Title

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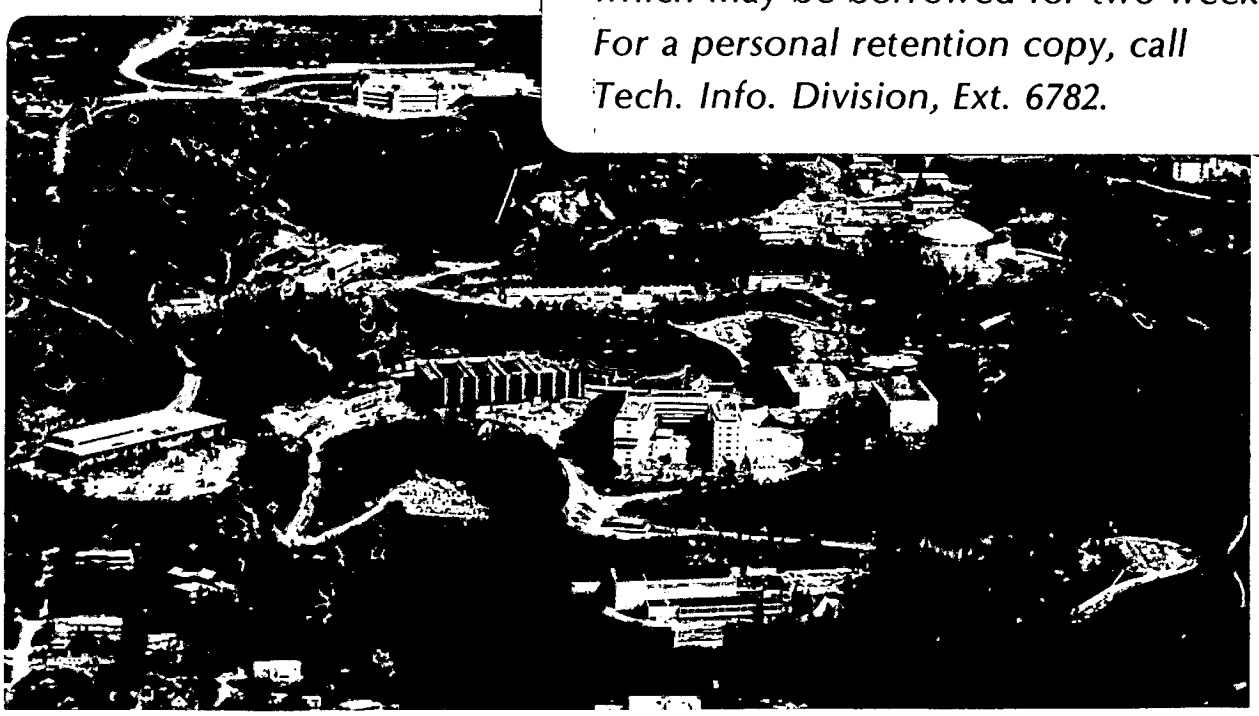
October 1983



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DISCLAIMER

DEEP LEVEL IMPURITIES IN GERMANIUM AND SILICON: LOW TEMPERATURE PASSIVATION OR REMOVAL TECHNIQUES

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Abstract

Deep level impurities and defects in high-purity germanium and silicon radiation detectors are often the cause of degraded spectral resolution. Exposure of the semiconductor diode to a low pressure hydrogen plasma may neutralize the electrical activity of a wide range of line and point defects and contaminating impurities, such as copper in Ge and gold in Si. The efficiency and thermal stability of this technique are discussed. The application of other novel methods of defect removal, such as the room temperature drifting of charged defects out of the depletion region under the action of the electric field in a diode, and the recombination enhanced annealing of radiation damage centers in Ge is also discussed.

Introduction

Radiation detectors fabricated from high-purity Ge and Si are sensitive to the presence of deep level recombination centers, either in the bulk of the semiconductor or on its surface. Electrons or holes created by ionizing radiation may be trapped at these centers causing degraded spectral resolution, characterized by tailing on the low energy side of photopeaks. Because of their ability to act as generation-recombination centers, these defects may also promote excess leakage current, preventing the application of the required detector operating bias. The deep levels may be present in the as-grown semiconductor crystal, they may be introduced during processing of the material or introduced during operation of the finished device, e.g. by radiation damage. The levels may be caused by lattice point or line defects (e.g. vacancies interstitials, or dislocations), chemical impurities, or complexes of these entities. In this paper, we report an investigation of several low temperature methods of defect passivation or removal.

Experiments

Hydrogenation of Surface and Bulk Defects

The use of hydrogenated amorphous germanium (a-Ge:H) coatings to passivate the surface of Ge nuclear radiation detectors is now a common practice[1], and a similar application for a-Si:H as a surface coating for Si radiation detectors is under investigation[2]. Previous experiments by RCA workers[3] showed that in low resistivity crystalline Si, surface states presumed to be related to Si dangling bonds could be substantially neutralized by hydrogenation. We looked for a similar effect in high-purity Ge and Si suitable for detector fabrication. Three standard high-purity p-type Ge detectors ($N_A - N_D = 2 \times 10^{10}$ cm^{-3}, $\varnothing = 2.5$ cm, thickness = 1 cm) with bare surfaces were exposed to a low pressure H plasma for 2 h at 50°C. We found only marginal improvement after the plasma treatment, and the decrease in leakage current was never as great as simply re-etching the surface in 4 HNO_3:1HF (Fig. 1). Similarly, repeating the experiment with two 1 kΩcm, 2 cm diameter, 0.3 cm thick p-type Si surface barrier detectors, we saw no consistent improvement in leakage current simply by H plasma exposure. Etching the surface or trying to set the surface states by various chemical treatments proved more effective in reducing the leakage current. This does not preclude the use of hydrogen plasmas to "tune" the hydrogen content of sputtered amorphous Si films on Si detector surfaces, where lower surface leakage currents have been found with increasing hydrogen content of the amorphous layer[2].

