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EFFECT OF AMBIENT ATMOSPHERE ON THE SURFACE CURRENT IN SILICON P-N JUNCTIONS

The influence of ammonia, water and ethylene vapors on I-V characteristics of forward and reverse currents, as well as on the kinetics of the surface current in silicon p-n structures was studied. All these vapors enhance both the forward and reverse currents. The gas sensitivity of p-n structures at forward biases is due to enhanced surface recombination, while at reverse biases a surface conductive channel shorts the p-n junction. The sensitivity to ammonia is much higher than to other vapors. It is explained as a result of donor properties of NH_3 molecules. The response time of silicon p-n junctions as gas sensors at room temperature is below 60 s.

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]. P-n junctions on wide-band semiconductors have high potential barriers for current carriers, which results in low background currents, high sensitivity and selectivity to the gas components [5, 6].

The sensitivity of p-n sensors to donor gases as ammonia 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]. This mechanism is valid only for adsorbed molecules which are ionized on the semiconductor surface. And it causes the gas selectivity of these sensors. The surface conducting channel is produced in these sensors under condition

$$N_s^m > N_s \,, \qquad (1)$$

where N_s^m and N_s are the surface densities of adsorbed molecules (ions) and surface electron states in the semiconductor, respectively. This determines the threshold gas concentration for these sensors.

Characteristics of p-n junctions in silicon as ammonia sensors were studied in previous works [7, 8]. It was shown that ammonia sensitivity of these structures is due to enhancing of the surface recombination, caused by NH_3 molecules adsorption. The difference in the sensitivity mechanism can lead to differences in selectivity and other characteristics of sensors.

The purpose of this work is a comparative study of the influence of ammonia, water and ethylene vapors on stationary surface currents in silicon p-n junctions, as well as on their kinetics.

2. EXPERIMENT

I-V measurements were carried out on silicon p-n junctions with the structure described in previous works [7, 8]. The effect of vapors over water solutions of several NH_3 concentrations, over distilled water and over liquid ethylene was studied on stationary *I-V* characteristics, as well as on kinetics of surface current in p-n junctions.

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 10 nA and 1mA the *I—V* curve can be described with the expression

$$I(V) = I_0 \exp(qV / nkT) \,, \qquad (2)$$

where I_0 is a constant; q is the electron charge; V denotes bias voltage; k is the Boltzmann constant; T is temperature; $n \approx 1.1$ is the ideality constant. Some deviation from the value n=1 can be ascribed to recombination on deep levels in p-n junction and (or) at the surface [9]. Curves 2, 3, 4 in Fig. 1 were obtained in air with vapors of water, ethylene, and ammonia, respectively. The partial pressures of water, ethylene and ammonia vapors were of 2000Pa, 5000Pa, and 50 Pa, accordingly. A comparison between curves 1, 2, and 3 in Fig. 1 shows that the sensitivity of p-n structures to ammonia vapors is the highest and to water — the lowest.

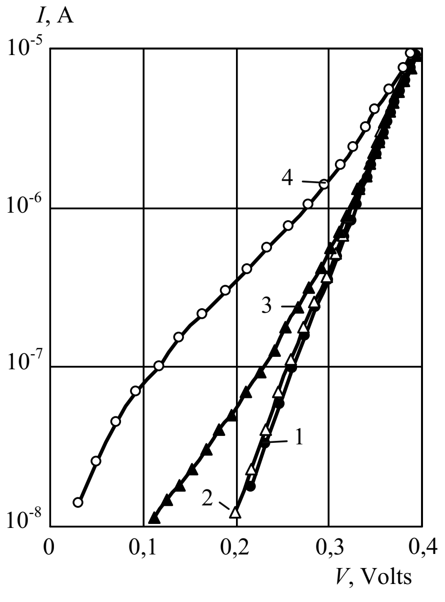

Fig. 1. Forward branches of *I-V* characteristics of a p-n structure in air (1) and in vapors of water (2), ethylene (3) and ammonia (4).

Fig. 2 represents *I—V* characteristics of the reverse current in a p-n junction. Curve 1 was measured in air, and curves 2—4 were obtained in air with vapors of water, ethylene, and ammonia, respectively. It is evident from Fig. 2 that the studied vapors strongly enhance the reverse current in silicon p-n structures.

