INFLUENCE OF ATOMIC HYDROGEN ON THE SURFACE AND THE NEAR-SURFACE LAYERS OF GERMANIUM CRYSTALS

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Influence of atomic hydrogen on single crystals of germanium at temperatures of 300–310 K, the pressure of 20 Pa in the working chamber, and the concentration of atomic hydrogen of about 10^{19} m^{-3} has been investigated. The specimens of n-Ge with a specific resistance $\rho = 15\ \Omega \cdot$ cm underwent a treatment for 100–300 s. To study the influence of atomic hydrogen on crystals, we measured the current-voltage characteristics (CVCs), specimen resistances, and the work function by the dynamic capacitor method. The influence of atomic hydrogen has been shown to change the electrophysical parameters of crystals, including the modification of a charge state of near-surface layers. A physical mechanism which explains the results of researches has been proposed.

Introduction

A pronounced trend in the development of modern science and technique lies in the change-over to nanoelectronics, which means the reduction of the dimensions of elements to the submicronic scale and, therefore, results in enhancing the role of elements' surfaces [1]. Among the methods which allow one to purposefully modify the surface properties is the treatment of the surface by active gas particles, in particular by atomic hydrogen. Such processes as the dissipation of the recombination energy of atomic hydrogen into molecular one [2], the action of chemically active atomic hydrogen on the surface, adsorption and desorption, the variation of a surface microrelief, generation of defects [3], and so on, which take place during the interaction of atomic hydrogen with crystals, will essentially affect the properties of semiconductor crystals. Earlier, the researches dealing with the cleaning of semiconductor surfaces in the atmosphere of atomic gases [4, 5], the stabilization of a state of the surface of semiconductor elements [6], the variation of structure parameters [7], and the low-temperature diffusion under the influence of atomic hydrogen [8] have been carried out. These studies showed that the interaction between atomic hydrogen and semiconductors is rather complicated and needs further researches. The present work is devoted to studying the interaction between atomic hydrogen and monoatomic semiconductors, the germanium crystals being taken as an example.

Experimental Method

We studied crystals of germanium of the n-type with the specific resistance $\rho = 15\ \Omega \cdot$ cm and the density of dislocations of 10^2 cm^{-2}. The sides of the crystals differed by the kind of a treatment (one side and and the other were mechanically and chemically polished, respectively), and, accordingly, by the degree of roughness.

Before the treatment, specimens were cleared. This procedure comprised chemical etching and washing out from organic contaminations. The crystal washing out consisted of the specimen degreasing in CCl_4 followed by its flushing in deionized water. The mixture of HNO_3, HF, and CH_3COOH in the proportion 5:3:3 was used for the chemical etching of germanium crystals [9]. After clearing, the crystals were held under ambient conditions for some time in order that the equilibrium state is recovered.

Atomic hydrogen was obtained by dissociation of molecular hydrogen in a plasma created by a high-frequency discharge. Molecular hydrogen was separated from a 20%-solution of KOH in distilled water by electrolysis with a current density of 0.01 A/cm^2. The small current density during electrolysis allowed us to lower the concentrations of oxygen and alkaline metal vapors in the environment of molecular hydrogen to the minimum, having reduced thus the influence of undesirable impurities on the specimens under investigation. Hydrogen was made pass through a forebaloon for the drops of KOH to be captured and through a drying column filled with granulated alkali KOH. Then, it entered into the working chamber, where its dissociation in the plasma into atomic hydrogen took place. Thus, the atom-molecular mixture entered into the chamber. The concentration of hydrogen atoms

was measured by the calorimetric method and was approximately 10^{14} cm^{-3} at a pressure of about 20 Pa in the working chamber.

The specimens to be studied were placed into the working chamber at a distance of 25 cm from the discharge region, which allowed the hydroxyl radicals and hydrogen ions to escape reaching the specimen [10]. The time of the exposure of the studied crystals to atomic hydrogen was varied from 100 to 300 s.