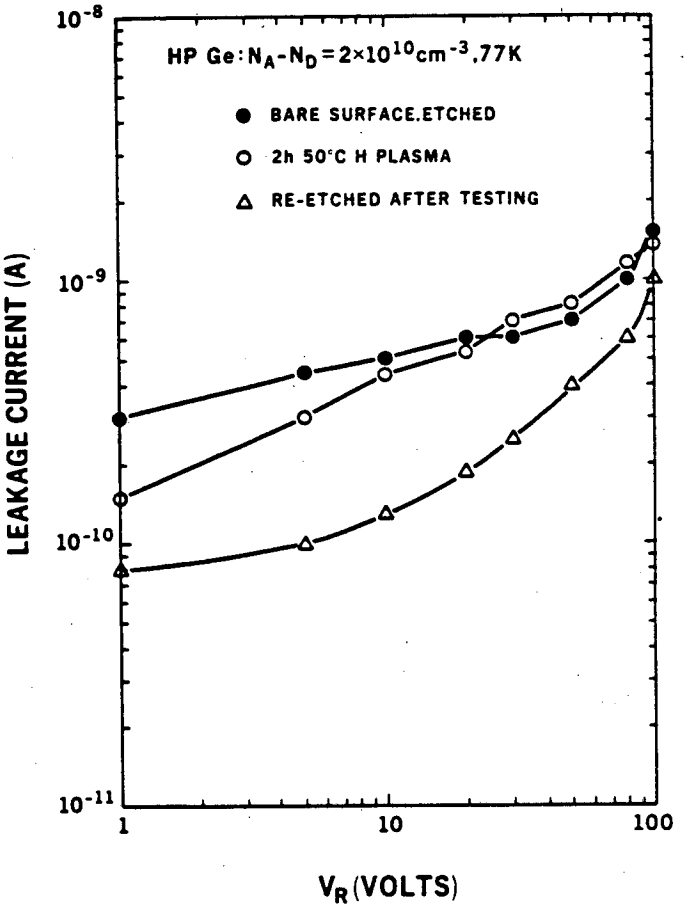

Fig. 1. Reverse leakage current-voltage characteristics for HP p-type Ge detector with bare surface, comparing effects of hydrogen plasma exposure with re-etching of the surface.

The use of hydrogenation to neutralize bulk defects is somewhat limited by the relatively slow diffusion of H at temperatures below ~ 600°C in crystalline Si and Ge. For a typical 3 h, 300°C plasma exposure, one can neutralize most transition metal-related trapping centers to depths of ~ 100 μm in Ge[4] and ~ 10 μm in Si[5]. An additional problem is severe plasma etching of Ge surfaces at temperatures above ~ 700°C. We have, however, seen significant improvement (25%) in detector

resolution of high-purity (60 kΩcm) Si surface barrier diodes exposed to H plasmas at 900°C for periods of several hours, for which the diffusion depth of atomic H is 3 - 4 mm[6]. DLTS scans had revealed no point defects present in the material, and the initial relatively poor detector performance was ascribed to swirl defects in the Si. This fact brings us to an important point. The diffusion of H is much more rapid in disturbed crystals, e.g. those containing high dislocation densities or lineage. As well, atomic hydrogen is known to neutralize the attractive potential of grain boundaries[7] and dislocations[8] for holes. Thus, we often have the reverse problem, i.e., not of introducing H into the material, but of preventing it from escaping the crystal and leaving line defects more active in trapping holes. This problem seems certain to become more evident as the technology of producing very large coaxial detectors improves, with the energy resolution becoming ever more sensitive to defects. The fact that very long collection paths of electrons and holes will be involved means that even small concentrations of trapping sites will be important in determining detector resolution. Modifications in crystal growing procedures may be necessary to prevent the outdiffusion of atomic hydrogen from dislocated or lineaged regions. As well, the effects of small concentrations of defects and impurities may be more obvious in high-purity detector material compared to the now obsolete Li-drifted detectors, because Li is known to passivate many of the acceptor defects that hydrogen does also[9]. In consequence, the loss of hydrogen from defect sites may be analogous to the precipitation of Li in Li-drifted detectors, both processes leading to worsened detector resolution.

