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Application of Precipitation Techniques to the Study of Defects in Germanium

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The role of oxygen content, gamma-ray bombardment, annealing temperature and solute concentration in the nucleation of lithium precipitates in germanium has been investigated. Analysis of the experimental data indicates that the primary nucleation site for lithium precipitation is an oxygen-vacancy defect pair. The evidence indicates that about 1% of the oxygen exists in this particular paired state. For the reaction

$$O+V=O-V$$

it is determined that the binding enthalpy of the pair is -0.6 eV and the concentration of $O-V$ defects is given by

$$[O-V]=2.6\times 10^4\ [O]\exp[-(1.4/kT)].$$

Lithium is also found to exist in the paired state with interstitial oxygen although these complexes apparently are not active as nucleating sites. At room temperature about 25% of the interstitial oxygen atoms are paired according to the reaction

$$Li^{+}+O=Li^{+}O.$$

The heat of binding of the pair is calculated to be about -0.5 eV.

I. Introduction

The purpose of this paper is to present results of an investigation aimed at determining the nucleation centers for precipitation processes in germanium. The particular system discussed here is the germanium-lithium system.

The initial work on the precipitation of lithium in germanium was performed by Morin and Reiss[1]. In their work, precipitation was investigated as a function of gamma irradiation, dislocation densities and variation of time and temperature of lithium saturation. From this study, Morin and Reiss suggested that lattice vacancies were acting as nucleation centers.

Further work was performed by Carter and Swalin[2]. In their research, further evidence was put forward regarding the dependence of the number of precipitate nuclei on the vacancy concentration. More importantly, evidence was presented that the precipitation rate was enhanced by increasing the oxygen content of the germanium crystals. On the basis of this work, it was suggested that one of two mechanisms could be active. Either oxygen-vacancy pairs or GeO_2 precipitate particles could act as nucleation centers.

The purpose of this investigation is to examine the problem further. Consequently, it was decided to investigate in detail the following points:

a) The dependence of the number of precipitate nuclei upon the vacancy concentration as determined by saturation annealing.

b) The quantitative dependence of the number of nuclei on the oxygen content of the crystal.

c) Influence of gamma bombardment on the nucleation process.

II. Experimental Techniques and Materials

A. *Basic Technique*

The general program consisted of a four-hour anneal of a pure sample at elevated temperatures followed by a quench. The samples were then saturated with lithium at 425°C, followed by a quench to the precipitation temperature. The precipitation process was followed isothermally by use of electrical resistivity techniques.

B. *Preparation of Samples*

The as-received germanium crystals were sliced parallel to a {111} plane into wafers 0.150 cm thick. These wafers were cut into rectangular blocks one cm long and 0.3 cm in width and were lapped with #600 carborundum.

A sample was sealed in a quartz capsule under one-half atmosphere of helium. It was then placed in a vertical tube furnace and annealed at temperatures between 600-900°C for four hours. After quenching to room temperature, the sample was lapped once again to remove any oxygen diffused layer. A lithium dispersion coating was applied to the sample. The sample was gently heated in an evacuated pyrex tube to vaporize the petrolatum. When the sample was dry and cool, it was encapsulated in pyrex under one-half atmosphere of helium.

C. *Saturation and Precipitation*

An annealed, encapsulated sample coated with lithium was suspended in a vertical tube furnace and saturated for 21 hours at 425°C. This saturation time exceeded the theoretical saturation time calculated from the diffusion data of Fuller and Severiens[3]. Upon completion of the saturation treatment, the sample was quenched to the precipitation temperature. The quenching medium for the low oxygen crystals was water at room temperature; the quenching medium for the high oxygen crystals was a solution of acetone-dry ice at −78.5°C. (Because of the large number of nuclei, rapid precipitation occurred at room temperature.)

The low oxygen crystals were lapped with #600 carborundum at room temperature, rinsed in distilled water and placed in the resistivity jig. For these crystals, zero time was assumed to be the instant of quenching.

The high oxygen crystals were lapped on a carborundum block in the acetone-dry ice mixture and then placed in the resistivity jig in a measuring medium of acetone packed in ice. The zero time for these crystals was assumed to be the instant the sample was placed in the measuring medium.

