The cooks understood, yet they looked crestfallen. 'But our beautiful units' they said. 'What about our goldplated pounds and ounces and drams? Look at that wonderful half-perch in yon corner, neatly subdivided in 99 inches. It would be ill-convenient to change all that.' The wise man smiled. 'There is no real need to change' he said. 'As long as you are sure to remember that ε_0 is just a way to change from one unit to another and that P and $\varkappa$ are the only physically relevant quantities, you can work in any system of units you like.'

The years went by. The wise man had died, new generations of cooks worked in the kitchen and got restive over the principles of tagenometry. 'How crazy', they said. 'Isn't it obvious that V and W are quite different quantities, since they are determined in quite different ways? And why should the volumetric constant of empty space be unity? Is a pot of rice not just as good or better than an empty pot?' These protests prevailed. It was decided at an international congress that even if volume and volumetric displacement were identical in magnitude the one should be measured in Euclid – this being a cubic centimetre – the other in Archimedes. The volumetric displacement of empty space – although equal to unity – had the dimension Archimedes/Euclid. And after having created order in this way, the new generation has returned to inches and pounds, and brands as reactionary anyone who heeds the wise lessons of the wise man.

That is how to-days cooks spend their moments of leisure; let us hope that their cuisine will not suffer.

Vacancy Diffusion in Germanium

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Abstract. The theory of precipitation from supersaturated solutions in elemental semiconductors for impurities with comparable substitutional and interstitial solubility is discussed. It is shown that the precipitation time constant is related to the vacancy diffusion coefficient. This relation can be used to estimate the migration energy of monovacancies. As an illustration Tweet's data on copper precipitation in germanium are analysed, giving ~ 0.2 eV for the monovacancy migration energy.

1. Introduction

The properties of simple point defects in silicon and germanium have recently received considerable interest, in part due to the practical importance of radiation effects in these semiconductors [1–5]. The detailed studies of monovacancies in *silicon* by means of electron spin resonance have led to surprisingly low energies of migration, namely

$$E_{1V}^M = (0.33 \pm 0.03) \text{ eV in } p\text{-type Si (neutral)},$$

$$= (0.18 \pm 0.02) \text{ eV in } n\text{-type Si (double negatively charged) [6]}.$$

Analogous electron spin resonance experiments have not yet proved feasible in *germanium*. There exist, however, recent experimental evidences that in germanium monovacancies are also mobile below room temperature, with activation energies of migration of the order of ~ 0.2 eV to 0.3 eV [7], in marked contrast to the widespread belief [8–10] that the vacancy migration energy is of the order of 1.0 eV to 1.3 eV. Sofar the migration energies of monovacancies in germanium have not yet been determined by a definitive experiment. If the monovacancy migration energy in germanium is indeed as low as 0.3 eV or 0.2 eV, we cannot hope to determine single vacancy properties by the (for metals) classical method of quenching and annealing because of the insuppressible interference of clustering. We have therefore to look for other, indirect, techniques for determining the migration energies of mono-vacancies in germanium. In the present note we should like to point out how experiments on the precipitation of impurities like Cu from supersaturated solid solutions can be used to deduce monovacancy properties in germanium (and also in silicon).

First, the theory of precipitation from such solutions is discussed. Then the proposed approach is illustrated by a reanalysis of Tweet's data on copper precipitation in germanium [11]. The results support a low migration energy for the monovacancy in germanium. More reliable information could be obtained from careful experiments specifically designed in order to investigate vacancy properties by this approach.

2. Theory of Precipitation from Solid Solutions

FRANK and TURNBULL [12] proposed the dissociative mechanism of impurity diffusion in order to explain the process of copper precipitation in germanium. In this section we consider an extended version of this theory. The basic assumptions are [13] that copper dissolves both interstitially and substitutionally in Ge and that the interstitial atoms diffuse much faster than the substitutional atoms (or ions). We have thus a system containing the following simple defects: monovacancies V_1, impurity atoms at interstitial sites, I, and at substitutional sites, S. These defects may react with each other to form divacancies V_2 or complexes X between substitutional impurity and vacancy. A divacancy can be converted to X by adsorbing an I. We describe the diffusion and interaction of these defects by the following system of equations:

$$\frac{\partial C_I}{\partial t} = D_I \nabla^2 C_I + k_1 C_S - k_2 C_I C_{1V} - k_7 C_I C_{2V} \tag{1.a}$$

$$\frac{\partial C_{1V}}{\partial t} = D_{1V} \nabla^2 C_{1V} + k_1 C_S - k_2 C_I C_{1V} + k_3 C_X - k_4 C_{1V} C_S$$

