

Precipitation of Cu in Ge

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The kinetics of precipitation of Cu from supersaturated solid solution in Ge have been studied as a function of temperature and dislocation density in the samples. The results can be expressed as an exponential decay with time of the unprecipitated fraction of Cu. We find that for a given dislocation density the time constant for the precipitation has a different temperature-dependence at high temperatures from its temperature-dependence at lower temperatures, and that the temperature of the break in the curve is a function of dislocation density. It is proposed that the high-temperature precipitation is limited by the diffusion of Cu to dislocations by the dissociative mechanism described by Frank and Turnbull. At lower temperatures the rate-limiting step is believed to be the actual process of dissociation of a substitutional Cu into a vacancy and an interstitial Cu atom. The measurements permit an estimate of the vacancy concentration in Ge at $\sim 715^\circ\text{C}$.

I. INTRODUCTION

LOGAN¹ has shown that the rate of precipitation of Cu from supersaturated solid solution in Ge is greatly accelerated at 500°C if the Ge has been deformed plastically. This paper presents a more complete and quantitative picture of the process, together with a proposed mechanism to explain the results.

II. EXPERIMENTAL

Bars of *p*-type Ge, 1 mm \times 3 mm \times 2 cm, with initial hole concentrations of $\sim 10^{14}/\text{cm}^3$, were twisted various amounts about $\langle 110 \rangle$ axes² and then twisted back flat, in order to facilitate electrical measurement. The deformation was performed in an atmosphere of N_2 at $\sim 520^\circ\text{C}$. A $\text{Cu}(\text{NO}_3)_2$ solution was applied and the samples were heated in H_2 to temperatures from 700°C to 850°C for periods of one hour and more to produce a solid solution of electrically active Cu. The samples were cooled in a few seconds to room temperature. After grinding and etching, carrier concentration was measured by the Hall effect, at a field strength of ~ 1600 gauss. The samples were reheated for various lengths of time, at temperatures below those used to dissolve the Cu, in order to precipitate a fraction of the Cu acceptors. Carrier density was again measured and this procedure continued until the acceptor concentration was between 1% and 10% of its original value. Typical data for several samples which were twisted $\pm 90^\circ$ are shown in Fig. 1. The ordinate represents the percentage of N_{ai} , the initial number of electrically active (unprecipitated) acceptors, remaining after precipitation at 450°C ; the time of precipitation, t , is the abscissa. If one assumes a single acceptor per Cu atom, this figure represents the percentage of unprecipitated Cu atoms. Cu introduces acceptor levels into Ge at 0.04 eV and 0.33 eV from the valence band and at 0.26 eV from the conduction band.³ Neglect of the upper Cu acceptor levels results in errors in concentration of 30% and 15% at Cu concentration

of $3 \times 10^{14}/\text{cm}^3$ and $10^{15}/\text{cm}^3$, respectively. Initial acceptor concentration in these samples was $\sim 10^{16}/\text{cm}^3$. The data fall quite well on a curve whose equation is

$$N_a(t) = N_{ai} e^{-t/\tau_p}, \quad (1)$$

where $N_a(t)$ is the number of acceptors due to Cu present after precipitation time t . N_{ai} is the acceptor concentration before precipitation. τ_p is ~ 50 minutes.