The work function for an electron was determined by measurements of the contact-potential difference (CPD) within the dynamic capacitor method [11]. The accuracy of measurements of the CPD was ± 2 mV.

The numerical value of the work function of a specimen, $A_{\rm sp}$, was determined as the difference between the work function $A_{\rm st}$ of a standard and the CPD Δ between the standard and the sample. The probe made of gold ($A_{\rm Au} = 4.3$ eV) served as a standard. The work function was determined according to the formula

$$A_{\rm sp} = A_{\rm Au} - \Delta.$$

The spread of values for the CPD over the surface did not exceed ± 0.05 eV for all the specimens.

The resistance was measured in two ways. In the first case, we used an ASM-100M standard installation for measuring the surface and specific resistances of semiconductor crystals, which allowed us to measure the relative variation of the surface resistance of the samples with an accuracy of 1%. In the alternative case, a test structure for researching the variation of the crystal resistance during its treatment was created. For this purpose, a lead film (lead and germanium make ohmic contact) was deposited through a mask onto a germanium crystal by thermal evaporation in vacuum. An elastic metal contact was pressed to the metal film. The film with contacts was covered by a protective layer proof against atomic hydrogen. The availability of the test structure allowed the variation of the structure resistance to be fixed with a high accuracy directly in the course of the treatment.

The measurements of the CPD and the resistance were carried out immediately before and after the treatment in the environment of atomic hydrogen, as well as after 24 and 48 h of the holding of the crystal under ambient conditions.

Experimental Results and Their Discussion

The results of test treatments, both short- and long- (up to 30 min) term, of the crystals in the environment of molecular hydrogen under the same conditions as for the atomic hydrogen environment revealed the stability and invariance of the CPD and the resistance of the crystals. At the same time, it was found that the treatment of germanium crystals by atomic hydrogen resulted in a change of the work function of an electron, i.e. it was the interaction of the crystal with atomic hydrogen that resulted in the variation of crystal characteristics. An increase of the work function was observed for all the specimens that underwent the treatment in the environment of atomic-molecular hydrogen during various time intervals. The increase of $A_{\rm sp}$ occurred at both the investigated surfaces of the specimens possessing different roughnesses. But, for all the samples, the work function at the mechanically polished surface, in general, was higher than that at the chemically etched one. This fact can be explained by the larger number of defects, the presence of which increases the work function at the rougher side of the crystal [12].

The measurements showed that the work function of an electron increased by no less than 0.2 eV for all the specimens staying in the environment of atomic hydrogen during various times.

The measurements of the quantity $A_{\rm sp}$ after the crystals being held for 24 and 48 h in the air under ambient conditions demonstrated the reduction of the work function for all the crystals. Besides, the crystals that were exposed to atomic hydrogen during different times differed by the degree of relaxation of the work function value. After 48 h of the specimen being held under ambient conditions, the quantity $A_{\rm sp}$ for the samples, which had been treated for a short term (100 s), was observed to diminish practically to the initial value. The work function for the crystals, which were exposed to atomic hydrogen for a longer time, remained larger than the initial value within 48 h.

The dependence of the work function on the holding time for crystals undergone a short-term exposure is presented in Fig. 1. As can be seen from the figure, the treatment of germanium in the environment of atomic hydrogen results in the increase of $A_{\rm sp}$, and the following holding leads to its relaxation.

The increase of $A_{\rm sp}$ may be connected to a change of the potential on the crystal surface owing to the adsorption of atomic hydrogen and its interaction with the crystal surface and to the corresponding bending of energy bands, since the process was carried out at room temperature during a short time interval. To explain the observed phenomenon, a model of the interaction of atomic hydrogen with the surface of germanium was proposed. Namely, owing to the interaction of atomic hydrogen with the semiconductor surface, surface