The effect on 1 kΩcm n-type Si of heating in a contaminated furnace is shown in the DLTS spectra of Fig. 2. The furnace's quartz tube had not been etched after previously being used for Au diffusions, and the samples were handled with stainless steel tweezers. The mention of the use of stainless steel tweezers is not a facetious one--a standard method of introducing iron onto Si wafers as a diffusion source is to scrape a piece of wire across the surface[10,11]. The featureless DLTS spectrum in Fig. 2(i) was displayed by the diode prior to heating. After annealing a similar section at 900°C for 2 h, we see the characteristic Au, Fe and Ni peaks in Fig. 2(ii). The effect of these impurities on reverse leakage current is shown in Fig. 3(ii). Heating this contaminated sample in a clean furnace for 2 h at 700°C in molecular hydrogen causes precipitation of a significant number of the metallic impurities [Fig. 2(iii)], with a consequent slight improvement in the reverse leakage characteristic. Heating in a H plasma, however, for 2 h at 700°C causes additional disappearance of the centers through neutralization [Fig. 2(ii)], and the current voltage characteristic displays a significant improvement. It should be emphasized that subsequent heating of the hydrogenated samples at elevated temperatures will cause at least some of the hydrogen to outdiffuse, or dissociate from the defect and recombine to form molecular hydrogen in the bulk of the sample. We also note that hydrogenation has limited application, and is no substitute for contamination-free material and clean handling conditions.

Drift of Charged Defects

At room temperature many deep level defects in Si and Ge are ionized, and we have investigated the deep level analog of the drift of Li under the action of an external field. We found that several defects such as the Cu and Ni centers in Ge[12], and the Au center in Si[13] could be drifted out of the depletion region of a reverse biased diode provided the electric field

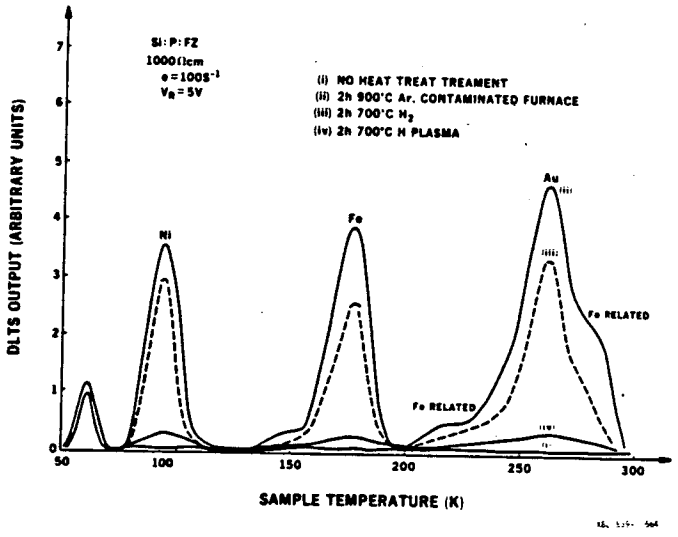

Fig. 2. DLTS spectra of 1000 Ωcm n-type Si: (i) as received, (ii) after annealing at 900°C for 2 h in a contaminated furnace, (iii) after further heating at 700°C for 2 h in a clean furnace under H_2, (iv) after heating at 900°C for 2 h in a H plasma.

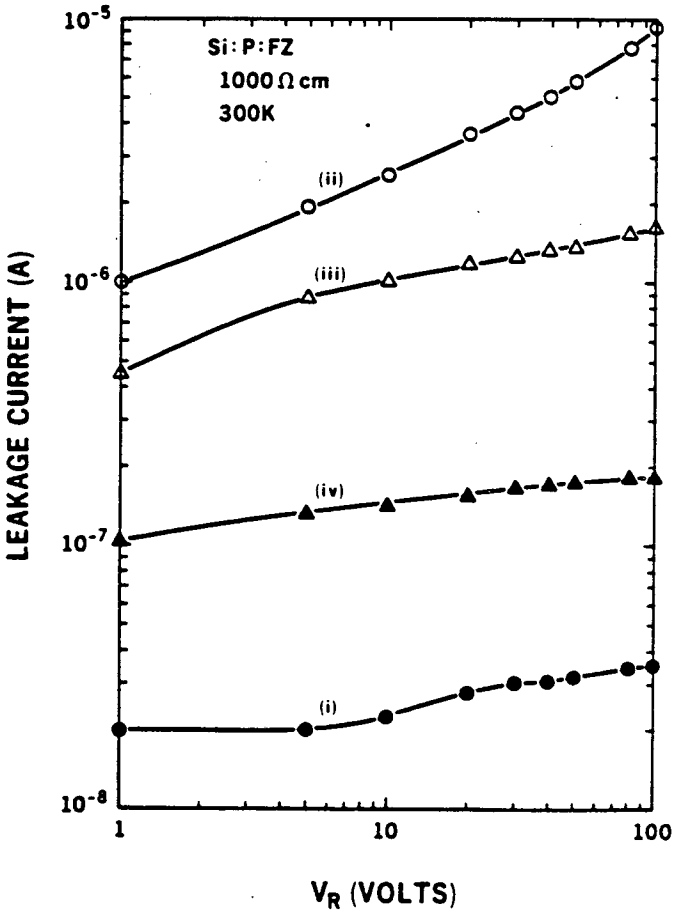

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Fig. 3.Reverse leakage current-voltage characteristics of the samples from Fig. 2, measured at 300 K.

strength is high enough. In material with net impurity contents > 5 x 10^{12} cm^{-3} this is easily attained; however, in detector grade material where $N_A - N_D$ ~ 10^{10} cm^{-3}, the resultant electric fields are too low to

obtain significant drift of the defects. We reverse biased two detectors ($N_A - N_D = 2 \times 10^{10}$ cm^{-3}) at 100 V (room temperature) for several thousand hours, but saw no significant change in the concentration of either the Cu-related levels (Cu-Li-H, Cu^{2-}), or the divacancy-hydrogen level. We note, however, that altering the charge state of a number of radiation induced defects in Si by isolating them in a depletion region may lower the temperature at which they can be annealed[14]. The possibility might therefore exist of annealing radiation-damaged Si radiation detectors in situ, as is done with neutron-damaged Ge detectors, but with a reverse bias applied.

