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THE EFFECT OF CRYSTAL GROWTH DIRECTION ON THE ENERGY RESOLUTION OF HIGH-PURITY GERMANIUM DETECTORS

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Abstract

[100] and [113] direction high-purity germanium crystals with dislocation densities > 10^4 cm^{-2} have been examined by Hall effect, Deep Level Transient Spectroscopy and gamma-ray spectrometer performance. High dislocation density in [100] crystals appears to give rise to acceptor levels which cause broadened and/or asymmetric photopeaks. [113] crystals with EPD > $10^4 cm^{-2}$ do not show these effects.

Introduction

High-purity single crystal germanium suitable for large volume radiation detectors is usually grown in the [100] orientation.[1,2] At times, the energy resolution of detectors fabricated from this material is worse than one would expect from charge production statistics and electronic noise.[3] This degradation in resolution, characterized by asymmetric and/or broadened photopeaks, has been correlated with a number of defects. Among these are the divacancy-hydrogen center in dislocation free germanium,[4] SiO complexes[5] and dislocations themselves. It has been shown by Glasow and Haller[6] that when the dislocation density, as revealed by chemical etching, exceeds 10^4 cm^{-2} the full width half maximum (FWHM), and particularly the FW 1/10 M, increase rapidly.

The electrical properties of dislocations induced in germanium by plastic deformation have been examined experimentally and theoretically for some time.[7-10] Unfortunately, the impurity concentrations [(N_A-N_D) $\sim 10^{12}$ - 10^{13} cm^{-3})] and etch pit densities (EPD $\sim 10^7$ - 10^8 cm^{-2}) in that work were several orders of magnitude higher than the nominal impurity concentrations and etch pit densities found in as-grown high-purity germanium. Furthermore, experimental methods which allow charge equilibrium, such as Hall effect, that have been used in studying deformed germanium are not easily interpreted for a non-equilibrium case such as the depletion region of a radiation detector. Consequently, there presently exists no fundamental understanding of the dislocation-induced charge trapping in high-purity germanium detectors.

From early experiments by Hansen we have germanium crystals grown in various directions including [100], [111] and [113]. Once a suitable etchant was developed to reveal the dislocation pattern of [113] crystal slices,[11] it was noticed that detectors made on this germanium which had an average dislocation density as large or greater than 10^4 cm^{-2} would still give good resolution (FWHM $\leq$ 2 keV) for a ^{60}Co 1.17 MeV gamma-photopeak. This finding was in apparent contrast to detectors made from [100] and [111] grown germanium.

In order to understand the surprisingly good detector performance of heavily dislocated [113] crystals and to attempt to achieve a more basic understanding of the electrical nature of dislocations in germanium detectors, we have utilized a variety of experimental methods. Variable-temperature Hall effect measurements with van der Pauw contact geometry were made over the range 300 K to 5 K. Deep Level Transient Spectroscopy,[12] (DLTS), was also used to examine the electrical effect of dislocations in a depletion layer and the gamma-ray spectrometer performance of various detectors was monitored using ^{60}Co and ^{241}Am. All devices for both DLTS and gamma-ray measurements were fabricated with Li diffused n^+ contacts and ^{11}B ion-implanted p^+ contacts. All gamma spectrometer measurements were taken with the detector at an operating voltage sufficiently high that the whole volume of the device was at an electric field $\geq$ 1000 V cm^{-1}. In this way, charge collection for different detectors could be reasonably compared since the velocity of all carriers is very near to the saturation velocity ($\sim 10^7$ cm/sec).[13]

Experimental Results

Dislocation Density

In order to fairly compare crystal slices grown with different orientations, it was necessary to count individual dislocations on suitably etched samples. This was done by cutting, lapping and polish-etching slices from both [113] and [100] crystals, then decorating the dislocations by means of a preferential etch. For [100] samples, a 1 - 2 min etch with a mixture of $CuNO_3$ (10%):HNO_3:HF (1:1:2) is sufficient. Revealing etch pits on a [113] surface required 6 - 10 min in a solution of $CuNO_3$ (10%):H_2O_2:HF (1:1:2) as described elsewhere.[11] The average etch pit size tends to be much smaller for [113] dislocations, accounting for the different appearance of density in photographs (see Fig. 1).