$$+ 2 k_5 C_{2V} - 2 k_6 C_{1V}^2 \tag{1.b}$$

$$\frac{\partial C_X}{\partial t} = D_X \nabla^2 C_X - k_3 C_X + k_4 C_{1V} C_S + k_7 C_I C_{2V} \tag{1.c}$$

$$\frac{\partial C_{2V}}{\partial t} = D_{2V} \nabla^2 C_{2V} - k_5 C_{2V} + k_6 C_{1V}^2 - k_7 C_I C_{2V} \tag{1.d}$$

$$\frac{\partial C_S}{\partial t} = D_S \nabla^2 C_S - k_1 C_S + k_2 C_I C_{1V} + k_3 C_X - k_4 C_{1V} C_S. \tag{1.e}$$

Here C_i denotes the concentrations, D_i the diffusion coefficients and k_i the reaction constants; subscripts indicate the type of defects involved.

The physical processes involved in Equations (1) may be visualized as follows: The substitutional impurity atoms S in supersaturated concentration precipitate out by dissociating into I and V_1, which then migrate independently to sinks. The substitutional impurities S act essentially as sources of defect production. The precipitation process is then limited by the removal rate of I and V_1 produced by the dissociation process.

The excess interstitials can either be absorbed by internal sinks or return to substitutional sites by recombining with a monovacancy V_1 or by reacting with a V_2 to form X, which may subsequently dissociate into V_1 and S. If the interstitials are highly mobile at the temperature of the precipitation experiment, the interstitial concentration remains practically at its equilibrium concentration C_I^e at all times. This condition is probably fulfilled in the Cu/Ge system. The copper interstitial is found to migrate with an activation energy of 0.33 eV [14] and the useful temperature range for precipitation experiments lies between 400° and 800 °C.

The annihilation of excess vacancies is more complicated than that of interstitials. The excess vacancies can only disappear at permanent sinks, e.g., jogs in dislocation lines, since the formation of V_2 and X does not remove the vacancy from the lattice. Such reactions serve only to trap the vacancy temporarily. The annihilation of vacancies is thus delayed by cluster formation. The binding energy of V_2 in crystals of the diamond structure is high. For Si, it is found to be ~ 1.6 eV [15], and the corresponding value for Ge should be also of the same order of magnitude [16]. This is connected with a large migration energy of V_2, since in the diamond structure the divacancy must dissociate first in order to migrate [17, 18]. We have at present little knowledge about the complexes X. Tweet [19] found some metastable complexes in his experiments on Cu precipitation in Ge below 450 °C, which he could not identify definitely. It is quite possible that one of these complexes is of type X. In view of the extraordinarily high divacancy binding energy we assume that the complexes X can dissociate more easily than V_2. The decay of V_2 occurs presumably by the reaction with I, resulting in the formation of X. The net production rate of X and V_2 is thus kept low. Since V_1 and S act as acceptors, they both carry negative charges in the ionized states. The repulsive Coulomb interaction will reduce the production rate of V_2 and X further.

The preceding discussion justifies the following simplifying assumptions:

1) The diffusion of defects is dominated by I and/or V_1, i.e. $D_I, D_{1V} \gg D_S, D_{2V}, D_X$. Therefore we neglect the diffusion of S, V_2 and X to sinks.

2) $C_I = C_I^e$ at all times.

3) C_X and C_{1V} are stationary, i.e. $\partial C_X/\partial t = 0$, $\partial C_{2V}/\partial t = 0$.

The system of Equations (1) reduces then to

$$\frac{\partial C_{1V}}{\partial t} = D_{1V} \nabla^2 C_{1V} + k_1 C_S - k_2 C_I^e C_{1V} \qquad (2.\text{a})$$

$$\frac{\partial C_S}{\partial t} = -k_1 C_S + k_2 C_I^e C_{1V}. \qquad (2.\text{b})$$

For simplicity, we suppose that all I are positively charged (ionized donors), and that vacancy has one single acceptor level E_{1V}. The vacancy will then exist partly in the neutral state and partly in the charged state. The total vacancy concentration is [18]

$$C_{1V} = C_{[1V^\circ]} + C_{[1V^-]} = (1 + \beta)\, C_{[1V^-]} \tag{3}$$

and the effective vacancy diffusion coefficient is

$$D'_{1V} = \frac{D_{[1V^-]}\, C_{[1V^-]} + D_{[1V^\circ]}\, C_{[1V^\circ]}}{C_{[1V^-]} + C_{[1V^\circ]}} \tag{4a}$$

