LBL-42[illegible]8

To be published in the Proceedings of the International Conference on Radiation Effects in Semiconductors, Dubrovnik 1976, The Institute of Physics, London and Bristol.

# DIVACANCY-HYDROGEN COMPLEXES IN DISLOCATION-FREE HIGH-PURITY GERMANIUM*

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* This report was done in part with support from the United States Energy Research and Development Administration.

## Abstract

A defect center with a single acceptor level at $E_v + 0.08$ eV appears in $H_2$ grown dislocation-free high-purity germanium. Its concentration changes reversibly upon annealing up to 650 K. By means of Hall-effect and conductivity measurements over a large temperature range the temperature dependence of the steady-state concentration between 150 K and 720 K as well as the transients following changes in temperature have been determined. The observed acceptor level is attributed to the divacancy hydrogen complex $V_2H$. The complex reacts with hydrogen, dissolved in the Ge lattice or stored in traps, according to: $V_2H + H \rightleftarrows V_2H_2$. An energy level associated with the divacancy-dihydrogen complex was not observed. These results are in good agreement with the idea that hydrogen in germanium forms a 'very deep donor' (i.e. the energy level lies inside the valence band).

## 1. Introduction

The development of high purity monocrystalline germanium with net concentration of electrically active impurities as low as $10^9$ cm$^{-3}$ - $10^{12}$ cm$^{-3}$ (Hall 1974a,b, Hansen and Haller 1974) and low degrees of compensation has opened new possibilities for the study of intrinsic properties of this semiconductor. Since in such material one can detect very small carrier concentrations it is possible to study small concentrations of intrinsic defects. An example is Hall's (1974) work on quenched-in acceptors in high-purity Ge with a dislocation density of [illegible] cm$^{-2}$. The present paper investigates a 'grown-in' defect center with an acceptor level at $E_v$ + 0.08 eV that always and so far only appears in hydrogen-grown dislocation-free Ge.

## 2. General Observations on the $E_v$ + 0.08 eV Level

In the early stages of high-purity Ge development for radiation detectors it was found that dislocation-free Ge was unsuitable for device fabrication. Severe trapping of charge created by ionizing radiation or particles showed that there were at least one and possibly several deep energy levels present (Hansen and Haller 1974). Hall-effect and conductivity measurements revealed an acceptor level at $E_v$ + 0.08 eV with a concentration of about 2 x $10^{11}$ cm$^{-3}$ in 'as grown' single crystals. By comparing the dislocated and undislocated sections of a monocrystalline slice cut perpendicular to the growth axis (i.e. parallel to the melt-solid interface) the defect center was found to be a single acceptor. Figure 1 shows the hole concentration vs 1/T for two samples cut from a partially dislocated slice of a crystal. The chemical background concentration due to shallow acceptors and donors, $N_A$-$N_D$, is constant throughout the slice. In the dislocation-free piece one observes a defect with an acceptor level at $E_v$ + 0.08 eV de-ionizing around 65 K. Another major difference between dislocation free and dislocated regions appears upon etching with preferential etchants. Figure 2 shows the (100) surface of a polish-etched Ge slice after a two-minute etch in $HF{:}HNO_3{:}Cu(NO_3)_2$ 10%(2:1:1). Hemispherical pits appear in the dislocation-free region whereas in the dislocated section only the well known dislocation etch-pits can be seen. It has been shown that the hemispherical etch-pits do not result from defects that give rise to detectable contrast in transmission electron microscopy (Seeger, Föll, Frank 1977).

The hemispherical pits are likely to be associated with vacancies that were grown-in at the crystallization temperature and which in dislocation-free Ge cannot annihilate at any sinks except for at the crystal surface. Since monovacancies are highly mobile they will form (much less mobile) divacancies and larger vacancy clusters (Seeger and Chik 1968). This suggests strongly that the observed acceptor center is linked to frozen-in vacancy-type defects, the divacancy possibly playing an important role.

