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RADIATION AND ANNEALING STUDIES ON OXYGEN-DOPED AND
LITHIUM DIFFUSED GERMANIUM

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ABSTRACT

Hall coefficient and resistivity measurements were used to determine the apparent carrier concentration and mobility of n-type Ge doped with specific impurities, or grown to contain oxygen, and then altered by annealing, Co^{60} photon irradiation, or Li diffusion. Annealing at 350°C increased the donor concentration and decreased the mobility of oxygen-doped Ge as a consequence of oxygen clustering. Subsequent annealing at 500°C decreased the donor concentration and increased the mobility as a consequence of oxygen dissociation. Clustering and dissociation were repeated many times with no apparent alteration of total oxygen content. The apparent rate of introduction of lattice defects by Co^{60} photons was essentially independent of oxygen concentration in Ge containing up to $\sim 10^{16}$ dissociated oxygen cm^{-3} . Formation of a primary defect state at $E_c - 0.2$ eV was observed for all concentrations. There was no evident interaction between the radiation induced defects and oxygen after defect formation, but some evidence was observed of defect stabilization against

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annealing in oxygen-doped Ge. There also was no evident interaction between Li and normal donors or oxygen in Ge after Li diffusion, precipitation, and annealing ($\sim 400^\circ\text{C}$), but Li interacted with "deep-level" acceptor impurities (Ag, Au or Cu) to form donors that were stable up to $\geq 500^\circ\text{C}$.

1. INTRODUCTION

The purpose of these experiments was to investigate the behavior of the apparent electrical carrier concentration and the mobility in selected samples of n-type Ge of known chemical dopant, initial carrier concentration, and oxygen content, as a consequence of annealing, Co^{60} photon irradiation and annealing, and Li diffusion, precipitation, and annealing.

The apparent rate of lattice defect introduction, energy level position, whether acceptors or donors were introduced, and subsequent changes on annealing have been investigated for semiconducting materials as irradiated at different temperatures by neutrons, photons, electrons, or charged particles. Cleland *et al.*¹ observed a step at $E_c - 0.2 \text{ eV}$ in the Hall coefficient and resistivity curves between ~ 200 and 250°K for fast neutron irradiated Ge; and suggested a defect model that consisted of a lattice atom vacancy (V) and Ge interstitial (I). Cleland and Crawford² observed a similar defect state for Co^{60} photon irradiated Ge; and suggested that two electrons were removed per defect pair; that the step in the Hall coefficient and resistivity curves was due to an ionization of (I); and that annealing (1 hr at 100°C) removed (I) to dislocations or clustering, making (V) a more effective double electron

trap up to intrinsic temperatures.

Watkins³ first reported the production of interstitial chemical impurities in Si by electron irradiation, and Hiraki *et al.*⁴ showed that one of the primary products of irradiation of Ge with electrons was interstitial chemical impurities (I) and lattice vacancies (V), and that the extent of any subsequent annealing involves some type of interaction between (I), (V), and the remaining substitutional chemical impurities (S_R). Pigg and Crawford⁵ observed that the carrier-removal rate was a function of the carrier concentration for Co^{60} photon irradiated Ge, and Cleland and Paciesas⁶ observed a difference in carrier-removal rate in electron irradiated Ge containing different chemical dopants. Hiraki *et al.*⁴ also indicated that considerable annealing occurred at room temperature, particularly for long exposure times, and that this would have a pronounced effect on apparent carrier-removal rates.

Emtzcv *et al.*⁷ did not observe the $E_c - 0.2$ level in Co^{60} photon irradiated Ge (that contained $\sim 3.5 \times 10^{16}$ oxygen cm^{-3}). They explained their results in terms of vacancy-donor and divacancy-donor complexes.⁸ Vavilov *et al.*⁹ also did not observe this level in 1.5 MeV electron irradiated Ge diffused with more than $\sim 3.5 \times 10^{14}$ Li cm^{-3} (that also contained $\sim 3.5 \times 10^{16}$ oxygen cm^{-3}). They suggested that Li pairs with some impurity X, thus preventing the radiation-induced primary defects from forming the $E_c - 0.2$ eV level; but they stated that X cannot be the (I) suggested by Hiraki *et al.*,⁴ nor could it be dissolved oxygen. Tkachev *et al.*,¹⁰ on the other hand, did not observe the $E_c - 0.2$ eV level initially ($\sim 20\%$ carrier removal) in Co^{60} photon irradiated Ge

