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Research Article

Coordinate dependent diffusion analysis of phosphorus diffusion profiles in gallium doped germanium

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Abstract

We have analyzed phosphorus diffusion profiles in an $In_{0.01}Ga_{0.99}As/In_{0.56}Ga_{0.44}P/Ge$ germanium structure during phosphorus co-diffusion with gallium for synthesis of the germanium subcell in multi-junction solar cells.. Phosphorus diffused from the $In_{0.56}Ga_{0.44}P$ layer simultaneously with gallium diffusion into the heavily gallium doped germanium substrate thus determining the specific diffusion conditions. Most importantly, gallium and phosphorus co-diffusion produces two *p*–*n* junctions instead of one. The phosphorus diffusion profiles do not obey Fick's laws. The phosphorus diffusion coefficient D_P depth distribution in the specimen has been studied using two methods, i.e., the Sauer–Freise modification of the Boltzmann–Matano method and the coordinate dependent diffusion method. We show that allowance for the drift component in the coordinate dependent diffusion method provides a better D_P agreement with literary data. Both methods suggest the D_P tendency to grow at the heterostructure boundary and to decline closer to the main *p*–*n* junction. The D_P growth near the surface *p*–*n* junction the field of which is directed toward the heterostructure boundary and its decline near the main *p*–*n* junction with an oppositely directed field, as well as the observed D_P growth with the electron concentration, suggest that the negatively charged $V_{Ge}P$ complexes diffuse in the heterostructure by analogy with one-component diffusion.

Keywords

phosphorus and gallium diffusion coefficient in silicon, coordinate dependent diffusion, vacancy diffusion model

1. Introduction

Phosphorus and gallium and the main doping impurities in germanium and therefore the interest to their diffusion emerged from the very start of the germanium *p*–*n* junction technology development. Study of diffusion in the 1950–1960's was based on *p*–*n* junction depth and spreading resistance measurements and diffusion profile description with Fick's laws which assume that the diffusion coefficient for a specific impurity depends only on temperature [1–5]. Since then the research into diffusion processes for different impurities has made a significant progress, with a number of theoretical and experimental investigations describing the effect of different factors (temperature, pressure, concentration, defects and accompanying impurities) on the diffusion coefficient. The view on this process de-

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veloped simultaneously with research into the crystalline structure of materials, types and parameters of intrinsic defects (mainly for intrinsic point defects), improvement of dislocation-free single crystal growth technologies and development of experimental measurement equipment and mathematical methods for diffusion process description. However there are still no universal impurity diffusion models even for basic semiconductors such as Ge. The main reason is that the research objects, i.e., the parameters of semiconductor substrates, accompanying impurities and diffusion conditions, are always different and often not described by authors of multiple works in detail.

There were many recent works on phosphorus diffusion in germanium. It was reported [6] that phosphorus diffusion coefficient D_P in pure germanium depends on phosphorus concentration; later on this observation was confirmed [7]. The authors analyzed SIMS diffusion profiles and calculated the diffusion coefficient using the Boltzmann–Matano method. They showed that if the boron concentration is higher than the intrinsic electron concentration at the diffusion temperature (n_i) the diffusion profiles are box-shaped and D_P is an almost linear function of the phosphorus concentration. Later on box-shaped diffusion profiles were analyzed in the assumption that phosphorus diffusion in germanium occurs by vacancy diffusion mechanism with the formation of germanium vacancy V_{Ge}P complexes in different charge states and the D_P *vs* C_P dependence is related with the charged vacancy concentration dependence on the electron concentration [8–16]. We believe [8, 9] to be the most practically valuable latest works primarily because they suggest numerical models allowing judging upon their applicability for diffusion process simulation in germanium. However diffusion coefficients vary noticeably between different authors' data which may be mainly due to different germanium compositions used.