$$= \frac{D_{[1V^-]} + \beta\, D_{[1V^\circ]}}{1 + \beta} \tag{4b}$$

with

$$\beta = 2 \exp\left\{- (E_F - E_{1V})/k\,T\right\}, \tag{5}$$

where E_F is the Fermi energy. The Coulomb interaction energy ΔH_C between two oppositely charged defects is approximated by

$$\Delta H_C = q_1\, q_2/\varepsilon\, r\,. \tag{6}$$

q_1 and q_2 are charges on the two defects, r their separation distance and ε the dielectric constant. The effect of the Coulomb attraction on the capture coefficient of the interstitial for a negatively charged vacancy is tentatively taken into account (in an admittedly rough way) by including a factor $\exp(\Delta H_C/kT)$ in the capture cross-section, where ΔH_C is evaluated from Equation (6). Substituting Equations (3) to (6) into (2), we have

$$(1 + \beta)\, \frac{\partial C_{[1V^-]}}{\partial t} = (D_{[1V^-]} + \beta\, D_{[1V^\circ]})\, \nabla^2 C_{[1V^-]} + k_1\, C_S$$
$$- \{\beta + \exp(\Delta H_C/k\,T)\} k_2\, C_I^e\, C_{[1V^-]} \tag{7a}$$

$$\frac{\partial C_S}{\partial t} = - k_1\, C_S + \{\beta + \exp(\Delta H_C/k\,T)\}\, k_2\, C_I^e\, C_{[1V^-]}\,. \tag{7b}$$

Equations (7) admit particular solutions of the form

$$C_S = U_\tau(r) \exp(- t/\tau), \quad C_{[1V^-]} = V_\tau(r) \exp(- t/\tau)\,. \tag{8}$$

U_τ and V_τ are now functions of the position vector r only. By eliminating U_τ we obtain

$$\nabla^2 V_\tau + \lambda^2\, V_\tau = 0\,, \tag{9}$$

where

$$\lambda^2\, D'_{1V} = \frac{1}{\tau} \left\{ 1 + \frac{k'_2\, C_I^e}{(k_1 - 1/\tau)} \right\} \equiv \frac{1}{\tau^{eff}} \tag{10}$$

$$k'_2 = k_2 \exp(\Delta H_C/k\,T)\, \{(1 + \beta \exp(- \Delta H_C/k\,T)/(1 + \beta)\} \tag{11}$$

and (in Equation (4))

$$D_{[1V^-]} = D^0_{[1V^-]} \exp(- E^M_{[1V^-]}/k\,T)\,, \tag{12a}$$
$$D_{[1V^\circ]} = D^0_{[1V^\circ]} \exp(- E^M_{[1V^\circ]}/k\,T)\,. \tag{12b}$$

The eigenvalue λ is related to the sink density.

Equation (9) can be solved for a regular array of dislocations of density ϱ_D, which act as the only sinks for the migrating defects. Penning [20] has treated the annihilation of vacancies in such an array of dislocations, assuming each dislocation to annihilate all excess vacancies within a circular cylinder of radius r_2, coaxial with the dislocation, where

$$\pi\, r_2^2 = 1/\varrho_D. \tag{13}$$

The boundary conditions are

$$C_{1V} = C_{1V}^e \quad \text{at} \quad r = r_1$$

(i.e. an equilibrium vacancy concentration is maintained at a distance r_1 from the core of the dislocation)

and
$$\frac{\partial C_{1V}}{\partial r} = 0 \quad \text{at} \quad r = r_2 \gg r_1.$$

Penning gave the general solution as

$$C_{1V} = C_0 \sum_{n=1}^{\infty} A_n\, R_n(r)\, \exp(-t/\tau^{(n)}), \tag{14}$$

where A_n are constants and $R_n(r)$ linear combinations of cylindrical functions. We identify the time constant for the first term in Equation (14) with the effective time constant in Equation (10). Then we obtain

$$\lambda^2 = \alpha\, \varrho_D \,^1). \tag{15}$$

According to Penning, α depends slightly on the magnitude of the dislocation density.

