succeeded to dope Si in a glow discharge, using hydrogen and admixtures of PH_3 or B_2H_6. The bombardment with the hydrogen ions is thought to produce an excess of vacancies which give rise to a greatly enhanced diffusion of these dopants into the silicon. Such enhancement is observed even at temperatures well below 750°C, probably even below 500°C. Therefore a mechanism different from the one in your experiments seems to be operating.

Curien, H.: In our laboratory, Dr. Authier has investigated by x-ray microscopy the effects of the proton irradiation on the silicon samples of Dr. Pfister and Baruch. His results can be summarized as follows; 1). One does not observe any significant displacement of the dislocation lines. 2). External scratches present before irradiation are erased due to thermal diffusion on the surface (the specimens were annealed at 800°C). 3). The bulk deformation of the exposed region is revealed by a set of fringes.

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Vacancies in Germanium-Properties of Quenched-in Vacancies

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After the oxidation of surface to prevent Cu-contamination, intrinsic Ge with various dislocation densities were quenched from high temperatures to introduce vacancies (acceptors). The concentration of vacancies was $N_v=3.7\times10^{23}\exp(-1.9\,\mathrm{ev}/kT)$/c.c. The Cu-concentrations in the heat-treated samples were below 5×10^{13} Cu-atoms/c.c. Annealing curves of exponential decay type were observed for samples with large dislocation densities ($n_D\sim5\times10^3\sim10^5$). The activation energy for diffusion and diffusion coefficient were 1.2~1.3ev and $D_v=2\exp(-1.2\,\mathrm{ev}/kT)\mathrm{cm}^2/\mathrm{sec}$. For samples with small dislocation densities ($n_D\sim$less than 10^3), some of the annealing curves deviated from the exponential decay.

The cluster-formation of vacancies were estimated from these curves. The acceptor level of vacancy at 0.02~0.03 ev from the valence band was obtained from Hall and resistivity measurements with temperature range from 20°K to room temperature.

1. Introduction

Many works have been made to investigate the properties of vacancies in Ge by various methods. But their definite properties may be said undetermined. Production of vacancies can be classified into "direct production" and "indirect production." Quenching and radiation damage are direct productions. There may be many kinds of indirect productions. One of them is application of characteristic diffusion behaviours of Cu or Ni-atoms in Ge known as "dissociative diffusion[1]." By annealing of supersaturated Cu or Ni-atoms which are in substitutional sites to become acceptors[2], vacancies are left behind because the substitutional atoms jump to the interstitial sites and diffuse very rapidly to nuclei of precipitation. This principle was tried in Si by Woodbury and Ludwig[3]. Mayburg[4], Logan[5], Zhidkov[6] and others made quenching and annealing experiments to know the formation of defect and their diffusion properties. As for the temperature dependence, the quenched-in defect-concentration was reported by Mayburg[4] and Logan[5] as $3\times10^{23}\exp(-2.01\,\mathrm{ev}/kT)$/c.c. and $10^{22}\exp(-1.8\,\mathrm{ev}/kT)$/c.c. respectively. Tweet got higher value by different method—$4.5\times10^{22}\exp(-1.7\,\mathrm{ev}/kT)$/c.c.[7] and $4.5\times10^{22}\exp(-1.8\,\mathrm{ev}/kT)$/c.c.[8] Mayburg[4]

and Logan[5] found rather complicated annealing curves of quenched-in defects. By analysis of these curves, Mayburg concluded that the defects might be of Frenkel-type. But Letaw proposed that the complexities of Mayburg's annealing curves came from the formation of vacancy-clusters during the annealing process and the defects could be understood as vacancies (Schottky-type).

Recently Zhidkov[10] found the similar annealing curves to some of those observed by Mayburg. He attributed the behaviours of the annealing to the existence of two kinds of Cu-atoms in the samples.* By the annealing of radiation damage, it is possible to know the diffusion properties of vacancy. The activation energy for diffusion of vacancy was estimated to be 1.2~1.3 ev[12]. Letaw *et al.*[13] obtained the self-diffusion coefficient of Ge by tracer technique—$D_{self}=8.7 \exp(-2.98\,\mathrm{ev}/kT)\mathrm{cm}^2/\mathrm{sec}$. If the self-diffusion in Ge proceeds by a "vacancy mechanism"—this assumption may be probably true from the experiments made by Valenta and Ramasastry[14] and the calculation made by Penning[15] — the diffusion property of single vacancy can be known from the vacancy solubility. Using the solubility reported by Mayburg[4], Letaw[9),13] got the diffusion coefficient of vacancy to be $D_v=1.2 \exp(-0.96\,\mathrm{ev}/kT)\,\mathrm{cm}^2/\mathrm{sec}$. Tweet[8] also got $D_v=8\exp(-1.2\,\mathrm{ev}/kT)\,\mathrm{cm}^2/\mathrm{sec}$ from the vacancy solubility obtained by the experiment on precipitation of Cu in Ge.

