Identification of vacancy charge states in diffusion of arsenic in germanium

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(Received 10 February 2000; accepted for publication 2 June 2000)

Diffusion of As into Ge from a GaAs overlayer deposited on *p*-type Ge substrates has been studied by means of secondary ion mass spectrometry. A concentration-dependent diffusion of As atoms was observed in addition to the concentration-independent diffusion of Ga and As atoms. The concentration dependence is explained by a Fermi-level-dependent diffusion model. Arsenic atoms are shown to diffuse through Ge vacancies with the charge states 2− and 0. No presence of the singly negatively charged vacancies was observed, indicating that Ge vacancy could be a negative *U* center. © *2000 American Institute of Physics.* [S0003-6951(00)00531-3]

The identification of point defects in semiconductors is of fundamental interest and important in device fabrication. Diffusion of impurity atoms can be a powerful tool to investigate point defects in semiconductors, and has successfully been used to identify charge states of vacancies and impurities.[1,2] The increasing importance of Ge in applications such as $Si_{1-x}Ge_x$ devices and multijunction GaAs/Ge and GaInP/GaAs/Ge solar cells[3,4] necessitates further studies on diffusion in Ge. Wojtczuk *et al.*[3] noticed that during growth of a GaAs layer on Ge a junction was created through the in-diffusion of Ga and As, resulting in a two-junction tandem cell. This process has been used to create *n*-type layers in Ge.

There are only a few studies on the diffusion of As in Ge,[5–7] and to our knowledge no results on concentration-dependent As diffusion in Ge has been reported. In a recent study on phosphorus diffusion into Ge, Söderval and Friesel[8] observed ''box-type'' penetration profiles, which are an indication of concentration-dependent diffusion. Mitha and co-workers[9–11] have investigated the effect of pressure on the diffusion of implanted As atoms in germanium. They concluded that the diffusion is not entirely mediated by vacancies. If, on the other hand, the diffusion proceeds only through vacancies, the vacancy formation volume must be unexpectedly low or the migration energy high. Further studies giving information on atomic defects in Ge acting as diffusion vehicles were conducted by Werner, Mehrer, and Hochheimer.[12] They studied the self-diffusion of Ge as a function of pressure, temperature, and doping, and concluded that this process is mediated by neutral and singly negatively charged vacancies. It is obvious that further studies are needed to determine the point defects responsible for diffusion in germanium. In this letter, neutral and doubly negatively charged Ge vacancies have been identified as the diffusion vehicles for As diffusion in germanium, while no contribution of the singly negatively charged vacancy was observed.

Commercially prepared samples of *p*-type ⟨001⟩-oriented single-crystal germanium, with Ga dopant concentrations of 2×10^{17} and 5×10^{18} atoms/cm^3, were used as substrates. The GaAs deposition on Ge was done by molecular beam epitaxy,[13] and the annealings were carried out using rapid thermal annealing *ex situ* in pure N_2, in the temperature range from 500 to 800 °C. The GaAs layer was then etched using a solution containing H_2SO_4, H_2O_2, and H_2O in a volumetric ratio of 1:1:1. The selective chemical etching was estimated to remove at most 2 nm of Ge, leaving a smooth surface for secondary ion mass spectroscopy (SIMS) measurements. Depth profiling of arsenic was carried out utilizing a double focusing magnetic sector SIMS.[13]

The diffusion profiles of As atoms consisted of two different parts, as illustrated in Fig. 1. In the region near the surface the As and Ga concentrations are very similar and drop very fast. In the second region beyond the surface region, the Ga concentration decreases to a doping level of 2×10^{17} cm^{-3}, while As has diffused deeper into the sample. In this letter we focus on the concentration-dependent As

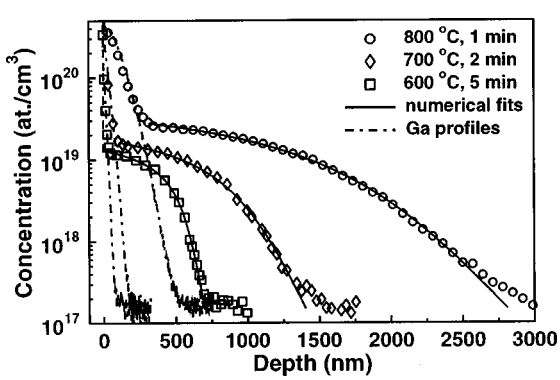

FIG. 1. Concentration profiles of As and Ga obtained in SIMS measurements for samples annealed at 600, 700, and 800 °C. The numerical fits are calculated for charge states 0 and 2− of Ge vacancies.

