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EFFECT OF AMMONIA VAPORS ON THE SURFACE CURRENT IN SILICON P-N JUNCTIONS

I—V characteristics of forward and reverse currents in silicon p-n junctions were measured in air, in air with ammonia vapors at several partial pressures of NH3, as well as in air after ammonia vapors treatment. The influence of adsorbed ammonia molecules on the forward current is explained by such processes: a) an increase in the surface recombination rate, caused by the electric field of ammonia ions, which are localized on the external side of the natural oxide layer; b) etching out some surface recombination states. The changes in the forward and reverse currents are reversible, so silicon p-n junctions can be used as ammonia vapors sensors.

INTRODUCTION

Physical processes that can be utilized for creation of gas sensors are extensively studied [1, 2]. Sensors on thin polycrystalline and amorphous layers have high sensitivity, low cost, simple technology. Disadvantages of such sensors are high working temperatures of 150—550°C [2], low controllability of the inter-crystallite contact properties, low technological compatibility with microelectronic elements. Sensors on the silicon Shottky barriers with a super-thin catalytic active metal layer Pt, Pd, Ni utilize a change in the dielectric permittivity of the depletion layer [3]. Such sensors work at elevated temperatures of 150°C, their sensibility strongly depends on the thickness and structure of the metal layer. Sensors on p-n junctions [4, 5] have crystal structure, high sensitivity at room temperature, selectivity, and can be manufactured in microelectronic technology. The surface current induced by adsorption of NH3 molecules in p-n structures on GaAs and AlGaAs linearly depends on the applied voltage and on the ammonia partial pressure. 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 [4]. The parameters of this channel must depend on the characteristics of the actual semiconductor material. Therefore it is of interest to study systematically this effect in p-n junctions on different semiconductors. Sensors on III—V semiconductors are hardly compatible with silicon microelectronic elements.

The purpose of this work is a study of silicon p-n junctions as ammonia vapors sensors.

1. I—V CHARACTERISTICS

I—V measurements were carried out on silicon p-n junctions manufactured in standard technology re-crystallization from the solution in melted Al on the n-silicon (111) plane substrate. The area of the p-n junction was of 0.25 mm^2, capacity ≈50 pF. 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.

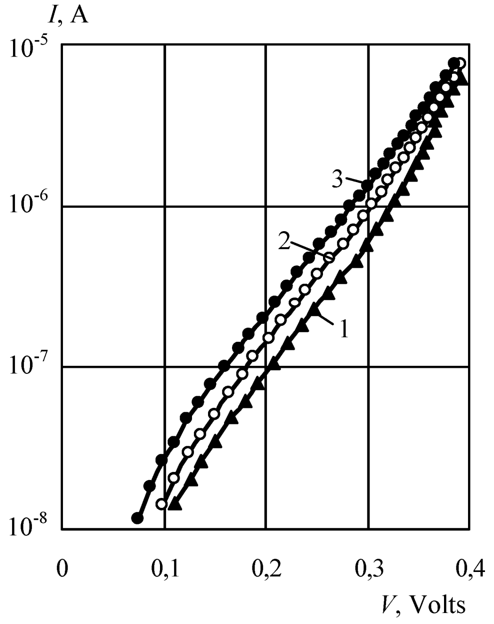

Fig. 1. Forward branches of I—V characteristics of a p-n structure: 1 — in air; 2 — at ammonia partial pressure 50 Pa; 3 — at 1000 Pa

Typical I—V characteristic of the forward current in studied p-n structures presented as curve 1 in Fig. 1 has an exponential section which can be described as

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

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 [6].

Curves 2 and 3 in Fig. 1 were obtained in air under ammonia vapors partial pressures of 50Pa and 1000Pa, correspondingly. These curves illustrate that adsorption of ammonia molecules strongly enhances the forward current in the p-n junction. Curves 2 and 3 have exponential sections described with equation (1) at the same ideality constant as curve 1. This is evidence that the forward current caused by adsorbed ammonia molecules in studied p-n structures is due to surface recombination.

