DISSOCIATIVE MECHANISM OF COPPER DIFFUSION IN GERMANIUM

V. V. SPIRIĆ and A. DAMJANOVIĆ

Institute »Boris Kidrič«, Beograd

Abstract: The dissociative mechanism of copper diffusion in germanium is studied. The rates of all processes taking place in diffusion are estimated. It is concluded that the diffusion of the copper atoms depends essentially on the diffusion of vacancies in the temperature region 650—750 °C if the thickness of the sample is about 1 mm and dislocation density below 10^3 cm^{-2}.

Using the sheet conductance and p—n junction methods, it is indicated experimentally that the copper atoms diffuse in germanium from all boundary surfaces, regardless of the exact location of copper before diffusion. This confirms directly the dissociative mechanism of copper diffusion in germanium. The diffusion coefficient of copper in the above temperature range is measured as a function of temperature.

1. Introduction

To explain many contradictory facts for the diffusion of copper in germanium the dissociative mechanism is assumed[1]. For example, the acceptor activity of copper in germanium[2] shows that it occupies the substitutional sites in the germanium crystal lattice. However, this is in disagreement with the observed values for the diffusion coefficient of about $2 \cdot 10^{-5}$ cm²/s at 800 °C[3, 4] and also with the drift of copper in the form of positive ions[5]. Therefore, it is supposed that the copper atoms occupy substitutional and interstitial positions in the crystal lattice of germanium. The copper atoms diffuse interstitially and form the substitutional atoms by going over into the vacant lattice sites[1]. Using this assumption many experimental results have been explained[6, 7, 8, 9, 10].

The purpose of this paper is to confirm directly a dissociative mechanism for the copper diffusion in germanium.

2. On the dissociative mechanism

Processes taking place during the diffusion of copper by dissociative mechanism are as folows: diffusion of the interstitial I copper atoms, difusion of vacancies V from boundary surfaces, generation of vacancies by their diffusion away from dislocations, and, finally the dissociation process $S \rightleftarrows I + V$. Let us calculate the rates for these processes assuming that they are mutually independent.

If copper was deposited before the diffusion on both sides of the sample of the thickness d, an average concentration of the interstitial copper atoms after the time interval t is given by[3]:

$$N_i(t) = N_i^\circ \left[1 - \exp \left(- \frac{t}{\tau_i} \right) \right]. \tag{1}$$

The time constant necessary to build up interstitial copper atoms is given by:

$$\tau_i = \frac{d^2}{\pi^2 D_i}, \tag{2}$$

where D_i denotes the diffusion coefficient of the interstitial copper atoms. In a similar way, the time constant necessary to build up vacancies by their diffusion from boundary surfaces is given by:

$$\tau_p = \frac{d^2}{\pi^2 D_v}. \tag{3}$$

where D_v denotes the diffusion coefficient of vacancies. The time constant necessary to build up vacancies by their diffusion away from dislocations is given by:

$$\tau_d = \frac{1}{\beta N_D D_v}. \tag{4}$$

where N_D denotes the dislocation density, and β is a function of the dislocation density[9]. Finally, the time constant for the dissociation process $S \rightleftarrows I + V$, τ_s, is the time defining the existence of a copper atom in a substitutional position.

The time constants vs. reciprocal temperature for the diffusion of copper in germanium are shown in Fig. 1. The sample thickness d and the dislocation density N_D are taken as parameters. From the published data we used the following magnitudes: the diffusion coefficient of interstitial copper determined by Hall and Racette[8]; the diffusion coefficient of vacancies determi-