(that contained $\sim 3.5 \times 10^{16}$ oxygen cm^{-3}), but evidence for this level was observed just before conversion from n- to p-type material. They attributed a considerably lower rate of defect introduction to an indication that oxygen atoms are the main sinks for free vacancies. Fukuoka *et al.*¹¹ irradiated n-type Ge, doped with Sb, As, oxygen, or Sb plus 10-20% Ga as introduced by transmutation experiments, and observed the $E_c - 0.2$ eV level in each case. The apparent carrier-removal rate at 77°K was $\sim 2 \times 10^{-1} \text{ cm}^{-1}$ for As-doped Ge, and $\sim 3 \times 10^{-1} \text{ cm}^{-1}$ for oxygen-doped Ge.¹² These data do not agree with Emtzev *et al.*⁷ who did not observe a level at $E_c - 0.2$ eV, or with Tkachev *et al.*¹⁰ who found a considerably lower carrier-removal rate in oxygen-doped Ge. Sinishchuk *et al.*,¹³ in a more recent publication, irradiated Sb-doped Ge containing $\sim 4.5 \times 10^{15}$ oxygen cm^{-3} , and $\sim 1.6 \times 10^{13}$ Li cm^{-3} , with Co^{60} photons, and observed a level at $E_c - 0.2$ eV with an initial carrier-removal rate of $\sim 1.5 \times 10^{-4} \text{ cm}^{-1}$.

The electrical behavior of oxygen in Ge has been of interest for many years. Infrared absorption band measurements (11.7 μ) have been used to detect the oxygen content, and quenching and annealing experiments have shown that ~ 4 oxygen atoms can combine to form a single donor.¹⁴ The electrical behavior of Li in Ge also has been of interest. Lithium diffuses rapidly as a singly-charged interstitial and acts as a donor. The solubility in pure Ge is $\leq 10^{14} \text{ cm}^{-3}$ at room temperature.¹⁵ Lithium diffusion has been used to electrically compensate chemical acceptor-type impurities to produce nearly intrinsic Ge. The unpredictable variation in Li drift mobility during attempts to fabricate Ge(Li) radiation detectors was finally attributed to the presence of oxygen.¹⁶

Good correlation was established between the amount of oxygen indicated by infrared absorption, and the electrical conductivity due to LiO^+ interactions, as indicated by room temperature conductivity measurements following Li diffusion. Lithium drift mobility measurements also have given a good correlation.¹⁷ The precipitation rate and the final conductivity are dependent on the diffusion temperature, crystal perfection, and the initial chemical impurity concentration, including any oxygen present. The resultant LiO^+ can be removed by annealing at $\sim 400^\circ\text{C}$.

The diffusivity, solid solubility, and acceptor or donor action of certain "deep level" impurities in Ge also has been investigated.¹⁸ Introduction of Cu into Ge by diffusion at an elevated temperature, followed by rapid quenching to minimize annealing, results in a stable supersaturated solution with Cu serving as a triple acceptor. Gold and silver impurity atoms also serve as triple acceptors,¹⁸ whereas Te serves as a double donor.^{18,19} The role of certain "deep-level" impurities as electron or hole traps in Ge(Li) detectors,²⁰ the use of Cu-compensation in detector fabrication,²¹ and an outline of some basic limitations in the use of Co^{60} photon compensation in detector fabrication²² also have been reported.

2. EXPERIMENTAL PROCEDURE

The starting material was ingot sections from single crystals of Ge grown from the melt with a specific chemical dopant or oxygen concentration,²³ or diffused at an elevated temperature and quenched to introduce copper. Bridge-type specimens were ultrasonically cut for Hall coefficient and resistivity measurements. Electrical contacts were

soldered to a freshly etched (CP-4) surface, using an indium-based solder, Cerroseal 35. Hall coefficient and resistivity measurements were taken between room temperature and 77°K. The magnetic field strength was 3,600 oersteds. Samples were irradiated at $\sim 30^\circ\text{C}$ with Co^{60} photons (flux $\sim 3 \times 10^{15} \text{ cm}^{-2} \text{ hr}^{-1}$). Vacuum anneals for 20 to 400 hr at 100 to 600°C were carried out after removing soldered contacts, etching, and boiling the sample in nitric acid to oxidize the surface to prevent contamination from copper during annealing. Selected ingot sections ($\sim 0.2 \text{ cm}$ thick) were coated with lithium in oil suspension, dried at $\sim 200^\circ\text{C}$, then held at $\sim 425^\circ\text{C}$ for $\sim 20 \text{ hr}$ in a helium atmosphere for complete diffusion.

