PHYSICAL REVIEW VOLUME 104, NUMBER 3 NOVEMBER 1, 1956

Mechanism of Diffusion of Copper in Germanium

F. C. FRANK* AND D. TURNBULL
General Electric Research Laboratory, Schenectady, New York

(Received July 23, 1956)

To explain the rapid diffusivity of copper in germanium and its dependence on structure, it is proposed that the copper be dissolved in two states, interstitial and substitutional. It is deduced that in the interstitial state the solubility of copper is about 10^{-2} times less and the diffusivity many orders of magnitude greater than in the substitutional state. Conversion from the interstitial to the substitutional state is effected by lattice vacancies which are generated at free surfaces and dislocations; this accounts for the structure dependence of the diffusivity observed by Tweet and Gallagher.

THE remarkably rapid penetration of copper into germanium, first studied by Fuller *et al.*,[1] has been found by Tweet and Gallagher[2] to be structure-sensitive. In gross, the depth of penetration to half-concentration, in 15 minutes at 710°C, is raised from 4×10^{-3} cm, in samples of high perfection, to 0.2 cm in samples which contain many small-angle boundaries or are deformed. The latter value corresponds to a diffusivity of about 4×10^{-5} cm^2/sec, comparing with $(3.2\pm0.8)\times10^{-5}$ cm^2/sec (practically independent of temperature from 700°C to 900°C) found by Fuller *et al.* In crystals of moderate perfection the distribution corresponds to Fick's law only at smaller depths than those stated. At greater depths there is a level of copper concentration which rises with time and is relatively independent of distance. A decrease of concentration with depth at 4 mm is appreciable in the 15-min run, but inappreciable at this depth in runs of longer duration. The measurements of Fuller *et al.* show evidence of a similar deviation from the Fick's law distribution. In closer detail, when copper diffuses into *n*-type germanium, converting it to *p*-type, the *p-n* junction is found to be at a shallow depth (of the order 4×10^{-3} cm) in perfect regions of the crystal, as judged from etch pits, with long protuberances of about the same radius, evidently along dislocation lines.

The immediate interpretation is that most of the copper is transported along the dislocation lines, but this raises serious difficulties. The apparent over-all diffusivity when there are about 10^6 dislocations/cm^2 is about 4×10^{-5} cm^2/sec. The interpretation then implies either that the diffusivity close to the dislocations is incredibly large (requiring mean free paths of many interatomic distances), or that the dislocations raise the diffusivity to a credible value at an inexplicably large distance from themselves.

We propose an alternative explanation which appears to be in agreement with all the known facts. This involves that copper dissolves in germanium in two states, which we suppose to be interstitial and substitutional, respectively. In interstitial solution it has a very high (but not incredibly high) diffusivity. Substitutionally, its diffusivity is low, but its solubility higher. Conversion from the interstitial to the substitutional state requires a supply of vacancies, which is not available except near to dislocations or the free surface.

Van der Maesen and Brenkman[3] had already proposed that copper dissolves both interstitially and substitutionally in germanium and that the rapid diffusion, reported by Fuller *et al.*, is effected by interstitial copper. However, they did not recognize the necessary provision of vacancies and the consequent importance of processes of vacancy diffusion from dislocations and free surfaces.

We attribute the deep penetration, substantially uniform to 4 mm after a diffusion run longer than 10^3 sec, to pure interstitial diffusion, and from this estimate the interstitial diffusivity D_i to be about 100 times the apparent diffusivity in imperfect crystals[4] (i.e., $D_i=4\times10^{-3}$ cm^2/sec). This is about what would be expected for a process of diffusion in a lattice when the activation energy is negligibly small.

In the presence of a high density of dislocations, we suppose that the concentrations of substitutional and interstitial copper, c_s and c_i, maintain equilibrium with each other in the ratio of their solubilities c_s' and c_i'. Then each copper atom spends only a fraction $c_i'/(c_s'+c_i')$ of its time in the state of high diffusivity, and the effective diffusivity becomes

$$D_{\text{eff}}=D_ic_i'/(c_s'+c_i').$$

Identifying the observed diffusivity in relatively imperfect crystals, 4×10^{-5} cm^2/sec, with D_{eff}, we infer that the solubility ratio $\alpha=c_s'/c_i'$ is about 100. The total solubility being about 10^{-7} (atoms per atom), the interstitial solubility at this temperature is estimated as 10^{-9}. The concentrations c_s, c_i of substitutional and interstitial copper and c_v of vacancies (c_s', c_i', and c_v' being their equilibrium values) will be related by an

---

* Permanent address: H. H. Wills Physical Laboratory, University of Bristol, Bristol, England.

[1] Fuller, Ditzenberger, and Wolfstirn, Phys. Rev. **93**, 1182 (1954).

[2] A. G. Tweet and C. J. Gallagher, Phys. Rev. **103**, 828 (1956).