Curves 1—4 in Fig. 2 are I—V characteristics of the excess forward current ΔI in p-n junction due to adsorption of NH_3 molecules, measured under partial pressures 10Pa, 50Pa, 200Pa, and 1000Pa, respectively. It is seen that I—V curves of the excess current are non-linear. Therefore the excess current in silicon p-n junctions unlike III—V broad-gap semiconductors cannot be ascribed to formation of a conductive surface channel with a voltage-independent electron concentration.

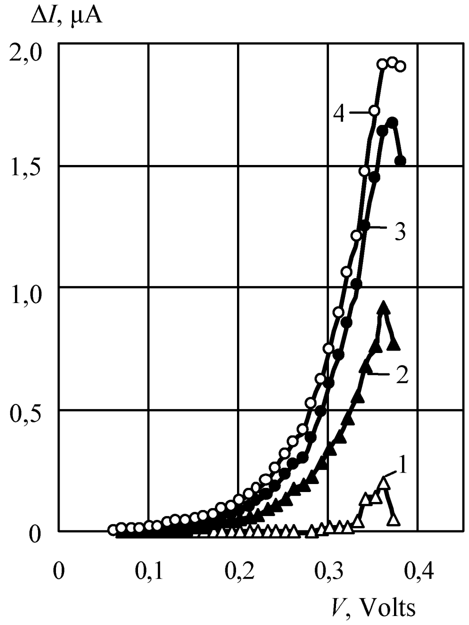

Fig. 2. I—V characteristics of the excess forward current due to ammonia molecules absorption at different NH_3 partial pressures, Pa: 1 — 10; 2 — 50; 3 — 200; 4 — 1000

Fig. 3 illustrates the dependence of the excess forward current in studied p-n structures on the ammonia partial pressure. Curves 1—3 were obtained from I—V characteristics and correspond to forward bias voltages 0.25V, 0.30V and 0.36V, respectively. The sensitivity of gas sensor can be defined as

$$S_I = \Delta I / \Delta P, \quad (2)$$

where ΔI is the change in the current, which corresponds to a change ΔP in the ammonia partial pressure. It is seen in Fig. 3 that S_I increases with bias voltage up to 0.36V and depends on the ammonia partial pressure. Maximum sensitivity was observed at $P < 100$ Pa.

2. MECHANISMS OF SENSITIVITY

Non-linear excess currents, due to NH3 molecules adsorption, were observed in p-n junctions on III—V semiconductors at sufficiently high forward biases [5] and explained as a result of the surface recombination enhanced by transverse electric field.

In the case of silicon p-n junctions, I—V curves measured in ammonia vapors are parallel to those obtained in air, as is seen from a comparison of curves 2 and 3 with curve 1 in Fig. 1. This suggests that the currents in air and in ammonia vapors are of similar mechanisms. The ideality coefficient of $n = 2$ corresponds to the current caused by the electron-hole recombination at deep states. For the current measured in air, these centers can be placed in the bulk depletion layer, as well as at the surface. And the recombination centers responsible for excess currents in ammonia vapors are localized at the surface.

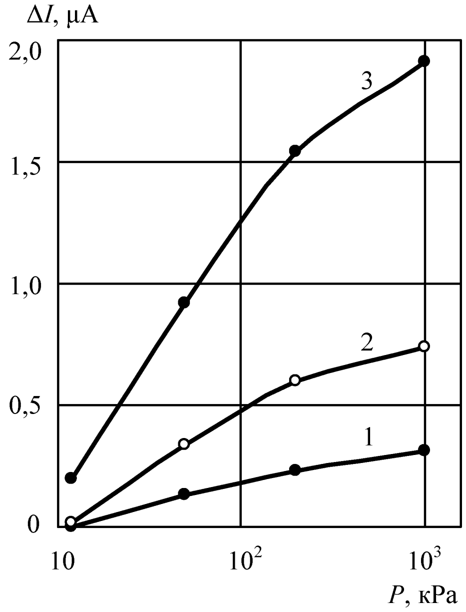

Fig. 3. Effect of the ammonia partial pressure on the excess forward current at different forward bias voltages: 1 — 0.25 V; 2 — 0.3 V; 3 — 0.36 V

