DEFECT-IMPURITY INTERACTIONS IN IRRADIATED GERMANIUM

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J. W. Cleland

Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830*

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The initial purpose of these experiments was to use electrical and infrared absorption measurements to investigate certain defect-impurity interactions in Ge which had a known concentration of chemical impurity dopant, and oxygen, and which had been irradiated at $\sim 300^\circ\text{K}$ with ^{60}Co photons,¹ 1.5-2.0 MeV electrons,² or thermal energy neutrons.³ However, it was discovered that certain impurity interactions occur during crystal growth and sample preparation, and that the nature and extent of these interactions must be determined before one can hope to understand defect-impurity interactions.

Single crystals of Ge were grown by the Czochralski process for use as Ge(Li) or Ge(HP) radiation detectors, and from P, As, or Sb-doped melts, and $\leq 10^{15}$ to $\geq 10^{17}$ oxygen cm^{-3} was added to the bottom part of certain crystals by introducing oxygen to the furnace chamber after $\sim 1/3$ of the crystal had been solidified. Hall coefficient and resistivity measurements (at 77 and 300°K) were used to determine the initial carrier concentration due to the chemical dopant and clustered oxygen,⁴ and infrared absorption measurements (at $11.7 \mu\text{m}$) were used to determine the dissociated oxygen concentration. Lithium was diffused from an oil suspension for 2-40 hr at ~ 500 - 700°K into sand blasted surfaces of selected ingot slices, and certain samples were coated with a visible layer of Cu prior to Li diffusion; or were coated with Cu and annealed for 100 hr at $\sim 820^\circ\text{K}$ in vacuum, to introduce $\sim 10^{14}$ Cu cm^{-3} as determined by independent electrical property measurements prior to Li diffusion or irradiation. The equipment and techniques used to fabricate specimens, make electrical property and infrared absorption measurements, and perform ^{60}Co photon¹ and 1.5-2.0 MeV electron² irradiations have been described. Thermal neutron irradiations were carried out in the D₂O tank attached to the Bulk Shielding Reactor at this laboratory. This facility is unique in that the thermal neutron flux is $\geq 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$ at 2 Mw, whereas the fast ($\geq 0.6 \text{ MeV}$) neutron flux is $\leq 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ at 2 Mw. This means that one can study (n, γ) recoil and subsequent transmutation effects in Si and Ge with only a very negligible contribution from fast neutron induced defect clusters or disordered regions.³

C. S. Fuller⁴ first demonstrated that dissociated oxygen did not contribute conduction electrons in Ge, but that long term annealing (up to 1500 hr at ~ 550 to 650°K) caused the formation of O_2 , O_3 , and eventually O_4 clusters, that served as single donors of conduction electrons. Short term annealing ($\sim 1/2$ hr at ~ 800 to 900°K) then quenching can be used to dissociate the clusters and remove their donor contribution. Repeated clustering and dissociation experiments were used to form and then dissociate up to $\sim 2 \times 10^{17}$ O_4 clusters cm^{-3} in the present experiments, with no appreciable loss of oxygen. However, the initial donor concentration was $\sim 10^{15}$ to $\sim 10^{16} \text{ cm}^{-3}$ for different samples from the middle (M) or bottom (B) portion of ingots that were pulled from melts that contained $\leq 5 \times 10^{13}$ As or Sb cm^{-3} in the top (T) portion, before oxygen was added to the furnace chamber. There was no correlation between the probable As or Sb concentration and the donor concentration as measured in M or B samples after crystal growth. Short term annealing then quenching reduced the donor concentration to a value that approached the probable As or Sb concentration as indicated by the T samples, however, the donor concentration of M or B samples could be increased markedly by very short (1 hr) anneals at ~ 550 to 650°K . The probable As or Sb concentration could only be estimated in M or B samples that contained $> 10^{16}$ oxygen cm^{-3} , since the donor contribution due to the clustered oxygen could not be completely removed by annealing and quenching.