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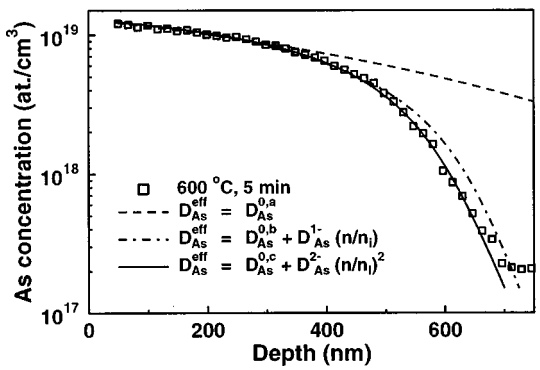

FIG. 2. Numerical fits to the As concentration profile obtained after the annealing at 600 °C for 5 min. Fits are calculated for different combinations of charge states for Ge vacancies. The parameter values are: $D^{0,a}_{As} = 363\ nm^2/s$, $D^{0,b}_{As} = 0.000\ nm^2/s$, $D^{0,c}_{As} = 38\ nm^2/s$, $D^{1-}_{As} = 47\ nm^2/s$, and $D^{2-}_{As} = 9.3\ nm^2/s$.

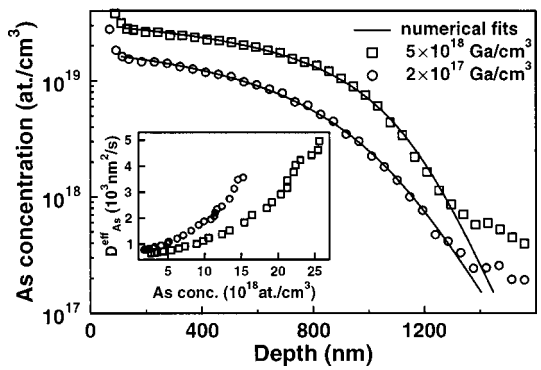

FIG. 3. Experimental and fitted As profiles for samples with different Ga doping concentrations annealed at 700 °C for 2 min. The inset shows the effective diffusion coefficients as a function of the As concentration.

diffusion in the second region. To model this behavior it is necessary to take into account that As is an n-type dopant in Ge and therefore occupies Ge lattice sites and diffuses through neutral and charged Ge vacancies. Positively charged vacancies can be ruled out in the second region where the As concentration is much higher than the concentration of p-type Ga. The amount of negatively charged vacancies increases with the increasing energy of the Fermi level, which depends on the As concentration. This leads to concentration-dependent diffusion and a diffusion equation where the change in the As concentration, $[As^+_{Ge}]$, is given as a function of depth x and time t as

$$\frac{\partial[As^+_{Ge}]}{\partial t} = \frac{\partial}{\partial x}\left(D^{eff}_{As}\left[\frac{\partial[As^+_{Ge}]}{\partial x} + \frac{[As^+_{Ge}]}{n}\frac{\partial n}{\partial x}\right]\right). \quad (1)$$

The second term is due to the electric field produced by the electrons and n is the extrinsic electron concentration. D^{eff}_{As} is the effective diffusion coefficient for As atoms diffusing through Ge vacancies and can be written as

$$D^{eff}_{As} = D^0_{As} + D^{1-}_{As}(n/n_i) + D^{2-}_{As}(n/n_i)^2, \quad (2)$$

where D^y_{As} are the diffusion coefficients of As diffusing through y charged Ge vacancies and n_i is the intrinsic electron concentration.[14] By applying the charge neutrality condition and using the semiconductor equality $pn = n_i^2$, where p is the hole concentration, we get the electron concentration as a function of As and Ga concentrations,

$$n = 0.5([As]-[Ga]+\sqrt{([As]-[Ga])^2+4n_i^2}). \quad (3)$$

The concentration-dependent diffusion equation (1) solved numerically with the effective diffusion coefficient calculated from Eqs. (2) and (3) results in a concentration distribution to be compared with an experimental profile. The diffusion coefficients D^0_{As}, D^{1-}_{As}, and D^{2-}_{As} were obtained by least-squares fitting.

Figure 2 shows the resulting fits to the 600 °C, 5 min annealed profile when the As diffusion through different vacancies is considered. Fitting with only neutral vacancies in Eq. (2) corresponds to the complementary error function solution of the diffusion equation. By fitting with neutral and singly negatively charged vacancies it was not possible to obtain fits that accurately follow the experimental ones. In this case the value for the parameter D^0_{As} was zero, indicating that no neutral vacancies exist or that they do not act as diffusion vehicles. The right concentration dependence for the effective diffusion coefficient for all profiles could only be achieved when diffusion through doubly negatively charged Ge vacancies was included. When fitting the profiles with all three coefficients in Eq. (2), it was observed that the fitting parameter for diffusion through singly negatively charged vacancy was zero or negligibly small compared to the parameters describing diffusion through neutral and doubly negatively charged vacancies. This result again indicates that only Ge vacancies with charges 0 and 2− need to be taken into account.