Among mechanisms of the current increase in silicon p-n junctions observed in ammonia vapors are: a) enhancing of the effective p-n junction area;

b) increase in the capture cross section of surface states as an effect of strong transversal electric field; c) enhancing of np product at the surface due to electric field of captured ammonia ions; d) a change in the surface states density.

Fig. 4. depicts a schematic of the silicon p-n structure in ammonia vapors. 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. 4, the n-layer surrounds the p-region at the perimeter, and the effective p-n junction area is

$$S_{eff} = S_0 + \pi d w_p, \tag{3}$$

where S_0 is the geometrical area of the p-n junction; d is diameter of the junction; w_p is the p-layer thickness.

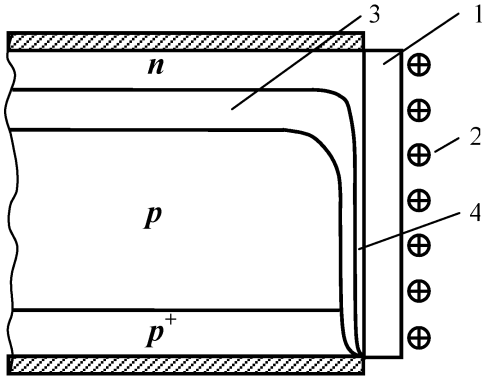

Fig. 4. Schematic of the p-n structure in NH_3 vapors: 1 — oxide layer; 2 — ions; 3 — depletion layer; 4 — conducting channel

The mechanism (a) is realized in the case, if the second item on the right in formula (3) is large enough. Than an increase in the current must occur at some ions surface density, and the current must be independent from the further raise of the vapors partial pressure. The maximum excess current predicted by this model is

$$\Delta I = I_0 \left(\pi d w_p / S_0\right), \tag{4}$$

where I_0 is the current in air.

In our case the second item on the right in formula (3) is small and cannot distinctly affect the current in p-n junction.

The mechanism (b) is due to an increase in the capture cross section of surface states as an effect of strong electric field due to captured ions. As the surface recombination occurs mainly in p-region, there is a potential barrier for holes recombining at surface states. And the cross section of surface states for holes capture can increase due to phonon-assisted tunneling [6] as

$$C_t = C_{t0} \exp\left[\frac{(q\hbar E_m)^2}{24 m_t (kT)^3}\right], \tag{5}$$

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 hole. As Em is proportional to the density of the adsorbed ions charge Q_i, the capture cross section (and the excess current) is predicted by this model to exponentially grow with the partial pressure of ammonia vapors. This effect must be observed in electric fields of the order of 10^5 V/cm. In studied structures, the excess current linearly (and sublinearly) increases with ammonia concentration, which disagrees with this model.

The model (c) takes into account an increase in np product at the surface due to transversal electric field. The excess forward current due to NH_3 molecules adsorption can be expressed as the sum of two components

$$\Delta I = I_{th} + I_S, \tag{6}$$

where I_{th} denotes the through current in the case of conductive channel formation; I_S is the surface recombination current

$$I_S = q l_P S \Delta n_0 L_{ns}, \tag{7}$$

where l_P is the free perimeter length of the p-n structure; S denotes the surface recombination velocity; Δn_0 is the maximum electron density at the surface in p-region; L_{ns} is the surface electron diffusion length, which can be expressed in equilibrium as

$$L_{ns} = \sqrt{D_{ns} w_{ns} / S}, \tag{8}$$

where D_{ns} is surface electron diffusion coefficient; w_{ns} is the effective thickness of the surface layer where electrons are localized in p-region; for the surface recombination velocity can be written

$$S = \sigma_{ns} v_n N_{se}, \tag{9}$$

where σ_{ns} is the cross section of surface states for electron capture; v_n denotes the thermal electron velocity; N_{se} is the density of empty surface states.