All radiation-detector-grade Ge is grown in a pure hydrogen atmosphere (1 atm). From early experiments, crystals grown in $N_2$, Ar and He were available. In none of these early crystals could the $E_v + 0.08$ eV level be detected in dislocation-free areas, nor did we find any hemispherical pits of the kind observed in dislocation-free hydrogen-grown Ge. The solubility of atomic H in solid Ge near the melting point is $2 \times 10^{15}$ cm$^{-3}$; the hydrogen diffusion coefficient is given by

$$D_H = 2.72 \cdot 10^{-3} \exp\left(- \frac{(0.38 \pm 0.01)\ \mathrm{eV}}{kT}\right) \frac{\mathrm{cm}^2}{\mathrm{s}} \qquad (1)$$

(Frank and Thomas 1960). With crystal growth rates of 12 cm/hr a large fraction of the dissolved hydrogen will be 'frozen' into the single crystals. Since in the present work the acceptor level at $E_v + 0.08$ eV and the hemispherical pits have been observed only in hydrogen-grown Ge we conclude that they are linked in some way to the presence of hydrogen.

The magnitude of $D_H$ indicates clearly that in Ge hydrogen is dissolved interstitially. Because of their smallness, interstitially dissolved hydrogen atoms are expected to constitute 'very deep donors' (with the donor level likely to be submerged in the valence band [Reiss 1956, Kaus 1958, Wang and Kittel 1973]); in the present experiments they turn out to be electrically inactive indeed.

An important property of the defect center discussed above is its sensitivity to annealing. One observes that its concentration <u>increases</u> with <u>increasing</u> annealing temperatures up to 650 K. It is the main purpose of this paper to present results for the steady-state concentration and the transients associated with temperature changes and to propose a model which explains these results.

## 2. Experimental

All experiments were performed with crystals grown from a melt of highly purified germanium. The melt was contained in a synthetic quartz crucible inside a graphite susceptor, which was RF heated. The surrounding atmosphere was palladium-diffused hydrogen (1 atm) unless otherwise stated. The residual shallow impurities were analyzed with Photothermal Ionization Spectroscopy (PTIS; Haller, et al. 1977). They were found to be B, Al and P with concentrations [illegible] $10^{11}$ cm$^{-3}$. In all quartz-crucible-grown crystals the concentration of oxygen as determined by lithium precipitation is known to lie below $10^{14}$ cm$^{-3}$ (Hall 1974).

P-type samples ([illegible] × 5 mm$^3$) consisting of one dislocation-free and one dislocated piece were selected from partially dislocated Ge crystals. The pieces were always taken from a slice cut perpendicular to the crystal growth axis. Several annealing techniques were explored to control the indiffusion of contaminants into the samples. The results obtained with Pb-Bi-eutectic, silicon oil, or argon atmosphere were comparable. The samples were annealed at the desired temperature for times sufficiently long to reach equilibrium and subsequently cooled to room temperature within a few seconds. A more rapid quench would result in the defects observed by Hall (1975). At room temperature the hole concentration does not change over many months. The samples were prepared for Hall effect measurements by etching in $HNO_3$:HF(4:1) for about [illegible] minutes, followed by rinsing with distilled, de-ionized water and blowing dry with boil-off nitrogen. Four InGa eutectic contacts were symmetrically applied to the samples. The hole concentration was obtained for both samples by Van der Pauw (1958) Hall measurements from 300 K down to 5 K. The heat treatment did not change the net concentration of the shallow levels by more than a few percent of the deep acceptor concentration. Since the deep acceptor concentration was changed by more than two orders of magnitude by anneals between [illegible] K and [illegible] K, we adopted a simplified technique and measured the hole concentration only at 77 K. At this temperature the deep acceptor is still ionized and its concentration is equal to the difference of the hole concentrations of the dislocation-free and the dislocated piece. As long as one stays below 650°C for not longer than a few hours, the deep acceptor concentration reaches, in a reversible manner, a well defined value for each temperature independent of sample history.

Figure 3 shows an Arrhenius plot of the steady-state concentration for the deep acceptor. Samples from different crystals all gave similar results with slight parallel shifts.

If dislocation-free samples are heated for very long times ($> 10^4$ min) or to temperatures above 720 K, the changes in the deep acceptor concentration become irreversible (i.e. the samples do not return to low levels at low temperatures). This may be understood by out diffusion of hydrogen from the Ge sample*. Low-temperature Hall-effect measurements also revealed the introduction of copper into the samples. The acceptor levels of substitutional copper are far enough separated from the $E_V + 0.08$ eV acceptor under investigation that they do not influence our results.

