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O. O. Ptashchenko[1], F. O. Ptashchenko[2], V. R. Gilmutdinova[1], G.V Dovganyuk

[1] Odessa National I. I. Mechnikov University, Dvoryanska St., 2, Odessa, 65026, Ukraine,
[2]Odessa National Maritime Academy, Odessa, Didrikhsona St., 8, Odessa, 65029, Ukraine

EFFECT OF AMMONIA VAPORS ON THE BREAKDOWN CHARACTERISTICS OF Si AND GaAs P-N JUNCTIONS

The influence of ammonia and water vapors on *I-V* characteristics of the reverse currents in Si and GaAs p-n junctions was studied. At most of the studied samples, the ammonia- and water vapors lover the breakdown voltage. At some devices an opposite effect was observed. This difference is due to dominance of different surface centers, which have donor or acceptor properties. And some p-n junctions exhibit a fixed breakdown voltage independently on the presence of ammonia and water vapors. This is due to the bulk location of the breakdown in these samples. Thus, the influence of ammonia vapors on the breakdown voltage provides some information on the localization of the breakdown and on the charge state of surface centers.

Key words: p-n junction, gas sensor, reverse current, breakdown voltage, surface center.

1. INTRODUCTION

The gas sensitivity of the p-n junctions at reverse bias is much higher than at the forward bias. It was shown on GaAs-, AlGaAs- [1, 2], GaP- [3], InGaN- [4] and Si [5-7] p-n junctions. The forward current, due to ammonia and (or) water molecules adsorption, is shortened by the bulk injection current at the bias voltages of 0,5 – 2,5 Volts, depending of the band gap. And reverse currents caused by adsorption processes are much higher than the bulk current. This enables to apply to the sample relatively high reverse bias voltages that provide higher gas sensitivity. The upper limit for this voltage is due to breakdown [8]. Ammonia- and water molecules are donors in III-V semiconductors and in silicon. 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 adsorption of electrically active molecules can change the breakdown voltage, which is dangerous for the using of p-n structures as gas sensors at reverse biases.

The purpose of this work is a study of the influence of ammonia and water vapors on stationary *I–V* characteristics and on the breakdown voltage of GaAs and silicon p-n junctions.

2. EXPERIMENT

The measurements were carried out on GaAs and silicon p-n junctions with the structure described in previous works [1, 2] and [5, 6], respectively. *I-V* characteristics were measured with an automatic system. The effect of vapors over water solutions of several NH_3 concentrations and over distilled water was studied on stationary *I-V* characteristics, as well as on the current kinetics in p-n junctions. The currents in the samples were limited to <5 μA in order to prevent non-reversible breakdown.

I–V characteristics of the reverse current in a GaAs p-n junction are shown in fig 1. Curve 1, measured in dry air, has a section with a steep ascent due to avalanche breakdown at a voltage of 18 Volts. A measurement in saturated water vapors (at a partial pressure of 1.2 kPa) gives the breakdown voltage of 5 Volts, as shown in curve 2. The breakdown voltage non-monotonously changed with partial pressure of wet ammonia vapors as illustrated in curves 3–6. Curve 4, measured under ammonia pressure of 10 Pa, demonstrates that the breakdown voltage in this sample can increase due to adsorption of NH_3 molecules. Such behavior of the breakdown voltage in ammonia vapors suggests that the breakdown in this sample is located at the surface of the crystal.

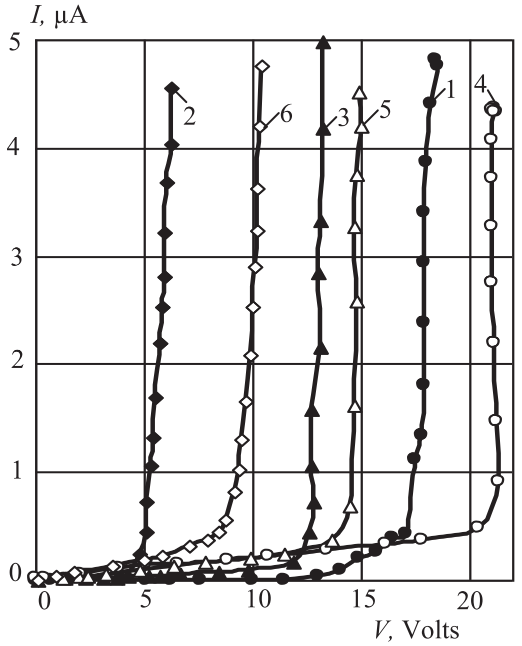

Fig. 1. *I-V* characteristics of the reverse current in a GaAs p-n junction, measured in dry air (curve 1) in water vapors (2) and in wet NH_3 vapors of several partial pressures, Pa: 3 — 1; 4 — 10; 5 — 20; 6 — 100.