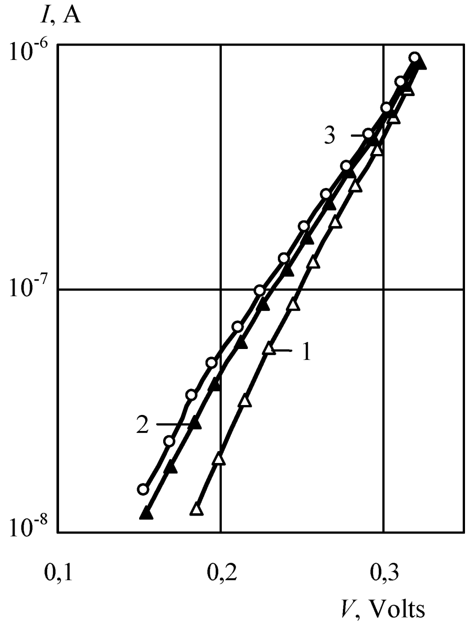

Fig. 5. Forward branches of I–V characteristics of a p-n structure in air after a treatment in ammonia vapors at NH_3 partial pressure 1000 Pa: 1 — after exposure in air 4 min; 2 — after 8 min; 3 — after 24 min

It is evident from equation (7) that an increase in the product of surface electron density Δn_0 and surface electron diffusion length L_{ns} can lead to an increase in the surface current due to ammonia molecules adsorption. This corresponds to mechanism (c). Computer calculations [4, 5] showed that transversal electric field, due to adsorbed ammonia ions, enhances both Δn_0 and L_{ns} in surface layer of a p-n junction.

The mechanism (d), namely a change in the surface states density can also take place. Fig. 5 presents I—V characteristics of a typical p-n structure measured in air after ammonia vapors treatment. Curves 1, 2 and 3 were obtained after exposition 4, 8 and 24 min in air, respectively. A comparison of curves 1 and 3 shows that ammonia vapors treatment decreases the currents in p-n junction to values lower than stationary ones. Therefore we can conclude that two effects can occur in p-n junctions in presence of ammonia vapors. First, the surface current increases due to enhancing of $\Delta n_0\ L_{ns}$ product in the electric field of adsorbed ions; and second, ammonia vapors partly etch out the surface recombination states that leads to a decrease in surface recombination current. These two processes are of different rate. The excess current is of electron nature and rises rapidly, while the change in the surface recombination states is due to chemical reaction and requires a time of 10 min. It is worth to note that an exposition in air restores the surface states density and the surface current in studied structures.

Reverse current in studied p-n junctions was more sensitive to ammonia vapors than the forward current. Fig. 6 presents I—V characteristics of a typical p-n structure measured in NH_3 vapors (curve 1) and after subsequent exposition in air. Curves 2, 3 and 4 were obtained after air-exposure of 2 min, 7 min and 23 min, correspondingly. The excess reverse current exceeds 5μA at ammonia partial pressure of 1000 Pa at a reverse bias voltage of 4 V.

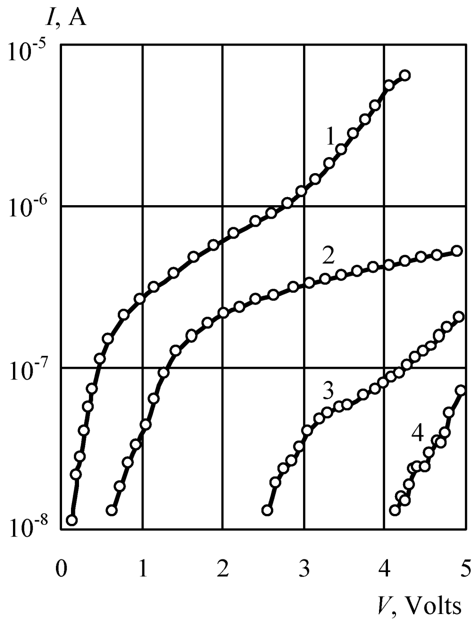

Fig. 6. Reverse branches of I—V characteristics of a p-n structure in ammonia vapors at NH_3 partial pressure 1000 Pa (1) and after subsequent exposure in air: 2 — 2 min; 3 — 7 min; 4 — 23 min