## 4. Time Effects

After increases in temperature the equilibrium concentration of the deep acceptor is reached in undetectably (< minutes) short times. This behavior suggests a dissociation process. A completely different situation occurs when the temperature is decreased. The equilibrium concentration is reached much more slowly, the time constants being the longer, the lower the annealing temperature is. Figure 4 shows two typical cases. For each measurement point, the samples were cooled rapidly to room temperature. After cleaning as described, contacts were applied and a Hall measurement was made at 77 K. After warming up, the contacts were removed, the samples were cleaned again by etching and then were brought quickly up to the annealing temperatures.

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* The extrapolation of the hydrogen-diffusion coefficient of Frank and Thomas (1960) to 720 K gives for the diffusion distance during $t = 1h: (\overline{x^2})^{1/2} = (2D^H t)^{1/2} = 2$ mm.

## 4. Divacancy-Hydrogen Model

Taking all the experimental observations into account we put forward the following model: The defect center with an acceptor level at $E_V + 0.08$ eV is a divacancy-hydrogen complex. The complex reacts with the free hydrogen in the Ge lattice according to:

$$V_2H + H \underset{\text{dissociation}}{\overset{\text{recombination}}{\rightleftharpoons}} V_2H_2 \tag{2}$$

Neither the free hydrogen nor the $V_2H_2$ complex have energy levels in the forbidden band (i.e. they are electrically neutral). When heating the sample, some of the $V_2H_2$ complexes dissociate almost instantaneously into mobile free hydrogen and virtually immobile $V_2H$ complexes. The recapture of free hydrogen by the $V_2H$ complexes at lower temperatures is controlled by the long-distance diffusion of hydrogen and/or by the release from traps, and hence much slower.

The formation of both $V_2H$ and $V_2H_2$ may be considered as the reaction of the 'very deep donor' hydrogen with acceptor centers. Recent experiments with Cu (Haller, Hubbard and Hansen 1977) have shown that H can indeed form complexes with multivalent acceptors in germanium. The valence of the complexes is reduced by one for each hydrogen atom and the energy levels are shifted towards the valence band. The copper-hydrogen complex formation is very similar to the interaction between lithium and multivalent acceptors (LoVecchio 1972).

Another analogous case is the formation of $V_2$ donor-centers, where the donor can be either P, As, Sb, Bi (Mashovets and Emtsev 1975), or LiO (Konopleva and Novikov 1974). The acceptor levels of these complexes increase with increasing atomic number from $E_V + 0.10$ eV (donor = P, LiO) to $E_V + 0.16$ eV (donor = Bi). The level position $E_V + 0.08$ eV associated with the 'very deep donor' H fits very well into this sequence and provides additional support for the view that the other partner of the observed complex centre is the divacancy $V_2$ (and *not* some larger multiple vacancy).

Let us denote the time-dependent concentrations by $C_i$, where $i = 1$ refers to $V_2H$, $i = 2$ to $V_2H_2$, $i = f$ to 'free' hydrogen (atomic hydrogen dissolved in the lattice), $i = t$ to trapped hydrogen. $N_H$ denotes the total hydrogen concentration, $N_{V_2}$ the total divacancy concentration (both taken as time-independent) and $N_t$ the concentration of hydrogen traps (the precise nature of which we may leave unspecified). The rate equations for the reactions described above read

$$\frac{dC_1}{dt} = -\sigma_1 C_1 C_f + \nu_2 C_2 \tag{3}$$

$$\frac{dC_f}{dt} = -\sigma_1 C_1 C_f + \nu_2 C_2 - \sigma_t N_t C_f + \nu_t C_t . \tag{4}$$

Two further rate equations may be integrated immediately to give

$$C_2 = N_{V_2} - C_1 \tag{5}$$

$$C_t = (N_H - 2 N_{V_2}) + C_1 - C_f , \tag{6}$$

(conservation of vacancies and of hydrogen atoms). In (3) and (4) $\nu_t$ and $\nu_2$ denote the escape frequencies of hydrogen atoms from traps and from $V_2H_2$, respectively. The capture rates $\sigma_i$ ($i = 1, t$) are given by

$$\sigma_i = 4\pi \, r_i \, D_H , \tag{7}$$

where $r_1$ is the capture radius of $V_2H$ and $r_t$ that of the hydrogen traps.

