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ELECTRONIC PROPERTIES OF SEMICONDUCTORS

Effect of Hydrostatic Pressure on the Static Permittivity of Germanium

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Abstract—The dependence of the static permittivity of single-crystal germanium on hydrostatic pressure up to $P \approx 7.4$ GPa is studied experimentally. As the pressure is increased to $P \approx 4$ GPa, the permittivity of Ge decreases by a factor of ~13 to $\varepsilon = 1.22$. As the pressure is increased further to $P \approx 7$ GPa, a moderate increase in ε to the initial value is observed. In the range 7–7.4 GPa, the permittivity increases to a value larger than 1000. The experimental dependences obtained in the study substantially differ from the previously known dependences.

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To date, no reliable data are available on such a fundamental electrical characteristic of single-crystal germanium as the dependence of its permittivity on hydrostatic pressure $\varepsilon(P)$. Studies of the dependence $\varepsilon(P)$ in the potential of interatomic interaction at distances smaller than equilibrium distances is of interest for a rather wide range of problems in semiconductor physics and technology. At present, there is a small number of studies concerned with the dependence $\varepsilon(P)$ of germanium and described in monographs [1, 2]. These experimental results markedly differ from those reported in [3] and experimentally obtained recently [4]. In [4], the dependence $\varepsilon(P)$ at pressures of up to 8 GPa is reported.

In all of the experimental studies, the pressure dependence of the polarizability is determined by the indirect method based on the Lorentz–Lorenz formula, in which the polarizability of a substance α is related to the refractive index n through the expression

$$R = V(n^2 - 1)/(n^2 + 2) = (4/3)\pi N\alpha. \tag{1}$$

Here, refraction R is expressed in units of volume V (cm^3 mol^{-1}) and the polarizability is $\alpha = 3R/4\pi N = 3/9630 \times 10^{-25}R$.

In these studies, the pressure dependence of the static permittivity $\varepsilon(P)$ is obtained by extrapolating the frequency dependence of the experimental refractive indices $n(\omega)$ to zero frequency. In [4], it is shown that the change in the static permittivity of Ge $\varepsilon(P)$ due to a pressure-induced change in the volume of the semiconductor up to $\Delta V/V_0 \approx 8\%$ can be described by the coefficient $r = d\ln(\varepsilon)/d\ln(V) = 1.58$. In [5], it is found that the coefficient $\eta \equiv \partial\ln(\chi)/\partial\ln(d)$ dependent on the interatomic spacing d is 2.4.

It is known that the permittivity of crystals, in which interatomic bonding is defined by the exchange interaction of valence electrons, is much larger than n^2. The replacement of ε by n^2 means that the refractive index is a constant measured at infinitely lone wavelengths. Therefore, the results of calculations heavily depend on the exactness of extrapolation of the refractive index to zero frequency.

In this study, we for the first time obtain the experimental dependence of the static permittivity of Ge on the hydrostatic pressure by direct measurements. The dependence $\varepsilon(P)$ is studied by a method based on recording the pressure dependence of the barrier capacitance of p–n structures with a stepwise change in the impurity concentration: $N_p \gg N_n$ (fused structures with an n-type semiconductor base) [6]. In this case, the static permittivity is expressed by the formula

$$\varepsilon = (1.44\times10^8 C_b^2 U_c)/\varepsilon_0 S^2 \cdot N_d, \tag{2}$$

where $\varepsilon_0 = 8.85416 \times 10^{-2}$ pF cm^{-1}.

From relation (2) with the experimental data for $C_b(P)$ and with the known quantities $U_c(P)$ and $S(P)$, we can determine the dependence $\varepsilon(P)$. The ionization energy of shallow impurities barely varies with pressure [7] and corresponds to the coefficient ~10^{-13} eV Pa^{-1}. At the same time, the variation in the band gap with pressure is described by the coefficient $dE_g/dP = 5 \times 10^{-11}$ eV Pa^{-1}. The change in the contact potential U_c with pressure was calculated with the known pressure coefficients [7, 8] for the extrema of the conduction band ($\gamma_{Ci}(L, \Delta_1)$) and the valence band (γ_Δ). For Ge, these pressure coefficients are

$$\gamma_{CL} = 83 \text{ meV GPa}^{-1}, \gamma_{C\Delta} = 8 \text{ meV GPa}^{-1},$$

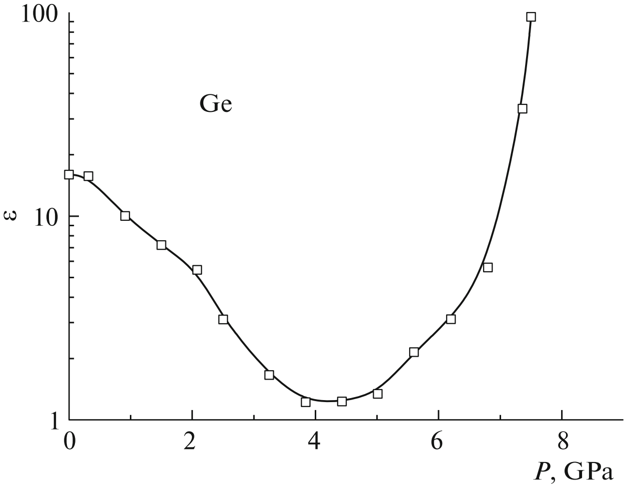

Fig. 1. Experimental dependence of the static permittivity of Ge on the hydrostatic pressure.

