *p* regions with boron. The surface of *p—n* junctions was not cowered, so there was only a natural oxide layer. The parameters of the studied samples are presented in Table 1. The samples were ranged in breakdown voltage. C—V characteristics of all the samples were linear in a plot $C^{-3}(V)$, so the *p-n* junctions were linear. The values of the doping concentrations gradient correlated with the breakdown voltages and were in the range between $4.5 \cdot 10^{21}$ cm^{-4} and $4{,}5 \cdot 10^{23}$ cm^{-4}, as evident from Tab. 1.

Table 1

Parameters of samples

Number of the sample	1	2	3	4
Breakdown voltage, Volts	3.3	5.1	8.2	18
Gradient of the doping concentrations, cm^{-4}	$4.5 \cdot 10^{23}$	$5.1 \cdot 10^{22}$	$2.6 \cdot 10^{22}$	$4.6 \cdot 10^{21}$
Ideality coefficient of *I—V* curve	1.82	2.89	1.44	2.92
Depletion layer width from *C—V* curve, nm	60	93	125	248
Depletion layer width from *I—V* curve, nm	44	37	54	36

I—V curves of the forward current in all the samples are presented in Fig. 1. Over the current range between 10 nA and 1 mA the *I—V* curve can be described with the expression

$$I(V) = I_0 \exp[qV/(n_t kT)], \qquad (1)$$

where I_0 for each sample is a constant; q is the electron charge; V denotes bias voltage; k is the Boltzmann constant; T is temperature; n_t is the ideality coefficient. The ideality coefficients for all the studied samples are presented in Tab. 1.

Ideality coefficients of all the *I—V* characteristics essentially exceed the ideal value $n_t = 1$.

Deviation from the value $n_t = 1$ can be ascribed to the local phonon-assisted tunnel recombination on deep levels in non-homogeneities of the p—n junction [10]. The local depleting layer wide in these non-homogeneities can be estimated from the expression [10]

$$n_t = n_{t0}\left[1 - \frac{qh^2}{6m_t(w_V kT)^2}\right]^{-1}, \qquad (2)$$

where $n_{t0} = 1$ or $n_{t0} = 2$ for related recombination mechanisms; h is the Plank constant; m_t is the tunnel effective mass of current carriers; w_V is a parameter of the non-homogeneity of the p—n junction, which is used in the expression

$$w = w_V\left(\frac{\varphi_0}{q} - V\right)^{\frac{1}{2}}, \qquad (3)$$

where w is the local p—n junction width at voltage V; φ_0 is the equilibrium barrier height in the p—n junction.

The local depletion layer widths of the p—n junctions, obtained from such analysis of I—V curves, are presented in Tab. 1. It is evident that the depletion layer widths in the non-homogeneities, responsible for the recombination current, are remarkably smaller, than the values, estimated from C—V curves. The maximum difference between these values is for the sample with a breakdown voltage of 18 V.

Fig. 2 presents I—V characteristics of reverse current in the p—n junctions. The samples with breakdown voltages of 3.3 and 5.1 V exhibit exponential rise of the current with the voltage. This corresponds to the tunnel breakdown mechanism. In the sample with a breakdown voltage of 8.2 V the current does not exceed 10^{-8} A at $V < 5$ Volts. And the sample with a breakdown voltage of 18 V exhibit anomalous high reverse current. This is in accordance with high forward current in this sample and anomalous thin depletion layer in the non-homogeneities, which are responsible for the recombination current.

Fig. 3 shows I—V characteristics of reverse current in the p—n junction with breakdown voltage of 5.1 Volts, measured in air and in air with ammonia vapors of several partial pressures. Adsorption of ammonia molecules strongly increases the current.

The (absolute, current-) gas sensitivity of a p—n junction as gas sensor can be defined as

$$S_I = \Delta I / \Delta P, \qquad (4)$$

where ΔI is the change in the current (at a fixed voltage), which is due to a change ΔP in the corresponding gas partial pressure [11]. An analysis of the data in Fig. 3 yields an estimation $S_I = 0.5$ μA/kPa at a reverse bias voltage of 1 V.