The dislocations thus revealed in our crystals were distributed in two ways: 1) a generally uniform background of isolated etch pits and 2) high density rows of etch pits generally termed lineages*. Early work by Vogel demonstrated in zone-melted [100] germanium that a lineage can be described as a series of purely edge dislocations defining a boundary between two crystals of slightly different orientation. Unfortunately, it has not been established whether the isolated dislocations in as-grown germanium are edge type screw type or the 60° dislocation described by Read[7] and encountered in work with plastically deformed germanium.[8] We shall return to this point later.

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* We will follow the generally accepted terminology that defines a lineage as any low angle grain boundary where the degree of misfit is < 1°.[14]

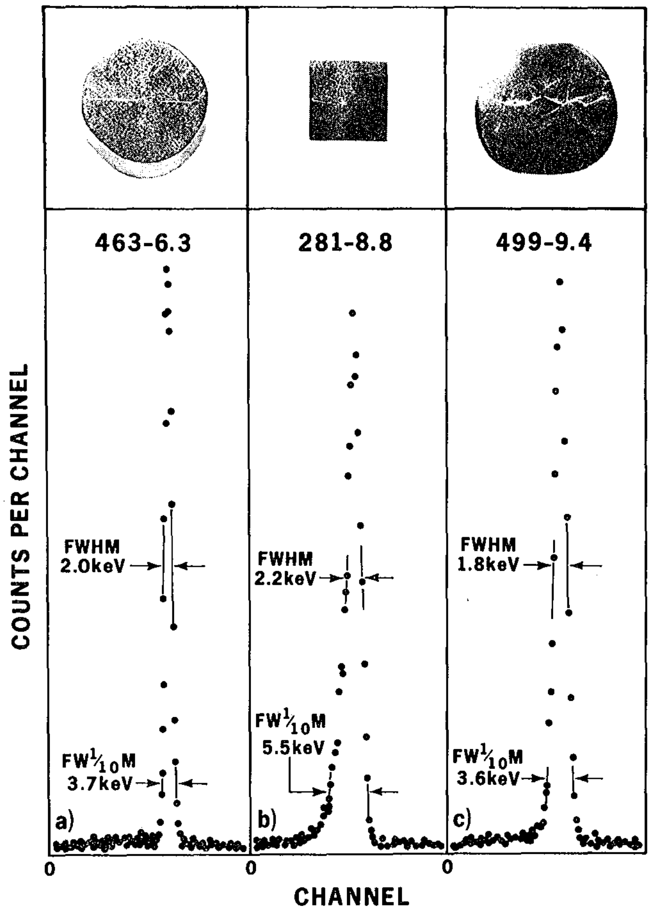

Fig. 1. ^{60}Co 1.17 MeV gamma-photopeaks and preferentially etched detector surfaces are shown. Detectors 463-6.3 and 281-8.8 are both from [100] crystals, average EPD 5×10^3 cm^{-2} and 1.1×10^4 cm^{-2} respectively. Device 499-9.4, from a [113] crystal, has an average EPD of 1.0×10^4 cm^{-2}. Device 281-8.8 was cut square to eliminate high EPD regions near the edge, making the average EPD more nearly that of 499-9.4. EPD at lineages (appearing as bright lines in photographs) are 4.5×10^4 cm^{-2}(463-6.3), 1×10^5 cm^{-2} (499-9.4 and 281-8.8).

An average dislocation density was computed by counting the number of etch pits in several representative areas and then figuring a weighted mean. This procedure was required since dislocations in [113] material develop in a much more non-uniform pattern than in [100] grown germanium and because lineages represent a high etch pit density for only a very small area. This latter constraint becomes important when one considers that the critical etch pit density of 10^4 cm^{-2} could be reached by having only isolated dislocations, only lineages, or some combination of the two.

Following this averaging procedure, it was found that the mean number of etch pits in a [113] crystal increased considerably more slowly from seed end to "tail" end than in a [100] direction crystal.

We have found that at a position near the "tail" representing 90% of the solid fraction of the crystal the average EPD for a [113] crystal may only be slightly > 10^4 cm^{-2}, whereas at a similar position a [100] grown crystal may have an EPD > 4×10^4 cm^{-2}. The only exceptions to this observation have been a few [113] crystals where a sudden, catastrophic change to severly disturbed crystallography has been noted.