The development of multi-junction solar cell (**MJSC**) technology raises the interest to germanium as substrate and first stage material for A^3B^5 compound base MJSC [17–20]. During first MJSC stage synthesis phosphorus diffuses from the InGaP buffer layer to heavily gallium doped germanium. As shown earlier [20] the Ga solubility at the InGaP/Ge interface is higher than that of P and therefore two *p–n* junctions form and the phosphorus profile has 3 sections delimited by these *p–n* junctions [20–22]. The aim of this work is to analyze diffusion profiles and calculate phosphorus diffusion coefficients in germanium for formation of the first MJSC stage *p–n* junction.

2. Specimen preparation

The specimens were grown by MOS hydride epitaxy in a Veeco E450 LDM reactor in the form of (100) gallium doped germanium substrates (N_{Ga} = 10^{18} cm^{-3}) and exposed to a phosphine gas flow at 635 °C for 2.5 min. Then the $In_{0.56}Ga_{0.44}P$ buffer layer (1 min at T = 635 °C) and the heavily doped $In_{0.01}Ga_{0.99}As$ layer (1.6 min at the same temperature) were deposited. The gallium, phosphorus and germanium profiles were measured by SIMS on a PHI-6600. As shown elsewhere [20] the phosphine gas treatment introduces a small phosphorus quantity, its main quantity being added during further layer growth and hence the diffusion time is 2.6 min. The 3 and 5 Mendeleev Table group elements form well-known compounds and therefore Ga and P co-diffusion analysis should take into account possible formation of complexes. However the low diffusion coefficients and the relatively large distances between the impurity atoms (greater than 10 nm) suggest that GaP formation can be neglected in this case.

3. Phosphorus diffusion coefficient calculation method

The phosphorus diffusion coefficient D_P was calculated using two methods, i.e., the Sauer–Freise modification of the Boltzmann–Matano method and [3] the coordinate dependent diffusion method [23]. For Sauer–Freise $D(C)$ calculation the experimental phosphorus distribution was approximated with a fourth power polynomial (Fig. 1) for the calculation range x = 0–165 nm counting from the InGaP/Ge interface and the limit concentrations

$$Y = \frac{C - C_R}{C_L - C_R};$$

$C_L = 1.41 \times 10^{21}$ cm^{-3}; $C_R = 4.7 \times 10^{17}$ cm^{-3} using the formula

$$D = \frac{1}{2t\left(\frac{\mathrm{d}C}{\mathrm{d}x}\right)_x} \times \left[(1 - Y)\int_x^{165}(C - C_R)\,\mathrm{d}x + Y\int_0^x (C_L - C)\,\mathrm{d}x\right], \tag{1}$$

C is the concentration of phosphorus depending on the depth (x). The $D_p(x)$ calculation results are presented in Fig. 2.

The coordinate dependent diffusion method deals with two atom migration mechanisms, i.e., due to the concentration gradient (proper diffusion) and drift at the velocity $V(x)$ caused by fields (electric or elastic stress). The continuity equation is written as follows:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x} - V(x)C\right). \tag{2}$$

The diffusion coefficient and the drift velocity are calculated using one parameter (the average distance between adjacent sites λ) and two variables, i.e., the probability of vacant sites for jump φ(x) and the frequency of jumps in unit time γ(x).

$$D = \varphi(x)\gamma(x)\lambda^2;$$

$$V(x) = \left(\gamma(x)\frac{\partial\varphi(x)}{\partial x} - \varphi(x)\frac{\partial\gamma(x)}{\partial x}\right).$$

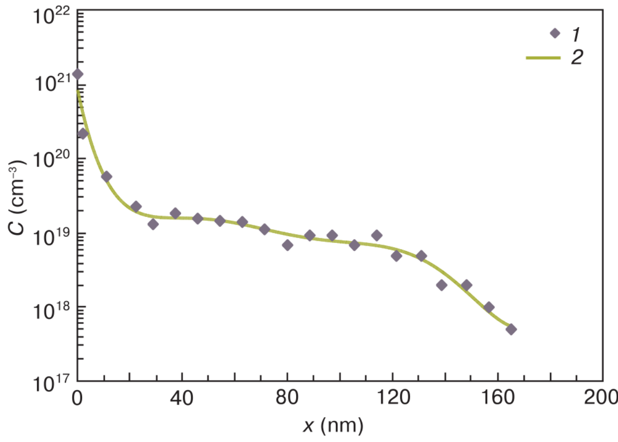

Figure 1. (*1*) experimental phosphorus profile in germanium and (*2*) fourth power polynomial approximation.