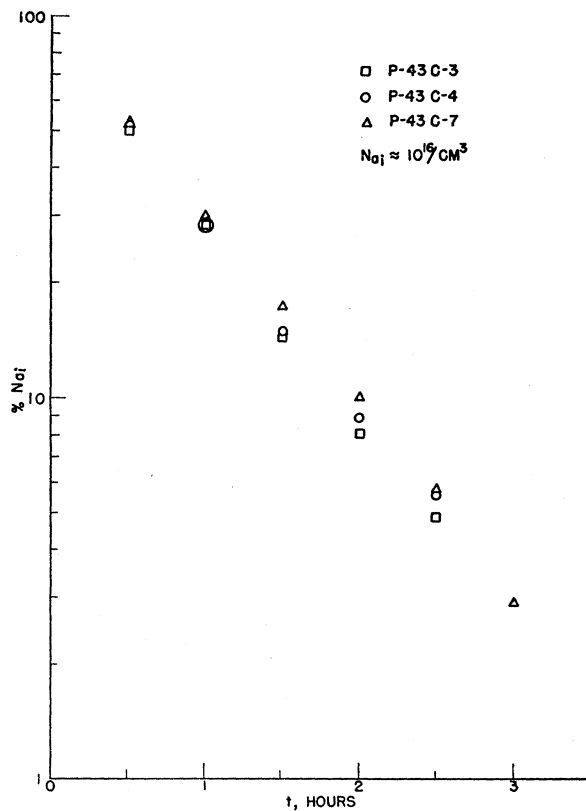


FIG. 1. Time-dependence of the precipitation of Cu from supersaturated solid solution in heavily deformed (dislocation density $\sim 10^7/\text{cm}^2$) Ge at 450°C . Ordinate is percent N_{ai} , the initial number of acceptors due to Cu. Abscissa is time of precipitation. Initial Cu concentration was $\sim 10^{16}/\text{cm}^3$.

¹ R. A. Logan, Phys. Rev. **100**, 615 (1955).

² Sample twisted about $\langle 111 \rangle$ axes behaved in the same way.

³ H. H. Woodbury and W. W. Tyler, Phys. Rev. **105**, 84 (1957).

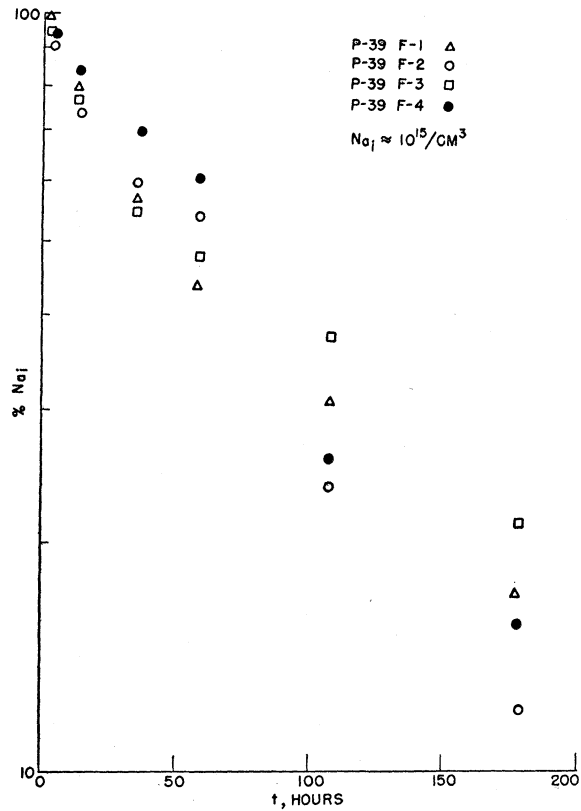


FIG. 2. Time-dependence of the precipitation of Cu in Ge with dislocation density $\sim 10^4/\text{cm}^2$ at 450°C . Ordinate is percent N_{ai} ; abscissa is time of precipitation. Initial Cu concentration $\sim 10^{16}/\text{cm}^3$.

Figure 2 shows similar data on undeformed samples of Ge (dislocation density $\sim 10^4/\text{cm}^2$), which were also precipitated at 450°C . Note the large differences in time scales and the scatter of the data for a single sample. This spread is probably related to variation in dislocation geometry from sample to sample. The average behavior of the collection of samples satisfies Eq. (1) fairly well, however, with a τ_p of ~ 95 hours.

A program was carried out to determine the dependence of the time constant, τ_p , for the precipitation process upon temperature and dislocation density, n_D , in the sample. The results are shown on Fig. 3 where we have plotted τ_p vs $1/T^\circ\text{K}$. The numbers attached to the different curves refer to dislocation densities in the samples. The numbers in parentheses are estimated on the basis of the amount of twist. The others refer to densities known from etch pit counts on crystals purposely slipped during growth. (We estimate that a twist of $\pm 5^\circ$ yields a dislocation density of $\sim 10^6/\text{cm}^2$ over a length of 1 cm in our samples, but it should be emphasized that the estimate is very crude.) The steeply sloped part of the τ_p curves labeled 1/g is given by

$$\tau_p = 3.6 \times 10^{-16} e^{+2.7 \text{ ev}/kT} \text{ sec}, \quad (2)$$

while the activation energy for the curves with smaller slope is ~ 1.3 ev. Note that at sufficiently low temperatures, the τ_p vs $1/T$ curves for all samples with dislocation densities, n_D , of $10^5/\text{cm}^2$ and higher merge with the curve labeled 1/g. The temperature of the break in each curve depends upon n_D .