Under conditions of thermal equilibrium ($dC_1/dt = dC_f/dt \equiv 0$) one obtains for the equilibrium concentration

$$C^{eq}_{V_2H} = C^{eq}_1 = \left[ \frac{\nu_2 N_{V_2}}{\sigma_1} \left( 1 + \frac{\sigma_t N_t}{\nu_t} \right) + \left( \frac{A}{2\sigma_1} \right)^2 \right]^{1/2} - \frac{A}{2\sigma_1} \tag{8}$$

where

$$A = (N_H - 2N_{V_2}) \, \sigma_1 + \nu_2 \left( 1 + \frac{\sigma_t N_t}{\nu_t} \right) \tag{8a}$$

Equation (8) may be fitted to the Arrhenius-type temperature dependence of $C^{eq}_{V_2}$ (Fig. [illegible]) observed between 500 K and 620 K* if and only if

$$\left(\frac{N}{2\sigma_1}\right) \; [illegible] \; \frac{\sigma_2 N_{V_2}}{\sigma_1} \tag{9a}$$

and

$$\sigma_t N_t \; [illegible] \; \sigma_t \; [illegible] \tag{9b}$$

We then have**

$$C^{eq}_{V_2H} = \left(\frac{\sigma_2 N_{V_2}}{\sigma_1}\right)^{1/2} . \tag{10}$$

Comparison with the experimental result gives us with $r_1 \approx 3\cdot 10^{-6}$cm and $\sigma_2 \approx 5\cdot 10^{13}\exp(-1.8\ \mathrm{eV}/kT)\,\mathrm{s}^{-1}$ the divacancy concentration $N_{V_2} \approx 3\cdot 10^{13}\mathrm{cm}^{-3}$, which is a reasonable order of magnitude. From (9a) one finds $N_H \approx 2N_{V_2} \approx 6\cdot 10^{13}\mathrm{cm}^{-3}$. This value compares well with the melting-point solubility of hydrogen of $\approx 10^{16}\mathrm{cm}^{-3}$.

The time-variation of an initial concentration $C_1(o)$ may be found analytically if either one of the two following simplifications are applicable:

i) The effects of traps are negligible; (4) may be replaced by (6) with $C_t = 0$. The solution is then given by

$$C_1(t) = - b + a\,\mathrm{Tg}\left\{ a\,\sigma_1\, t + \mathrm{Artg}\,\frac{C_1(o)-b}{a} \right\} \tag{11}$$

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* The deviations from the Arrhenius law above 620 K are irreversible in nature and associated with out-diffusion of hydrogen, presumably accompanied by the reaction $V_2H \rightleftarrows V_2+H$ not taken into account in the present theory. The deviations at low temperatures may be attributed to violations of (9a) or (9b).

** Other Arrhenius type approximations to (8) which do not satisfy (9a) and (9b) are unable to account for the order of magnitude $10^{18}\mathrm{cm}^{-3}$ of the preexponential factor in the Arrhenius dependence of (10).

with

$$a = \frac{1}{2}\left(C_1^{eq} + \frac{\nu_2 N_{V_2}}{\sigma_1 C_1^{eq}}\right); \quad b = \left(C_1^{eq} - \frac{\nu_2 N_{V_2}}{\sigma_1 C_1^{eq}}\right) . \qquad (11a,b)$$

Equation (11) describes the gradual decay of an initial acceptor concentration $C_1(o)$ after a rapid temperature change to a lower temperature. The validity of (11) may be tested by comparing the measurements immediately after the temperature change with the long-time behavior. The comparison is not satisfactory at high annealing temperatures, where the 'tail' extends to longer times than predicted by (11). It comes out much better at low annealing temperatures, particularly if one allows for the fact that because of the H out-diffusion at high temperatures there may be a gradient of the H concentration from the surface to the interior.