In all cases, it was possible to determine resistivity within 5 minutes after quenching. The resistivity of the samples was measured as a function of time without disturbing its position in the jig. Measurements were made at appropriate intervals during the experiment.

D. *Measurement of Electrical Resistivity*

The technique for the measurement of electrical resistivity used in this work is discussed in detail in a paper by Carter and Swalin[2].

E. *Determination of Oxygen Content of Crystals*

The oxygen content of the crystals was determined by use of a method devised by Fuller, Kaiser and Thurmond[4]. Basically, this technique involved the annealing of samples at temperatures between 350-550°C for 100-600 hours and measurement of the change in electrical resistivity. After this long term, low temperature anneal most of the dissolved oxygen is present as O_4 donors which can be detected electrically. The measured donor concentration is 1/4 the oxygen concentration. At higher temperatures the O_4 clusters dissociate.

In the present work it was noted that there is a correlation between the oxygen concentration of the crystal and the plateau value of the donor concentration after precipitation was completed. This will be discussed in more detail later. Pell[5] found a similar phenomenon in silicon.

Samples covering a thousand fold range of oxygen contents were investigated. The oxygen concentrations ranged from $2\times10^{14}/\mathrm{cm}^3$ to $2\times10^{17}/\mathrm{cm}^3$*.

III. Results

A. *Influence of Annealing Treatment Prior to Saturation with Lithium.*

A very pronounced influence of prior annealing of the pure crystal upon the number density of precipitate particles was observed. For a crystal containing 2×10^{14} oxygen atoms/cm^3, an as-received crystal saturated with lithium at 425°C and having no prior annealing treatment contained about 1.6×10^{11} particles/cm^3. If the wafer had been annealed at 900°C prior to the introduction of lithium at 425°C, the number of particles increased to $8\times10^{12}/\mathrm{cm}^3$. There appears to be an exponential relation between the number density of particles and the reciprocal of the annealing temperature, as shown in Fig. 1.

Obviously the concentration of nucleating centers had increased upon high temperature

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* Thanks are due to P. Penning from Phillips Research Laboratory for providing samples covering a wide range of oxygen contents and to Dr. Morin of Bell Telephone Laboratories for provision of a single crystal.

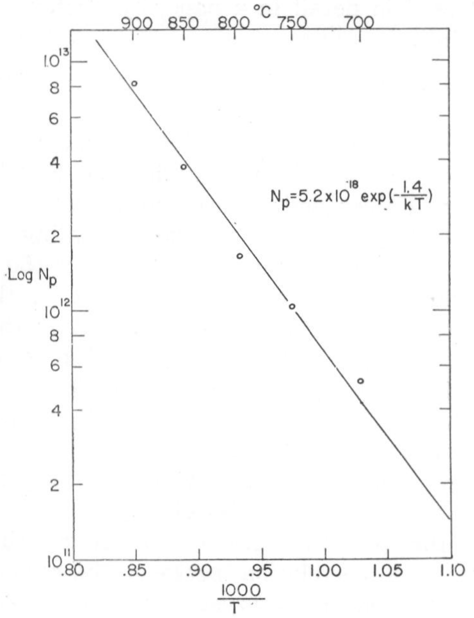

Fig. 1. Number density of precipitate particles N_p as a function of annealing temperature.

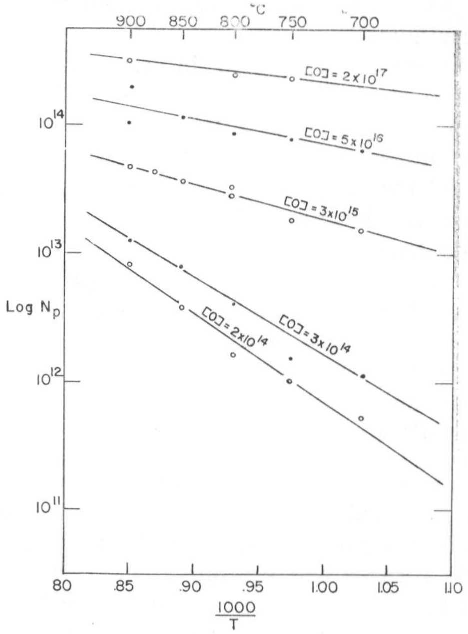

Fig. 2. Number density of precipitate particles N_p as a function of annealing temperature and oxygen content.

annealing. It was desired to determine if the number of centers introduced by the annealing process were introduced in a reversible fashion or irreversible fashion. An experiment was performed in which a sample was annealed at 900°C, cooled slowly to 700°C, and quenched to room temperature. The sample was saturated with lithium and the precipitation followed. The results were the same as those obtained from a crystal of the same oxygen content given a standard 700°C anneal. This experiment showed that the number of precipitate nuclei was a function only of the final anneal temperature and not of the path taken to reach that temperature. That is, the nuclei are formed reversibly.