3. RESULTS

3.1 Oxygen-Doped Germanium

Hall coefficient and resistivity measurements were made as a function of temperature on Ge with an apparent oxygen concentration of $\sim 1.1 \times 10^{16} \text{ cm}^{-3}$, as indicated by infrared absorption, and the results are shown in Fig. 1, which is a graph of log Hall coefficient vs inverse temperature. The initial electron concentration was $\sim 2.5 \times 10^{12} \text{ cm}^{-3}$, and the initial mobility was $\sim 26,000 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ at 77°K (Curve I). Vacuum annealing (155 hr at 350°C) increased the electron concentration to $\sim 7 \times 10^{14} \text{ cm}^{-3}$, and decreased the mobility to $\sim 23,200 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ at 77°K (Curve II). A subsequent anneal (16 hr at 500°C) decreased the electron concentration to $\sim 6.2 \times 10^{12} \text{ cm}^{-3}$, and increased the mobility to $\sim 33,000 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ at 77°K (Curve III). The results of yet another anneal at 350°C (Curve IV), and identical results on other

oxygen-doped specimens, suggest that oxygen atoms cluster to provide electrically active donors at $\sim 350^\circ\text{C}$; that these clusters are dissociated on annealing at $\sim 500^\circ\text{C}$; and repeated experiments at these temperatures have no apparent effect on the total oxygen content. No attempt was made to determine the total oxygen content by this technique, since previous experiments¹⁴ have indicated that ~ 1500 hr anneals were required. No indication of a sizeable change in apparent carrier concentration or mobility was observed for Ge with $\leq 10^{15}$ oxygen cm^{-3} as a consequence of annealing for ~ 100 hr at 350°C .

3.2 Compensated Germanium

Dakhovskii *et al.*²⁴ have published a method for a determination of the degree of compensation of n-type Ge from the Hall mobility measured in a weak magnetic field. Single crystals, grown by the Czochralski method, were doped with Sb to provide an uncompensated region, then Ga was introduced during the pulling procedure to provide a compensated region. The compensation coefficient ($K = N_a/N_d$) when N_a is the number of acceptors and N_d is the number of donors, was thus altered from a low value (uncompensated) to nearly unity (heavily compensated), and an experimental determination of the Hall mobility gave the total concentration of ionized impurities ($N_i = N_a + N_d$). Crawford and Cleland^{25,26} have studied the effect of thermal neutron absorption, capture γ -ray emission, defect formation by lattice atom recoil, annealing of such recoil-induced defects, and the subsequent introduction of donor and acceptor-type impurities in Ge by transmutations. One can alter the compensation coefficient by this technique almost exactly, since the isotopic neutron absorption cross sections are well known for Ge. A

preliminary examination of data (largely unpublished) for a large number of transmutation compensated samples of Ge has been made, and these data agree qualitatively with the results obtained by Dakhovskii *et al.*²⁴ by crystal growth techniques. It is evident that the measured Hall mobility gives an indication of the total concentration of ionized impurities ($N_i = N_a + N_d$), whereas Hall coefficient and resistivity measurements only indicate the net donor or acceptor impurity concentration.

Transmutation-induced impurities were used to compensate oxygen-doped crystals of Ge to provide samples that ranged from uncompensated high resistivity n-type to heavily compensated medium resistivity p-type material. Subsequent annealing experiments at ~ 350 and 500°C indicated that the process of oxygen donor formation (clustering) and donor removal (dissociation) was not altered in any detectable manner by the presence of a large excess of p-type acceptor impurities. These data thus provided an additional confirmation of the results obtained by Dakhovskii *et al.*²⁴