$$\gamma_V = 28 \text{ meV GPa}^{-1},$$

$$\Delta E_{g(V-CL)} = 55 \text{ meV GPa}^{-1} \ (P = 0\text{–}2.5 \text{ GPa}),$$

$$\text{and } \Delta E_{g(V-C\Delta)} = -20 \text{ meV GPa}^{-1} \ (P \geq 2.5 \text{ GPa}).$$

The $p-n$ structures to be studied were fabricated by alloying the In–Pb–Ga (10% Pb, 0.7% Ga, 89.3% In) and Pb–Sn–Sb (65% Pb, 30% Sn, 5% Sb) alloys into n-Ge with an impurity concentration of $N_D - N_A = 4.0 \times 10^{14}$ cm^{-3} and crystallographic orientation in the [100] direction.

To create a pressure in the range 0–10 GPa, we used a high-pressure apparatus of the type of a flat anvil with an indentation and a toroidal support [9]. The pressure dependences of the barrier capacitance were recorded at a frequency of 1 MHz at the measurement signal level 0.1 V. In calculating $\varepsilon(P)$, we took into account the change induced in $C(P)$ by the pressure-induced change in the geometric dimensions of the structures $\Delta V(P)/V_0$. The last-mentioned quantity corresponds to –0.25% GPa^{-1}.

Figure 1 shows the dependence of the static permittivity of Ge on the hydrostatic pressure at a temperature of 300 K. As can be seen from the experimental results, in the initial portion of the dependence, we observe a slight increase in the permittivity. A further increase in the pressure yields a substantial decrease in the static permittivity (by a factor of ~13) to $\varepsilon = 1.22$ at $P \approx 4$ GPa. In the range from 4.0 to 7 GPa, we observe a moderate increase in ε to the initial value, and in the range 7–7.4 GPa, the permittivity increases to more than 1000.

It is known that, in Ge, hybrid orbitals possess a lower symmetry than the constituent atomic orbitals and the distribution of the electron density is shifted from the atomic nucleus along the symmetry direction of the hybrid orbital. At the same time, in order of magnitude, the atomic polarizability is equal to the atomic volume; i.e., atoms with a large radius of the electron orbit can be easily polarized. A decrease in the interatomic spacings (–0.368% GPa^{-1}) enhances hybridization of the s and p orbitals and provides more efficient overlapping of the electron orbits of neighboring atoms; in this case, the potential in the middle of the spacing between two interacting atoms at the point of branching remains unchanged and equal to zero.

The change in the static permittivity of Ge under hydrostatic pressure is defined by mutually competing factors. These are as follows:

(i) Under hydrostatic pressure, the Coulomb repulsion of atoms and the effect of the superposition of electron shells of neighboring atoms yield an increase in the kinetic energy of bonding electrons. In this case, as the radii of electron orbits decrease, the velocity of valence electrons increases as

$$V_P = V_0 \cdot r_0 / r_P. \quad (3)$$

Here, V_0 is the electron velocity at $P = 0$, r_0 is the electron radius at $P = 0$, and r_P is the electron radius under hydrostatic pressure.

The electron polarization is inversely proportional of the electron velocity squared: $P \approx k/V_e^2$. Therefore, as the interatomic spacings decrease, the permittivity coefficient decreases as well.

(ii) The electric field of bonding atoms exhibits a point of branching in the middle of the bond between atoms. At the point of branching, the field strength is zero, and the equipotential surface intersects itself. The variation in the electric potential in relation to the electron radius under hydrostatic pressure r_P and to the distance h in the direction orthogonal to the line connecting the atoms can be represented as [10]

$$\varphi_\perp \approx -k \cdot h^2 / r_P^3. \quad (4)$$

Here, k is the proportionality coefficient.

From relation (4), it follows that, as the interatomic spacing decreases, the potential of bonding atoms in the direction orthogonal to the bond between them decreases, which is bound to result in strengthening of the effect of an external polarizing electric field.

(iii) An increase in the permittivity is promoted also by an increase in the electron density localized in the space between atoms with decreasing interatomic spacings.

From the aforesaid, it follows that the decrease in the polarization in Ge at pressures below 4 GPa is due to the dominant effect of the electron kinetic velocity which increases as the pressure is increased. A further increase in the polarization at $P \geq 4$ GPa is defined by saturation of the kinetic energy of charge carriers and by a decrease in the field strength in the space between interacting atoms as well as by an increase in the electron density localized in the space between atoms.

The above interpretation of the experimentally observed changes in the static permittivity of Ge under hydrostatic pressure refers to the region of pressures below the pressure corresponding to the onset of structural phase transformations. According to the data reported in [11] (see also references therein), the phase transition in Ge from the diamond-like structure (I) to the β-Sn-like structure (II) occurs in the range of pressures from 6.7 to 10.6 GPa.

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