In Fig. 1 is also shown, for the low oxygen crystal, the relationship between the number density of precipitate particles, the oxygen content, and the number of intrinsic vacancies. It is seen that for this crystal the number of precipitate nuclei is less than the oxygen content and has an enthalpy of formation different from that for the production of intrinsic vacancies.

In addition to the low oxygen crystal ($[O] \sim 2 \times 10^{14}/\text{cm}^3$) discussed previously, a series of similar experiments were performed on crystals of greater oxygen content. The results of these experiments are presented in Fig. 2.

In conjunction with an investigation of annealing effects in the low oxygen content germanium the effect of the presence of dislocation was studied. A crystal containing about 2×10^{14} oxygen atoms/cm^3 was obtained which was dislocation-free*. The results from this crystal were compared with the results from a crystal containing about 10^4 dislocations per cm^2 and of the same oxygen content. The results indicated that dislocations were not active in the nucleation process.

B. *Irradiation Effects*

Irradiation experiments were performed on crystals of various oxygen contents. It was found that irradiation increases the precipitation rate, and that the irradiation effect is greater in low oxygen content germanium.

C. *Influence of Oxygen Content*

It has already been shown in Fig. 2 that the number of precipitate particles is a function not only of annealing temperature but also of oxygen content. Therefore, it

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* Thanks are due to Parma Research Laboratory, Union Carbide Corporation, for provision of this crystal.

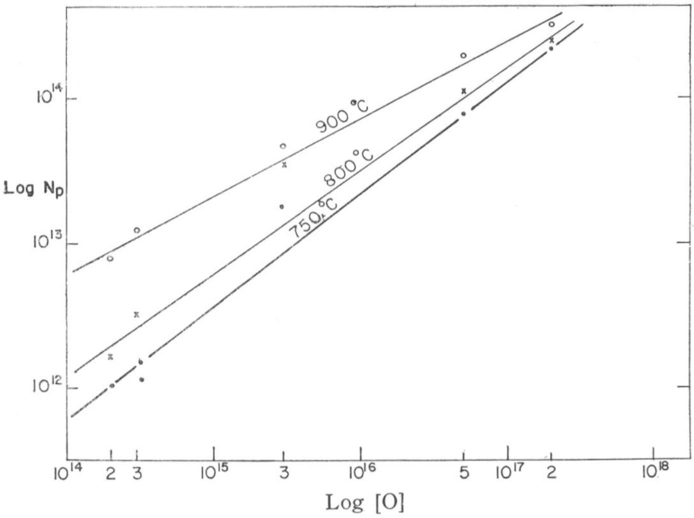

Fig. 3. Isothermal dependence of the number density of precipitate particles N_p on oxygen content.

is of interest to investigate the isothermal dependence of the number density of precipitate particles on the oxygen content of the crystal. In Fig. 3 is shown the isothermal relationships. From this curve it is found that the slope ranges from 3/4 at 750°C to 1/2 at 900°C. This information verifies the strong dependence of the number density of nuclei on the oxygen content of the crystal. There is some uncertainty involved in the determination of oxygen as well as in N_p. These curves indicate that $N_p \sim [O]$ within experimental accuracy. At high oxygen contents, there is some evidence that secondary defects play a role.

In the course of this study it was found that there appeared to be a direct relationship between the oxygen concentration of the crystal and the final carrier concentration. This same type of phenomena was found by Pell[5] to exist in silicon. Pell's relationship was $N_f = (1/50)[O]$. In this case of lithium, the number of carriers N_f is equivalent to C_f, the concentration of dissolved lithium. In Fig. 4 is shown the relationship between N_f and the oxygen concentration of the crystal. Our data for germanium yield the relationship

$$N_f = (1/4)[O].$$

IV. Discussion

The following general conclusions result from the data of the previous section.