3.3 Co⁶⁰ Photon Irradiation Experiments

Hall coefficient and resistivity measurements were made as a function of temperature on selected samples of Ge (with apparent oxygen contents of $\leq 10^{14}$, 1.6×10^{15} , 5×10^{15} , and $1.1 \times 10^{16} \text{ cm}^{-3}$) before irradiation, after irradiation with Co⁶⁰ photons, and after annealing for 20 hr at 100°C . The apparent rate of removal of conduction electrons was $\sim 4 \times 10^{-4} \text{ cm}^{-1}$ for several specimens with $\leq 10^{14}$ oxygen cm^{-3} , and $\sim 3 \times 10^{-4} \text{ cm}^{-1}$ for all of the oxygen-doped specimens investigated. No evidence of a considerably lower rate of defect introduction in oxygen-doped Ge, as reported by Tkachev *et al.*,¹⁰ was observed in these

experiments. They stated that oxygen atoms were the main sinks for free vacancies, and that an initial rate of removal of conduction electrons of $1.3 \times 10^{-3} \text{ cm}^{-1}$ decreased to $1.5 \times 10^{-4} \text{ cm}^{-1}$, and approached a constant rate of introduction of (IV) complexes of $\sim 1.7 \times 10^{-4} \text{ cm}^{-1}$. Hiraki *et al.*⁸ indicated that considerable annealing of (IV) complexes can occur at room temperature over a period of time as short as several hours, hence the large decrease in apparent removal rate over long exposure periods as observed by Tkachev *et al.*¹⁰ may have been due to (IV) annealing, rather than their suggestion that oxygen serves as the main sink for vacancies.

Figure 2, which is a graph of log Hall coefficient and resistivity vs inverse temperature, shows typical data for a sample containing $\sim 5 \times 10^{15} \text{ oxygen cm}^{-3}$ before irradiation (Curves I), after Co^{60} photon irradiation (Curves II), and after annealing for 20 hr at 100°C (Curves III). Formation of the $E_c - 0.2 \text{ eV}$ level is indicated, however there is virtually no evidence for preferential annealing of this level as was observed in Ge with $\leq 10^{14} \text{ oxygen cm}^{-3}$. Similar results were obtained for other samples containing $\sim 1.6 \times 10^{15}$ to $\sim 1.1 \times 10^{16} \text{ oxygen cm}^{-3}$. These data suggest that the (IV) defect is stabilized by oxygen against annealing, even though the defect introduction rate and formation of the $E_c - 0.2 \text{ eV}$ level is not affected by the presence of $\sim 10^{16} \text{ oxygen cm}^{-3}$.

3.4 Lithium Diffusion Experiments

No attempt was made to determine the apparent donor concentration, conductivity, or mobility immediately after Li diffusion in the present experiments. Previous experiments,^{16,17} using a 4-point resistivity

probe technique, have indicated $\geq 10^{17}$ donors cm^{-3} immediately following such diffusion. The time required to prepare samples for Hall coefficient and resistivity measurements in the present experiments was such that some precipitation already had occurred; but the initial donor concentration was not of particular interest as long as sufficient Li was diffused into the material.

Samples of high resistivity p-type Ge, high resistivity n-type Ge, and of Sb, As, or P doped n-type Ge with different initial carrier concentrations were Li diffused, allowed to anneal at room temperature for ~ 20 days, and then vacuum annealed for 16-20 hr at 375-450°C. None of these samples had an absorption band at 11.7 μ that indicated the presence of a significant amount of oxygen. The experimental data all agreed with the general picture of initial donor action, precipitation during annealing, and removal of any remaining donor action by annealing at 375-450°C. There was some variation in the rate of precipitation, and the apparent donor concentration after ~ 20 days at room temperature was usually somewhat larger than that of the starting material, but this difference was $\leq 10\%$, and probably could be attributed to incomplete precipitation, a small oxygen content, or interaction with deep-level acceptor-type impurities (see below). In summary there was no real evidence for any direct interaction between Li and $\sim 10^{13}$ to $\sim 5 \times 10^{15}$ Sb, As, or P atoms cm^{-3} in Ge as a final consequence of diffusion, precipitation, and annealing.