Fig. 4 presents I—V characteristics of reverse current in the p—n junction with break-

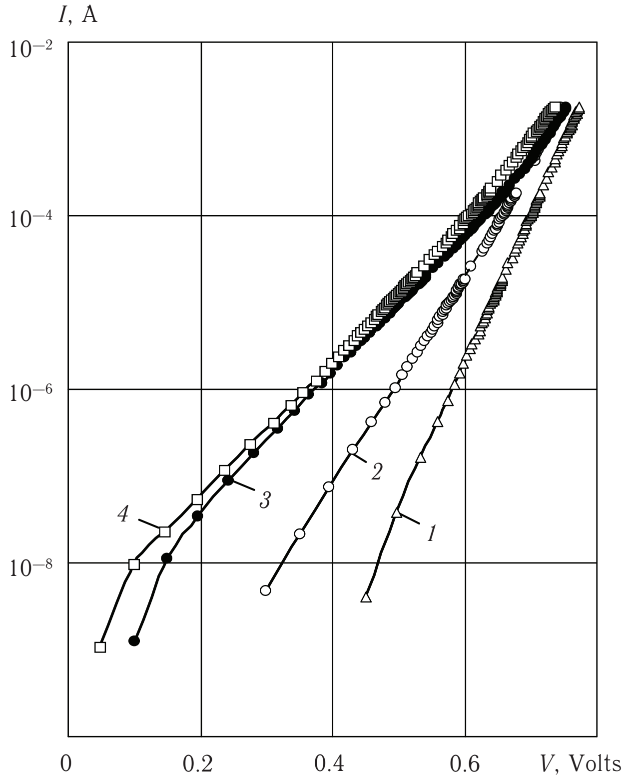

Fig. 1. I—V characteristics of the forward current in p—n structures with different breakdovn voltages, Volts: *1* — 8.2; *2* — 3.3; *3* — 5.1; *4* — 18

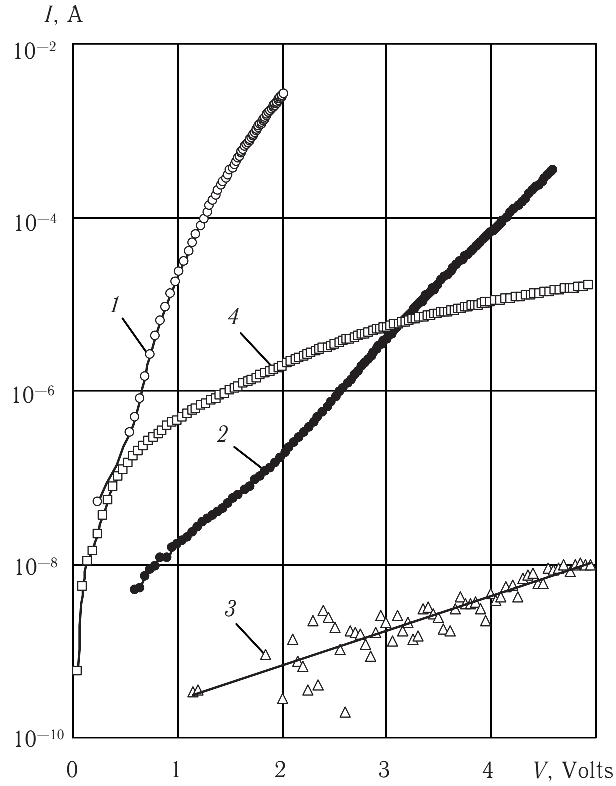

Fig. 2. I—V characteristics of the reverse current in p—n structures with different breakdovn voltages, Volts: *1* — 3.3; *2* — 5.1; *3* — 8.2; *4* — 18

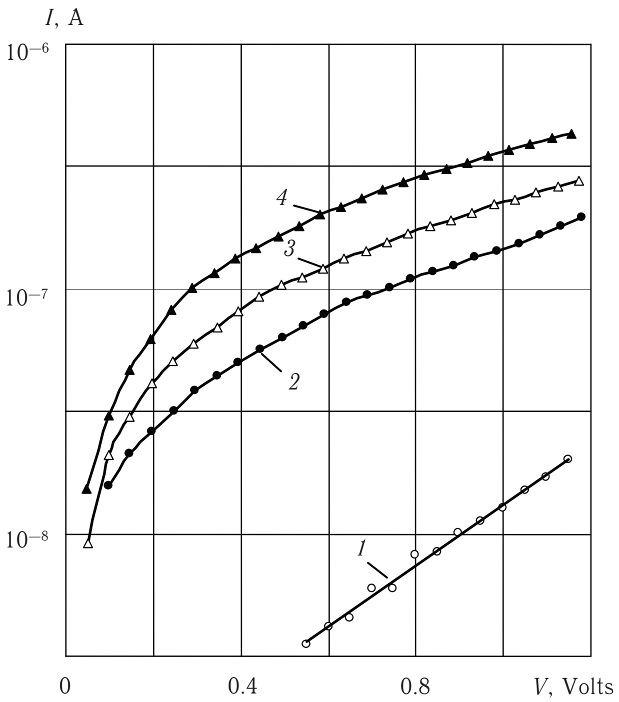

Fig. 3. *I—V* characteristics of the reverse current in *p—n* structure with breakdown voltage of 5.1 Volts, measured in air (*1*) and in air with ammonia vapors of partial pressure: *2* — 100 Pa; *3* — 500 Pa; *4* — 1000 Pa