A prominent lattice defect state has been observed at ~ 0.2 eV below the conduction band ($E_c - 0.2$ eV) as a consequence of irradiation of n-type Ge at $\sim 300^\circ\text{K}$ with ^{60}Co photons,^{1,5,6} 1.7 MeV electrons,² thermal neutrons,³ or fast neutrons.⁷ These investigators suggested that the $E_c - 0.2$ eV level was formed as a consequence of migration of an irradiation produced vacancy (V) to the vicinity of a substitutional chemical impurity donor (D), to form a stable (VD) defect state. Goncharov *et al.*⁸ did not observe a defect state at $E_c - 0.2$ eV as a consequence of irradiation of n-type Ge with ^{60}Co photons. They suggested that the Ge used by all previous investigators contained more oxygen than their material, which contained $\sim 3 \times 10^{15}$ oxygen cm^{-3} , and that any observation of a defect state at $E_c - 0.2$ eV was due to the formation of a (VO) defect state. Tkachev *et al.*,⁹ on the other hand, observed a defect state at $E_c - 0.2$ eV in ^{60}Co photon irradiated n-type Ge that contained $\sim 3.5 \times 10^{16}$ oxygen cm^{-3} , but they also observed a considerably lower rate of defect introduction, that they attributed to the formation of (VO) defect states.

It has previously been reported¹ that ^{60}Co photon irradiation at $\sim 300^\circ\text{K}$ of n-type Ge that contained $\leq 10^{14}$ to 10^{16} oxygen cm^{-3} produced a defect state at $E_c - 0.2$ eV. These experiments have now been continued on As or Sb doped T, M, and B samples that contained $\leq 10^{14}$ to $\geq 7 \times 10^{17}$ oxygen cm^{-3} , after the samples were annealed then quenched to dissociate the oxygen. The rate of introduction of lattice defects was larger for As than for Sb-doped Ge, and increased for Ge with a larger initial As or Sb concentration, but there was no indication that the rate was decreased as a consequence of the presence of oxygen, and formation of a defect state at $E_c - 0.2$ eV was always observed. These data indicate that the $E_c - 0.2$ eV defect state is not a (VO) defect state, as suggested by Goncharov *et al.*,⁸ and these data also indicate that the rate of introduction of lattice defects in n-type Ge by irradiation is not decreased as a consequence of any increase in the rate of formation of any type of (VO) defect state, as suggested by Tkachev *et al.*⁹

Lithium acts as an electrical donor when first introduced into Ge by diffusion techniques, and $\geq 10^{17}$ donors cm^{-3} can be introduced initially. The saturation solubility of Li in Ge is $\sim 10^{14}$ cm^{-3} at 300°K , and the donor concentration due to Li in Ge will decrease with time to this value, unless other defects or impurities are present. Morin and Reiss¹⁰ presented evidence that (V) served as Li precipitation centers, removing the donor contribution due to the Li, and that dislocations or electron irradiation provided additional (V) to increase the precipitation rate. Carter and Swalin,¹¹ and later Weltzin and Swalin,¹² in contrast, presented evidence that (VO) pairs served as Li precipitation centers, that dislocations had no evident effect, that ^{60}Co photon irradiation increased the precipitation rate, but that a simultaneous diffusion of as few as $\sim 10^{13}$ Cu cm^{-3} formed an atmosphere of Cu atoms around the precipitation centers that prohibited Li precipitation.

Vavilov *et al.*¹³ did not observe a primary defect state at $E_c - 0.2$ eV in 1.5 MeV electron irradiated n-type Ge that contained 3×10^{14} to 3×10^{15} As or Sb cm^{-3} , $3\text{--}5 \times 10^{16}$ oxygen cm^{-3} , and $\sim 3 \times 10^{14}$ Li cm^{-3} as introduced by diffusion. They suggested that the Li pairs with some impurity X, thus preventing radiation induced defects from forming the $E_c - 0.2$ eV level, but they stated that X could not be As, Sb, or oxygen, so was some type of electrically inactive residual impurity in Ge that interacted with (V) to form a (VX) defect state if Li was not present. Sinischuk *et al.*,¹⁴ on the other hand, observed a primary defect state at $E_c - 0.2$ eV in ^{60}Co photon irradiated n-type Ge that contained 1.5×10^{12} Sb cm^{-3} , $\sim 4 \times 10^{15}$ oxygen cm^{-3} , and $\sim 1.6 \times 10^{13}$ Li cm^{-3} as introduced by diffusion. However, the rate of introduction of defects by ^{60}Co photons was less by more than a factor of five for the Li diffused samples, than for control samples, so they suggested that Li pairs with (V) to form an electrically inactive (LiV) defect state, whereas the $E_c - 0.2$ eV defect state is due to a (VI) complex.