ii) The hydrogen concentration in the lattice is stationary (i.e. $dC_f/dt = 0$. Then (4-6) give us

$$C_f = \frac{(\nu_2 - 2\nu_t)N_{V_2} + \nu_t N_H + (\nu_t - \nu_2)C_1}{\sigma_1 C_1 + \sigma_t N_t + \nu_t} . \qquad (12)$$

Insertion of (12) and (5) into (3) results in the differential equation

$$\frac{dC_1}{dt} = \frac{\sigma_1 \nu_t (C_1 + \gamma)}{\alpha + \sigma_1 C_1} (C_1 - C_1^{eq}) \qquad (13)$$

with

$$\alpha \equiv \nu_t + \sigma_t N_t \; ; \; \gamma \equiv \nu_2 N_{V_2} \cdot \frac{\alpha}{\sigma_1 \nu_t C_1^{eq}} . \qquad (13a,b)$$

The short-time behavior follows immediately from (13):

$$C_1(t) = C_1(o) + \frac{dC_1}{dt}\Big|_o \cdot t + \frac{1}{2} \frac{d^2 C_1}{dt^2}\Big|_o \cdot t^2 + \dots \qquad (14)$$

with

$$\left.\frac{dC_1}{dt}\right|_o = -\sigma_1\nu_t\,\frac{C_1(o)+\gamma}{\alpha+\sigma_1C_1(o)}\,(C_1(o)-C_1^{eq}) \qquad (14a)$$

$$\left.\frac{d^2C_1}{dt^2}\right|_o = -\sigma_1\nu_t\,\left.\frac{dC_1}{dt}\right|_o\left[\alpha\,\frac{C_1(o)-C_1^{eq}}{(\alpha+\sigma_1C_1(o))^2}+\gamma\,\frac{\alpha+\sigma_1C_1^{eq}}{(\alpha+\sigma_1C_1(o))^2}+\frac{C_1(o)}{\alpha+\sigma_1C_1(o)}\right] . \qquad (14b)$$

As in the case of (11) the long-time behavior obeys an exponential law

$$C_1 = C_1^{eq} + B\exp(-t/\tau) \quad . \qquad (15)$$

The time constant is now given by

$$\tau = \frac{1}{\sigma_1\nu_t}\,\frac{\alpha+\sigma_1C_1^{eq}}{C_1^{eq}+\gamma} \quad . \qquad (15a)$$

From the integral of (13)

$$\frac{t}{\tau} = \frac{\sigma_1\gamma-\alpha}{\sigma_1C_1^{eq}+\alpha}\,\ln\frac{C_1(o)+\gamma}{C_1(t)+\gamma} + \ln\frac{C(o)-C_1^{eq}}{C_1(t)+C_1^{eq}} \qquad (16)$$

we find

$$B = \left\{C_1(o)-C_1^{eq}\right\}\left[\frac{C_1(o)+\gamma}{C_1^{eq}+\gamma}\right]^{\frac{\sigma_1\gamma-\alpha}{\sigma_1C_1^{eq}+\alpha}} \qquad (17)$$

Evaluation of two annealing curves (A: equilibration at 573 K, annealing at 378 K; B: equilibration at 573 K, annealing at 473 K (△ in Fig. 10) yields using Eq. (17): $\sigma_1(A) = 2.8 \times 10^{-16}$cm$^3$s$^{-1}$ and $\sigma_1(B) = 2.2 \times 10^{-17}$cm$^3$s$^{-1}$. The $\sigma_1$ together with the experimental time constant $\tau$ determine in Eq. (15a) the hydrogen escape frequencies $\nu_t$(A) =