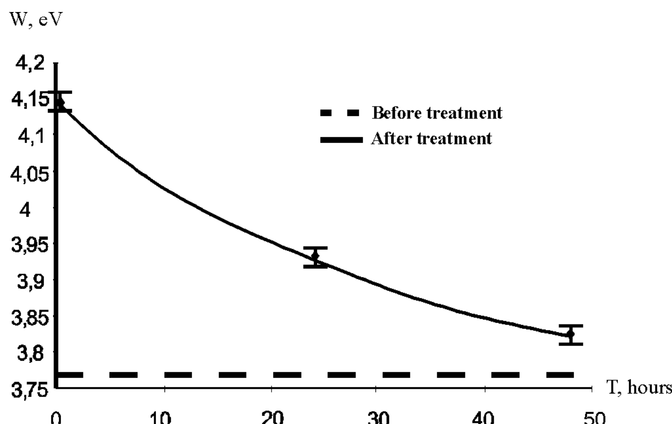

Fig. 1. The variation in time of the work function of n-Ge crystals exposed to atomic hydrogen for 100 s

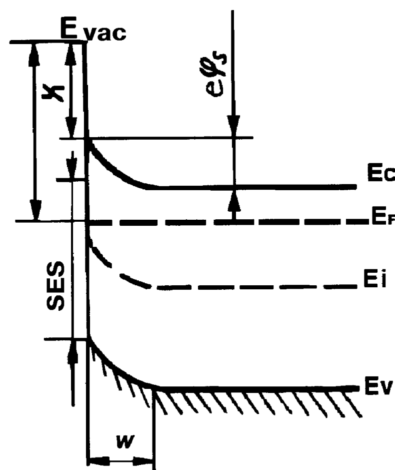

Fig. 2. Emergence of the surface states in semiconductors of the n-type

electron states (SESs) appear, and, therefore, the modification of the electrophysical properties of near-surface layers in germanium takes place. According to the direction of the band bending, which corresponds to an increase of the work function, the surface states belong to the acceptor type [13]. It is to be noted that the adsorption of hydrogen can possess either the donor or the acceptor type [14]. According to [14], the surface of an adsorbent is charged positively if a small amount of hydrogen is absorbed, because the chemosorbed atoms of hydrogen execute the donor function. Provided absorption should reach a certain level, the sign on the surface charge can change and the surface will be charged negatively [14]. Thus, the interaction of atomic hydrogen with the surface of a single crystal of germanium has a rather complicated character. Taking into account the sign of the charge of arising levels, it is possible to admit that there was the strong absorption of hydrogen in the near-surface layers of the semiconductor followed by the formation of surface acceptor levels.

The presence of a negative charge at the surface states of the acceptor type results in the bending of energy bands upwards in the energy scheme by a value of φ_s (Fig. 2). The negative charge creates a surface barrier to electrons, owing to which the region of space charge will include the near-surface electron-depleted layer. Provided that the bands at the surface are planar before the interaction, the work function A will increase by the value of the band bending φ_s:

$$A = \chi + (E_C - E_\mathrm{F}) + \varphi_s, \qquad (1)$$

where χ is the electron affinity, E_F is the position of the Fermi level reckoned from the vacuum one, E_c is the bottom energy of the conduction band, and φ_s is the surface potential.

Therefore, the emergence of a negative surface potential is accompanied by the increase of the work function, the bending of energy bands near the surface, and the redistribution of the concentration of current carriers, that is, by a variation of the resistance of near-surface layers. The width w of the near-surface layer, which will have the larger specific resistivity in comparison with the bulk of the crystal, depends on the concentration of the doping impurity and the barrier height [15]:

$$w = \sqrt{\frac{2\varepsilon\varepsilon_0\varphi_s}{eN_d}} \qquad (2)$$

where $\varepsilon\varepsilon_0$ is the dielectric permittivity of the semiconductor, N_d is the impurity concentration, and e is the electron charge.

