

Physics

Dependence between the Energy-Gap Width and Shallow Impurities in Semiconductors with Tetrahedral Symmetry

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ABSTRACT. According to the common model of the impurity center, the dependence between the energy-gap width and concentration of impurity is calculated in this paper. The individual role of impurities in decreasing the energy-gap width is shown. There is a good correspondence with the experimental results. © 2011 Bull. Georg. Natl. Acad. Sci.

Key words: semiconductor, impurity, energy-gap.

Implantation of a large amount of impurities in semiconductors can cause major distortion of the zonal structure. “Large amount” means such concentration when the average distance $\frac{1}{\sqrt[3]{N_I}}$ becomes less than Bohr orbit radius $\frac{1}{\sqrt[3]{N_I}} \ll a_\beta$, where $a_\beta = \left(\frac{m}{m^*}\right) \varepsilon a_0$. m^* is the effective mass of the atom in the given semiconductor, m is the free electron’s mass, ε is the dielectric constant, a_0 is the electron’s Bohr orbit radius in hydrogen atom. In these conditions there appears the impurity band and in the case of donor impurities it joins the conduction band and in the case of acceptor impurity – the valence band. This causes major changes of the density of states. At the edge of the appropriate band there appear tails of the density of states and they drag the edge of the band to the energy-gap. This causes narrowing of the energy-gap. Studies of this process began about 50 years ago, continuing to the present day. First papers on this topic appeared when it became feasible to perform zonal structure defining experiments. These studies were contrapositive and mutually exclusive, e.g.: reflection measurement experiments showed [1] that an increase of impurity concentration causes an increment of the effec-

tive mass of electron, but the calculations in [2] do not confirm these results. Pankove [3] investigated the spectral dependence of the absorption coefficient during interzonal optical transitions in heavily doped germanium with shallow arsenic impurity and calculated the dependence between the energy-gap width and concentration of impurities. He defined that increasing the impurity concentration causes a decrease of the energy-gap in germanium. In the case of impurity concentration $4.5 \cdot 10^{19} \text{cm}^{-3}$ the band width decreases by 0.1 eV. The experiments were conducted at 4.2 K. Haas [4] performed similar calculations in heavily doped germanium with phosphorus and arsenic at 80 K temperature. He also defined the decrease of the energy-gap width when the impurity concentration increased, but not so much as in [3]. Other authors, e.g. [5] said that the reason of the difference is the wrong absorption extrapolation of uncombined carriers in Haas’s main absorption area. Besides, it is quite hard to compare these results because these experiments were performed in heavily doped hole germanium. The fact of reduction of the energy-gap width was also investigated in [6] in which some investigations of infrared absorption were conducted in heavily doped germanium with gallium at 80 K and 293 K temperatures. At 80 K the authors found that the difference between direct and indirect transitions is

0.16 eV, but they explained this fact by heavy doping Fermi energy entering the valence band and the interzonal transitions beginning there. The value of the energy-gap width reduction in such case when impurity concentration $\sim 10^{19} \text{cm}^{-3}$, according to the authors' calculations, is 0.05 eV.

In heavily doped compensated germanium narrowing of the energy-gap was theoretically calculated by Keldysh and Proshko [7]. They followed the conception of random distribution of impurities and calculated the value of energy-gap width reduction caused by the fluctuations of impurity potential. This potential is represented as Coulomb potential. The formula of band width reduction is:

$$\Delta E_g = 2 \left(\frac{e^2}{a_H} \right) \frac{1}{\varepsilon} \left(\frac{m}{m_v} \left(1 + \frac{m_v}{m_e} \right) \varepsilon \right)^{\frac{1}{5}} \left(n a_0^3 \right)^{\frac{2}{5}} \sqrt{\left(\frac{m_v}{m_c} \right)^{\frac{2}{5}} - 1}, \quad (1)$$

where m_e and m_v are effective masses of electrons and holes. The values of energy-gap width reduction, calculated using (1) formula, are small, e.g. for germanium when $n \sim 10^{19} \text{cm}^{-3}$, $\Delta E_g \sim 10^{-3} \text{eV}$. These values are also small when using Hamman's formulas [8] for germanium and silicon. They are based on the Coulomb potential of the impurity center. Hamman calculated the decrease of energy-gap energy in semiconductors, using the variational method. With taking into account the Fermi energy changes caused by the charge carrier concentration increment and without it, he derived the formulas for Ge and Si:

$$\text{Ge: } \Delta E_g(\mu, n) = \Delta E_g(n) - 6.63 \left(n / 10^{18} \right)^{\frac{2}{3}} \quad (\text{eV})$$

$$\Delta E_g(n) = 0.741 - 4.89 \left(\frac{n_0}{10^{18}} \right)^{\frac{1}{3}} - 8.2 \left(\frac{n_0}{10^{18}} \right)^{\frac{1}{4}} - 3 \quad (\text{eV}), \quad (2)$$