$2 \times 10^{14}s^{-1}$ and $\nu_t(B) = 10^{14}s^{-1}$. The $\sigma_1$ and $\nu_t$ which are obtained from the long-time behavior can be used in Eq (14a) to determine the initial slope of the annealing curves. For annealing curve A we obtain $dC_1/dt|_0 = -8.4 \times 10^7 cm^{-3}s^{-1}$ compared with the experimental value of $-4.5 \times 10^8 cm^{-3}s^{-1}$ and for curve B $-6.1 \times 10^7 cm^{-3}s^{-1}$ compared with the experimental value of $-1.5 \times 10^8 cm^{-3}s^{-1}$. The agreement between long-time and short-time behavior is now satisfactory. This suggests that the assumption of stationarity of the free hydrogen concentration ($dC_f/dt = 0$) was indeed admissable. The trapping rate $\sigma_1$ comes out smaller than expected from an extrapolation of the high-temperature values of $D_H$. (Using Eq. (7) and $r = 3 \times 10^{-8}$cm one obtained $\sigma_1(A) = 1.5 \times 10^{-13}cm^3s^{-1}$ and $\sigma_1(B) = 9.3 \times 10^{-14}cm^3s^{-1}$). This may indicate that in the preceeding treatment the 'hydrogen diffusion coefficient' is to be considered as an effective quantity. In the temperature range of the present experiment hydrogen diffusion may be slowed down by a tendency to form hydrogen molecules in the lattice and/or by temporary association of hydrogen with some of the electrically non-active impurities (e.g. oxygen) that remained in the present samples.

## 6. Summary

Our main findings may be summarized as follows:

i) The single acceptor at $E_v + 0.08$ eV can only and always be found in hydrogen-grown dislocation-free high-purity germanium. This strongly suggests that this acceptor is related to a complex consisting of vacancies (V) and hydrogen (H). The divacancy-hydrogen complex ($V_2H$) is the most probable candidate.

ii) The concentration of the acceptor is sensitive to annealing. A model based on the reaction $V_2H + H \rightleftarrows V_2H_2$ and on hydrogen trapping and detrapping at larger traps describes both the stationary concentration of the acceptor centre as well as the response to sudden temperature changes.

iii) The model is supported further by (a) excellent correspondence between the energy levels of divacancy-donor complexes and the $V_2H$-centre and (b) the recently discovered complexes of hydrogen with multivalent acceptors (similar to multivalent acceptor-lithium complex formation).

## Acknowledgements

We would like to thank F. S. Goulding for many discussions and his continuous interest in our work.

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## Figure Captions

Fig. 1. Hole concentration versus reciprocal temperature 1/T of a dislocated and an undislocated Ge sample cut from the same crystal slice. The net-impurity concentration of shallow acceptors and donors is equal for both samples. The $E_V$ + 0.08 eV acceptor only appears in the dislocation-free piece; its concentration depends on the annealing temperature.

Fig. 2. Photograph of a partially dislocated <100> surface of a hydrogen-grown Ge crystal. The large etch pits with four-fold symmetry in the right half of the picture are due to dislocations. The hemispherical pits in the left half of the picture are attributed to vacancy and hydrogen complexes.

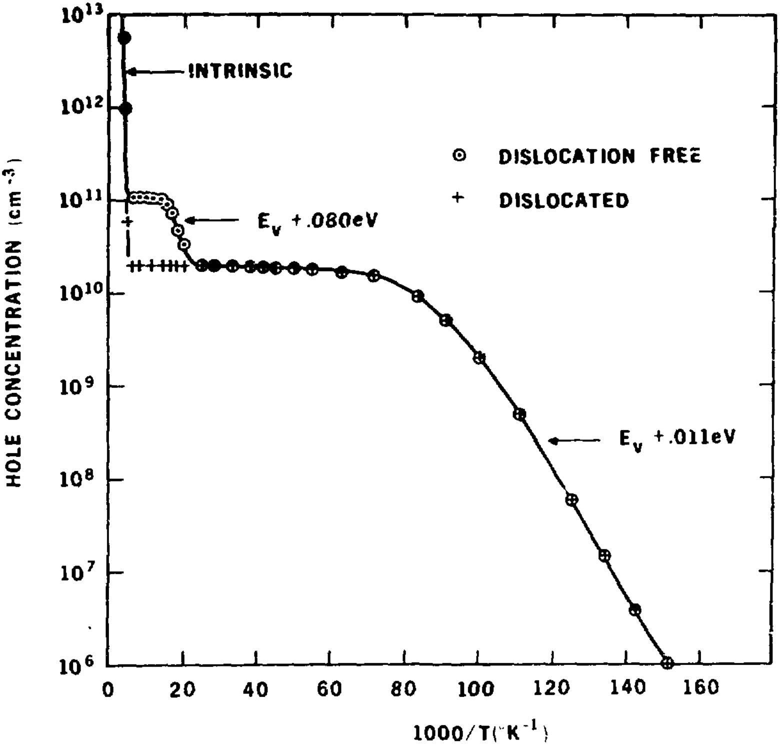
Fig. 3. Steady-state concentration of the $E_V$ + 0.08 eV acceptor of two dislocation-free samples. Δ sample cut from center of a crystal (crystal ∅ = 35 mm). Θ sample cut near crystal surface. The error for each measurement point is of the order of 5 to 10% for the concentration and less than 2% for the temperature. The dashed line corresponds to $1.04 \cdot 10^{18} \exp(-0.71\ \text{eV}/kT)\ \text{cm}^{-3}$.