The effect of the Ga doping concentration on the As diffusion was studied by annealing two samples with different Ga doping concentrations of 2×10^{17} and 5×10^{18} atoms/cm^3 for 2 min at 700 °C. The resulting As profiles shown in Fig. 3 are different due to the change in the electron concentration, see Eq. (3), which influences the effective diffusion coefficient in Eq. (2). Both experimental As profiles are reproduced with the same diffusion coefficients if the correct Ge vacancies participating in the diffusion process are used in fitting these profiles. The vacancy combination 1− and 2− as well as 0 and 1− resulted in drastically different diffusion parameters D^{1-}_{As} and D^{2-}_{As}, and D^0_{As} and D^{1-}_{As}, respectively, for the two Ga doping concentrations. Therefore we can rule out these vacancy combinations. However, the diffusion coefficients D^0_{As} and D^{2-}_{As} obtained for the vacancy charge state combination 0 and 2− were within the experimental uncertainties the same, see the 700 °C points in the Arrhenius plot in Fig. 4. This fact strongly supports the conclusion that the vacancies responsible for As diffusion are the neutral and doubly negatively charged ones. No presence of diffusion through singly negatively charged vacancies is observed. Hence, we suggest that the Ge vacancy could thus be a negative-U center,[15] which changes directly from neutral to double negative charge state without occupying the 1-state.

In Fig. 1 the fits are plotted for the profiles observed after annealing at 600 °C for 5 min, 700 °C for 2 min, and 800 °C for 1 min. It can be noted that the calculated profiles are in excellent agreement with the experimental ones. Figure 4 shows the resulting Arrhenius plots, where the diffusion is well described by the Arrhenius equation D

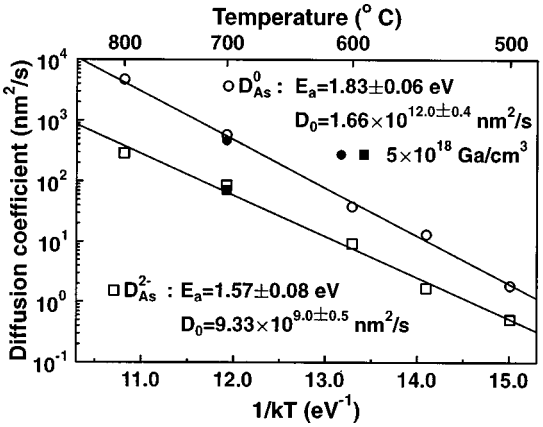

FIG. 4. Arrhenius plots for diffusion of As atoms via neutral and doubly negatively charged Ge vacancies. The open and closed symbols correspond to the Ga doping levels 2×10^{17} and $5\times10^{18}\,\mathrm{cm}^{-3}$, respectively. The fitted activation energies and preexponential factors are also given.

$=D_0\exp(-E_a/k_BT)$. The values for the preexponential factor D_0 and the activation energy E_a are given in Fig. 4. k_B is Boltzmann's constant and T is the absolute annealing temperature.

The experimental steep penetration profiles, obtained for P diffusion in germanium by Söderval and Friesel,[8] can according to the current observations also be explained by introducing diffusion through neutral and doubly negatively charged vacancies. Werner, Mehrer, and Hochheimer[12] suggested that neutral and singly negatively charged vacancies are responsible for the self-diffusion in Ge. This conclusion was made when the linear dependency of the effective self-diffusion coefficient as a function of n/n_i was observed. The linearity was deduced from only four experimental diffusion coefficients at 700 °C with n/n_i values 0.25, 0.7, 1.0, and 1.3. The discrepancy between the conclusions by Werner, Mehrer, and Hochheimer and the current interpretation can be understood by examining the As concentration profiles in more detail. In Fig. 1 it can be seen that at 600 °C the curvature of the profile is steeper and therefore the concentration dependency of the diffusion is stronger than at 700 °C. This fact can also be seen in the Arrhenius plots in Fig. 4, where the ratio of the concentration-dependent to the independent coefficient, $D^{2-}_{\mathrm{As}}/D^{0}_{\mathrm{As}}$, becomes bigger at lower temperatures. Then at high temperatures for values of n/n_i close to one, it is difficult to distinguish if the concentration-dependent part is proportional to n/n_i or $(n/n_i)^2$, see Eq. (2).

As can be seen in Fig. 4, the preexponential factors for the diffusion through neutral and doubly negatively charged vacancies differ by more than two orders of magnitude. This difference can be attributed to the ratio of the correlation factors[16] f^{2-}/f^0 related to the As diffusion through the two different vacancy types. Because a substitutional As atom has charge 1+ it attracts a doubly negatively charged Ge vacancy, resulting in a small correlation factor $f^{2-}<f^0$. The attraction retards the migration of As atoms: $D=f^{2-}D_{\mathrm{real}}$, where D is the observed diffusion coefficient and D_{real} is the diffusion coefficient one would obtain if there were no correlation between the successive atom jumps.

In summary, we have studied concentration-dependent diffusion of As into germanium from a GaAs overlayer as a function of temperature and doping concentration. Deeply extended As diffusion was observed in the SIMS concentration profiles. This behavior is quantitatively explained by the diffusion of substitutional As through Ge vacancies with charge states 0 and 2−.

This work has been supported by the Academy of Finland (Project No. 1018553). The authors thank Dr. Kimmo Saarinen (Helsinki University of Technology) for comments on the manuscript and Dr. Joseph Campbell (Helsinki University of Technology) is gratefully acknowledged for helpful discussions.

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