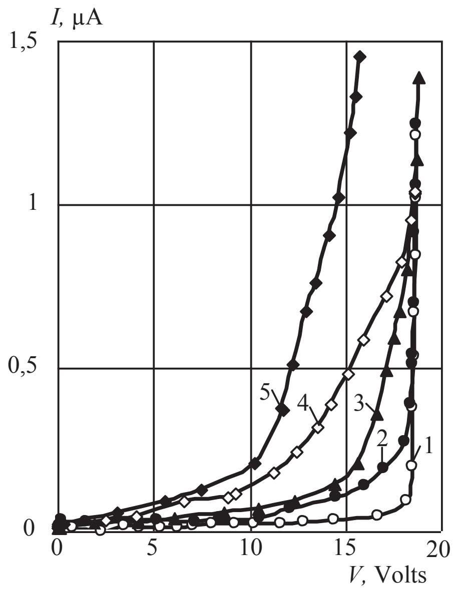

Fig. 2 presents *I-V* characteristics of the reverse currents in another GaAs p-n junction, measured in dry air and in NH_3 vapors of several partial pressures. As seen in this figure, the breakdown voltage in this sample is 18 Volts and does not change in ammonia vapors.

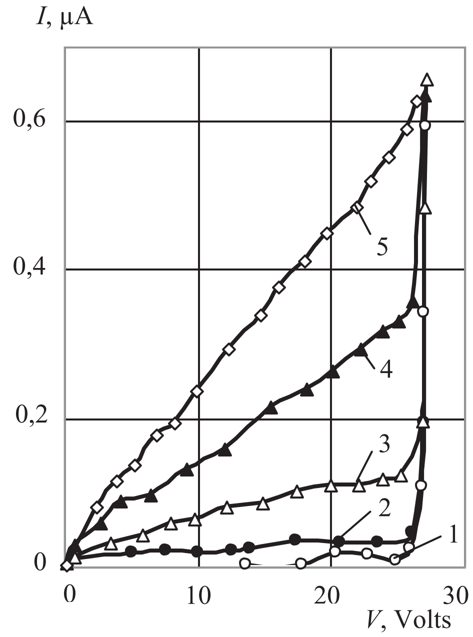

Fig. 3. *I-V* characteristics of the reverse current in a Si p-n junction, measured in dry air (curve 1) and in wet NH_3 vapors of several partial pressures, Pa: 2 – 5; 3 – 10; 4 – 20; 5 – 100; 6 –200.

Similar behavior is characteristic of some Si p-n junctions, as illustrated in fig. 3. It is evident from curves 5–6 in fig. 3 that the breakdown voltage in this Si p-n junction amounts to 28 Volts and does not change in water and ammonia vapors. This means that additional ionized donor centers due to adsorbed water- and ammonia molecules does not affect the electric field in the region of the depletion layer where the breakdown occurs. This argues that the avalanche breakdown in referred samples of GaAs and Si p-n junctions occurs in the crystal bulk and is not associated with the crystal surface.

3. DISCUSSION

The dependence of the avalanche breakdown voltage on the parameters of an asymmetrical abrupt p-n junction can be described as

$$V_B = 60(E_g/1,1)^{3/2}(N_B/10^{16})^{-3/4}, \qquad (1)$$

where E_g is the band gap of the actual semiconductor; N_B denotes the impurity concentration in the region of lower doping in the p-n junction [9].

This expression can be used for an estimation of the impurity concentration in a p-n structure by using of the measured breakdown voltage as

$$N_B = 10^{16}(60/V_B)^{4/3}(E_g/1{,}1)^2 \ . \qquad (2)$$

The irregular change of the breakdown voltage with the ammonia concentration in the ambient atmosphere, illustrated in fig. 1, can be explained, as we assume the presence of several non-homogeneities with different local concentrations of donors and acceptors at the surface in this sample.

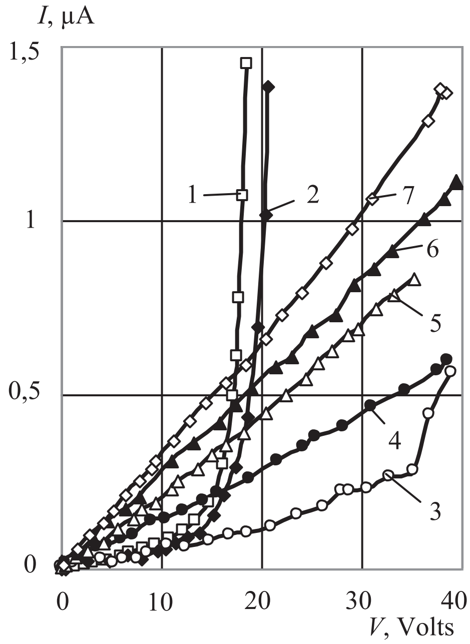

Fig. 4. *I-V* characteristics of the reverse current in a Si p-n junction, measured in dry air (curve 1), in water vapors (2) and in wet NH_3 vapors of several partial pressures, Pa: 3 — 1; 4 — 5; 5 — 10; 6 — 20; 7 — 100.