The solution for τ can be written explicitly from Equation (10) and (15) as

$$\frac{1}{\tau_{1,2}} = \frac{1}{2}\left\{(k_1 + k_2'\, C_I^e + \alpha\, \varrho_D\, D_{1V}') \pm \sqrt{(k_1 + k_2'\, C_I^e + \alpha\, \varrho_D\, D_{1V}')^2 - 4\, \alpha\, \varrho_D\, D_{1V}'\, k_1}\right\}. \tag{16}$$

The following two special cases are of practical interest:

1) If $k_1 + k_2'\, C_I^e \gg \alpha\, \varrho_D\, D_{1V}'$, e.g. for small ϱ_D, the time constants are

$$\frac{1}{\tau_1} = \frac{\alpha\, \varrho_D\, D_{1V}'\, k_1}{(k_1 + k_2'\, C_I^e + \alpha\, \varrho_D\, D_{1V}')}\left\{1 + \frac{\alpha\, \varrho_D\, D_{1V}'\, k_1}{(k_1 + k_2'\, C_I^e + \alpha\, \varrho_D\, D_{1V}')^2} - \cdots\right\} \tag{17a}$$

$$\frac{1}{\tau_2} \cong k_1 + k_2'\, C_I^e \gg \frac{1}{\tau_1} \tag{17b}$$

The precipitation rate is determined by τ_1.

2) If $\alpha\, \varrho_D\, D_{1V}' \gg k_1 + k_2'\, C_I^e$, we have

$$\frac{1}{\tau_1} = k_1, \tag{18a}$$

$$\frac{1}{\tau_2} \simeq \alpha\, \varrho_D\, D_{1V}' \gg \frac{1}{\tau_1}. \tag{18b}$$

τ_1 is again rate-determining.

If the precipitation time constant τ_1 is measured over a sufficiently wide range of temperatures it can be approximated by a superposition of the two special cases

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[1]) In Penning's paper, the symbol β is used instead of α.

discussed above (Fig. 1). τ_1 of type I (corresponding to case 1) depends on the dislocation density. Curves for different dislocation densities merge into a single curve represented by Equation (18a), which corresponds to type II. From the temperature dependence of τ_1 of type II we are therefore able to determine k_1 experimentally.
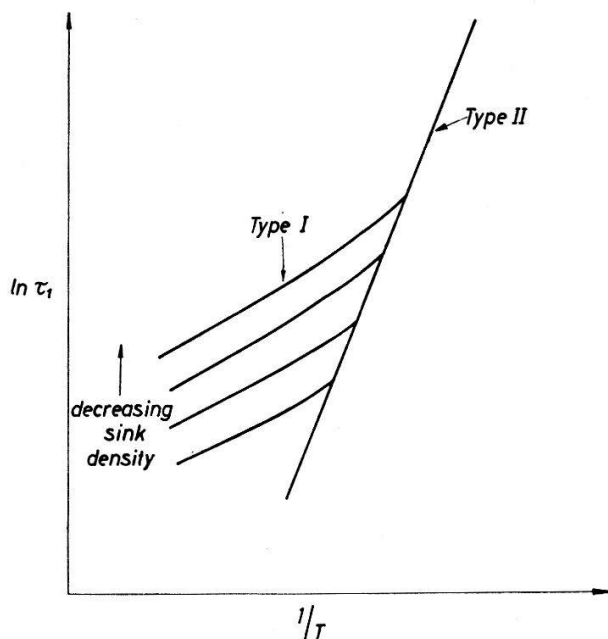

Figure 1

Variation of precipitation time constant τ_1 with temperatures (schematic).
Each type I curve corresponds to one value of sink density.

PENNING [21] was the first to point out the relation of τ_1 to the diffusion coefficient for a vacancy self-diffusion mechanism. His relation can be derived from Equation (17a) by putting the term in brackets equal to unity and eliminating k_1, k_2 and C_I^e using the relation

$$k_1 C_S^e = k_2 C_I^e C_{1V}^e, \qquad (19)$$

where the superscript e denotes equilibrium and C_S^e is the equilibrium substitutional solubility of the impurity atom.

We should like to point out here that τ_1 according to Equation (17a) is directly related to the diffusion coefficient of monovacancies. If k_2' and C_I^e are derived from other sources, we can deduce the vacancy diffusion coefficient from precipitation experiments. In order to determine the activation energy of migration $E_{[1V^-]}^M$ of negatively charged monovacancies, it suffices to study the *temperature dependence of* τ_1 for a wide range of temperatures in crystals of different dislocation densities covering both type I and type II precipitation (see Section 3). In order to obtain the *absolute value* of the diffusion coefficient, accurate determinations of sink densities are required in addition.