ned by Hiraki[7] and the time constant τ_s determined by Tweet[10]. Let us take into consideration the following conditions: the temperature region 600 — 800 °C, sample thickness about 1 mm, and dislocation density below $10^3/cm^2$. If these conditions are fulfilled, the $\tau_t \gg \tau_p \gg \tau_i \gg \tau_s$.
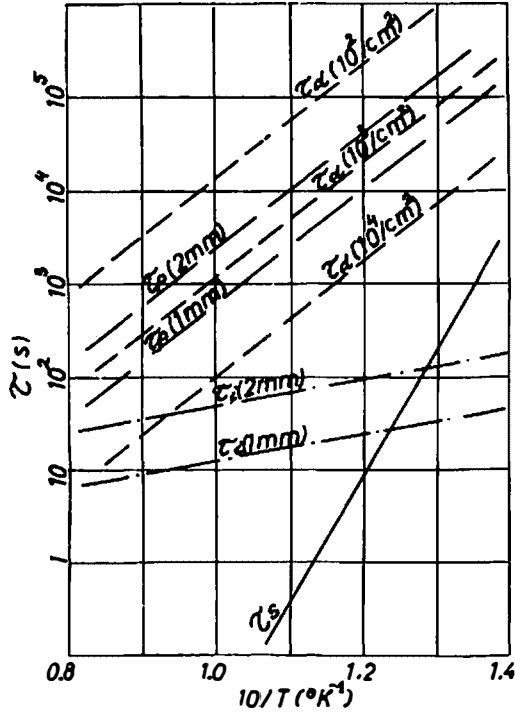

Fig. 1. Plot of time constants τ_i, τ_F, τ_d and τ_s for copper diffusion in germanium as a function of $1/T$.

Since the dissociation process is considerably faster than all the others, a local equilibrium of concentration will exist, which can be expressed by:

$$\frac{N_s}{N_i N_v} = \frac{N_s^\circ}{N_i^\circ N_v^\circ} . \tag{5}$$

where N_s, N_i and N_v are concentrations of substitutional and interstitial copper atoms and vacancies, respectively and N_s°, N_i° and N_v° are the corresponding solubilities at the diffusion temperature.

Since the interstitial diffusion of copper is considerably faster than diffusion of vacancies ($\tau_i \ll \tau_p$) ,it can be supposed that $N_i \equiv N_i^\circ$, and that vacancies are formed mainly by the diffusion from the boundary surfaces ($\tau_p \ll \tau_d$).

It can be concluded that distribution of concentration of the substitutional atoms will follow distribution of concentration of vacancies. Therefore, the build up of substitutional copper atoms will be equivalent to the diffusion process with an effective diffusion coefficient[11]:

$$D_{eff} = D_v \frac{N_v^o}{N_v^o + N_s^o} \cdot \qquad (6)$$

If before the diffusion copper is deposited on one side of the sample then the same distribution of concentration of the substitutional copper atoms from both sides of the sample can be expected. In case of diffusion from the constant surface source, this distribution can be expressed by[11]:

$$N_s = N_s^o \, \mathrm{erfc} \left[\frac{x}{2 \, (D_{eff} \cdot t)^{1/2}} \right]^* \cdot \qquad (7)$$

If the relation $D_v N_v^o = D_{Ge} N_L$ is used[3] (where D_{Ge} is a coefficient of the germanium self-diffusion[16] and N_L concentration of crystal lattice sites), then D_{eff} is given by:

$$D_{eff} = D_{Ge} \cdot \frac{N_L}{N_s^o} \cdot \qquad (8)$$

3. Experimental

Germanium single-crystals of n-tipe with specific resistivity of $5 - 8 \, \Omega \cdot$ cm. and dislocation density of 2000/cm² were used. The germanium samples were of rectangular shape with dimensions $20 \cdot 8 \cdot 1$ mm. After mechanical polishing and etching in CP-4A solution, to clean up the surface from copper the samples were washed in the solution of KCN[12].