(1) The number density of precipitate particles is approximately proportional to the oxygen content of the crystal. Thus it appears that oxygen is directly involved in the nucleation process. Not all oxygen atoms are effective however, but only a small fraction (about 1%).

(2) Annealing at high temperatures increases in a reversible nature the number density of particles, presumably by increasing the effectiveness of some of the oxygen.

(3) Gamma irradiation of samples increases the number density of particles.

(4) The number density of precipitate nuclei is the same in dislocation-free crystals as in samples containing dislocations, for two crystals having the same oxygen content.

(5) The number density of nuclei does not depend on the initial lithium concentration.

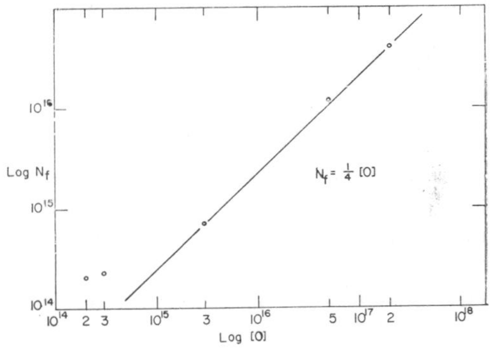

Fig. 4. Relationship between oxygen content and final concentration of charge carriers N_f.

The question then arises as to the nature of the predominant nucleating site. From the above summary, it is clear that the normal interstitial oxygen atoms are not effective and that the oxygen must be in some abnormal state. The predominant nucleating site cannot be equilibrium O_n complexes (where $2 \leq n \leq 4$), particularly at low oxygen concentrations. This follows since at any annealing temperature, there is the following equilibrium

$$nO = O_n \qquad K_1 = \frac{[O_n]N^{n-1}}{[O]^n} \tag{1}$$

where N is the number of lattice sites per cm^3. If O_n are assumed to be nucleating centers, then N_p may be identified with $[O_n]$. Thus for a given annealing temperature

$$N_p = K_1[O]^n.$$

This investigation shows that the exponent n is approximately equal to one. Similar analysis rules out complexes of oxygen and lithium. GeO_2 particles are eliminated from consideration since in all cases the oxygen content of the crystal is below the solubility of GeO_2 as determined by Kaiser and Thurmond[6].

It is clear then that the effective nucleating agent must be a single oxygen atom paired with some lattice defect. This defect cannot be residual impurity atoms X, as the following analysis will show. Suppose that O-X defect pairs are formed through the following reaction.

$$O + X = O\text{-}X \qquad K_2 = \frac{N[O\text{-}X]}{[O][X]}\,. \tag{2}$$

The dependence of K_2 upon temperature is

$$K_2 = A\mathrm{e}^{-\Delta H_b/kT}$$

where A is an entropy factor and ΔH_b represents the binding energy of the O-X complex. If there is an attraction between O and X, ΔH_b must have a negative sign and equating [O-X] to N_p we see that

$$N_p = A[O][X]\mathrm{e}^{-\Delta H_b/kT} \tag{3}$$

which indicates that N_p would be *increased* as the temperature is *decreased*. Figs. 2 and 3 indicate just the opposite relationship.

If X is not a residual impurity atom but an equilibrium defect, the situation may be considered different however. The irradiation experiments result in the formation of an increased number of interstitial germanium atoms and lattice vacancies which in turn results in an increased number of nuclei. This cannot be a kinetic effect since both lithium and oxygen are normally in the interstitial state. Thus their respective diffusion constants should not be influenced by the concentration of vacancies. Let us suppose then that lattice defect X is a vacancy.