Recombination-Enhanced Annealing

A further low temperature method of defect removal investigated was to use electronic stimulation of the annealing process in radiation-induced centers. The recombination of electron-hole pairs at defects can give rise to enough locally deposited vibrational energy to anneal the defect at a much lower temperature than that at which simple thermal dissociation occurs[15,16] (Fig. 4). This phenomenon, common in compound semiconductors, has been observed in ^{60}Co γ-ray damaged Ge. By forward biasing the radiation-damaged diode at injection current densities as low as 0.2 A cm^{-2}, substantial annealing occurred at room temperature for defects which are thermally stable to 200°C[17].

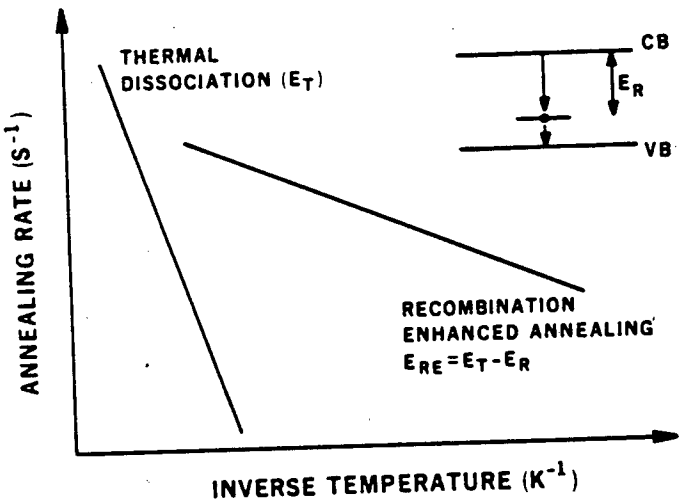

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Fig. 4. Schematic diagram of annealing rates for a purely thermal process, and a recombination enhanced mechanism. The activation energy for dissociation is lowered by the electronic transition energy, E_R (after Kimerling, Ref. 16).

The most important type of damage from a Ge radiation detector viewpoint is neutron damage. To examine the effect of injection-enhanced annealing on neutron-induced point defects, several large (2.5 cm diameter, 0.5 cm thick) planar Ge detectors with diffused Li n^+ contacts and implanted B p^+ contacts which had been irradiated with fast neutrons to a dose of 5 x 10^9 cm^{-2} were investigated with DLTS. Figure 5 shows the DLTS spectra from the two high purity samples given the same dose in 1979, and stored at room ambient since that time[18]. In the detector taken from the crystal grown under a hydrogen atmosphere, there are a number of prominent levels not seen in the sample taken from the

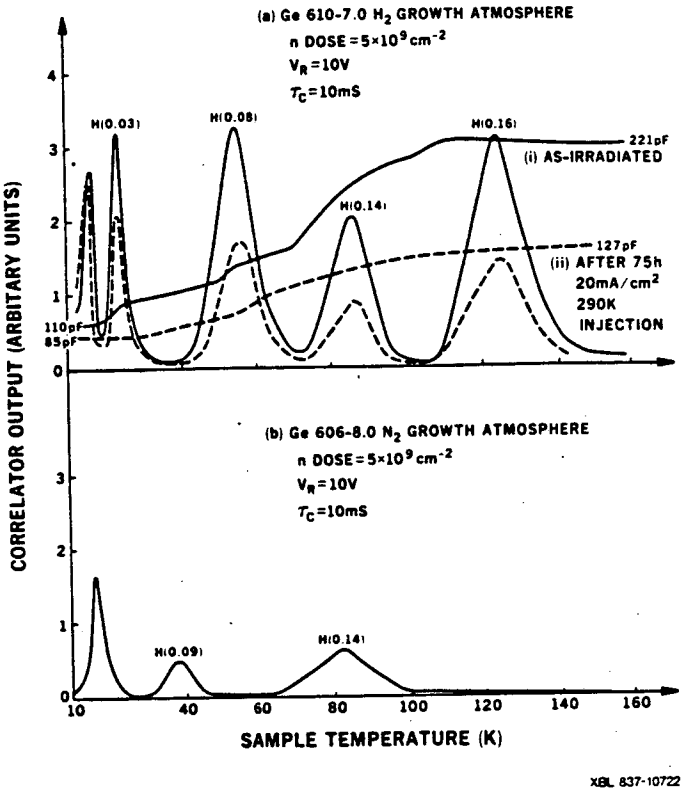

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Fig. 5. DLTS spectra of fast neutron irradiated Ge (a) sample grown under H_2 atmosphere, (b) sample grown under N_2 atmosphere. Most of the defect levels are annealed by forward bias injection of electrons.

crystal grown under a nitrogen atmosphere, which tentatively identifies these levels as being hydrogen-related since all other growth conditions were similar. Figure 5(a) also shows the injection-enhanced annealing of several hole traps during injection at 290 K. These hole traps were thermally annealed at 180°C after 2 h. We saw a similar effect in neutron-transmutation-doped Ge (neutron dose ≈ 10^{17} cm^{-2}) which had first been thermally annealed to repair amorphous regions created by the irradiation. Injection of electrons at room temperature caused annealing of point defects, which were thermally dissociated only at 300°C (Fig. 6). Figure 7 shows the lowering of the dissociation energy of the neutron-induced defects by the recombination-enhanced mechanism, compared to simple thermal annealing[19].