But to know the vacancy solubility precisely, as suggested by Tweet[7] and Zhidkov[6], is a very difficult problem. So the direct knowledge of diffusion coefficient of the vacancy is necessary. The acceptor level of vacancy may be estimated from many experimental results. In the process of precipitation of Ni in Ge, Penning observed the occurrence of new acceptor level at 0.02 ev from the valence band. From the principle of "indirect production of vacancy" mentioned above, he concluded this level might correspond to a single vacancy. Acceptor levels supposed to be those of vacancy at 0.01 and 0.05 ev from the valence band were found by Tyler and Woodbury[16] in the experiments similar to that performed by Penning.

From the data of radiation damage, acceptor level at 0.01~0.02 ev from the valence band were found probably due to vacancy[17]. The purpose of our experiment was to get diffusion properties of vacancy taking the effect of dislocations into account and the position of its acceptor level.

2. Production of Vacancies by Thermal Quenching

Quenching is the simplest and the most common way of producing the vacancies into a crystal. But if Cu-atoms exsist on the surface of Ge, they are known to diffuse into the bulk very rapidly at high temperatures and become acceptors at lower temperatures. Then, without the complete surface treatment to avoid Cu, it is impossible to quench the acceptors due to vacancy only in Ge[6),10]. Many authors[4),5),6),18] tried to quench vacancies without Cu by various surface treatments. Weiser[19] found that heat treatment of Ge in wet oxygen gas raised the lifetime—high rate oxidation reaction plays the gettering and leaching effect of impurity recombination centers (especially Cu[20]). Applying this phenomenon to quenching procedures, we put Ge samples in the furnace with wet oxygen atmosphere, heated them slowly to the quenching temperature and put them out into the air at the cooling rate of 800°C/sec. We could protect Cu-contamination below the level of less than 5×10^{13} Cu-atoms/c.c.* in the heat-treated samples. The formation energy (E_F) of vacancy was difficult to determine due to the anneal during the quenching.** Intrinsic samples with dislocation density (n_D) of 10^3 were used. Taking the largest numbers of quenched-in acceptors at each quenching temperature, Fig. 1. was obtained***. E_F and the concentration of vacancies (acceptors) were approximately 1.9 ev and $N_V=3.7\times10^{23}$

* Penning annealed the supersaturated Ni-atoms in Ge and the annealing curves were quite similar to Zhidkov's.

* Cu-concentration in the heat-treated samples were kindly measured by spectroscopy at Toshiba Electric Co. Ltd. after condensing the Cu by zone melting method.

** For example, into the samples with $n_D\sim10^5$ we could not quench more than 10^{14} vacancies/c.c. at a cooling rate of 200°C/sec from 800°C.

*** One acceptor level per one vacancy was assumed.

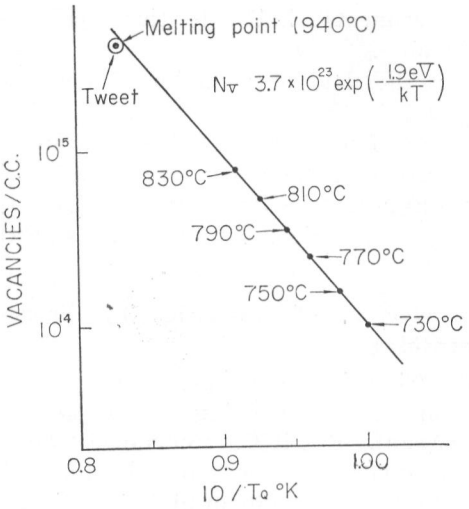

Fig. 1

$\exp(-1.9\,\text{ev}/kT)$/c.c. respectively.

3. Diffusion Properties of Vacancy

Diffusion properties of quenched-in vacancies could be known by annealing experiments at low temperatures (450°~650°C).

Annealings were performed in the furnace with wet oxygen atomosphere previously mentioned to prevent Cu-contamination during the annealing. From the Hall and resistivity measurements, it was found that the carrier (hole) mobility was not appreciably affected by quenching—Hall mobility (μ_H) of heat-treated samples was about 3000 ~2900 (cm^2/volt-sec) at 25°C. So, the annealing curves of quenched-in vacancies (acceptor) were obtained by four points resistivity measurement at 25°C—number of unannealed acceptors as a function of annealing time at each annealing temperatures. As seen from typical annealing curves in Fig. 2 and Fig. 3 the charactor of annealing depends