3.4.1 Tellurium-doped Ge

Several ingot sections of single crystal n-type were obtained from material grown from pure zone-refined Ge in a sealed horizontal

leveling operation with no chemical dopant added except tellurium. The initial donor concentration was $\sim 1.1 \times 10^{14} \text{ cm}^{-3}$ and the initial mobility was $\sim 28,000 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ at 77°K . This type of growth process is expected to introduce more oxygen than the Czochralski technique, and infrared absorption measurements indicated $\sim 2 \times 10^{15} \text{ oxygen cm}^{-3}$. The apparent donor concentration decreased to $\sim 6 \times 10^{15} \text{ cm}^{-3}$ and the mobility increased to $\sim 13,000 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ at 77°K after several days at room temperature, but there was virtually no further change in the apparent carrier concentration and mobility after three and up to fifteen days. These data would suggest that the Li rapidly precipitated to form LiO^+ donors or a (LiTe) donor complex. Experiments on high resistivity p-type Ge, with or without a detectable oxygen concentration, have indicated that LiO^+ donors are unstable, and Li eventually precipitates on dislocations or diffuses to the surface, thus removing any donor-type activity. The final carrier concentration of Sb, As, or P doped samples of n-type Ge was virtually the same as the initial carrier concentration, after Li diffusion, precipitation, and annealing, so there was no evident interaction between Li and normal donor-type impurity atoms. The samples of n-type Te doped Ge were also high resistance, nearly intrinsic, after annealing ($\sim 16\text{-}20 \text{ hr}$ at $375\text{-}450^\circ\text{C}$), so there was no evident interaction between the Li and the double donor Te atoms, or the $\sim 2 \times 10^{15} \text{ oxygen cm}^{-3}$, that remained after Li diffusion, precipitation, and annealing.

3.4.2 Silver-doped Germanium

Several samples of single crystal Ge were obtained from an ingot grown by the Czochralski process with no chemical dopant added except

silver. There was only a very marginal indication of an infrared absorption that suggested the presence of $\leq 10^{14}$ oxygen cm^{-3} . The maximum solubility of Ag in Ge is less than 10^{15} cm^{-3} , and Ag serves as a triple acceptor¹⁸ in Ge, but this material had an apparent initial donor concentration of $\sim 5 \times 10^{13} \text{ cm}^{-3}$. The initial Hall mobility was $\sim 17,000 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ at 77°K, as compared to a typical value of $\sim 35,000 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ at 77°K for high purity (undoped) Ge. These data would suggest that the crystal was heavily compensated with an unknown donor-type impurity, hence the actual concentration of any Ag could only be estimated as $\leq 10^{15} \text{ cm}^{-3}$ by the technique employed by Dakhovskii *et al.*²⁴ The apparent donor concentration after Li diffusion was $\geq 10^{16} \text{ cm}^{-3}$ at 77°K, and decreased to $\sim 5 \times 10^{15} \text{ cm}^{-3}$ at 77°K after several days at room temperature, but then remained at approximately that value out to 20 days at room temperature. This behavior was identical to that for the Te-doped Ge that contained oxygen (Section 3.4.1), but infrared absorption did not indicate a significant amount of oxygen in the Ag-doped Ge. Vacuum annealing (16 hr at 375-425°C) removed any evidence of any remaining donor action that could be attributed to Li in the Sb, As, P, or Te-doped Ge, but a similar anneal only reduced the apparent donor concentration of the Ag-doped Ge to $\sim 2 \times 10^{15} \text{ cm}^{-3}$ at 77°K. Vacuum annealing (16 hr at $\sim 600^\circ\text{C}$) was required to remove most of the donor type behavior introduced by Li diffusion and precipitation in the Ag-doped Ge. These data indicate that Li interacts with "deep level" acceptor-type Ag, or with Ag that is in the lattice but electrically inert (interstitial?), as readily as it interacts with oxygen, and that the (LiAg) complex is more stable against annealing than is the LiO^+ complex.

A second crystal was grown by the Czochralski technique with both Sb and Ag added as dopants. The apparent initial donor concentration was $\sim 4.4 \times 10^{15} \text{ cm}^{-3}$ at the outset; $\sim 3.3 \times 10^{16} \text{ cm}^{-3}$ immediately after Li diffusion; and $\sim 1.0 \times 10^{16} \text{ cm}^{-3}$ after ~ 20 days at room temperature and vacuum annealing (20 hr at 450°C). The apparent donor concentration was still $\sim 5.3 \times 10^{15} \text{ cm}^{-3}$ after a second vacuum anneal (16 hr at 500°C), which again indicates that the (LiAg) complex is more stable against annealing than is the LiO^+ complex.