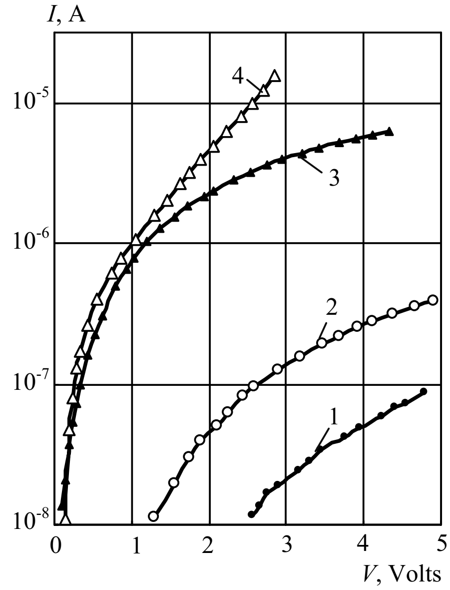

Fig. 2. Reverse branches of *I-V* characteristics of a p-n structure in air (1) and in vapors of water (2), ethylene (3) and ammonia (4).

Curves 1, 2 and 3 in Fig. 3 depict *I—V* characteristics of the additional current in a p-n structure, due to adsorption of water, ethylene, and NH_3 molecules, accordingly. It is seen that, at a high enough reverse voltage, the additional reverse currents are higher than the corresponding forward currents.

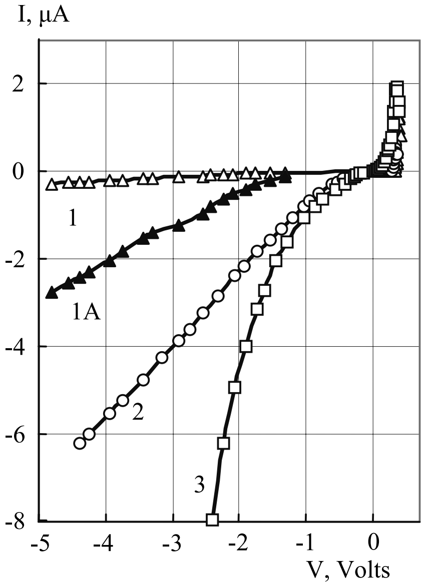

Fig. 3. *I-V* characteristics of the additional currents in a p-n structure in vapors of water (1, 1A), ethylene (2) and ammonia (3). Ordinates of curve 1A are multiplied by 10.

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

$$S_I = \Delta I / \Delta P \, , \tag{3}$$

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 [10]. And the relative sensitivity is

$$S_R = \Delta I / (I_0 \Delta P) \, , \tag{4}$$

where I_0 denotes the current in the pure air at the same bias voltage.

The sensitivities of studied p-n junctions to water, ethylene (C_2H_5OH) and ammonia vapors at a forward bias voltage of 0.25 V and a reverse bias voltage of 3 V are presented in Tab. 1.

Table 1

Gas sensitivities of p-n structures

	H_2O	C_2H_5OH	NH_3
S_I (0.25 V), nA/kPa	6	11	11000
S_I (−3 V), nA/kPa	70	800	20000
S_R(0.25 V), 1/kPa	0.1	0.23	200
S_R(-3 V), 1/kPa	3	50	900

It is seen in Tab. 1 that the studied p-n structures can be used, practically, as ammonia selective sensors. In an ammonia-free atmosphere these structures are sensors of water and ethylene. The reverse bias is preferable for the sensors.

Fig. 4 illustrates the kinetics of forward (*a*) and reverse (*b*) currents in a p-n structure after let in- and out of ammonia vapor with a partial pressure of 50 Pa. Similar curves were measured for water- and ethylene vapors. The response time t_r for current rise was estimated as the duration of the current increase to 90% of its stationary value after letting in the corresponding vapor into the container with the sample. And the decay time t_d was obtained in a similar way, for the current decrease from the stationary value to 10% of it. These procedures were carried out in regimes of forward and reverse bias. The resulting response- and decay times are presented in Tab. 2.