$$\text{Si: } \Delta E_g(\mu, n) = \Delta E_g(n) - 3.34 \left(n / 10^{18} \right)^{\frac{2}{3}} \quad (\text{eV}),$$

$$\Delta E_g(n) = 1.156 - 6.47 \left(\frac{n_0}{10^{18}} \right)^{\frac{1}{3}} - 13.1 \left(\frac{n_0}{10^{18}} \right)^{\frac{1}{4}} - 8.1 \quad (\text{eV}), \quad (3)$$

where n is the concentration of free electrons, $\Delta E_g(\mu, n)$ is the value of energy-gap reduction. When the impurities are ionized, electron gas is too much distorted and the chemical potential enters the band. So, this is the distance between the chemical potential and the edge of another band, and $\Delta E_g(n)$ is the energy-gap width reduction value without taking this fact into account, so it is the distance from one band's edge to another. This method also gives small values, e.g. for Ge when concentration

$n = 5 \cdot 10^{19} \text{cm}^{-3}$, $\Delta E_g(n) \sim 0.02 \text{eV}$. The papers by Overstraeten and Mertens [9] contain numerous results of calculations of the dependence between impurity concentration and the energy-gap width. They used electric measurements in these experiments. In these papers the results of 5 different authors are shown.

In regard to Ge, at low temperatures (4.2K), the energy-gap vs. impurity concentration dependence is shown in [3]. These experimental data, together with our theoretical results, are shown at the end of this article in Figs. 1 and 2.

The concentration of electrons is low at low temperatures when it makes sense to measure the energy-gap width in heavily doped germanium and silicon. According to the theories considered above, neutral impurities cannot take part in changing the energy-gap narrowing process. In [10] an impurity center model is proposed in which the impurity atom in the first coordination sphere is considered to be a free atom in vacuum and outside of it – as usual – using the continuum approximation. According to this conception the impurity center potential formula is:

$$\Phi(r) = \frac{Z^* e}{r} \theta(r_0 - r) + \frac{Ze}{\varepsilon r} \theta(r - r_0), \quad (4)$$

according to Slater [12] $Z^* = n^* \sqrt{\frac{1}{E_H}}$, n^* is the effective

principal quantum number of the valence band of the impurity atom, which is defined using Slater's Principle. I is the appropriate state energy of the free atom of impurity. At $T=0 \text{K}$ the impurity atom is neutral, so for $PI=0.8 \text{eV}$ and for $As I=1.07 \text{eV}$. E_H is the ionization energy of hydrogen free atom and $\theta(x)$ is the Heaviside step function.

As the dielectric constant spatial dependence is limited by the first coordination sphere, the potential (4) needs

some corrections. $\frac{1}{\varepsilon(r)}$ dependence according to [11]

can be described thus:

$$\frac{1}{\varepsilon(r)} = \left(1 - \left(1 - \frac{1}{\varepsilon} \right) \frac{r}{r_0} \right) \theta(r_0 - r) + \frac{1}{\varepsilon} \theta(r - r_0). \quad (5)$$

After this kind of correction (4) will transform into:

$$\Phi(r) = n^* \sqrt{\frac{I}{E_H}} \frac{e}{r} \left(1 - \left(1 - \frac{1}{\varepsilon_0} \right) \frac{r}{r_0} \right) \theta(r_0 - r) + \frac{Ze}{\varepsilon r} \theta(r - r_0), \quad (6)$$

where n^* is the principal quantum number of the valence

layer of the impurity atom, which is calculated using Slater's rule [12]. I is the ionization energy of the corresponding state of the free impurity atom. E_H is the ionization energy of the free atom of hydrogen. $\theta(x)$ is the Heaviside step function. n^* and E_I parameters automatically describe the individuality of each impurity. This model was successfully confirmed by investigations of charge carriers' dispersion on ionized impurities, as well as emitted and non-emitted transitions and other problems [12-14].

We tried to use the impurity center common model and investigate the dependence of energy-gap narrowing vs. impurity density. We assume that the impurity is randomly distributed and the screened potential of (4) energy according to Debye and Hewkel will be:

$$\Phi(r) = n^* \sqrt{\frac{I}{E_H}} \frac{e}{r} \left(1 - \left(1 - \frac{1}{\varepsilon} \right) \frac{r}{r_0} \right) \theta(r_0 - r) + \frac{Ze}{\varepsilon r} e^{-qr} \theta(r - r_0), \quad (7)$$

where q is the inverted value of Debye radius in whole substance. The correlation function of potential energy of randomly distributed n impurity is:

$$\langle u(r_1)u(r_2) \rangle = \frac{N}{V} \int d\vec{r} u(\vec{r} + \vec{r}_1) u(\vec{r} + \vec{r}_2), \quad (8)$$

where $u(r) = e\Phi(r)$. If we replace $u(\vec{r} + \vec{r}_1)$ and $u(\vec{r} + \vec{r}_2)$ functions in (8) with the Fourier transformation we shall obtain the formula:

$$\langle u(r_1)u(r_2) \rangle = \frac{N_I}{(2\pi)^3} \int e^{i\vec{k}(\vec{r}_1 + \vec{r}_2)} u(\vec{k}) u(-\vec{k}) d\vec{k}, \quad (9)$$

$$u(k) = 4\pi e^2 \left\{ \sqrt{\frac{I}{E_H}} \frac{n^*}{k^2} \left(\frac{1}{\varepsilon} (1 - \cos kr_0) + \left(1 - \frac{1}{\varepsilon_0} \right) \times \left(1 - \frac{\sin kr_0}{kr_0} \right) \right) + \frac{z}{\varepsilon(k^2 + q^2)} \left(\frac{q}{k} \sin kr_0 + \cos kr_0 \right) \right\}, \quad (10)$$

where $N_I = \frac{N}{V}$ is impurity concentration, $u(k)$ is the Fourier transformation of $u(r)$ function.

As we see, $u(k) = u(-k)$ so at the $r_1=r_2$ point for potential energy fluctuation we shall have the formula:

$$\langle u^2(r) \rangle = \frac{N_I}{(2\pi)^3} \int |u(k)|^2 d\vec{k}. \quad (11)$$

If we put formula (10) in (11) and take into account $\Delta E_g(N_I) = \sqrt{\langle u^2(r) \rangle}$ expression, after long, but simple transformations we shall get:

$$\Delta E_g(N_I) = \sqrt{\frac{8\pi}{\varepsilon} (N_I a_0^3) E_H \left\{ 2 \left(\frac{r_0}{a_0} \right) I + \frac{z^2}{\varepsilon} E_H \frac{e^{-2qr_0}}{qa_0} \right\}} \quad (12)$$

This formula shows that the inner as well as the outer area of impurity center affects the energy-gap narrowing process. Besides, the universality of our conception is

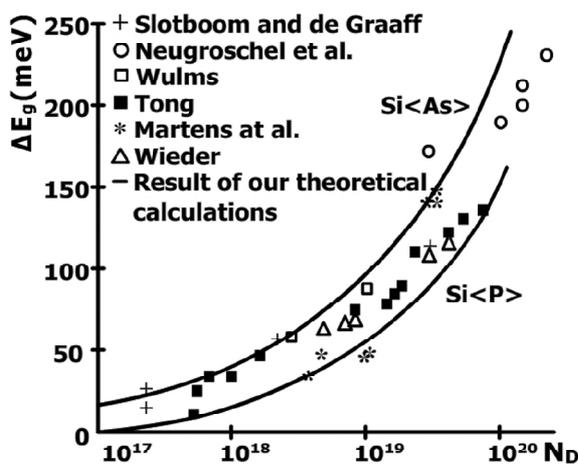


Fig. 1. Energy-gap vs. impurity concentration dependence diagram for Si. Figures show the experimental data [9] and the line – the result of our theoretical calculations.

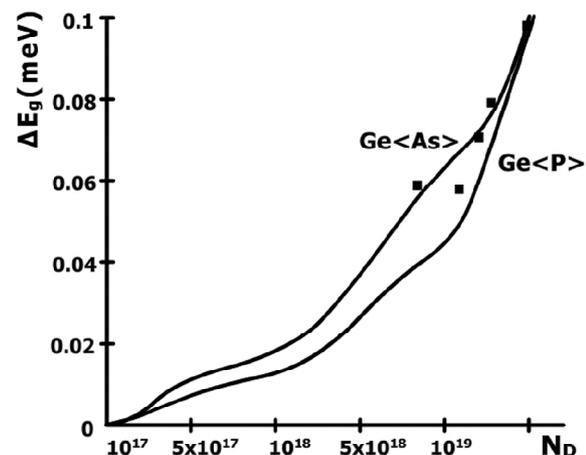


Fig. 2. Energy-gap vs. impurity concentration dependence diagram for Si. Figures show the experimental data [3] and the line – the result of our theoretical calculations according to formula (13).

that formula (12) shows the difference in the individuality of each impurity and different kind of influence in the energy-gap narrowing process. Energy-gap width reduction at $T=0$ according to (12) will be:

$$\Delta E_g(N_I) = 4n^* \sqrt{\frac{\pi}{\varepsilon} (IE_H) \left(\frac{r_0}{a_0}\right) (N_I a_0^3)}. \quad (13)$$

According to formula (13) we built energy gap vs. impurity concentration $\Delta E_g(N_D)$ dependence diagrams for Si<As>, Si<P>, Ge<As> and Ge<P>, which are shown in the Figures below. The experimental data are also given, that are taken from [9] for Si and [3] for Ge<As>. As we see, the similarity is satisfactory.

ფიზიკა

ტეტრაედრული სიმეტრიის ნახევარგამტარებში აკრძალული ზონის სიგანის დამოკიდებულება თხელ მინარევეებზე

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