Fig. 4 presents *I-V* characteristics of the reverse current in a Si p-n junction, measured in dry air, in water vapors and in ammonia vapors of several partial pressures. Curve 1, obtained in dry air, exhibits a breakdown voltage of 17,8 Volts, that corresponds to an impurity concentration of $5{,}0\cdot10^{16}$cm^{-3}. As measured in water vapors of a H_2O partial pressure of 12 kPa, the breakdown voltage was 20 Volts, which yields for the impurity concentration an estimation $4{,}3\cdot10^{16}$cm^{-3}. A comparison of both this values, estimated from the measurements in dry air and in water vapors, suggests that the avalanche breakdown in this sample is located at the crystal surface. The adsorbed water molecules partly compensate the electrically active centers, which are responsible for the surface breakdown.

Curve 3 in fig. 4, measured in ammonia vapors with a partial pressure of 5 Pa, shows a breakdown voltage of 35,2 Volts, that corresponds to a concentration of electrically actives centers of $3{,}0\cdot10^{16}$cm^{-3}. The ammonia vapors of higher partial pressures give the further rise of the breakdown voltage. An analogues effect was observed on the breakdown voltage in GaAs p-n junctions.

The effect of ammonia vapors on the breakdown voltage in Si and GaAs p-n junctions is schematically illustrated in fig. 5. The model takes into account that water and NH_3 molecules are donors on the surface of Si and GaAs crystals. Fig 5*a* depicts the donors and acceptors distributions in a local section of p-n junction, which is responsible for the surface breakdown. The donor concentration N_D in the n-side of the depletion region of this p-n junction is much higher than the acceptor concentration N_A in the corresponding layer of this region:

$$N_D >> N_A. \qquad (3)$$

Therefore the breakdown voltage V_{B1} is controlled by the acceptor concentration at the p-side of the p-n junction. The value V_{B1} can be calculated from the expression (1), where

$$N_B = N_A . \qquad 4)$$

Fig. 5*b* illustrates the structure of the same local p-n junction at the crystal surface under presence of ammonia vapors in ambient atmosphere. Since adsorbed ammonia molecules are donors, they partly compensate the acceptors, which results in a widening of the local depletion region, as shown in fig. 5*b*. In this case the breakdown voltage is determined with the same formula (1), where

$$N_B = N_A - N_D^{\text{add}}, \qquad (5)$$

where N_D^{add} is an additional donor concentration due to ammonia molecules adsorption. It is evident from formulas (1) and (5), that an increase in N_D^{add} enhances the breakdown voltage.

An analysis of curves 1–3 in fig. 4 using relation (2) yields for N_D^{add} values $0{,}7\cdot10^{16}cm^{-3}$ and $2\cdot10^{16}cm^{-3}$, respectively, for local donor concentrations, produced by water- and ammonia molecules (under a partial pressure of 5 Pa) adsorption.

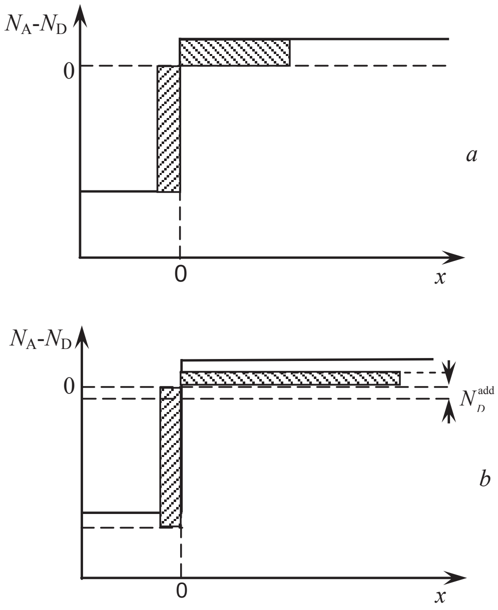

Fig. 5 The donors and acceptors distributions in a local section of p-n junction, which is responsible for the surface breakdown: *a*) — in dry air: *b*) — in wet ammonia vapors. The dashed areas correspond to the depletion region.

