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EFFECT OF WATER VAPORS ON THE TIME-RESOLVED SURFACE CURRENT INDUCED BY AMMONIA MOLECULES ADSORPTION IN GaAs P-N JUNCTIONS

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The time-resolved surface current in an n-conducting channel, due to ammonia and water molecules adsorption in GaAs p-n structures was studied. It is shown that the presence of water vapors in the ambient atmosphere strongly affects the current decay curves after the ammonia vapors removal. The current decay curve in this case has three exponential components with different characteristic times: , and , as well as a component with . The results are explained in terms of a simple model taking into account a dynamic equilibrium between the free electrons in the conducting channel and electrons on slow surface centers. Each decay curve exponential component is due to the emptying of corresponding centers. The characteristic time of a current decay curve exponential component is determined by the depth and density of the corresponding surface levels, as well as the conducting channel thickness.

Key words: p-n structure, ammonia vapors, water vapors, adsorption, conducting channel, current decay, surface centers.

1. Introduction

Barrier structures on Si and GaAs, such as *p-n* junctions [1–4], porous membranes [5, 6], and nanowires [7], are promising materials for the gas sensors development. The Si *p-n* junctions can be combined in a transistor, which has much higher gas sensitivity than a single junction [8]. They can be easy integrated into microelectronic circuits. And the GaAs *p-n* junctions have a very high gas sensitivity, as well as a threshold ammonia vapors partial pressure of 0,1 Pa [4].

The sensitivity of the mentioned barrier structures, as well of GaP [9] and InGaN [10] *p-n* junctions, to ammonia vapors was observed only in presence of water vapors.

The aim of this work is a study of the influence of water vapors on the time resolved surface current in GaAs *p-n* structures, due to ammonia molecules adsorption.

2. Experiment

The measurements were carried out on GaAs *p-n* structures, described in the previous paper [10]. *I-V* characteristics of the forward and reverse currents were measured in air with various concentrations of ammonia vapors and saturated water vapors at T=290 K. The chemical composition of the ambient atmosphere was changed in 2 s by placing the sample in an appropriate container.

The curve 1 in Fig.1 represents the time dependence of the forward current, measured at V=0,3 Volts in a *p-n* structure, which was first placed in dry air; at t_1=200 s – in air with wet ammonia vapors (NH_3 partial pressure P=200 Pa); at t_2=3800 s – in dry air. After changing the ambient atmosphere from wet ammonia vapors to dry air (at $t>t_2$) the current drops from I_{max}=122 nA to 0,1 I_{max} in a time of 71 s. In the case of the curve 2, at t_2=3800 s the sample was placed in the atmosphere, containing air and saturated water vapors. And after 3 hours, at t_3=14600 s the sample was placed in dry air.

It is seen that the current decay curve 2 has three different sections: a "fast" section; a "slow" section; and a drop after the atmosphere changing from wet air to dry air.

Fig. 2 shows the time dependence of the current in the same sample for a following atmosphere change: dry air → (t_1) air + water vapors→(t_2) dry air. It is seen from Fig. 2, that maximum current in wet air is of 8,2 nA, which is considerably lower than in the “slow” component of the curve 2 in Fig. 1. This indicates that the slow decrease in the current after the atmosphere change from wet ammonia vapors to wet air can be explained only taking into account the presence of some electrically active centers on the crystal surface.

3. Discussion

The experimental results can be explained with the model, depicted in fig. 3 [11]. Ionized ammonia molecules 2 are located on the natural oxide surface

Their electric field bends the depletion layer 3 and forms a *n*-conducting channel 4. The forward current consists of two components. Arrow *a* corresponds to the through component I_t of the current in the channel

And arrow *b* represents the current component I_i due to electron injection from the channel into the p$^+$ layer at the contact.

The adsorbed water molecules (without ammonia molecules) also form such an *n*-conducting channel and remarkably enhance the current in the *p-n* junction, which is evident in Fig. 2.