The quality of the data is markedly better on the portions of the time constant curve with the steep slope than on the sections with a smaller temperature dependence. On the samples with etch pit densities of $10^4/\text{cm}^2$ especially, there was difficulty in getting samples to behave consistently upon precipitating at a particular temperature, redissolving the Cu, and reprecipitating at a lower temperature. It proved expedient to carry precipitation part way to completion in a sample, then continue the process at a lower temperature in the same sample. By interleaving the temperatures of a number of such two-stage precipitations, we obtained a more reliable temperature dependence of τ_p . (We tentatively attribute these difficulties to the occurrence of spontaneous nucleation of precipitates independent of the dislocations at supersaturation of $\gtrsim 100$ times the solubility. Thus it is possible actually to increase the rate of precipitation by lowering the temperature, perhaps because such a procedure will satisfy the conditions for spontaneous nucleation.)

In collecting the data for Fig. 3, we also ascertained a number of other facts.

1. τ_p is independent of initial Cu concentration when τ_p is on the steep part of the curve in Fig. 3.
2. A heavily deformed sample may be run through several cycles of solution and precipitation with no changes in τ_p .
3. It is immaterial in which order deformation and saturation with Cu are carried out.
4. Cu requires < 2 minutes to redissolve at high temperature in heavily deformed samples.
5. We found that the role of the dislocations is to provide nuclei for precipitation, not diffusion short circuits for diffusion of the Cu to the surface of the samples. This was shown by grinding heavily on the surface of a deformed sample in which Cu had been precipitated. It was then cleaned carefully in KCN and heated to the temperature at which the Cu had originally been dissolved. The Cu concentration came up to nearly its original value. A control sample changed very little upon being given the same treatment.⁴

III. DISCUSSION

Turnbull⁵ has pointed out that the precipitation kinetics epitomized in Eq. (1) are consistent with a diffusion-limited precipitation in which the Cu diffuses to dislocations⁶ which serve as nuclei for the precipita-

⁴ The work of Dash [W. C. Dash, J. Appl. Phys. 27, 1193 (1956)] has made this particular experiment unnecessary.

⁵ D. Turnbull (private communication). The author is indebted to Dr. Turnbull for stimulating conversations about this work.

⁶ C. Zener, J. Appl. Phys. 20, 950 (1949).

tion. If one assumes that

$$D\tau_p \approx L^2 \approx 1/n_D, \quad (3)$$

where D is the Cu diffusion coefficient, L the spacing between dislocations, and n_D the dislocation density, then the low-activation energy portions of the time-constant curves in Fig. 3 are consistent both in magnitude and temperature-dependence with $D = D_s$, where D_s is the coefficient given by Frank and Turnbull⁷ for the mechanism of dissociative diffusion of Cu in Ge. The dissociative mechanism had been verified experimentally, by Fuller and Ditzenberger⁸ and by the author. Thus we believe that portions of the τ_p curves with a 1.3-ev activation energy correspond to dissociative diffusion of Cu to dislocations.

However, an attempt to fit the high-activation-energy portion of the τ_p curve with an equation such as (2) leads to a diffusion coefficient with the impossibly high D_0 of 10^7 cm²/sec for samples with an n_D of $\sim 10^7$ /cm². Moreover, it is difficult to see why D_s , if operative at low temperatures, would not short-circuit any other, slower diffusion process.

IV. PROPOSED MECHANISM

In the dissociative mechanism of Cu diffusion, account is taken of the fact that Cu can be present in Ge in both the interstitial and substitutional positions. D_i , the interstitial diffusion coefficient, is $\sim 10^{-4}$ cm²/sec at 700°C and presumably very insensitive to temperature, while the substitutional Cu probably diffuses with approximately the self-diffusion coefficient of Ge. However, there is an equilibrium mass action principle relating n_s and n_i , the number of substitutional and interstitial Cu atoms, respectively, to n_v , the number of vacancies:

$$n_s = K n_i n_v, \quad (4)$$

where

$$K = \left(\frac{n_s'}{n_i'} \right) \left(\frac{1}{n_v'} \right) = \frac{\alpha}{n_v'}$$

Primes indicate thermal equilibrium values. We have measured α at 715°C and find that it is $\sim 6 \pm 2$. Thus, substitutional Cu dissociates into vacancies and interstitials which diffuse separately until trapped again. The rate of advance of substitutional Cu into initially Cu-free Ge, then, is limited by the dissociative diffusion coefficient D_s which is equal to D_v , the diffusion coefficient of vacancies, multiplied by the fraction of the time the vacancy spends free, i.e., untrapped by an interstitial Cu.