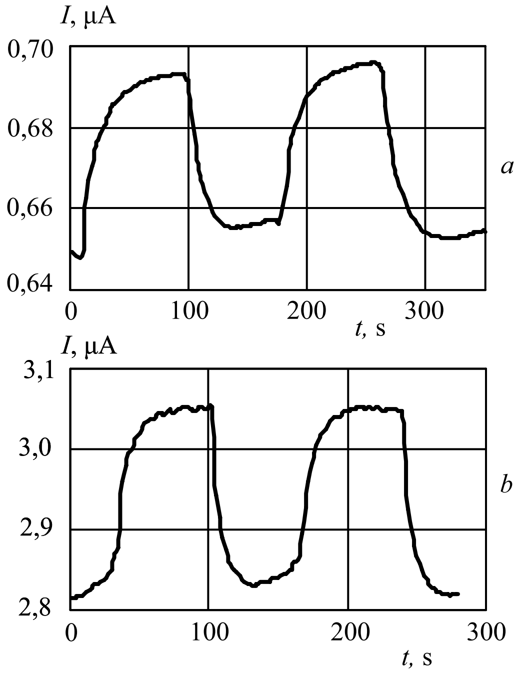

Fig. 4. Kinetics of forward (*a*) and reverse (*b*) currents in a p-n structure after let in- and out of ammonia vapor with a partial pressure of 50 Pa.

Table 2

Rise- and decay times of p-n gas sensors

	H_2O	C_2H_5OH	NH_3
t_r (0.25 V), s	30–35	10–16	25–40
t_d (0.25 V), s	10–15	5–8	20–30
t_r (-3 V), s	35–55	50–55	25–30
t_d (-3 V), s	25–30	10–12	8–9

The data in Tab. 2 show that the rise time of the signal for all the studied vapors is longer than the decay time in both regimes. And the response time of the p-n structures as gas sensors does not exceed 55 s.

3. DISCUSSION

The mechanism of the ammonia sensitivity of the forward current in silicon p-n structures was discussed in previous works [7, 8]. Adsorbed and subsequently ionized molecules of a donor gas form the electric field which bends down c- and v- bands in the crystal at the surface. Under a high enough gas partial pressure, a surface channel with electron conductivity is formed. This situation is realized in p-n structures on wide-band semiconductors at low enough biases [1, 2, 5, 6]. With an increased bias voltage, electrons and holes are injected into the channel, and a regime of double injection is realized which results in a superlinear rise of the current [6]. The double injection leads, at high enough injection current, to destruction of the channel.

In the case of silicon p-n junctions, the destruction of the channel by injected charge currents occurs at relatively low forward bias voltages of ~0.1V, and the linear section of *I–V* curve practically is not realized [6]. Our experiments confirm this conclusion. Curve 4 in Fig. 1 has a large section that corresponds to formula (1) with ideality coefficient n=2.6. Such value of n suggests that the excess current, due to ammonia molecules adsorption, can be ascribed to the phonon-assisted tunnel recombination at deep surface states [9].

I–V characteristics 2 and 3 in Fig. 1, measured in water- and ethylene vapors, respectively, have pronounced linear sections in a semi-logarithmic plot, with ideality coefficients of 1.13 and 2.1, which argues that the increase of the forward current in these vapors is due to enhanced surface recombination. Thus, the mechanism of the sensitivity of silicon p-n junctions to ammonia-, ethylene- and ammonia vapors is the same.

I–V characteristics of the excess reverse current, due to water- and ethylene molecules adsorption, which are plotted as curves 1and 2 in Fig. 3, have large linear sections. This means that the surface conductive channel, formed as a result of water- and ethylene molecules adsorption, is not destroyed at a reverse bias. And this channel is responsible for gas sensitivity of silicon p-n structures at reverse biases.

Curve 3 in Fig. 3, as *I–V* characteristic of the excess reverse current in ammonia vapors, is superlinear. This can be tentatively ascribed to injection processes or (and) strong-field effects.

An interesting result of our study is that the sensitivity of silicon p-n structures as gas sensors is higher at reverse bias than at forward bias. Gas sensitivity of the forward current was observed only at low bias voltages V<0.4 Volts. The limiting of gas sensitivity of the forward current is caused by two factors. First, with the forward bias voltage exponentially rises the bulk injection current, and the surface current becomes negligible. And second, the electrons and holes, injected into the surface channel at a high enough forward bias, screen the electric field of adsorbed ions and suppress its effect on the electrons distribution at the surface.