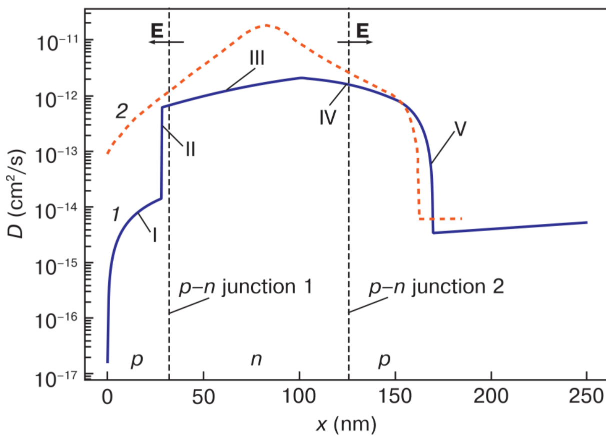

Figure 2. Phosphorus diffusion coefficient distribution in depth: (*1*) Sauer–Freise method; (*2*) coordinate dependent diffusion method. Arrows are the direction of the electric field vector of the *p-n* junctions.

For the calculations λ was accepted equal to the germanium lattice parameter $a = 0.566$ nm. The $\varphi(x)$ and $\gamma(x)$ functions were determined by fitting for the three profile sections: 0–28 nm, 28–165 nm and 165–200 nm from the heterostructure interface. The calculation results are also shown in Fig. 2.

The coordinate dependent diffusion calculated D_P data are expectedly lower than the Sauer–Freise ones since we took into account the phosphorus atom drift component for their calculation. The only exclusion is a small portion in the hole conductivity region at the phosphorus distribution tail, but with account of the calculation inaccuracy in this region one can consider these results to be approximately equal, i.e., the drift component is negligible beyond the second *p–n* junction. Further analysis included free carrier concentration calculation at the diffusion temperature.

Figure 3 shows the experimental phosphorus and gallium profiles and free election (n) and hole (p) concentrations calculated using the electrical neutrality equation (Eq. (3)) at the diffusion temperature (T).

$$C_P^+(x) + p(x) - n(x) - C_{Ga}^-(x) = 0. \quad (3)$$

We did not take into account the concentrations of germanium vacancies (V_{Ge}) and possible P–V_{Ge} complexes due to their negligibility compared with the doping impurity concentration [11].

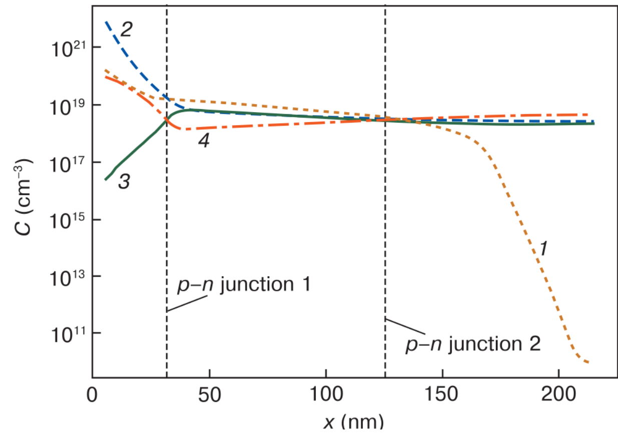

Figure 3. Phosphorus, gallium and free carrier concentration profiles in germanium: (*1*) C_P; (*2*) C_{Ga}; (*3*) n; (*4*) p.

The element concentrations at the heterostructure interface exceed the density of states in the conduction band (N_C) and in the valence band (N_V) at the diffusion temperature, i.e., germanium is degenerate in this region and hence we calculated the electron and hole concentrations using the Fermi–Dirac distribution function [24]:

$$n = N_C F_{1/2}(\eta),\ p = N_V F_{1/2}(-\eta - \varepsilon_i), \quad (4)$$

where $F_{1/2}(\eta)$ is the Fermi integral having a value of approx. 1/2:

$$F_{1/2}(\eta) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{\varepsilon^{\varepsilon-\eta} + 1},$$

$$\varepsilon = \frac{E - E_C}{kT},$$

$$\eta = \frac{F - E_C}{kT},$$

$$\varepsilon_i = \frac{E_C - E_V}{kT},$$

F is the Fermi level, E_C and E_V are the conduction band bottom and valence band top, respectively, and k is the Boltzmann constant.