In the uniform section of the channel, the following equation can be written

$$N_{ns} = N_i - N_{sf}^- - N_{ss}^- + N_{sD}^+ - N_{sA}^-, \qquad (1)$$

where N_{ns} is the free electrons number in the channel per 1cm^2 of the surface; N_i is the adsorbed ions surface density; N_{sf}^- and N_{ss}^- are the densities of filled fast and slow acceptor surface centers, respectively; N_{sD}^+ is the ionized donor surface centers density; N_{sA}^- is the number of ionized acceptor centers in the surface depletion layer per 1cm^2 of the surface:

$$N_{sA}^- = N_A^- w_s; \qquad (2)$$

N_A^- is the ionized acceptor concentration in *p*- region; w_s is the surface depletion layer thickness [10].region; w_s is the surface depletion layer thickness [10].

The section of the curve 2 in Fig. 1 at $t > t_2$ can be decomposited in three exponential components, presented in Fig. 4. The characteristic times for the fast component, presented in Fig. 4a is $\tau_1 = 30$ s.

For two “slow” components, showed in Fig. 4b, $\tau_2 = 1900$ s and $\tau_3 = 9400$ s, respectively, are obtained.

The mentioned decomposition includes also a “constant” component with a characteristic time $\tau_4 \gg \tau_3$ with the amplitude $I_4^0 = 30$ nA. The fast decay component of the curve 2 in Fig. 1 can be ascribed to the desorption of ammonia ions. An analogous component has curve 1 in Fig. 1.

The components 2, 3 and 4 of the curve 2 in Fig. 1 can be explained taking into account presence of some slow centers on the naturally oxidized GaAs surface [4, 12, 13]. These centers are responsible for the peculiarities of the stationary characteristics [4] and the response time [13] of GaAs p-n structures as gas sensors.

The gradual descent in the curve 2 in Fig. 1 at $t > t_2$ is due to gradual decrease in the density of filled slow acceptor surface centers N_{ss}^- in (1). After an atmosphere ammonia → water vapors changing, the ions surface density drops. Therefore the electrons number N_{ns} in the conducting channel strongly falls down, which corresponds to the «fast» exponential component of the current decay curve, presented in Fig. 4A. And the electrons number N_{ss}^- on slow acceptor surface centers gradually decreases due to their thermal transitions to the conduction band. These transitions generate free electrons in the channel, slowing the decrease of the current. This effect can be described with a differential equation

$$\frac{d(N_{ns} + N_{ss}^-)}{dt} = G - N_{ns}/\tau, \qquad (3)$$

where G is the electrons generation rate in the cannel due to donors (water molecules) adsorption; τ is the electrons life time in the channel. In the case of a dynamic equilibrium between the free and captured electrons, a relation is valid

$$N_{ss}^- = N_{ns} N_{ss} /(N_c d) \exp[(E_c - E_{ss})/(kT)], \qquad (4)$$

where N_{ss} is the full density of slow acceptor surface centers; N_c denotes the effective states density in the c-band; *d* is the channel thickness; $E_c - E_{ss}$ is the slow surface acceptor level depth; *kT* is the Boltzmann factor.

The initial condition for equation (3) is

$$N_{ns}(0) = N_{ns}^{0} > G\tau \,, \qquad (5)$$

because at t=0 the ambient atmosphere is changed from wet ammonia to water vapors.

Equation (3) under this initial condition has a solution

$$N_{ns}(t) = G\tau + \left(N_{ns}^{0} - G\tau\right)\exp(-t/\tau_{eff}) \,, \qquad (6)$$

where

$$\tau_{eff} = (1+\nu)\tau \,, \qquad (7)$$

and

$$\nu = N_{ss}/(N_c d)\exp[(E_c - E_{ss})/(kT)] \,. \qquad (8)$$

It is seen from (7) and (8) that the channel current decay time after an ammonia → water vapors atmosphere change depends from the depth and density of slow surface levels, as well from the channel thickness. Two exponential components of the current decay curve, presented in Fig. 4b, are due to the presence of two slow surface centers on the GaAs natural oxide.

4. Conclusions

A change from wet ammonia vapors to water vapors in the ambient atmosphere results in a decrease of the surface current in GaAs *p-n* junctions. The current decay curve has a fast exponential component with a characteristic time τ_1<100 s and three slow components with $\tau_4 \gg \tau_3 \gg \tau_2 \gg \tau_1$.