As is seen from Figs. 5 and 6, the kinetics of reverse current restoration in air after ammonia vapors treatment is slower than kinetics of forward current. After placing in air, the reverse current in p-n junctions monotonously decreases for ≈30 min.

Kinetics of excess forward and reverse currents of silicon p-n junctions in ammonia vapors also was different. The excess forward current rapidly increased after introduction of ammonia vapors into the container with the sample, and than slowly decreased. And the reverse current slowly monotonously increased.

CONCLUSIONS

Silicon p-n structures can be used as ammonia sensors. The change of I—V curves caused by ammonia molecules adsorption is reversible.

Two effects of adsorbed NH_3 molecules on I—V characteristics of the forward current were observed: a rapid increase of current and subsequent slow decrease. The sensitivity of silicon p-n structures to NH_3 vapors is caused by an increase in the surface recombination rate due to enhancing of electron density and the effective diffusion length of electrons in the surface layer. Ammonia vapors partly etch out surface recombination states in silicon, however these states are restored during an exposure of 30 min in air.

Maximum ammonia-sensibility of the forward current in silicon p-n junctions is observed at bias voltages of 0.35—0.36 V, which is remarkably lower than in III-V semiconductors. The sensibility S_I is constant at ammonia partial pressures P<100 Pa and reaches $2\cdot 10^{-8}$ A/Pa. At P>100 Pa the sensitivity lowers.

Adsorbed ammonia molecules dramatically change the reverse current in silicon p-n junctions, so that the absolute value of the excess reverse current $\Delta Ir >> \Delta I_f$. Therefore the regime of reverse bias is preferable for the ammonia sensor on silicon p-n junction.

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ВПЛИВ ПАРІВ АМІАКУ НА ПОВЕРХНЕВИЙ СТРУМ У КРЕМНІЄВИХ P-N ПЕРЕХОДАХ

Досліджено ВАХ прямого і зворотного струмів в кремнієвих p-n переходах в повітрі, в повітрі при наявності парів аміаку при різних значеннях парціального тиску NH_3, а також в повітрі після обробки в парах аміаку. Вплив адсорбованих молекул аміаку на прямий струм пояснюється такими процесами: а) зростанням інтенсивності поверхневої рекомбінації, зумовленим електричним полем іонів аміаку, локалізованих на зовнішній поверхні шару власного оксиду; б) стравлюванням частини поверхневих рекомбінаційних центрів. Зміни прямого і зворотного струмів оборотні, так що кремнієві p-n переходи можна використовувати як сенсори парів аміаку.

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ВЛИЯНИЕ ПАРОВ АММИАКА НА ПОВЕРХНОСТНЫЙ ТОК В КРЕМНИЕВЫХ P-N ПЕРЕХОДАХ

Исследованы ВАХ прямого и обратного токов в кремниевых p-n переходах в воздухе, в воздухе при наличии паров аммиака при различных значениях парциального давления NH_3, а также в воздухе после обработки в парах аммиака. Влияние адсорбированных молекул аммиака на прямой ток объясняется такими процессами: а) ростом интенсивности поверхностной рекомбинации, обусловленным электрическим полем ионов аммиака, локализованных на внешней поверхности слоя собственного оксида; б) стравливанием части поверхностных рекомбинационных центров. Изменения прямого и обратного токов обратимы, так что кремниевые p-n переходы можно использовать как сенсоры паров аммиака.