Numeric calculations of Eq. (3) were carried out using the Newton method. The origin of coordinates in Fig. 3 is at the $In_{0.56}Ga_{0.44}P$/Ge heterostructure interface. The first *p–n* junction is at a 28–30 nm depth and the second one is at a 120–125 nm depth which agrees with the *p–n* junction depth estimates using electrochemical etching [22]. For the *p–n* junction space charge regions the electrical neutrality equation is not valid and the intrinsic carrier concentrations are calculated using Poisson's ratio but at high impurity concentrations the first space charge region is only within 5–6 nm and we therefore considered it safe to ignore that region and calculate n and p based on the electrical neutrality equation.

The electric field of the first *p–n* junction is directed toward the heterostructure interface and that of the second

p–n junction is opposite. One can expect that the field of the first *p–n* junction will accelerate the diffusion of negatively charged atoms or complexes (Ga and (V_{Ge}P) complexes) and decelerate the diffusion of positively charged (P^+) atoms. The field of the second deeper *p–n* junction will act in the opposite direction. Both methods suggest the following phosphorus diffusion coefficient behavior: D_P growth near the first *p–n* junction and decrease near the second one. This is possible if phosphorus diffuses within negatively charged complexes such as phosphorus/germanium vacancies. Germanium vacancies are acceptors with the charge state ranging from one to three resulting in the *V*GeP complexes being neutral, single- or double-negative charged [11]. It is thus confirmed that phosphorus bound into negatively charged V_{Ge}P complexes co-diffuses with gallium.

To analyze the diffusion coefficient dependence on material's parameters we plotted D_P vs *n* graphs (Fig. 4). Figure 4 also shows literary data for the so-called cubic ($D_P \sim n^3$ [7]) and quadratic ($D_P \sim n^2$ [6]) diffusion mechanisms. If n_i is exceeded ($n_i = 3.2 \times 10^{18}$ cm^{-3} for $T = 908$ K) the dependence is as follows (for the cubic mechanism):

$$\grave{u}_{\grave{u}} = {}^{2-}\left(\frac{n}{n_i}\right)^2 + {}^{3-}\left(\frac{n}{n_i}\right)^3,$$

$$D^{2-} = 11.1\exp\left(-\frac{2.93}{kT}\right), \quad (5)$$

$$D^{3-} = \grave{u}\grave{u}\grave{u} \left(-\frac{2.92}{kT}\right)$$

or (for the quadratic mechanism):

$$D_P = \grave{u}\grave{u}\grave{u}^{+5.3}_{-3.4} \left(-\frac{2.85^{+0.04}_{-0.04}}{kT}\right)\left(\frac{n}{n_i}\right)^2 \quad (6)$$

The regions in Fig. 4 are numbered beginning from the heterostructure interface. Region 1 is the *p* conductivity region at the heterostructure interface, Regions 2 and 5 are the first and second *p–n* junctions, respectively, and Regions 3 and 4 are the electron conductivity regions between the two *p–n* junctions.

It can be seen from Fig. 4 that the D_P data of this work are higher compared with literary data but in the region close to the intrinsic one the coordinate dependent diffusion method data agree well with earlier results [3] and there is a general tendency of D_P growth with *n* that is typical of the diffusion of phosphorus bound into negatively charged V_{Ge}P complexes.

The general D_P growth with the concentration *n* is confirmed although there are some specific features most likely associated with gallium participation in diffusion and with the effect of the *p–n* junction electric fields on diffusion.