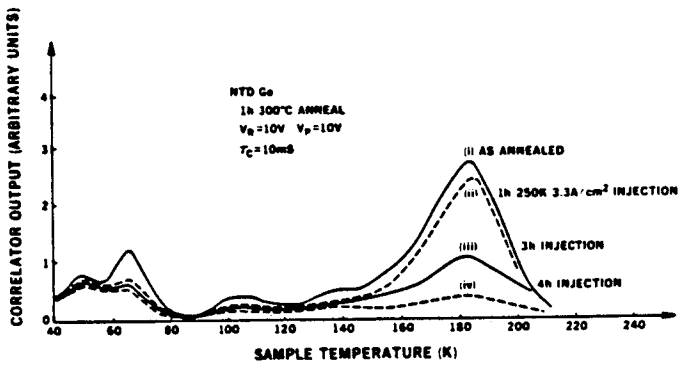

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Fig. 6. DLTS spectra of NTD Ge annealed at 300°C for one hour, then subjected to an injected current density of 3.3 A/cm^2 for various periods at 250 K.

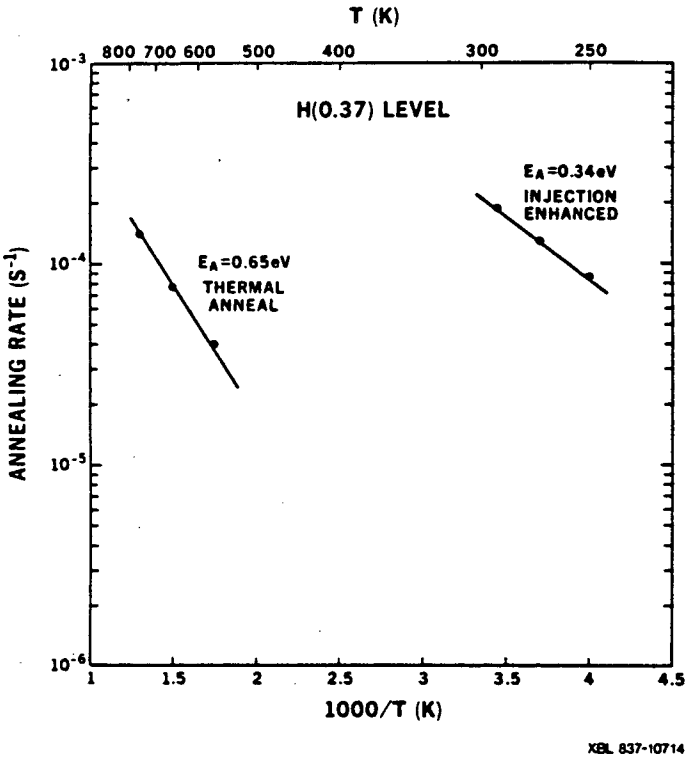

Fig. 7. Annealing rate of the H(0.37) level in NTD Ge as a function of temperature for thermal and injection enhanced annealing.

This observation of a recombination-enhanced annealing mechanism may have application to proton and neutron damaged detectors, which are usually thermally annealed in their cryostats at ~ 150°C for several days. However, this can be a hazardous process because of the presence of low-melting-point In foil used within the cryostat, and the fact that extended thermal annealing thickens the Li-diffused n^+ contacts on these detectors[20]. It is possible that simply forward biasing the detector for periods of 8 - 10 hours at temperatures of 50 - 80°C or even lower may be sufficient in some instances to restore adequate detector resolution. However, a problem for large detectors is that the injection-enhanced mechanism is effective only within the electron recombination length from the Li contact, which will limit the annealed region to depths of 5 mm or less. Similarly, in the case of annealing defects at lower temperatures than normal by using the charge state dependent annealing discussed in the previous section, this will be useful only within the depletion region created by the reverse bias, which will be small at elevated temperatures.

Discussion

In high-purity p-type Ge of good crystallinity, the bulk defects which cause most problems are the well-known copper-related centers, and in dislocation-free material, the V_2H centers. Most Ge crystal growing facilities are able to eliminate copper contamination most of the time. As this problem is solved, and detector users press for larger devices with good resolution, we feel that the effect of less well-known defects such as precipitates and dislocations, will become more evident.

There is also a problem in regularly producing large, high quality n-type crystals for the manufacture of coaxial detectors; the possible role of point defects and impurities in limiting the performance and yield of these devices is not yet clear. The resistance of these detectors to radiation damage makes this a topic which requires a careful correlation of growth conditions, detector performance and materials analysis. The techniques discussed in this paper may have limited application for certain types of detectors, but obviously there is no substitute for truly pure Ge and Si. The clean conditions of modern microelectronics industry fabrication procedures must at least in part be applied to Si detector manufacture where high temperatures are required (oxidation, annealing of implanted contacts) for a reasonable chance of high yields.