The complicated shape of the current decay curve can be explained in terms of a simple model taking into account a dynamic equilibrium between the free electrons in the conducting channel and electrons on slow surface centers. Each decay curve exponential component is due to the emptying of corresponding centers.

The characteristic time of a current decay curve exponential component is determined by the depth and density of the corresponding surface levels, as well as the conducting channel thickness.

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Summary

The time-resolved surface current in an *n*-conducting channel, due to ammonia and water molecules adsorption in GaAs *p-n* structures was studied. It is shown that the presence of water vapors in the ambient atmosphere strongly affects the current decay curves after the ammonia vapors removal. The current decay curve in this case has three exponential components with different characteristic times: $\tau_1 = 30$ s, $\tau_2 = 1900$ s and $\tau_3 = 9400$ s, as well as a component with $\tau_4 \gg \tau_3$. The results are explained in terms of a simple model taking into account a dynamic equilibrium between the free electrons in the conducting channel and electrons on slow surface centers. Each decay curve exponential component is due to the emptying of corresponding centers. The characteristic time of a current decay curve exponential component is determined by the depth and density of the corresponding surface levels, as well as the conducting channel thickness.

Key words: *p-n* structure, ammonia vapors, water vapors, adsorption, conducting channel, current decay, surface centers

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ВПЛИВ ПАРІВ ВОДИ НА КІНЕТИКУ ПОВЕРХНЕВОГО СТРУМУ, ІНДУКОВАНОГО АДСОРБЦІЄЮ МОЛЕКУЛ АМІАКУ В P-N ПЕРЕХОДАХ НА ОСНОВІ GaAs

Резюме

Досліджено кінетику поверхневого струму в *n*-провідному каналі, обумовленому адсорбцією молекул аміаку і води, в *p-n* переходах н основі GaAs. Показано, що наявність парів води у навколишньому середовищі сильно впливає на криві спадання струму після видалення парів аміаку. Крива спадання струму в цьому випадку має три експоненціальні компоненти з різними значеннями характеристичного часу: $\tau_1 = 30$ с, $\tau_2 = 1900$ с і $\tau_3 = 9400$ с, а також компоненту з $\tau_4 \gg \tau_3$. Результати пояснюються в рамках простої моделі, яка враховує динамічну рівновагу між вільними електронами у провідному каналі та електронами на повільних поверхневих центрах. Кожна експоненціальна компонента обумовлена спустошенням відповідних центрів. Характеристичний час кожної експоненціальної компоненти кривої спадання струму визначається глибиною і щільністю відповідних поверхневих рівнів, а також товщиною провідного каналу.

Ключові слова: *p-n* структура, пари аміаку, водяні пари, адсорбція, провідний канал, спадання струму, поверхневі центри.

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ВЛИЯНИЕ ПАРОВ ВОДЫ НА КИНЕТИКУ ПОВЕРХНОСТНОГО ТОКА, ИНДУЦИРОВАННОГО АДСОРБЦИЕЙ МОЛЕКУЛ АММИАКА В P-N ПЕРЕХОДАХ НА ОСНОВЕ GaAs

Резюме

Исследована кинетика поверхностного тока в *n*-проводящем канале, обусловленном адсорбцией молекул аммиака и воды, в *p-n* переходах н основе GaAs. Показано, что наличие паров воды в окружающей среде сильно влияет на кривые спадания тока после удаления паров аммиака. Кривая спадания тока в этом случае имеет три экспоненциальные компоненты с различными значениями характеристического времени: $\tau_1 = 30$ с, $\tau_2 = 1900$ с и $\tau_3 = 9400$ с, а также компоненту с $\tau_4 \gg \tau_3$. Результаты объясняются в рамках простой модели, которая учитывает динамическое равновесие между свободными электронами в проводящем канале и электронами на медленных поверхностных центрах. Характеристическое время каждой экспоненциальной компоненты кривой спадания тока определяется глубиной и плотностью соответствующих поверхностных уровней, а также толщиной проводящего канала.

Ключевые слова: *p-n* структура, пары аммиака, водные пары, адсорбция, проводящий канал, спадание тока, поверхностные центры.