MODIFICATION OF THE ELECTROPHYSICAL PROPERTIES OF A REAL GERMANIUM SURFACE ATTENDING THE ADSORPTION OF HYDROGEN ATOMS

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Adsorption of hydrogen atoms on a real surface of a germanium monocrystal vacuumed at 700°K results in a significant rise in the monotonic component of the surface recombination rate at virtually unchanged capture of charge carriers onto fast surface states. The quasicontinuous spectrum of recombination nuclei is independent of the spectrum of fast states.

Chemosorption of hydrogen atoms is frequently employed as a convenient model system in analytic studies of surface physics [1,2]. The few experiments with adsorption of hydrogen atoms were performed primarily on atomically pure Ge surfaces [2,3] and in the Ge-electrolyte system [4]. The real Ge surface, bordering on the vacuum, has been least explored in this respect.

We employed a combined experimental field-effect facility [5] for measuring the modification of the surface potential Y_s, capture onto fast surface states Q_{fs} and rates of surface recombination S on a real (111) Ge surface following adsorption of hydrogen atoms. The n-Ge monocrystals (ρ = 30-35 ohm•cm) were etched in a standard peroxide etching agent and then dehydrated for 5 min in oil-free vacuum of approximately 10^{-8} mm Hg at T_B = 500°K (Ge-500) and 700°K (Ge-700). The molecular hydrogen was fed to the vacuum system through a zeolite trap and a palladium capillary. Atomic hydrogen was obtained by hydrolizing H_2 on a hot tungsten wire and in a high frequency discharge.

Unlike the study by Neizvestnyi with his coworkers [6], adsorption of molecular hydrogen did not modify the electrophysical properties of the surfaces of Ge-500 and Ge-700 specimens. The latter is confirmed by data of Kompaniets [7], according to which the adhesion factor of H_2 is less than 10^{-8}. Adsorption of hydrogen atoms on the Ge-500 specimen shifted Y_{s0} by 1.5-2 kT/q in the direction of positive values and virtually had no effect on S and Q_{fs} (Fig. 1). After heating of specimens at 700°K in accordance with the technique of Novototskii-Vlasov [5], only the monotonic component of the surface recombination rate S_m was observed (Fig. 2). Adsorption of atomic hydrogen resulted in shifting Y_{s0} by 1.5-3 kT/q into the positive region (see the arrows in Fig. 2), which does not contradict the results of Surnev and Bliznakov [3]. Simultaneously with the change in Y_{s0}, and with approximately the same kinetics the value of S_m increased, as can

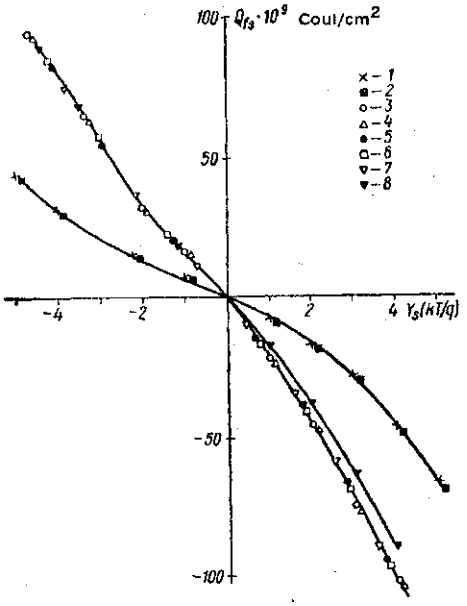

Fig. 1

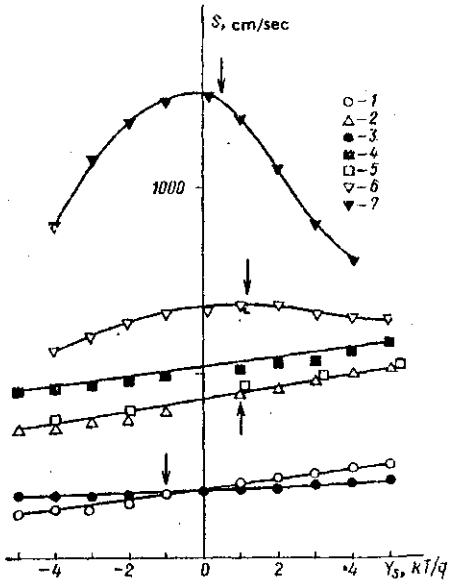

Fig. 2

Fig. 1. Curves of capture onto fast surface states: 1) Ge-500 specimens; 2) after adsorption of atomic hydrogen on Ge-500 specimens; 3) Ge-700 specimens; 4) after adsorption of atomic hydrogen on Ge-700 specimens; 5) after heating of Ge(H) specimens at 600°K; 6) after adsorption of pyridine on Ge(H) specimens; 7) after adsorption of H_2O on Ge(H) specimens; 8) after heating of Ge(H) specimens in O_2.