Acknowledgments

The authors acknowledge useful discussions with J. T. Walton and the technical assistance of A. A. Williams, D. Alexiev and P. J. Lee. This work was supported by the Director's Office of Energy Research, Office of Health and Environmental Research, U. S. Department of Energy under Contract Number DE-AC03-76SF00098.

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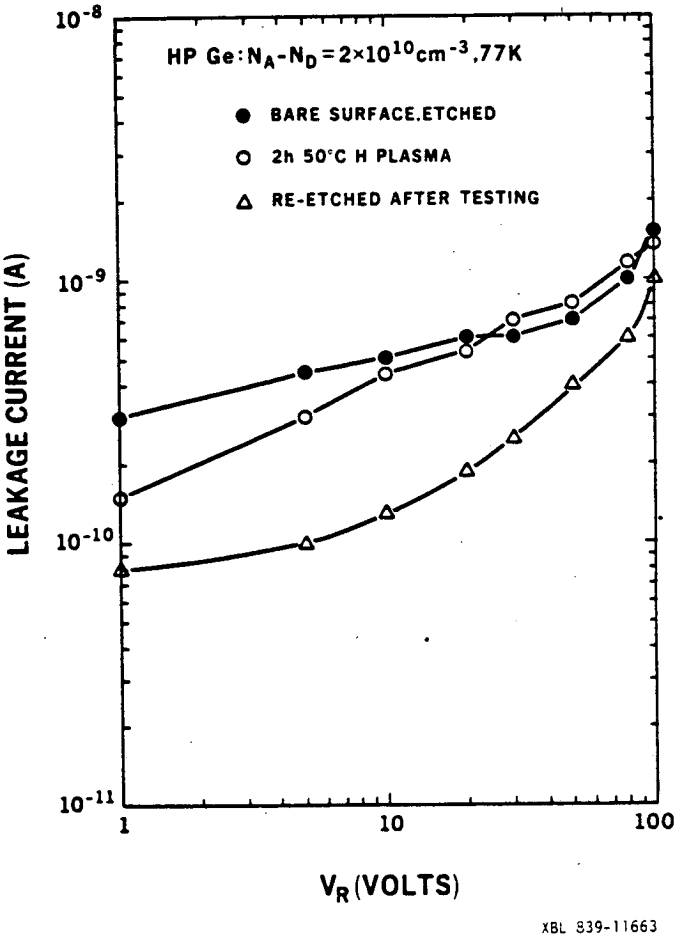

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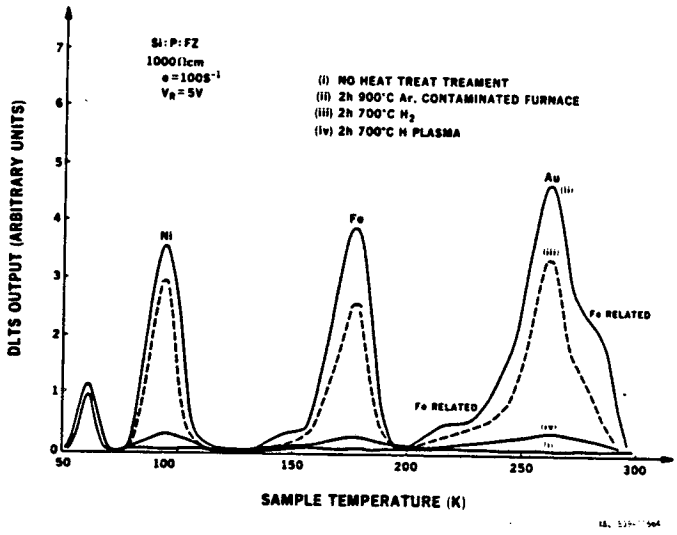

Fig. 2. DLTS spectra of 1000 Ωcm n-type Si: (i) as received, (ii) after annealing at 900°C for 2 h in a contaminated furnace, (iii) after further heating at 700°C for 2 h in a clean furnace under H_2, (iv) after heating at 900°C for 2 h in a H plasma.