3. Application: Precipitation of Cu in Ge

The precipitation of Cu in Ge is at present the only system that has been investigated in enough detail to allow an estimate of $D_{[1V^-]}$ by the method outlined in

Section 2. TWEET [11] has studied the temperature dependence of τ under conditions which cover both type I and II precipitation of Cu in Ge. He found

$$k_1 = 2.8 \times 10^{15} \exp(-2.7 \text{ eV}/kT) \text{ sec}^{-1}. \tag{20}$$

The diffusivity of interstitial Cu in Ge was reported by HALL and RACETTE [14] as

$$D_I^{Cu/Ge} = 0.004 \exp(-0.33 \text{ eV}/kT)\text{cm}^2/\text{sec}. \tag{21}$$

C_I^e can be read directly from Figure 3 in [14]. The vacancy acceptor level E_{1V} in Ge is not known exactly. Earlier investigations suggested that it lies near the valence band [8]. It can be shown that for $E_F > E_{1V}$ the correction terms involving β in Equation (10) and (11) can be neglected in the temperature range of interest. Therefore in the following calculations we left out all terms involving β.

The quantity k_2 represents the probability that the interstitial I will jump into a vacancy. We may relate this to the diffusivity of the impurity interstitial by

$$k_2 = 32 \ (D_I^0/a^2) \exp(-E_I^M/kT), \tag{22}$$

where D_I^0 is the preexponential factor for the impurity diffusion coefficient and a the lattice constant.

The Coulomb interaction energy ΔH_C is estimated from Equation (5) as

$$\Delta H_C = 0.36 \text{ eV}, \tag{23}$$

taking $\varepsilon = 16$ and $r = $ distance between nearest neighbours. We can write Equation (10) as

$$\frac{1}{\lambda^2 \tau^{eff}} \simeq D_{[1V^-]}^0 \exp(-E_{[1V^-]}^M/kT). \tag{24}$$

The slope of $\ln 1/\lambda^2 \tau^{eff}$ against $1/T$ gives $E_{[1V^-]}^M$ directly. If we wish to evaluate $E_{[1V^-]}^M$ only (and not the absolute magnitude of the monovacancy diffusion coefficient), we do not have to know the absolute value of λ^2 (i.e., the density of the dislocations acting as sinks). We may consider λ^2 as an adjustable parameter characteristic for a
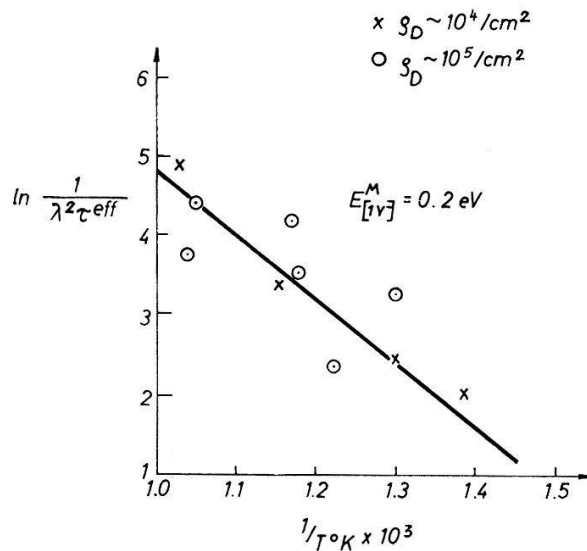

Figure 2

Determination of mono-vacancy migration energy, according to Equations (10) and (24).

specimen with a given dislocation density, and choose the λ^2-values for different specimens such as to give the best overlapping for $(\lambda^2 \tau^{eff})^{-1}$. Figure 2 shows the results, using two sets of data for $\varrho_D \simeq 10^5/\text{cm}^2$ and one set of data $\varrho_D \simeq 10^4/\text{cm}^2$ from TWEET [11]. The plot gives

$$E^M_{[1V^-]} \simeq 0.2 \text{ eV} . \tag{25}$$

This result agrees with other experimental evidences [7, 22]. $E^M_{[1V^-]}$ can be also derived by two other evaluations of the data, which, however, are less accurate and which will be briefly discussed in [22].

The preexponential factor $D^0_{[1V^-]}$ of the diffusion coefficient of the negatively charged monovacancy can be estimated, using the dislocation densities ϱ_D as determined by TWEET from etch-pit counts, as about 0.1 cm²/sec. This is a reasonable order of magnitude and supports the results of the preceding analysis, in particular the low value of the monovacancy migration energy in germanium. However, it is clear that the reliability and accuracy of these results could be substantially increased by carrying out experiments designed specifically for evaluation in terms of the present theory. In addition to careful determinations of the characteristic precipitation times, investigations by transmission electron microscopy in order to determine density, character and distribution of the dislocations acting as sinks in the precipitation process should be undertaken. Furthermore, an extension to other impurities, such as nickel and gold, and to silicon would be desirable. Experiments on solid solutions in silicon would permit a critical test of the present approach by comparing the results with electron spin resonance experiments.

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