If the dissociation is a temperature-activated process, with an activation energy greater than that for D_s , at sufficiently low temperatures dissociation of vacancies and interstitials could become the rate-limiting step in

⁷ F. C. Frank and D. Turnbull, Phys. Rev. **104**, 617 (1956).

⁸ C. S. Fuller and J. A. Ditzenberger, J. Appl. Phys. **28**, 40 (1957).

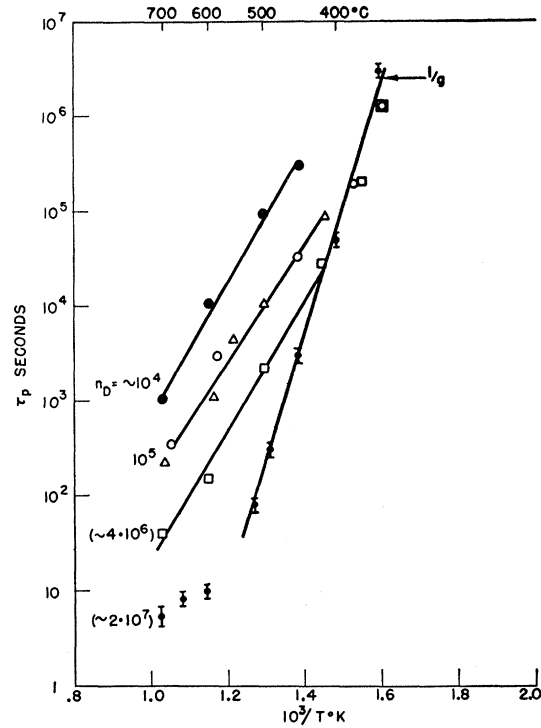


FIG. 3. Plot of τ_p , the time constant⁷ for Cu precipitation in Eq. (1), vs $1/T^\circ\text{K}$. Curves are labeled with dislocation densities. Smaller densities were measured from etch pit counts. Larger densities (numbers in parentheses) were estimated crudely from amount of deformation.

the precipitation process. This will occur whenever the vacancy concentration is low enough so that the free path against trapping of an interstitial by a vacancy is comparable with the spacing between dislocations. Greater spacing between dislocations will require smaller vacancy concentrations and hence lower temperatures to satisfy this criterion for the breakdown of the dissociative diffusion mechanism. We see that this conclusion is consistent with the fact that the breaks in the curves on Fig. 3 take place at lower temperatures for smaller dislocation densities.

The foregoing proposal leads to the conclusion that Eq. (2), which describes the part of the τ_p vs $1/T$ curve at temperatures below the break, should be interpreted as the reciprocal of the vacancy-interstitial generation rate, g . This interpretation is supported by the following consideration.⁹ Assume that ΔG is the free energy barrier for dissociation of vacancies and interstitials. Then

$$\begin{aligned} 1/\tau_p &= g = \nu_0 e^{-\Delta G/RT} \\ &= \nu_0 e^{\Delta S/R} e^{-\Delta E/RT}, \end{aligned} \quad (5)$$

where $\nu_0 \sim 10^{13}$ /sec, the reststrahlen frequency of the Ge lattice. Comparing Eqs. (2) and (5), we find that $\Delta S = 11.2$ calories/mole $^\circ\text{K}$. This is in reasonable agree-

⁹ The author is indebted to W. T. Read, Jr., for helpful discussion of this point.

ment with the value of 9.0 calories/mole $^{\circ}$ K given by the Zener theory,¹⁰ in which $\Delta S = -\Delta E(d \ln \mu / dT)$, where μ is the shear modulus of Ge.¹¹

If the interpretation of τ_p given in Eq. (5) is correct, we can calculate the vacancy concentration in a certain concentration range by the following argument.¹²