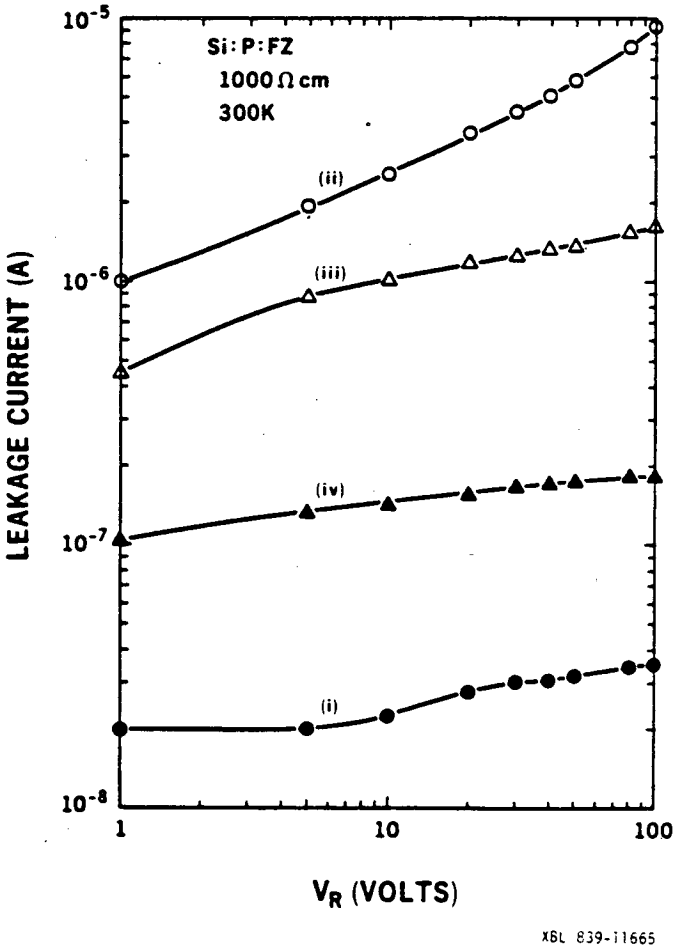

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Fig. 3.Reverse leakage current-voltage characteristics of the samples from Fig. 2, measured at 300 K.

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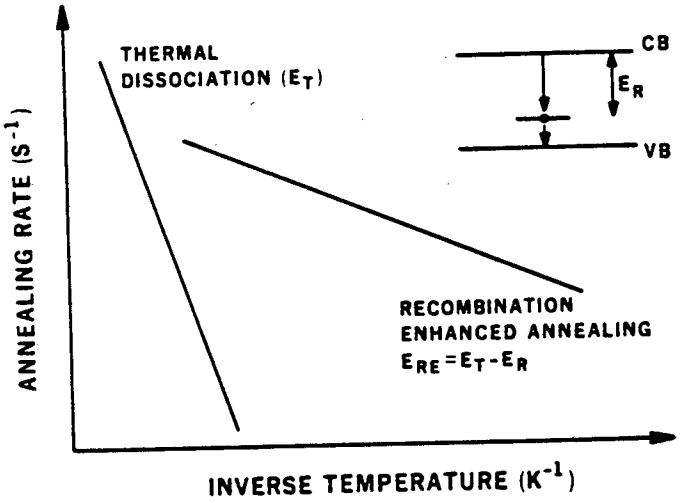

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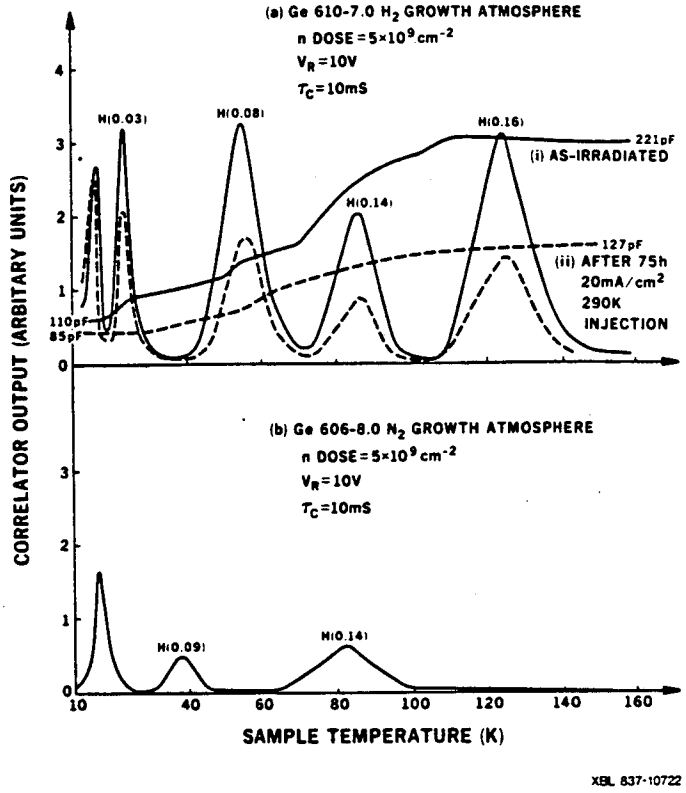
Fig. 4. Schematic diagram of annealing rates for a purely thermal process, and a recombination enhanced mechanism. The activation energy for dissociation is lowered by the electronic transition energy, E_R (after Kimerling, Ref. 16).

The most important type of damage from a Ge radiation detector viewpoint is neutron damage. To examine the effect of injection-enhanced annealing on neutron-induced point defects, several large (2.5 cm diameter, 0.5 cm thick) planar Ge detectors with diffused Li n^+ contacts and implanted B p^+ contacts which had been irradiated with fast neutrons to a dose of 5 x 10^9 cm^{-2} were investigated with DLTS. Figure 5 shows the DLTS spectra from the two high purity samples given the same dose in 1979, and stored at room ambient since that time[18]. In the detector taken from the crystal grown under a hydrogen atmosphere, there are a number of prominent levels not seen in the sample taken from the



XBL 837-10722

Fig. 5. DLTS spectra of fast neutron irradiated Ge (a) sample grown under H_2 atmosphere, (b) sample grown under N_2 atmosphere. Most of the defect levels are annealed by forward bias injection of electrons.

crystal grown under a nitrogen atmosphere, which tentatively identifies these levels as being hydrogen-related since all other growth conditions were similar. Figure 5(a) also shows the injection-enhanced annealing of several hole traps during injection at 290 K. These hole traps were thermally annealed at 180°C after 2 h. We saw a similar effect in neutron-transmutation-doped Ge (neutron dose = 10^{17} cm^{-2}) which had first been thermally annealed to repair amorphous regions created by the irradiation. Injection of electrons at room temperature caused annealing of point defects, which were thermally dissociated only at 300°C (Fig. 6). Figure 7 shows the lowering of the dissociation energy of the neutron-induced defects by the recombination-enhanced mechanism, compared to simple thermal annealing[19].