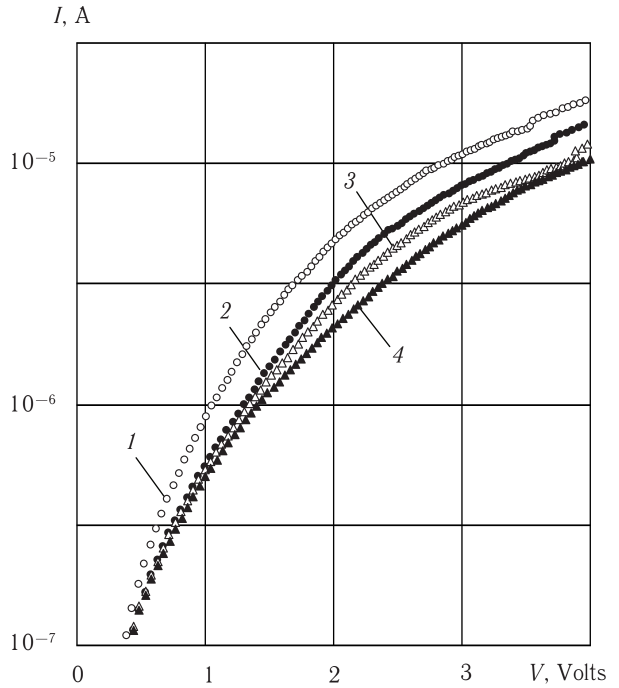

Fig. 4. *I—V* characteristics of the reverse current in *p—n* structure with breakdown voltage of 18 Volts, measured in air (*1*) and in air with ammonia vapors of partial pressure: *2* — 100 Pa; *3* — 500 Pa; *4* — 1000 Pa

down voltage of 18 Volts ("anomalous sample"), obtained in air and in air with ammonia vapors of various partial pressures. A comparison between curves *1—4* shows that adsorption of ammonia molecules does not increase the current. The current in ammonia vapors is lower, than in dry air. And the sensitivity of this sample is negative, namely $S_I = -20$ μA/kPa at a bias voltage of 4 V and $S_I = -0.7$ μA/kPa at $V = 1$ V. The absolute value of the negative sensitivity of this sample is some higher, than the sensitivity of "normal" samples.

The relative sensitivity of a gas sensor is defined as

$$S_R = \Delta I/(I_0 \Delta P), \qquad (5)$$

where I_0 denotes the current in the pure air at the same bias voltage. An analysis of the data in Figs. 3 and 4 gives for the relative sensitivity of a "normal" sample $S_R = 10$ kPa^{-1} at V = 1 V and for the "anomalous" one $S_R = -0{,}7$ kPa^{-1} at the same bias. A relative sensitivity of this sample reaches a value of -10 kPa^{-1} at V = 4 V. It is remarkable that the current noise in "anomalous" samples is higher, than in "normal" junctions. It is because the current of the "anomalous" samples in the pure air is high.

3. DISCUSSION

The negative sensitivity to a donor gas, namely, a decrease in the current as a result of the donor molecules adsorption can be explained under an assumption that some acceptor centers are present on the *n*-region surface. The corresponding schematic of the *p—n* structure is presented in Fig. 5. Ionized acceptors (not shown) at (on) the surface of *n*-region form an electric field, which bends up the c- and v-bands. Therefore the depletion region *3* is bent, as shown in Fig. 5. A channel of *p*-type conductivity *4* is produced at enough high number of ionized acceptors. This channel shorts the *p—n* junction, and therefore the forward and reverse currents in dry air are high. When the *p—n*

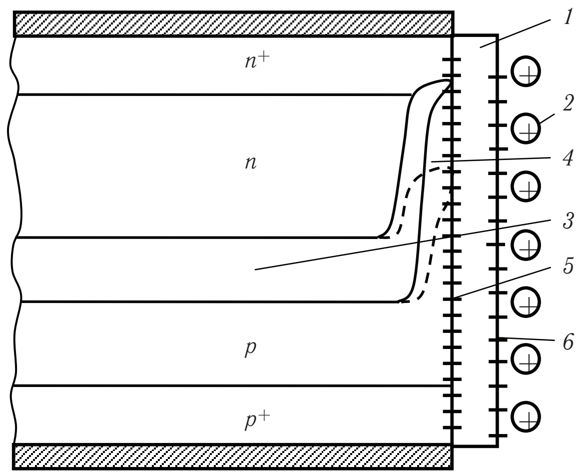

Fig. 5. Schematic of the *p—n* structure in NH_3 vapors: *1* — oxide layer; *2* — ions; *3* — depletion layer; *4* — conducting channel; *5* — surface states (rapid centers); *6* — states on the oxide surface (slow centers). *Dashed* — the depletion layer after adsorption of donor molecules