Fig. 4. Concentration of $E_V$ + 0.08 eV acceptor level and of shallow levels (as measured at 77 K).

Θ : Sample equilibrated at 623 K, quenched to and annealed at 548 K.

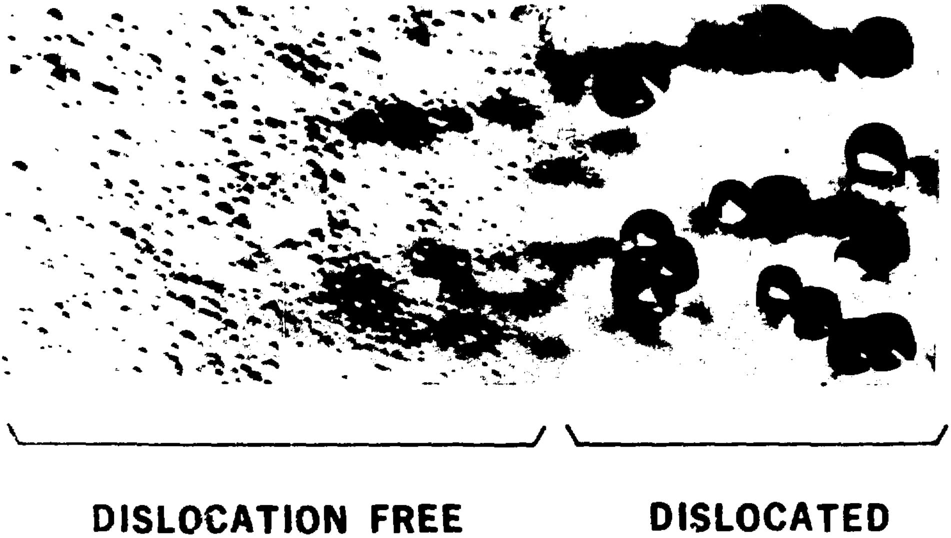
Δ : Sample equilibrated at 573 K, quenched to and annealed at 473 K.

+ : Shallow net-acceptor concentration.