3.4.3 Gold or Copper-doped Germanium

Similar experiments were carried on Au-doped Ge, material doped with Au and Sb to an initial donor concentration of $\sim 5 \times 10^{15} \text{ cm}^{-3}$ at 77°K , and on samples of Sb-doped Ge (initial carrier concentration $\sim 4 \times 10^{14} \text{ cm}^{-3}$ at 77°K) that were coated with a visible layer of Cu, held at 520, 550 or 580°C for 100 hr, then quenched. Infrared absorption measurements did not indicate a significant oxygen concentration in any of these samples. Lithium diffusion and precipitation gave indication of a donor-type interaction between the Li and the acceptor type Au or Cu, and vacuum annealing (20 hr at $\geq 500^\circ\text{C}$) was required to remove this donor-type action. These data indicate that Li interacts with the "deep level" acceptor-type Au or Cu, and that the resulting complex is stable against annealing at temperatures up to $\sim 500^\circ\text{C}$.

DISCUSSION

4.1 Co^{60} Photon Irradiation

The apparent rate of introduction of lattice defects in n-type Ge by Co^{60} photons was found to be essentially independent of the dissociated

oxygen concentration for material containing up to $\sim 10^{16}$ oxygen cm^{-3} , and formation of a primary energy level at $E_c - 0.2$ eV was observed. No evident interaction between the irradiation-produced defects and oxygen, of the type reported by Tkachev *et al.*,¹⁰ was observed. Some evidence of a stabilization against annealing of radiation-induced defects was observed for samples that contained $\sim 10^{16}$ oxygen cm^{-3} .

A sample of heavily compensated Ag-doped Ge (see Section 3.4.2) also had a comparable rate of introduction of lattice defects as a consequence of irradiation with Co^{60} photons, gave evidence for the formation of the $E_c - 0.2$ eV state, and there was no evident interaction between the irradiation-produced defects and the "deep level" acceptor type Ag. Annealing (20 hr at 100°C) removed $\sim 10\%$ of the radiation-induced defects, but did not remove the $E_c - 0.2$ eV level. The Li diffusion data (Section 3.4.2) indicated that this material was heavily compensated, with up to 1×10^{15} Ag cm^{-3} , but the fact that this concentration of Ag had no apparent effect on the rate of introduction of lattice defects, or formation of the $E_c - 0.2$ eV level, can be taken as an indication that an excess concentration of electrically inactive impurities, whether oxygen or Ag, has no apparent effect on the apparent rate of defect formation by irradiation.

The early model of Cleland and Crawford^{1,2} of a primary defect state that consists of a vacancy (V) and an interstitial Ge atom (I) has been replaced by a model proposed by Watkins³ for Si and Hiraki *et al.*⁴ for Ge that consists of a vacancy (V) and an interstitial chemical impurity (I). One must assume that the $E_c - 0.2$ eV state is due to a second ionization of the chemical impurity (I), and that

removal of the state is as a consequence of migration of (I), leaving (V) as a more effective double electron trap up to nearly intrinsic temperatures.

Hiraki *et al.*⁴ also suggested that (VI) annihilation occurred at room temperature, particularly for long exposure times, unless (V) was trapped by a substitutional chemical impurity (S_R). Emtzev *et al.*,^{7,8} Vavilov *et al.*,⁹ and Tkachev *et al.*¹⁰ did not observe the $E_c - 0.2$ eV state, but their Ge contained $\sim 3.5 \times 10^{16}$ oxygen cm^{-3} . Fukuoka *et al.*¹¹ observed this defect state (oxygen content not specified), and Sinishchuk *et al.*¹³ observed this state in Sb-doped Ge that contained $\sim 4.5 \times 10^{15}$ oxygen cm^{-3} . The fact that the $E_c - 0.2$ eV defect state was not observed in Ge that contained $\sim 3.5 \times 10^{16}$ oxygen cm^{-3} may be due to (VI) annihilation during irradiation, or trapping (stabilization) of (V) by substitutional chemical impurities (S_R).

Hiraki and Fukunaga²⁷ have compared the apparent rate of introduction of lattice defects at room temperature by 1.5 MeV electrons in Sb-doped Ge with that for high purity (40 ohm cm) oxygen-doped Ge that had been annealed to produce $\sim 10^{16}$ donors cm^{-3} . The apparent rate of introduction of lattice defects was only $\sim 1/3$ as large for the oxygen-clustered Ge. One would not expect an interaction between an irradiation produced Ge interstitial (I) and an oxygen cluster, hence one would expect (VI) annihilation in the oxygen-doped specimen, and (VS_R) stabilization in the Sb-doped Ge.