In the present experiments Li was diffused into T, M, or B ingot slices that contained $\leq 10^{14}$ to $\geq 10^{17}$ oxygen cm^{-3} as determined by infrared absorption measurements, and as confirmed by independent O_4 clustering experiments. The samples were annealed then quenched to dissociate any oxygen before Li diffusion. The donor concentration was determined at 77 and 300°K as a function of time at 300 or 373°K. Rapid precipitation of Li to form a stable (LiO) donor was observed if oxygen was present, in agreement with Swalin *et al.*^{11,12} and Fox,¹⁵ but these data did not indicate the rapid (1-2 day) approach to a final Li saturation solubility of $\sim 10^{14}$ cm^{-3} observed by previous investigators^{10-12,15} for Ge in which they had detected no oxygen or other impurity concentration.

Similar results were obtained for a sample from an ingot of radiation detector quality p-type Ge that contained $\sim 1 \times 10^{14}$ Ga cm^{-3} , and for which lithium-drift mobility measurements indicated that virtually no oxygen was present. The donor concentration due to diffused Li was determined as a function of time at $\sim 300^\circ\text{K}$, then redetermined as a function of time after the donor concentration due to the Li was reactivated by heating the sample in vacuum for ~ 5 min at 670°K . There was some loss of the donor contribution due to the Li as a consequence of the removal of soldered electrical leads, etching, and reactivation, but this sample was reactivated to an initial Li donor concentration $> 10^{17}$ cm^{-3} four times; with no apparent effect on the precipitation rate or final donor concentration. These data indicate that the donor concentration due to diffused Li in Ge of low oxygen or other impurity content may eventually approach a saturation solubility of 10^{14} cm^{-3} if the sample is held at $\sim 300^\circ\text{K}$ for months, or at $\sim 373^\circ\text{K}$ for many days, however these data also indicate that $\geq 10^{17}$ Li cm^{-3} can be present in Ge, but electrically inactive under certain conditions.

These experiments were also carried out on two samples from a slice from a Ge ingot that was unique in that one side had a dislocation distribution of $\sim 10^3$ cm^{-2} , but the other side was dislocation free. Similar results were obtained for these samples, for samples from vacuum grown Ge, hydrogen grown Ge, and for samples that contained $\sim 10^{14}$ Cu cm^{-3} . There was no apparent effect of dislocations, hydrogen, or Cu on the Li precipitation rate, or rate of approach to a final saturation solubility of $\sim 10^{14}$ cm^{-3} after months at $\sim 300^\circ\text{K}$ or many days at $\sim 373^\circ\text{K}$. These experiments are still in progress, but they indicate that dissociated oxygen is the only well established precipitation site for diffused Li in Ge; and that the role of dislocations, hydrogen, or Cu as a precipitation site appears to be negligible. It is evident that $\geq 10^{17}$ Li cm^{-3} can be present in Ge, electrically inactive under certain conditions, but electrically active under certain other conditions. Hence, a satisfactory model for a defect-impurity structure as a consequence of irradiation experiments cannot be established for Li diffused Ge until the precipitation site for Li in Ge is better understood.

N-type samples of Ge containing $\sim 2-5 \times 10^{15}$ or $2-5 \times 10^{16}$ P, As, Sb, or O_4 clusters cm^{-3} were irradiated at $\sim 300^\circ\text{K}$ with thermal energy neutrons, and the apparent rate of removal of conduction electrons was determined as a consequence of lattice defects introduced by (n, γ) recoils. The rate of introduction of lattice defects was larger for P and As than for Sb-doped Ge, and increased slightly for Ge with a larger initial impurity concentration. There was no electrical evidence for multiple defect creation,³ or for any (VO) type defect state. However, the rate of introduction of lattice defects was less by a factor of three for n-type Ge in which the donor concentration was due to O_4 clusters. Hiraki and Fukunaga¹⁶ suggested that one might improve the radiation resistance of Si or Ge p-n devices by the use of oxygen clusters to provide donors instead of conventional impurities, and these data are in general agreement with their observations.

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