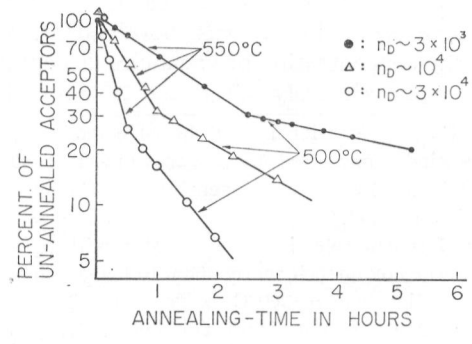

Fig. 2

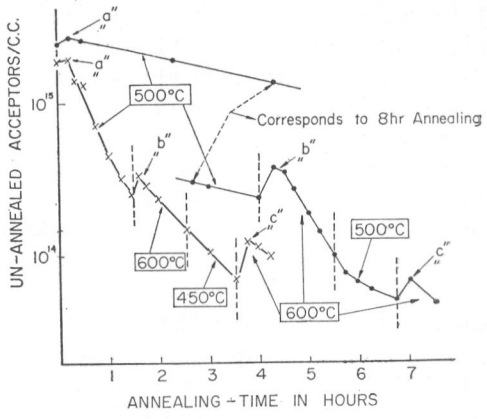

Fig. 3

strongly upon the dislocation density (n_D)—for samples with large dislocation density (n_D~5×10^3~10^5), the curves are of exponential decay type, on the other hand, the complicated decay curves are sometimes observed for dislocation free or of small dislocation density (n_D~less than 10^3) samples. The dislocation densities were measured by etch pit counts.

3A. Annealing of Vacancies in the Case of Large Dislocation Density (Exponential Decay)

As shown in Fig. 2, the time constants of exponential decays were almost proportional to the dislocation density indicating that the dislocations were sinks of vacancies to disappear. The works on annealing of quenched-in vacancies in metals were made by several authors[21] and their results and conclusions are very suggestive to our work. The theory of annealing or annihilation of excess vacancies at dislocations were proposed by Penning[22]. It was concluded that in the case of equally spaced distribution of dislocations the decrease in average concentration of excess vacancy ($\bar{c}$) was described by the equations given below indicating the exponential decay except at the very beginning of the annealing where the abrupt annealing was observed.

$$\frac{d\bar{c}}{dt}=-\frac{\bar{c}}{\tau} \quad \text{with } 1/\tau=\beta(n_D)\cdot n_D\cdot D_V$$

$$\sim\beta(n_D)\cdot\left(\frac{n_D}{n_0}\right)Az\upsilon\exp\left(\frac{E_D}{kT_{\text{anneal}}}\right)$$

where $\beta(n_D)$ is "proportionality factor" defined by Penning which is 0.63 for n_D~10^4 and 0.69 for n_D~10^5.

D_V is the diffusion coefficient of vacancy, so that $D_V = D_0 \exp(-E_D/kT_{\text{anneal}})$ with $D_0 = (a^2/8) \times Az\upsilon$ cm^2/sec. and a: lattice constant; 5.65×10^8 cm

A: entropy factor for diffusion; to be determined experimentally $\sim 10^2$

z: co-ordination number; 4

υ: characteristic frequency; $\sim 10^{13}$ cycle/sec[23]

E_D: activation energy for diffusion

T_{anneal}: annealing temperature

n_0: number of Ge atoms in cm^2 $\sim 8/a^2 \sim 2.5 \times 10^{15}$

Thus, it was possible to get the activation energy for diffusion (E_D) from the time constant "τ" of the exponential type annealing curves. From the conventional reason, we defined "adjusted decay time ($\tau'_{1/2}$)" as follows $\tau'_{1/2}(T_{\text{anneal}}) = \tau_{1/2}(n_D T_{\text{anneal}}) \cdot \beta(n_D)$ ($n_D/2 \times 10^3$) so as $\tau'_{1/2}(T_{\text{anneal}})$ to correspond to 10 hours.

$\tau_{1/2}(\fallingdotseq 0.735\,\tau)$ is the observed decay time, time required to anneal half of quenched-in

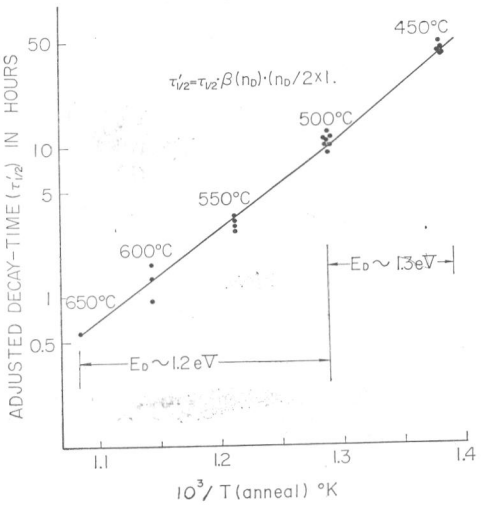

Fig. 4

acceptors. E_D was 1.2 ev for higher temperatures and 1.3 ev for lower temperatures as seen in Fig. 4.