It is not the primary intent of this paper to suggest that the $E_c - 0.2$ eV defect state is now understood; but rather to indicate why this state was not observed in some previous experiments. The oxygen

content of Ge has been ignored in many previous investigations of radiation-induced defects that included vacuum annealing at ~ 300 - 500°C to remove such defects, and Hall mobility indications of an appreciable compensation by impurities also have been ignored in many previous experiments. The present work does not permit one to differentiate between the dissociated and clustered oxygen content, as regards any possible effect on defect formation, migration, or annealing, but it does serve to indicate that the total oxygen content is of importance in certain radiation-induced defect studies.

4.2 Lithium Diffusion Experiments

There was no obvious interaction between Li and normal donor-type impurities (Sb, As, or P), a double-donor type impurity (Te), or a modest oxygen concentration ($\sim 2 \times 10^{15} \text{ cm}^{-3}$) in Ge that remained after Li diffusion, precipitation at room temperature, and annealing (365 - 425°C); however, diffused Li and certain "deep-level" acceptor type impurities (Ag, Au, Cu) formed a complex that resisted annealing up to $\geq 500^\circ\text{C}$. Vavilov *et al.*⁹ did not observe the $E_c - 0.2 \text{ eV}$ defect state in 1.5 MeV electron irradiated Ge diffused with more than $\sim 3.5 \times 10^{14} \text{ Li cm}^{-3}$, but his material contained $\sim 3.5 \times 10^{16} \text{ oxygen cm}^{-3}$, and formation of a sizeable concentration of relatively unstable LiO^+ complexes would be expected to mask the effect of any interaction between radiation-induced defects and any remaining Li^+ interstitial atoms. Sinishchuk *et al.*¹³ observed the $E_c - 0.2 \text{ eV}$ state in Li drifted Ge that contained $\leq 4 \times 10^{15} \text{ oxygen cm}^{-3}$, but formation of unstable LiO^+ complexes again would be expected to mask the formation of any electrically inactive (LiV) type complexes.

5. SUMMARY

The previously suggested model of a lattice vacancy (V) and interstitial chemical impurity (I) as a primary radiation-induced defect has not been altered as a consequence of experiments that involved oxygen-doped Ge. The apparent rate of introduction of lattice defects by Co^{60} photons was essentially independent of the oxygen concentration up to $\sim 10^{16} \text{ cm}^{-3}$, and formation of a defect state at $E_c - 0.2 \text{ eV}$ was observed in every case. No obvious interaction between radiation-induced defects and oxygen was apparent as a consequence of defect formation, but some indication of defect stabilization against annealing was observed. There also was no evident interaction between diffused Li and n-type Ge, with or without an oxygen content, after Li diffusion, precipitation and annealing, but electrical donor interactions with "deep-level" acceptor-type impurities was evident. Previous experiments have indicated that oxygen must be removed from Ge to permit fabrication of Ge(Li) radiation detectors. These data suggest that removal of "deep-level" acceptor-type impurities is of equal importance. Alternatively, some thought might be given to the fabrication of radiation detectors from Li drifted Ge that contained Ag, Au, or Cu to ascertain if detectors of this type could be stored at ambient temperatures without appreciable loss of Li by migration.

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FIGURE CAPTIONS

Fig. 1 Log of Hall Coefficient vs Reciprocal Temperature of Oxygen-Doped Ge after Successive Annealing at 350°C (II), 500°C (III) and 350°C (IV).

Fig. 2 Log of Hall Coefficient and Resistivity vs Reciprocal Temperature of Oxygen-Doped Ge after Co⁶⁰ γ -Radiation (II) and Annealing at 100°C (III).

W. A. # 69400
 Date 12-7777

N-type Ge
 ($\sim 1.1 \times 10^{16}$ oxygen / cm^3)

Fig I

N. O. # 69400
DATE 7-2-77

N-type Ge
($\sim 1.1 \times 10^{16}$ oxygen/cm³)

2
Fig I

Resistivity, Ohm-cm

10^7

10

69644

[illegible]

III- type Ge

 $(\sim 5 \times 10^{15} \text{ oxygen/cm}^3)$

10⁴

69694
 Lot. 72-7776

N-type Ge
 (~ 5 x 10¹⁵ oxygen/cm³)

Resistivity, ohm cm. 10²

Fig. II