XBL 759-8019

FIG.1



XBB 758-6503

FIG.2

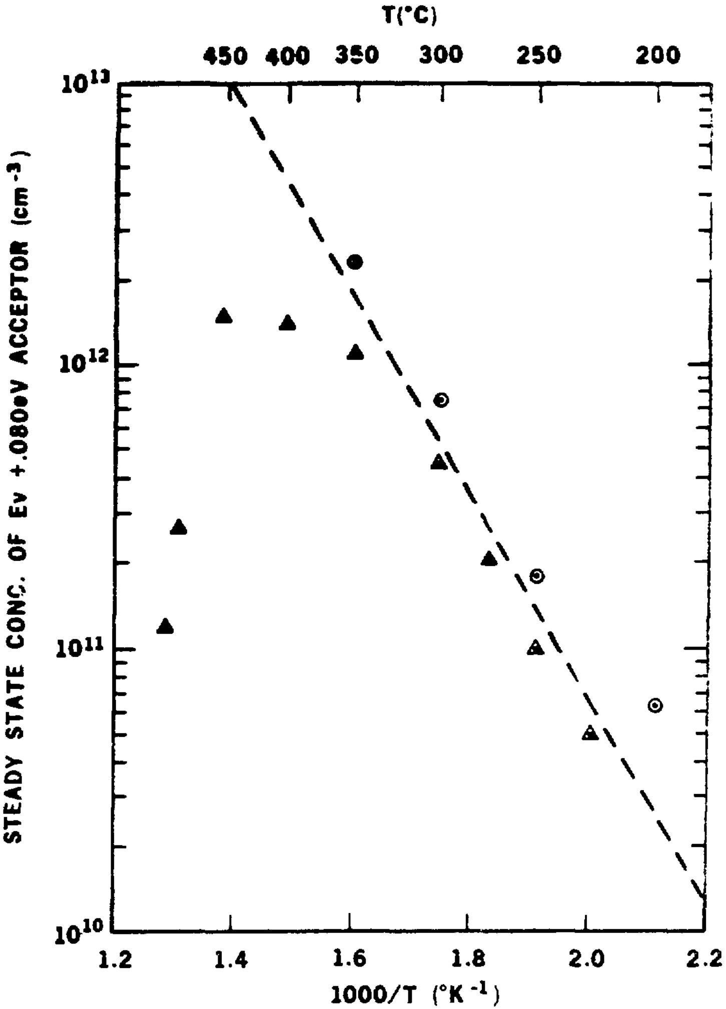


FIG.3

XBL 767-8912

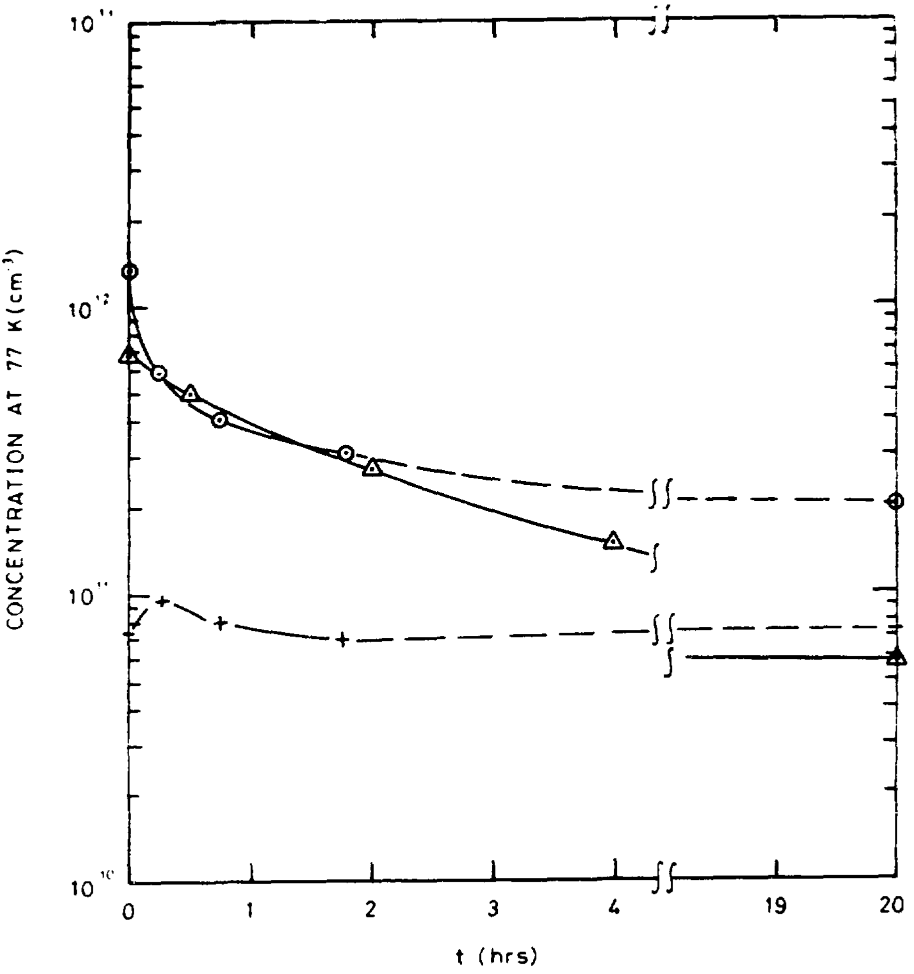

CONCENTRATION AT 77 K (cm$^{-3}$)
10$^{13}$
10$^{12}$
10$^{11}$
10$^{10}$
0
1
2
3
4
19
20
t (hrs)

FIG.4