The calculated thickness w of the depleted layer of the researched structure 450 μm in thickness was about 2.23×10^{-3} mm for the surface potential of 0.3 eV, which corresponds to a variation of the effective resistance of such a structure by about 0.5%. This correlates with the data obtained when measuring the resistance of the test structure during and after its treatment in the chamber (Fig. 3) in the assumption that the potential of the surface is greater during and immediately after the treatment prior to the chamber depressurization and the contact of a specimen with the environment, than that measured after the latter.

The researches of the resistance of the specimens showed an increase of the surface resistance of the crystals, while the measurements of the effective

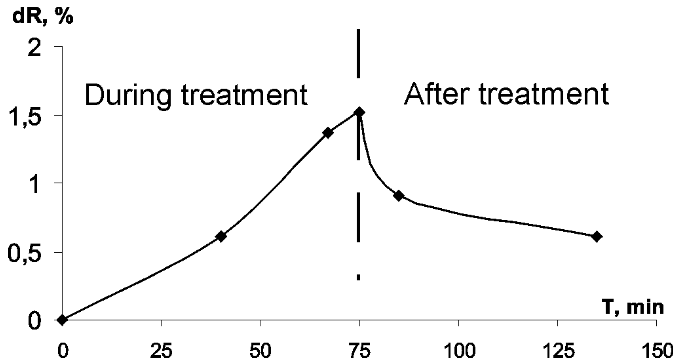

Fig. 3. Relative variation of the test structure resistance during the treatment by atomic hydrogen and immediately after it

resistance of the test structure, being exposed to the atmosphere of atomic hydrogen, showed an increase in the resistance of the specimen, i.e. confirmed the proposed model. Under the treatment, the effective resistance of the investigated n-Ge structure increased by 1–2% (Fig. 3) for the crystal 450 μm in thickness. After the termination of the atomic hydrogen action upon the structure, a reduction of the resistance was observed, which was explained by a reduction of the negative charge in the surface states, i.e. the variation of the resistance correlated with the variation of the surface potential of the specimens concerned.

Conclusions

Hence, the process of interaction of germanium crystals with the environment of atomic hydrogen is accompanied by a complicated complex of physical and chemical processes, which results in a modification of the electrophysical parameters of the crystals. But the interaction of the crystals with the environment of molecular hydrogen for a long time (up to 120 min) does not lead to such variations.

Owing to the interaction of atomic hydrogen with the surface of the germanium crystals, the formation of acceptor surface states takes place. As a result, the bands in the energy diagram of the semiconductor become bent and the work function increases by no less than 0.2 eV, as the experimental data evidence for. Owing to the bending of the bands in the near-surface layers of the semiconductor, an electron-depleted near-surface layer appears. That is, the treatment of germanium crystals results in a variation of the resistance of the near-surface layers, which is corroborated experimentally.

The effect of the crystal surface treatment by atomic hydrogen gradually decreases under the action of the environment. While the crystals are staying under ambient conditions, the negative charge in the surface electron states decreases, which corresponds to a reduction of the work function of electrons in experiment and to a reduction of the resistance of the n-germanium specimens.

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ВПЛИВ АТОМАРНОГО ВОДНЮ НА ПОВЕРХНЮ
ТА ПРИПОВЕРХНЕВІ ШАРИ КРИСТАЛІВ ГЕРМАНІЮ

Є.Л. Жавжаров, В.М. Матюшин

Р е з ю м е

Досліджено вплив атомарного водню на монокристали германію при температурах 300—310 К тиску у робочій камері 20

Па та концентрації атомарного водню порядку 10^{19} м$^{-3}$. Зразки германію n-типу з питомим опором $\rho = 15$ Ом·см обробляли на протязі 100—300 с. Для вивчення впливу атомарного водню на кристали вимірювали вольт-амперні характеристики (ВАХ), опір зразків та роботу виходу методом динамічного конденсатора. Показано, що вплив атомарного водню приводить до зміни електрофізичних параметрів кристалів, у тому числі і до зміни зарядового стану приповерхневих шарів. Запропоновано фізичний механізм, який пояснює результати досліджень.