junction is placed in ammonia vapors, NH_3 molecules are adsorbed and ionized on the crystal surface. The ionized donors *2* partly compensate the acceptors mentioned and decrease the band bending. Therefore the conduction channel becomes shorter, as shown with dashed lines in Fig. 5, and the current in the channel decreases.

4. CONCLUSIONS

Silicon *p—n* junctions can have negative sensitivity to donor vapors, such as ammonia. In these structures the forward and reverse currents decrease in the atmosphere of donor gases. Such *p—n* structures have acceptor centers on (at) the surface of the *n*-layer. The electric field of the ionized acceptors bends up c- and v-bands and, at enough high density of acceptors, forms a channel with *p*-conductivity at the *n*-layer surface. This channel shorts the *p—n* junction, causing an additional current at forward and reverse biases. Adsorption of donor molecules, such as NH_3, partly compensates acceptors mentioned and decreases the surface currents at forward and reverse biases.

The absolute (current-) and relative sensitivities of such *p—n* structures is negative, which extends the functional possibilities of *p—n* junctions as gas sensors.

The negative sensitivity to ammonia vapors of the silicon *p—n* junctions with acceptor surface doping is of the same order, as the positive sensitivity of *p—n* structures without such doping.

The response time of the sensors with positive and negative sensitivity at room temperature is of 100 s.

The current noise in the sensors with negative sensitivity is higher, than in other structures of positive sensitivity because of higher current in pure air.

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Abstract

The influence of ammonia vapors on *I—V* characteristics of the forward and reverse currents in silicon *p—n* junctions with different doping levels was studied. Some samples had anomalous high forward and reverse currents. They had negative sensitivity to ammonia vapors. The forward and reverse currents decreased with increasing ammonia partial pressure in the ambient atmosphere. This effect is explained under an assumption that some ionized acceptor centers are present on the *n*-region surface and form a surface conductive channel, which shorts the *p—n* junction. Adsorption of ammonia molecules, which are donors in Si, compensates the surface acceptors and diminish the conductivity of the channel.

Key words: gas sensor, p-n junction, surface states, conductive channel, sensitivity.

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НЕГАТИВНА ЧУТЛИВІСТЬ КРЕМНІЄВИХ *p—n* ПЕРЕХОДІВ ЯК ГАЗОВИХ СЕНСОРІВ

Резюме

Досліджено вплив парів аміаку на ВАХ прямого і зворотного струмів кремнієвих *p—n* переходів з різним рівнем легування. Деякі зразки мали аномально високі прямий і зворотний струми. Вони мали негативну чутливість до парів аміаку. Прямий і зворотний струми зменшувалися зі зростанням парціального тиску аміаку в навколишній атмосфері. Даний ефект пояснюється у припущенні, що на поверхні *n*-області знаходяться іонізовані акцепторні центри і формують провідний канал, який закорочує *p—n* перехід. Адсорбція молекул аміаку, які є донорами в Si, компенсує поверхневі акцептори і зменшує електропровідність каналу.

Ключові слова: газовий сенсор, *p-n* перехід, поверхневі стани, провідний канал, чутливість.

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ОТРИЦАТЕЛЬНАЯ ЧУВСТВИТЕЛЬНОСТЬ КРЕМНИЕВЫХ *p—n* ПЕРЕХОДОВ КАК ГАЗОВЫХ СЕНСОРОВ

Резюме

Исследовано влияние паров аммиака на ВАХ прямого и обратного токов кремниевых *p—n* переходов с различным уровнем легирования. Некоторые образцы имели аномально высокие прямой и обратный токи. Они имели отрицательную чувствительность к парам аммиака. Прямой и обратный токи уменьшались с ростом парциального давления аммиака в окружающей атмосфере. Данный эффект объясняется в предположении, что на поверхности *n*-области находятся ионизированные акцепторные центры и формируют проводящий канал, который закорачивает *p—n* переход. Адсорбция молекул аммиака, которые являются донорами в Si, компенсирует поверхностные акцепторы и уменьшает электропроводность канала.

Ключевые слова: газовый сенсор, *p—n* переход, поверхностные состояния, проводящий канал, чувствительность.