In equilibrium,

$$G = n_s' g = n_i' \nu (\phi c_v') = R. \quad (6)$$

That is, the total generation rate, G , is equal to the total recombination rate, R . R is equal to the number of interstitial atoms times the number, ν , of jumps each makes per second times the probability that any jump ends in a vacancy. This latter quantity will be proportional to the equilibrium fraction, c_v' , of the lattice sites which is occupied by vacancies. The proportionality constant, ϕ , will be related to the effective cross section for recombination, and will be close to unity if there are no attractive forces between vacancies and interstitials. We can set

$$\nu = D_i / b^2, \quad (7)$$

where D_i is the interstitial diffusion coefficient, and b is the jump distance, which we take to be $\sim 3 \times 10^{-8}$ cm. Then, letting $\phi = 1$, which gives an upper limit on c_v' :

$$c_v' = \left(\frac{n_s'}{n_i'} \right) g \left(\frac{b^2}{D_i} \right) = \frac{\alpha b^2}{D_i \tau_p}. \quad (8)$$

Extrapolating the experimental data for τ_p to 715 $^{\circ}$ C, the temperature at which α and D_i are known, yields $c_v' \sim 10^{-9}$. (All estimates in this paragraph are to be considered as good only in order of magnitude.) This satisfies the condition for dissociative diffusion that $n_v' < n_i'$. Assuming

$$c_v' = e^{-E_v/kT}, \quad (9)$$

we get $E_v = 1.8$ ev. Since no pre-exponential entropy term has been used in this calculation, 1.8 ev is a lower limit on E_v . From knowledge of the self-diffusion coefficient of Ge,¹³ $D_{Ge} = 8e^{-3 \text{ ev}/kT}$, we get the vacancy diffusion coefficient D_v :

$$D_v = D_{Ge} / c_v' = 8e^{-1.2 \text{ ev}/kT}. \quad (10)$$

The ambiguity in the correct division of the entropy term in the Ge self-diffusion coefficient between D_v and c_v' must be emphasized. In addition, the arbitrary selection of $\phi = 1$ in Eq. (6), reflecting our ignorance of the vacancy-interstitial recombination cross section, is a troublesome point.

¹⁰ C. Zener, J. Appl. Phys. 22, 372 (1951).

¹¹ H. J. McSkimin, J. Appl. Phys. 24, 988 (1953).

¹² The author is indebted to J. Bardeen for pointing out this argument.

¹³ Letaw, Portnoy, and Slifkin, Phys. Rev. 102, 636 (1956).

It might prove possible to evaluate the cross section by a treatment which can be given crudely as follows. The interstitial mean free path against capture by a vacancy, λ_i , is given by

$$\lambda_i = b N_i = D_i \tau_f^i / b, \quad (11)$$

where b is the jump distance, N_i the number of jumps, D_i the interstitial diffusion coefficient, and τ_f^i the mean free time between successive captures. Now σ , the capture cross section, is given by

$$\sigma = 1 / n_v \lambda_i. \quad (12)$$

Hence, if a theory giving n_v and τ_f^i were available, σ could be calculated. Note that n_v is not necessarily the thermal equilibrium value of the vacancy density. At temperatures well below the breakpoint in the τ_p curves, the vacancy-interstitial dissociation rate is small enough and the vacancy diffusion coefficient large enough, so that vacancy equilibrium with the lattice can be maintained by unhindered vacancy diffusion to the dislocations. But at temperatures above the breakpoint, the dissociation rate is rapid enough so that Eq. (4) applies. The interstitial and vacancy densities are then above the thermal equilibrium values.

V. SUMMARY

In the foregoing sections, we have described the dependence of τ_p , the time constant for precipitation of Cu in Ge, upon temperature and dislocation density in the samples. For a given dislocation density, the time-constant curve exhibits a high-temperature range, where the temperature dependence has an activation energy of ~ 1.3 ev, and a low-temperature range where the activation energy is 2.7 ev. We attribute the high-temperature behavior to a diffusion-limited migration of Cu atoms to dislocations, in which the diffusion coefficient is that for dissociative diffusion⁷ of the Cu. We believe that on the low-temperature part of the curve the rate-limiting step is the dissociation rate of vacancies and Cu atoms.

Some speculation as to the equilibrium vacancy concentration and the creation energy for vacancies are made on the basis of this model.

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