The diffusion process was performed in the apparatus shown in Fig. 2

The ends of the germanium sample enter the rectangular holes on tantalum electrodes, so that the sample was in contact only with tantalum. It is a measure to protect the sample against contamination during the diffusion process. The sample was directly heated by the alternating current in

---

$$* \, \mathrm{erfc} \, (y) = 1 - \frac{2}{\pi^{1/2}} \int_o^y \exp \, (- z^2) \, dz$$

vaccuum of the order of 10^{-6} mm Hg. At the temperature 500 °C copper was deposited on the low side of the sample by evaporation and then temperature was suddenly increased to the diffusion temperature. Diffusion was perfor-
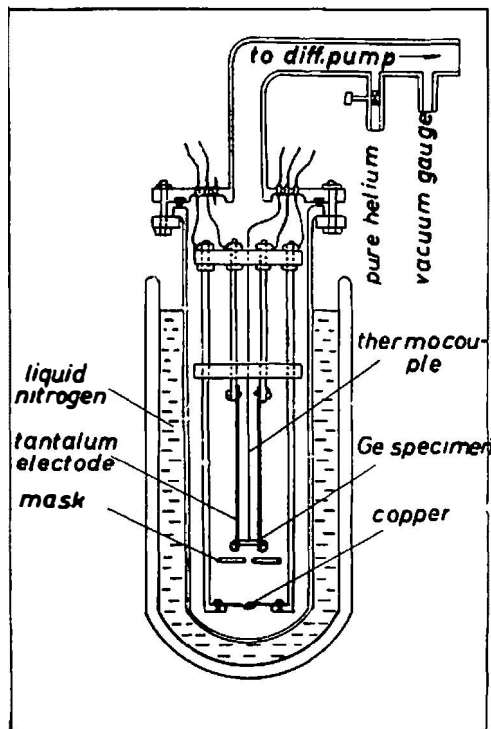

Fig. 2. Apparatus for diffusion.

med in the temperature region 650 — 800 °C for 5 to 20 minutes. The quenching of sample was done by disconnecting the power supply and by introducing pure helium into the diffusion chamber. The initial cooling rate of 100 — 200 °C/s was obtained.

After the diffusion process the sample was taken out of the chamber and the distribution of concentration of copper atoms was determined. The method of successive removal of thin layers with measuring the electric conductivity at room temperature after each removal of the layer was applied[3, 13]. The electric conductivity was measured using the four points probes method[14]. The two magnitudes from the distribution of concentration of copper atoms were determined: solubility and diffusion coeficcient of copper in germanium. The diffusion coefficient was also determined using the p — n junction method[3, 13].

Before the diffusion process the sample was heated at the diffusion temperature without depositing copper. The equilibrium concentration of ther-

mal acceptor v. s. diffusion temperature was determined from the changes
of sample specific resistivity before and after heating.

4. Results and discussion

The experimental results confirmed our assumptions and indicated some
new problems.

The distributions of concentration of copper atoms on semi-erfc paper are
given in Fig. 3. As can be observed, the symmetrical distributions are obtained
if the copper was deposited only on one side of the sample. The copper atoms
diffused symmetrically as also established by measuring the depth of p — n
junction.

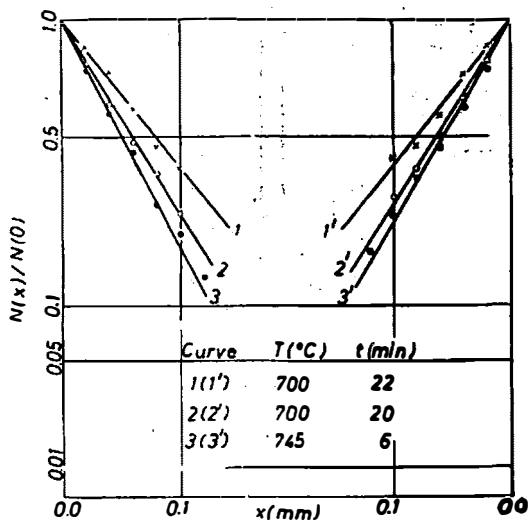| Curve	T(°C)	t (min)
1(1')	700	22
2(2')	700	20
3(3')	745	6

Fig. 3. Semierfc plots of the distribution of copper atoms after diffusion. Before
diffusion copper was deposited only on the left side of the germanium sample.