The next question is the mechanisms of processes that determine the response time of p-n junctions as gas sensors. The rise- and decay curves of the surface current forward currents in a p-n structure after let in- and out of ammonia, ethylene and water vapors are plotted in Fig. 5. For the rise curves parameter ΔI was taken $\Delta I = I_0 - I(t)$, where I_0 is the stationary value of I; for decay curves $\Delta I = I(t)$. It is seen that all the curves have pronounced linear sections in a semi-logarithmic plot. This means that there is a single process which is responsible for the inertia of current rise and decay. The estimated values of characteristic rise time τ_r and decay time τ_d for the excess forward and reverse currents in p-n structures are presented in Tab. 3

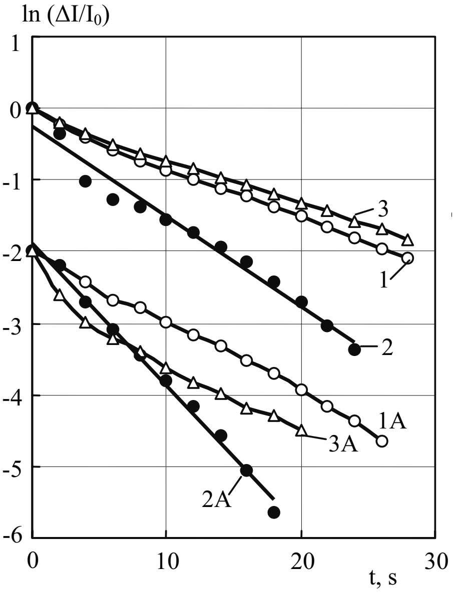

Fig. 5. Rise (1–3) and decay (1A–3A) curves of the forward currents in a p-n structure after let in- and out of vapors: 1, 1A – ammonia; 2, 2A – ethylene; 3, 3A – water. Curves 1A – 3A are shifted down by 2.

Table 3

Characteristic rise- and decay times of p-n structures

	H_2O	C_2H_5OH	NH_3
τ_r (0.25 V), s	16.1	7.9	14.0
τ_d (0.25 V), s	8.9	5.0	10.2
τ_r (-3 V), s	14.3	14.5	9.3
τ_d (-3 V), s	11.5	3.2	8.6

The inertia of the p-n structures as gas sensors can be due to molecular processes at the surface of the oxide layer and (or) to electron transitions at fast surface states on the boundary silicon–oxide and slow states on the external surface of the oxide. The electronic mechanism is preferable in light of the fact that the characteristic rise- and decay times τ_r and τ_d for three studied vapors are of the same order of magnitude, while the sensitivities differ by three orders. For the electronic mechanism is also characteristic inequality $\tau_r > \tau_d$, which was observed for all studied gases at forward and reverse biases, as seen in Tab. 3. Tentatively, the response time of the studied p-n gas sensors is due to the recharging of surface states, as a result of the adsorption of molecules from the ambient atmosphere.

4. CONCLUSIONS

Forward and reverse currents in silicon p-n junctions are sensitive to ammonia, ethylene and water vapors in the ambient air. The sensitivity to NH_3 vapor is by orders of magnitude higher than to other studied vapors. Therefore silicon p-n junctions can be used as selective ammonia vapor sensors. Selectivity of the sensor is due to donor properties of NH_3 molecules.

The sensitivity of silicon p-n structures to the mentioned vapors at forward biases is caused by enhancing of surface recombination, as a result of band bending in p-region, due to electric field of adsorbed ions.

The gas sensitivity of studied p-n structures at reverse biases is due to forming of a surface conductive channel which shorts the p-n junction.

The forward bias voltage of the sensor is limited by exponential rise of bulk injection current and screening of the electric field, induced by adsorbed ions, by injected electrons and holes. Therefore the reverse bias is preferable for the sensors and provides higher gas sensitivity, than the forward bias.

The response time of silicon p-n sensors is below 60 s at room temperature for all the studied vapors at forward and reverse biases. This time can be ascribed to recharging of slow surface centers.