In the hole conductivity region at the heterostructure interface D_P grows with *n*. The diffusion coefficient grows simultaneously with the electron concentration as one approaches the first *p–n* junction. Since the Fermi level tends to the middle of the band gap one can expect an increase in the share of vacancies with the highest charge

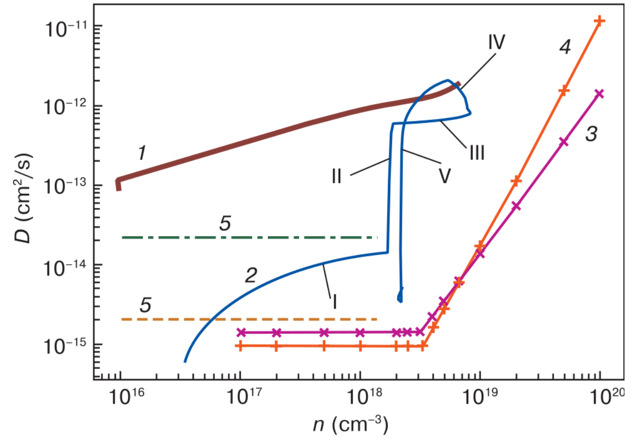

Figure 4. D_P as a function of electron concentration: (*1*) Sauer–Freise method calculation; (*2*) coordinate dependent diffusion method ((I) 0 < *x* <25 nm; (II) 25 < *x* <33 nm; (III) 33 < *x* <60 nm; (IV) 60 < *x* < 100 nm; (V) *x* >100 nm); (3—5) calculation according to Ref. [8], [9] and [6], respectively.

state and a transition from the quadratic to the cubic diffusion mechanism. D_P growth deceleration may be caused by a decrease in the overall vacancy concentration since Eqs. (5) and (6) were derived in the assumption of constant overall vacancy concentration. It should be noted that the phosphorus diffusion coefficient was first studied in this work for a hole conductivity region in germanium.

In the electronic conductivity region of the structure between the two *p–n* junctions D_P depends on *n* but slightly. This may be for a number of reasons, primarily, V_{Ge}P complex deceleration by *p–n* junction fields.

4. Conclusion

The diffusion coefficient calculated as a function of a distance from the heterostructure interface using the Sauer–Freise modification of the Boltzmann–Matano method and the coordinate dependent diffusion method. It is shown that diffusion in a *p–n–p* structure, i.e., two *p–n* junctions, exhibits a D_P growth tendency closer to the first *p–n* junction whose field should accelerate the negatively charged centers, and a D_P decline tendency moving away from the second *p–n* junction whose field should decelerate the negatively charged centers. Therefore, diffusing phosphorus is bound to the negatively charged centers, i.e., V_{Ge}P complexes with a charge of -1 or -2. The Sauer–Freise method overestimates D_P whereas the coordination dependent diffusion method gives a better D_P agreement with literary data. The latter is because the coordinate dependent diffusion method takes into account both the diffusion and the drift phosphorus atom diffusion components in germanium lattice. For two *p–n* junctions the drift component can be associated with the charge particle movement in the *p–n* junction electric fields.

The D_P growth tendency with *n* also corroborates the assumption of the vacancy phosphorus diffusion mechanism in germanium. It seems that in simultaneous Ga and P diffusion, the P diffusion is also by the vacancy mecha-

nism, similarly with phosphorus diffusion without other impurities.

The D_P data for the hole region also shows the D_P growth tendency with *n,* although according to the suggested phosphorus diffusion models D_P should be constant at phosphorus concentrations of below n_i. This discrepancy may originate from the former assumption made for the phosphorus diffusion formulas that $n = C_P$ which is not valid for the heavily compensated *p* conductivity region where an increase of the Fermi level can be accompanied by a change in the charge state of the vacancies and hence a different degree of D_P dependence on *n*.The D_P data for the hole region also show the D_P growth tendency with *n* although according to the suggested phosphorus diffusion models D_P should be constant at phosphorus concentrations of below n_i. This discrepancy may originate from the former assumption made for the phosphorus diffusion formulas that $n = C_P$ which is not valid for the heavily compensated *p* conductivity region where an increase in the Fermi level can be accompanied by a change in the charge state of the vacancies and hence a different degree of D_P dependence on *n*.

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