Diffusion coefficient of vacancy was obtained $D_V(T) = 2 \exp(-1.2 \text{ ev}/kT)$cm^2/sec.*

3B. Annealing of Vacancies in the Case of Small Dislocation Density — Possibility of Vacancy-Cluster Formation

As was reported by Tweet[7),24)], the formation of vacancy-clusters could be observed in the dislocation free sample produced by the Dash technique. This is understood that in the process of cooling from the melt vacancies which were introduced in the equilibrium concentration at the melting temperature could not find any sinks or dislocations to anneal and they began to aggregate to form vacancy-clusters for relieving the supersaturation. In interpretating the annealing curves as shown in Fig. 3, we imagine that probably the same phenomena may have happened in our samples.

In our present stage only a qualitative explanation can be made. In the process of quenching, the vacancies introduced at the quenching temperature have a tendency to anneal at sinks. But, as there are no dislocations, they aggregate with each other in spite of coulomb repulsions which come from the trapped electrons by acceptor vacancies, to form clustered vacancies. As for the stability of clustered vacancies, two types may be considered—one is very stable and large as observed by Tweet[7),24)] and the other is unstable that might be the cause of complexity of our annealing curves. Here "unstable" may be understood as "thermally unstable." So, in the clusters, vacancies aggregate with weak attraction and by raising the temperature they are easily evaporated from the surfaces of the clusters.

These unstable clusters are supposed to be electrically inactive as stable ones[7),24)]. In the annealing process at 500°C the increase (as indicated by the peak "a" in Fig. 3) in number of acceptors was at first observed and the exponential decrease followed. The increase was considered to be induced by vapourization of vacancies from the surfaces of unstable clusters because of the sudden raise of temperature. After the vapourization, vacancies were expected to anneal again to the remaining clusters—the exponential decays were observed and from the decay time constants which were equivalent to the case of large dislocation densities ($n_D \sim$ more than 10^4) as already mentioned in 3A—indicating that the density of clusters were more than 10^{11} clusters/c.c. Same phenomena could be observed by rais-

* The experimental values

$\tau_{1/2}(500°\text{C}, 5\times10^4) = 0.5$ hr

and

$\tau_{1/2}(500°\text{C}, 5\times10^3) = 2.5$ hr

were used as $\tau_{1/2}(T_{\text{anneal}}, n_D)$ in the calculation.

ing the annealing temperature from 500°C to 600°C—the peaks "b" and "c" in Fig. 3. But in the case of lowering the annealing temperature, such peaks did not of course appear.

4. Acceptor Level of Vacancy

The Hall and resistivity measurements as a function of temperatures (from 20°K to 300°K) were made. Magnetic field of 4000 gausses was used. From the analysis of $(R_H(T)T^{3/2})$ to $(1/T)$ curves, the acceptor level at 0.02~0.03 ev from the valance band was estimated but precise value was not yet determined. From the lifetime measurement, it was supposed there might be at least another higher level. Compensation technique as made by Woodbury and Tyler[2] is requested to know precise level diagram and this is now being undertaken.

5. Discussions

From the diffusion coefficient*, the entropy for the motion of a vacancy (ΔS: $A = \exp(\Delta S/R)$) was obtained about 10 cal/mol-deg.

By the E.P.R. studies of vacancies in Si, it has been proposed that a single vacancy moves with low activation energies whose value depend on the charge states[27] of the vacancy. Divacancy in Si moves with higher activation energy which is consistent with the nature of diamond structure 1.3 ev was proposed by Watkins and Corbett[28].

This value was quite similar to the value of our diffusion energy of vacancy (1.2~1.3 ev). But it should not be concluded that the vacancy we observed may correspond to divacancy in Ge.

The E.P.R. studies, life time measurements, calculation of diffusion of single vacancy and so on are requested to solve this problem and some of them are now undertaken.

Acknowledgement

We should like to express sincere thanks to Dr. H. Yonemitsu, Dr. H. Muraoku of Toshiba Electric Co. Ltd. and Mr. P. Son of Osaka University for their many helps and discussions.

* As the number of oxygen atoms were less than 10^{14}/c.c., the effect of trapping vacancies at about 500°C was negligible in the estimation of E_D and also entropy factor if the binding energy was less than 1 ev.

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DISCUSSION

Thomson, R.: Was any other method besides electrical measurement used to check the vacancy density?

Hiraki, A.: The measurement of such as change of volume, lattice constant and so on were not made because of the small amount of quenched-in vacancies (about 10^{15} vacancies/cc). But ESR and life-time studies which can make clear the charge states of single vacancy or divacancy and also the order of their densities are now being prepared. From these studies, I think, clearer correspondence between the density of electrically measured acceptors and real density of vacancies can be made.