The question is imposed whether copper could appear on the side of the
sample where it was not deposited. Frank and Turnbull rejected the possi-
bility of transport along dislocations, because the diffusion coefficient
should have an unexpected value[1]. Also, the possibility of transport via
surfaces should be refuse the unexpected value of surface diffusion coeffi-
cient. In this way we undoubtedly confirmed that copper diffuses in germa-
nium by dissociative mechanism.

On the other hand, it is evident from the shapes of N(x)/N(0) curves that
the distribution of concentration is given by the erfc function so that Eq. (7)
is confirmed.

To determine the diffusion coefficient the slope of distribution curves and the p — n junction depth are used. The obtained results are represented in Fig. 4. and compared with the diffusion coefficient D_{eff} according to Eq. (8).

Since Eq. (8) is a direct consequence of the dissociative mechanism, a satisfactory agreement of experimental results with theory represent one more confirmation of applicability of the dissociative mechanism to diffusion of copper in germanium.
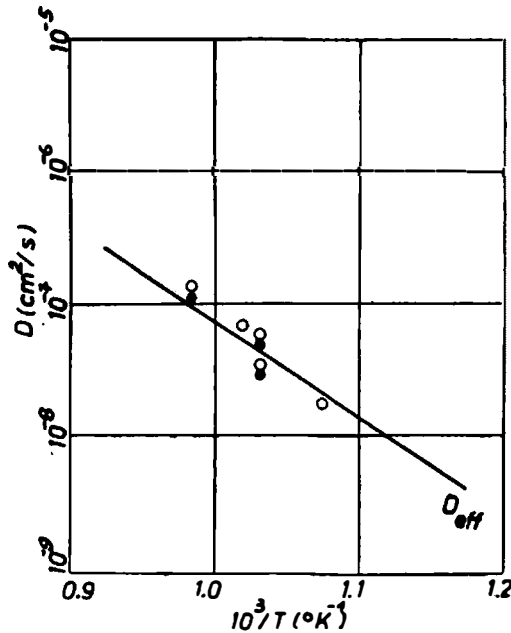

Fig. 4. Diffusion coefficient of copper in germanium as a function of $1/T$.

The experimental values of copper solubility in germanium and the vacancy solubility with the corresponding literature values of Fuller[15, 16, 17, 18] and Hiraki[7] were compared in Fig. 5.

It can be observed that our solubility values of vacancies are greater than those of Hiraki. The reason for this disagreement probably results from the differences in thermal treatment[19].

Our results show that at room temperature only substitutional atoms of copper can be detected. The experiments in which the diffusion was done for a short time in order to »freeze in« only interstitial copper atoms in germa-

nium gave negative results. We suppose that this is either the result of the neutrality of interstitial copper atoms or their very fast annealing.
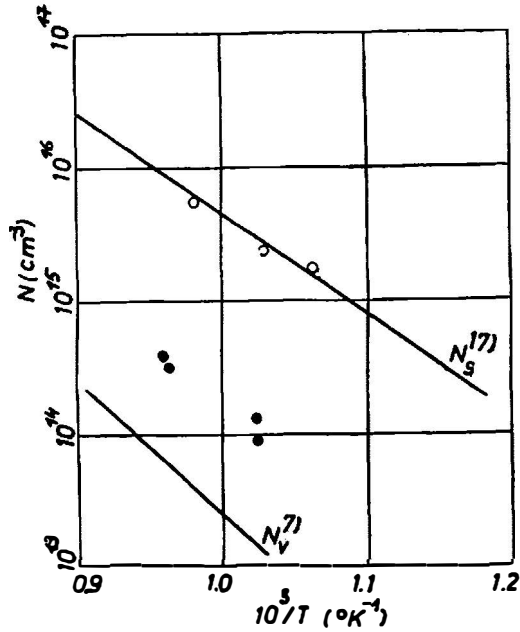

Fig. 5. Plot of solubility for copper and vacancies in germanium.
○ Copper
● Vacancies

5. Conclusion

The assumption of the dissociative mechanism of copper diffusion in germanium is confirmed in two ways:

1. The diffusion coefficient of copper in germanium (the sample thickness about 1 mm, the dislocation density about $10^3/cm^2$) in the temperature range 650 — 750 °C is determined. The direct dependence of this coefficient from the diffusion coefficient of vacancies is established according to Eq. (6).