[3] F. van der Maesen and J. A. Brenkman, J. Electrochem. Soc. **102**, 229 (1955).

[4] Numerical estimates in this note are significant only as to order of magnitude.

equilibrium equation:

$$c_s = K c_i c_v, \tag{1}$$

where

$$K = c_s'/c_i'c_v' = \alpha/c_v' \sim 100/c_v'. \tag{2}$$

With an initial concentration of vacancies c_v', and introduction of copper with no immediate supply of further vacancies, we have

$$c_s + c_v = c_v', \tag{3}$$

and hence

$$c_v = c_v'/(1 + K c_i). \tag{4}$$

Thus the vacancy concentration will be temporarily depressed by a factor of more than 2 provided that $c_i > 1/K = c_v'/\alpha = c_i'c_v'/c_s'$; i.e., essentially, if $c_v' < c_s' \sim 10^{-7}$. This requirement for the interpretation is almost certainly met.

If we estimate that the activation energy for self-diffusion in germanium,[5] 73.5 kcal, can be divided as 50 for vacancy formation and 23.5 for vacancy migration,[5] the equilibrium vacancy concentration at 710°C will be about 10^{-10}, and therefore, as required, will be substantially suppressed by the interstitial copper concentration when it is near to its equilibrium value $c_i' \sim 10^{-9}$.

In the light of this theory, the principal mechanism for diffusion of substitutional atoms of copper will be that they dissociate into vacancies and interstitial copper atoms, which diffuse independently. Compared with this, we can neglect the "genuine" diffusivity of substitutional copper which is likely to be of a similar order of magnitude to the self-diffusion coefficient of germanium, $D_{\mathrm{Ge}} \sim 6\times 10^{-15}$ cm^2/sec. For diffusion by this dissociative mechanism, we shall have

$$D_s = D_v \cdot c_v/(c_v + c_s), \tag{5}$$

the migration rate being that of the slower moving species, the vacancies, multiplied by a factor representing the proportion of time that the vacancies are free (from combination with copper). Thus

$$D_s = \frac{D_v}{1 + K c_i} = \frac{c_v' D_v}{c_v' + \alpha c_i} = \frac{D_{\mathrm{Ge}}}{c_v' + \alpha c_i}. \tag{6}$$

This diffusivity is thus not a constant, but diminishes with the interstitial copper concentration. If the latter is very low, D_s becomes equal to D_v, about 6×10^{-5} cm^2/sec hypothetically. When the high interstitial diffusivity maintains c_i near to its equilibrium value c_i', we have essentially

$$D_s \sim D_{\mathrm{Ge}}/c_s' \sim 6\times 10^{-15}/10^{-7}\ \mathrm{cm^2\ sec} = 6\times 10^{-8}\ \mathrm{cm^2/sec}.$$

This value (giving an effective penetration of 8×10^{-3} cm in 10^3 sec) agrees in order of magnitude with the distribution of acceptors around dislocations, and near the surface of perfect regions of crystal.

The estimated value, 100, for the solubility ratio, α, is sufficiently high to explain the substantial agreement between radioactive and electrical assessments of copper content if we assume that each substitutional copper atom is an acceptor, whatever the electrical behavior of interstitial copper. It is reasonable to suppose that the interstitial copper atoms are donors, and this is supported by the observation[6] that at 800°C copper migrates electrolytically as a positive ion.

A qualitative prediction from this theory, that acceptors are produced around dislocations having no close connection with the surface source, is verified in A. G. Tweet and C. J. Gallagher's[7] observations that, after diffusion, certain regions having no apparent connection with the surface are marked by radiocopper.

The mechanism of diffusion of copper into silicon appears to be similar. Phenomena of this kind in crystals of relatively high perfection are to be anticipated, in pronounced form, whenever the solubility is smaller, but the product of solubility and diffusivity larger, for the interstitial than for the substitutional state, and at the same time the total solubility exceeds the equilibrium vacancy concentration.

The present interpretation helps to explain the observations of Dash[8] with regard to the formation of copper precipitates at dislocations in silicon. The copper migration for precipitate growth is no doubt interstitial, but silicon atoms must also be removed to make space for the precipitate. The necessary vacancy supply is available close to dislocations, where the precipitation is observed, and is less easily available from screw dislocations, where precipitation either does not occur, or occurs to a smaller extent than at other dislocations.

ACKNOWLEDGMENT

Our interest in this problem was stimulated by conversations with A. G. Tweet and L. Apker to whom we are also indebted for reviewing the manuscript.

---

[5] Letaw, Slifkin, and Portnoy, Phys. Rev. **93**, 892 (1954).

[6] J. C. Severiens and C. S. Fuller, Phys. Rev. **92**, 1322 (1953).

[7] A. G. Tweet and C. J. Gallagher (private communication).

[8] W. C. Dash, J. Appl. Phys. **27**, 1193 (1956).