References

1. Птащенко О. О., Артеменко О. С., Птащенко Ф. О. Вплив газового середовища на поверхневий струм в *p-n* гетероструктурах на основі GaAs–AlGaAs // Фізика і хімія твердого тіла . — 2001. — Т. 2, № 3. — С. 481 — 485.
2. Птащенко О. О., Артеменко О. С., Птащенко Ф. О. Вплив парів аміаку на поверхневий струм в p-n перреходах на основі напівпровідників A^3B^5 // Журнал фізичних досліджень. — 2003. — Т. 7, №4. — С. 419 — 425.
3. Бугайова М. Е., Коваль В. М., Лазаренко В. І. та ін. Газові сенсори на основі оксиду цинку (огляд) // Сенсорна електроніка і мікросистемні технології. — 2005. — №3. — С. 34 — 42.
4. Балюба В. И., Грицык В. Ю., Давыдова Т. А. и др. Сенсоры аммиака на основе диодов Pd-n-Si // Физика и химия полупроводников. — 2005. — Т. 39, № 2. С. 285 — 288.
5. Ptashchenko O. O., Artemenko O. S., Dmytruk M. L. et al. Effect of ammonia vapors on the surface morphology and surface current in p-n junctions on GaP // Photoelectronics. — 2005. — No. 14. — P. 97 — 100.
6. Ptashchenko F. O. Effect of ammonia vapors on surface currents in InGaN p-n junctions // Photoelectronics. — 2007. — No. 17. — P. 113 — 116.
7. Птащенко Ф. О. Вплив парів аміаку на поверххневий струм у кремнієвих p-n переходах // Вісник ОНУ, сер. Фізика. — 2006. — Т. 11, №. 7. — С. 116 — 119.
8. Ptashchenko O. O., Ptashchenko F. O., Yemets O. V. Effect of ammonia vapors on the surface current in silicon p-n junctions // Photoelectronics. — 2006. — No. 16. — P. 89 — 93.
9. Ptashchenko A. A., Ptashchenko F. A. Tunnel surface recombination in p-n junctions // Photoelectronics. — 2000. — № 10. — P. 69 — 71.
10. Вашпанов Ю. А., Смынтына В. А. Адсорбционная чувствительность полупроводников. — Одесса: Астропринт, 2005. — 216 р.

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Abstract
The influence of ammonia, water and ethylene vapors on *I-V* characteristics of forward and reverse currents, as well as on the kinetics of the surface current in silicon p-n structures was studied. All these vapors enhance both the forward and reverse currents. The gas sensitivity of p-n structures at forward biases is due to enhanced surface recombination, while at reverse biases a surface conductive channel shorts the p-n junction. The sensitivity to ammonia is much higher than to other vapors. It is explained as a result of donor properties of NH_3 molecules. The response time of silicon p-n junctions as gas sensors at room temperature is below 60s.

Key words: ambient atmosphere, surface current, silicon.

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ВЛИЯНИЕ ОКРУЖАЮЩЕЙ АТМОСФЕРЫ НА ПОВЕРХНОСТНЫЙ ТОК В КРЕМНИЕВЫХ P-N ПЕРЕХОДАХ

Резюме
Исследовано влияние паров аммиака, воды и этилена на ВАХ прямого и обратного токов, а также на кинетику поверхностного тока в кремниевых p-n структурах. Все указанные пары повышают и прямой, и обратный токи. Газовая чувствительность p-n структур при прямом смещении обусловлена ростом интенсивности поверхностной рекомбинации, а при обратном смещении проводящий канал закорачивает p-n переход. Чувствительность к аммиаку значительно выше, чем к другим парам. Это объясняется донорными свойствами молекул NH_3. Время срабатывания кремниевых p-n переходов как газовых сенсоров при комнатной температуре не превышает 60 с.

Ключевые слова: поверхностный ток, окружающая атмосфера, кремний.

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ВПЛИВ НАВКОЛИШНЬОЇ АТМОСФЕРИ НА ПОВЕРХНЕВИЙ СТРУМ У КРЕМНІЄВИХ P-N ПЕРЕХОДАХ

Резюме

Досліджено вплив парів аміаку, води і етилену на ВАХ прямого і зворотного струмів, а також на кінетику поверхневого струму в кремнієвих p-n структурах. Всі указані пари підвищують і прямий, і зворотний струми. Газова чутливість p-n структур при прямому зміщенні обумовлена зростанням інтенсивності поверхневої рекомбінації, а при зворотному зміщенні провідний канал закорочує p-n перехід. Чутливість до аміаку значно вища, ніж до інших парів. Це пояснюється донорними властивостями молекул NH_3. Час спрацювання кремнієвих p-n переходів як газових сенсорів при кімнатній температурі не перевищує 60 с.

Ключові слова: поверхневий струм, навколишня атмосфера, кремній.