Fig. 2. Curve of the surface recombination rate vs. Y_s: 1) Ge-700 specimens; 2) after adsorption of atomic hydrogen on Ge-700 specimens; 3) after heating of Ge(H) specimens at 600°K; 4) after adsorption of atomic hydrogen on Ge-700 upon supply of negative (with respect to Ge) potential to the grid; 5) after adsorption of pyridine on a Ge(H) specimen; 6) after adsorption of H_2O on a Ge(H) specimens; 7) after heating of Ge(H) specimens in O_2.

be seen in Fig. 2. The steady state values of Y_{s0} and S_m were attained after holding the specimen for 40 min in an atmosphere of hydrogen atoms. Curves of capture onto the fast states virtually did not change after adsorption of atomic hydrogen (see Fig. 1). The evacuation of the specimen, which was performed at 300°K after adsorption virtually did not change Y_{s0}, Q_{fs} and S_m. However, when T_B was raised to 600°K the above parameters took on values close to starting values (with respect to adsorption), which is in agreement with data on desorption of hydrogen [7]. Adsorption of atomic hydrogen, obtained both by pyrolysis and in the high frequency discharge, resulted in the same changes in Y_{s0}, Q_{fs} and S_m. To establish the existence of adsorption of charged particles (H^+) a grid, charged with respect to Ge, was placed between the specimen and the source. The application to the grid of potentials of different signs virtually did not change S_m - see Fig. 2. The presence of H^+ on the surface is also contraindicated by data on adsorption of proton-acceptor pyridine molecules (PyH^+ complexes). Adsorption of Py had no effect on Q_{fs} and S_m (see Figs. 1 and 2).

The significant change in S_m upon adsorption of atomic hydrogen is an additional confirmation of the data of Neizvestnyi et al. [8], who showed that this component of the surface recombination rate is not related to recombination in the region of the space charge. The steep rise in S_m at constant Q_{fs} apparently points to the fact that the system of nuclei responsible for recombination is independent of the system of fast states. Most probably chemosorption of atomic hydrogen is accompanied by breaking of Ge-Ge or Ge-O-Ge bonds on the Ge-GeO_2 boundary and restructuring of the boundary layer structure. This involves formation of the GeH hydride groups, which is confirmed by IR spectra [9]. In the case of atomically pure surface of Ge the reconstruction of the surface and formation of GeH groups are indicated by data of diffraction of slow electrons and of UV spectroscopy [2]. Hydrogen atoms at such surfaces interact with free Ge radicals [1], and then the surface acquires a negative charge [3]. In the case of Ge-700 specimens the interaction of hydrogen atoms with chemically saturated bonds results in formation of GeH and GeOH groups, with positive charging of the surface. The Ge-vacuum interface differs from that of Ge-electrolyte. In the presence of an electrolyte the adsorption of hydrogen was accompanied by cymbate growth of the bell-shaped component of the surface recombination rate and of Q_{fs} [4].

Holding a specimen with hydrated surface (Ge(H)) in water vapor ($p \approx 8$ mm Hg) for 2 hr resulted in some distortion of linearity of $S_m(Y_s)$; the bell-shaped component manifested itself more clearly after heating the Ge(H) specimen in dry oxygen at 400°K - see Fig. 2. Note that H_2O was found to precipitate in spectra of thermodesorption from the Ge(H) specimens, following adsorption of O_2 [7]. Adsorption of O_2 and H_2O involves partial breakup of GeH groups and additional oxidation of the Ge surface. These processes result in restructuring of the subsurface region of the semiconductor so that a part of states may drop out from the quasicontinuous spectrum of recombination levels. The latter, according to the model of Neizvestnyi and Ovsyuk [10], will result in appearance of the bell-shaped component of the surface recombination rate.

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