If an opposite to (3) inequality takes place in the non-homogeneity, an increase in the local donor concentration, due to donor molecules adsorption, lowers the breakdown voltage.

The samples of Si and GaAs p-n junctions with the breakdown located in the crystal bulk, as well as those with the breakdown voltage, enhanced by donor molecules adsorption, can be used as water- and ammonia vapors sensors, which can work at reverse biases, having higher sensitivity, than at forward biases.

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

$$S_I = \Delta I / \Delta P, \qquad 6)$$

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]. An analysis of the data in figs 2 and 3 yields for the maximum sensitivities of the corresponding GaAs and Si p-n junctions to ammonia vapors values of 60 μAPa^{-1} and 20 μAPa^{-1}, respectively.

4. CONCLUSIONS

The reverse bias is preferable for the gas sensors on Si and GaAs p-n junctions, as far as it provides a higher gas sensitivity, than the forward bias. The upper limit for the reverse bias voltage is due to breakdown voltage, which can depend on the partial pressure of the investigated vapors.

A simple model is proposed to explain the dependence of the p-n junction breakdown voltage on the ammonia partial pressure in the ambient atmosphere. In terms of this model the adsorbed ammonia molecules produce ionized donor centers, that partly compensate acceptors in local surface non-homogeneities, which are responsible for the breakdown. Depending on the donor- and acceptor local concentrations, this can result in either decrease or increase of the breakdown voltage.

The behavior of the breakdown voltage in ammonia vapors can be used for diagnostics of surface non-homogeneities in p-n junctions. Such diagnostics can be applied to a choose of samples, which can work as gas sensors under reverse biases, having higher sensitivity.

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Summary

The influence of ammonia and water vapors on *I-V* characteristics of the reverse currents in Si and GaAs p-n junctions was studied. At most of the studied samples, the ammonia- and water vapors lover the breakdown voltage. At some devices an opposite effect was observed. This difference is due to dominance of different surface centers, which have donor or acceptor properties. And some p-n junctions exhibit a fixed breakdown voltage independently on the presence of ammonia and water vapors. This is due to the bulk location of the breakdown in these samples. Thus, the influence of ammonia vapors on the breakdown voltage provides some information on the localization of the breakdown and on the charge state of surface centers.

Key words: p-n junction, gas sensor, reverse current, breakdown voltage, surface center.

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О. О. Птащенко, Ф. О. Птащенко, В. Р. Гільмутдінова, Г. В. Довганюк

ВПЛИВ ПАРІВ АМІАКУ НА ХАРАКТЕРИСТИКИ ПРОБОЮ P-N ПЕРЕХОДІВ НА ОСНОВІ Si ТА GaAs

Резюме

Досліджено вплив парів аміаку та води на вольт-амперні характеристики зворотних струмів у p-n переходах на основі Si та GaAs. В більшості досліджених зразків пари аміаку та води зменшують напругу пробою. На деяких зразках спостерігався зворотний ефект. Ця різниця обумовлена домінуванням різних поверхневих центрів, які мають донорні або акцепторні властивості. Деякі p-n переходи мають фіксовану напругу пробою незалежно від присутності парів аміаку та води. Дана поведінка обумовлена локалізацією пробою в об'ємі кристалу в таких зразках. Таким чином, вплив парів аміаку на напругу пробою дає інформацію про локалізацію пробою і про зарядовий стан поверхневих центрів.

Ключові слова: p-n перехід, газовий сенсор, зворотний струм, напруга пробою, поверхневий центр.

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О. О. Птащенко, Ф. О. Птащенко, В. Р. Гильмутдинова, Г. В. Довганюк

ВЛИЯНИЕ ПАРОВ АММИАКА НА ХАРАКТЕРИСТИКИ ПРОБОЯ P-N ПЕРЕХОДОВ НА ОСНОВЕ Si И GaAs

Резюме

Исследовано влияние паров аммиака и воды на вольт-амперные характеристики обратных токов в p-n переходах на основе Si и GaAs. В большинстве исследованных образцов пары аммиака и воды уменьшают напряжение пробоя. На некоторых образцах наблюдался обратный эффект. Это различие обусловлено доминированием различных поверхностных центров, имеющих донорные либо акцепторные свойства. Некоторые p-n переходы имеют фиксированное напряжение пробоя независимо от присутствия паров аммиака и воды. Такое поведение обусловлено локализацией пробоя в объеме кристалла в таких образцах. Таким образом, влияние паров аммиака на напряжение пробоя дает информацию о локализации пробоя и о зарядовом состоянии поверхностных центров.

Ключевые слова: p-n переход, газовый сенсор, обратный ток, напряжение пробоя, поверхностный центр.