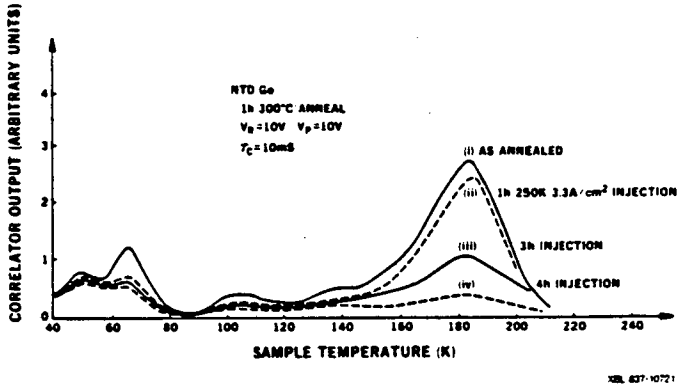


Fig. 6. DLTS spectra of NTD Ge annealed at 300°C for one hour, then subjected to an injected current density of 3.3 A/cm^2 for various periods at 250 K.

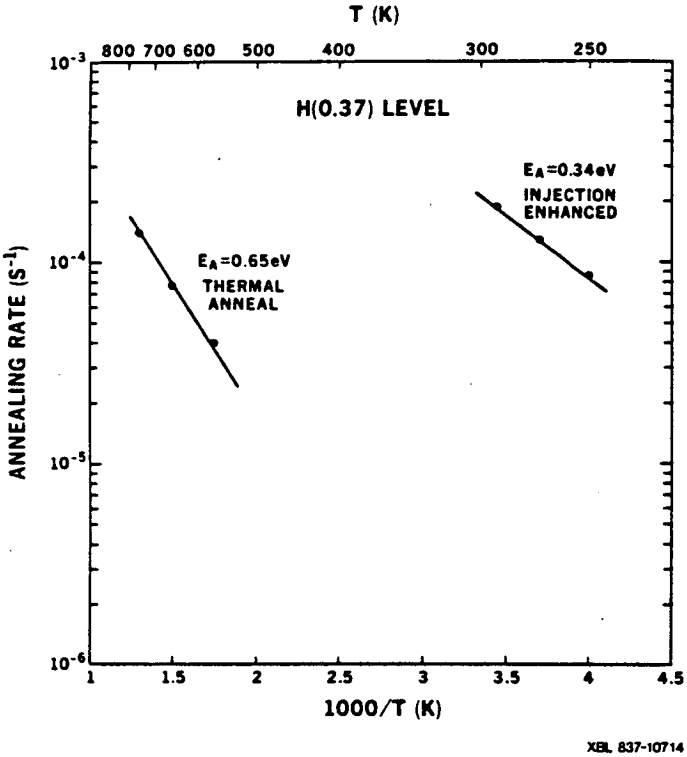


Fig. 7. Annealing rate of the H(0.37) level in NTD Ge as a function of temperature for thermal and injection enhanced annealing.

This observation of a recombination-enhanced annealing mechanism may have application to proton and neutron damaged detectors, which are usually thermally annealed in their cryostats at ~ 150°C for several days. However, this can be a hazardous process because of the presence of low-melting-point In foil used within the cryostat, and the fact that extended thermal annealing thickens the Li-diffused n^+ contacts on these detectors[20]. It is possible that simply forward biasing the detector for periods of 8 - 10 hours at temperatures of 50 - 80°C or even lower may be sufficient in some instances to restore adequate detector resolution. However, a problem for large detectors is that the injection-enhanced mechanism is effective only within the electron recombination length from the Li contact, which will limit the annealed region to depths of 5 mm or less. Similarly, in the case of annealing defects at lower temperatures than normal by using the charge state dependent annealing discussed in the previous section, this will be useful only within the depletion region created by the reverse bias, which will be small at elevated temperatures.

Discussion

In high-purity p-type Ge of good crystallinity, the bulk defects which cause most problems are the well-known copper-related centers, and in dislocation-free material, the V_2H centers. Most Ge crystal growing facilities are able to eliminate copper contamination most of the time. As this problem is solved, and detector users press for larger devices with good resolution, we feel that the effect of less well-known defects such as precipitates and dislocations, will become more evident.

There is also a problem in regularly producing large, high quality n-type crystals for the manufacture of coaxial detectors; the possible role of point defects and impurities in limiting the performance and yield of these devices is not yet clear. The resistance of these detectors to radiation damage makes this a topic which requires a careful correlation of growth conditions, detector performance and materials analysis. The techniques discussed in this paper may have limited application for certain types of detectors, but obviously there is no substitute for truly pure Ge and Si. The clean conditions of modern microelectronics industry fabrication procedures must at least in part be applied to Si detector manufacture where high temperatures are required (oxidation, annealing of implanted contacts) for a reasonable chance of high yields.

Acknowledgments

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