Then the number density of nuclei particle will be identified as O-V pairs (or physically oxygen atoms in substitutional positions). We have the following reaction

$$\mathrm{O} + \mathrm{V} = \mathrm{O\text{-}V}$$

$$K_3 = \frac{N[\mathrm{O\text{-}V}]}{[\mathrm{O}][\mathrm{V}]} = \mathrm{e}^{-\Delta G_b/kT} = \mathrm{e}^{+\Delta S_b/k}\mathrm{e}^{-\Delta H_b/kT}. \tag{4}$$

The intrinsic concentration of vacancies in germanium has been determined by Logan[7] and is given as a function of temperature as

$$[\mathrm{V}] = 1.3 \times 10^{24}\mathrm{e}^{-2.0/kT}.$$

Substitution into Eq. (4) and identifying [O-V] with N_p we find that

$$N_p = 26\,[\mathrm{O}]\,\mathrm{e}^{\Delta S_b/k}\mathrm{e}^{-(\Delta H_b+2.0)/kT}. \tag{5}$$

Thus we see that N_p is proportional to the interstitial oxygen content, which agrees with experimental observation. For the low oxygen material we find experimentaly that

$$N_p = 2.6 \times 10^4\,[\mathrm{O}]\exp\left(-\frac{1.4}{kT}\right). \tag{6}$$

Comparing Eqs. (5) and (6) we see that the binding enthalpy between an interstitial oxygen and a lattice vacancy is $-0.6\,\mathrm{eV}$, which appears to be a reasonable quantity. The vibrational entropy change ($\Delta S_b/k$) is calculated to be 10. This number appears to be rather large but in any case must be considered to be appropriate in view of the experimental uncertainty in the pre-exponential terms.

It would appear therefore that oxygen-vacancy pair (or oxygen atom in a substitutional site) appears to act as the nucleating defect in this system, and therefore that thermodynamic information about the defect-complex may be obtained.

Other experimental evidence for a defect of this type in semiconductors exists. Watkins and Corbett[8], for example, using electron spin resonance (ESR) has postulated the existence of an O-V pair in silicon. This is called an "A" center in their work. In order to detect these defects with ESR techniques, a large quantity must be introduced.

For high oxygen samples, the slope of the plot of log N_p *versus* $1/T$ is reduced. This effect is not completely understood. It is hypothesized however, that for high oxygen contents and at low temperatures, other oxygen complexes become active as nucleation centers.

Let us turn our attention now to the relationship of the final value of lithium C_f to the oxygen content. From the data it would appear that at room temperature 25% of the oxygen atoms are firmly bound with lithium in the form of Li^+-O complexes. The concentration of these complexes is much larger, it might be added, than the number of precipitate particles, so it would appear that they are not effective in nucleation. From the data in Fig. 4 it is possible to estimate the binding enthalpy of the Li^+-O pair. The defect pair forms according to the following reaction.

$$Li^+ + O = Li^+O \qquad K_4 = Ae^{-\Delta H_b/kT}$$

$$K_4 = \frac{N[Li^+O]}{[Li^+][O]} .$$

We have the experimental relation that $[Li^+O] = (1/4)[O]$, at 300°K and the intrinsic lithium solubility in germanium at 300°K is $[Li^+] = 2\times10^{14}/cm^3$.[1] Assuming a small entropy change so that A is unity, we find that $\Delta H_b \simeq -0.5$ eV. For the same reaction in silicon, Pell[5] found a value of $\Delta H_b = -0.52$ eV.

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DISCUSSION

Watkins, G. D.: We have performed an experiment in which you may be interested. As you mentioned, we can observe the single vacancy-oxygen pair by electron spin resonance in silicon. We have looked for such defects in samples quenched for us by E. M. Pell from near the melt and found no evidence of them. This means that the concentration quenched in is $\lesssim 10^{13}$ cm^{-3}. Do you feel this is consistent with the precipitation experiments in silicon?

Swalin, R. A.: The concentration I am talking about here is of order of 10^{11} to 10^{13} of these defects which is generally below the resolution of ESR technique and may be a supplement to this. We can find in silicon actually 10^8 or 10^9 of these particles.

Dienes, G. J.: I did not quite understand your value of 1.4 eV for the formation energy of the nuclei since the number of nuclei depend on the oxygen concentration differently at different temperatures. Is the formation energy a strong function of the oxygen concentration?

Swalin, R. A.: Value of formation energy is a function of oxygen concentration. We have a suspicion that at high oxygen concentrations some kind of complex is going on which we do not understand at present. This is the result for low oxygen material.

Inuishi, Y.: We have measured the annealing of lifetime in γ irradiated Si, and got tentative value of 0.7~0.8 eV for the binding energy of vacancy-oxygen complex.