2. The symmetrical distribution of copper concentration after the diffusion at a given temperature is obtained, independently of where copper before the diffusion was deposited. This form of the distribution represents an original and direct confirmation of the reaction $Cu_i \rightleftarrows Cu_s + V$, i. e. the dissociative mechanism of copper diffusion in germanium.

Acknowledgement

References

1) F. C. Frank and D. Turnbull, Phys. Rev. **104** (1956) 617;
2) H. H. Woodbury and W. W. Tyler, Phys. Rev. **105** (1957) 84;
3) B. I. Boltaks, »Difuzija v poluprovodnikah« Fizmatgiz, Moskva, 1961;
4) C. S. Fuller and J. A. Ditzenberger, J. Appl. Phys. **28** (1957) 40;
5) C. S. Fuller and J. C. Severiens, Phys. Rev. **92** (1953) 1322, ibid. **96** (1954) 21;
6) A. G. Tweet and O. J. Gallagher, Phys. Rev. **103** (1956) 828;
7) A. Hiraki, J. Phys. Soc. Japan **21** (1966) 34;
8) R. N. Hall and J. H. Racette, J. Appl. Phys. **35** (1964) 379;
9) P. Penning, Philips Res. Repts. **14** (1959) 337;
10) A. G. Tweet, Phys. Rev. **106** (1957) 221;
11) M. D. Sturge, Proc. Phys. Soc. **73** (1959) 297;
12) F. Van Der Maesen and J. A. Brenkman, J. Electroch. Soc. **102** (1955) 229;
13) B. N. B. Hannay, »Semiconductors«, Reinhold Publ. Corp. New York, 1960;
14) F. M. Smits, B. S. T. J. **37** (1958) 711;
15) C. S. Fuller et al., Phys. Rev. **93** (1954) 1182;
16) H. Letaw et al., Phys. Rev. **102** (1956) 636;
17) K. Wolfstirn and C. S. Fuller, Phys. Chem. Solids **7** (1958) 141;
18) C. S. Fuller and K. Wolfstirn, Phys. Chem. Solids **26** (1965) 1463;
19) M. Stojić, Ph. D. Thesie, University of Tokyo, 1967.

DISOCIJATIVNI MEHANIZAM DIFUZIJE BAKRA U GERMANIJUMU

V. V. SPIRIĆ i A. DAMJANOVIĆ

Institut »Boris Kidrič«, Beograd

Sadržaj

Analiziran je disocijativni mehanizam difuzije bakra u germanijumu. Ocenjene su vrednosti brzina svih procesa koji se dešavaju pri difuziji ovim mehanizmom. Data je zavisnost brzina svih procesa od temperature difuzije, debljine uzoraka u kojima se vrši difuzija i od gustine dislokacija. Utvrđeno je da postoji određena temperaturna oblast u kojoj difuzija bakra direktno zavisi od difuzije vakansija. Zaključeno je da se kod ovakve difuzije supsticioni atomi bakra moraju ugrađivati u kristalnu rešetku na granicama svih površina germanijuma bez obzira gdje je primesa bakra pre difuzije nanesena.

Korišćenjem metode skidanja tankih slojeva i merenjem električne provodnosti, eksperimentalno je dokazana simetrična raspodela atoma bakra u germanijumu posle difuzije iako je bakar nanesen samo na jednu površinu germanijuma. Za difuziju bakra u germanijumu disocijativni mehanizam je time na originalan način potvrđen. Određen je i koeficijent difuzije bakra u temperaturnom opsegu 650 — 750 °C.