Gamma-Ray Spectrometer Performance

The significance of the manner in which dislocations are distributed is shown in Fig. 1. Photograph 1a shows the shape of the 1.17 MeV ^{60}Co line for a detector (463-6.3) made from [100] Ge whose average EPD is $\sim 5 \times 10^3$ cm^{-2}, but which contains lineages where the EPD is $\sim 4.5 \times 10^4$ cm^{-2}. Nevertheless, the device exhibits a FWHM of 2.0 keV with no visible asymmetry in the peak. Scanning the lineage with ^{24}Am 59.6 keV gamma radiation shows an increase in the FWHM and peak asymmetry in those high-density areas. This type of charge trapping is seen more clearly in Fig. 1b for detector 281-8.8. This detector has an EPD of $\sim 1.1 \times 10^4$ cm^{-2} and its ^{60}Co resolution suffers seriously as predicted by Glasow and Haller. By contrast, the third device 499-9.4 (Fig. 1c) has an average EPD of 1.0×10^4 cm^{-2}, but a FWHM of 1.8 keV and good peak symmetry. This difference is underscored by comparing the results of scanning with 59.6 keV ^{241}Am gamma-rays as seen in Fig. 2. Using a 0.5 mm collimator, the radiation was scanned across the defect in the center of 281-8.8 (a sort of lineage twisted around itself - EPD $\sim 10^5$ cm^{-2} and across the sharp lineage observed on detector 499-9.4 (EPD $\sim 10^5$ cm^{-2}). By collecting counts for four minutes at each position and plotting the resultant peak in a logarithmic scale, the low energy "tailing" associated with lattice disorder in crystal 281 is clearly shown. Both the n^+ and p^+ contacts were scanned and it was found that the tailing was seen only when irradiating the p^+ contact, as found in other work.[6]

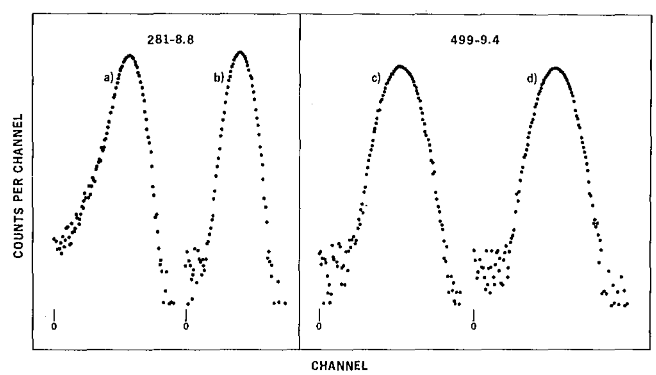

Fig. 2. Collimated 59.6 keV gamma-rays from ^{241}Am were scanned across lineages in both detectors. The counts in each peak were accumulated for four minutes and plotted on a logrithmic scale. The amplifier setting was more sensitive for detector 499-9.4 to exaggerate any tailing, giving rise to the apparent difference in peak width as compared to 281-8.8. Peaks a) and c) were collected at the lineages (EPD $\sim 10^5$ cm^{-2}), peaks b) and d) were collected at a reference position (EPD $\sim 10^4$ cm^{-2}).

Surprisingly, the lineage in detector 499-9.4 (made of [113] material) affects the ^{241}Am resolution very little or not at all. To establish whether the influence of the dislocations was due to the crystal growth direction or the orientation of the defects with respect to the contacts and hence electric field lines, a [113] grown crystal with EPD > 10^4 cm^{-2} was optically aligned so that a [100] slice could be cut. The etch pit density and distribution was found to be the same for both directions and the FWHM was excellent in both cases.

Hall Effect Measurements

A series of samples from [100] and [113] crystals with high EPD were prepared with van der Pauw contact geometry. Using a variable temperature Hall effect apparatus constructed for earlier studies of impurities in Ge,[15] measurements were taken from 300 K to 5 K with a maximum magnetic field of 6000 gauss. Two typical measurements on p-type samples are shown in Figs. 3 and 4. Sample 281-7.6 (taken adjacent to the detector in Fig. 1b) contains the same defect scanned by 59.6 keV gamma-rays in Fig. 2.

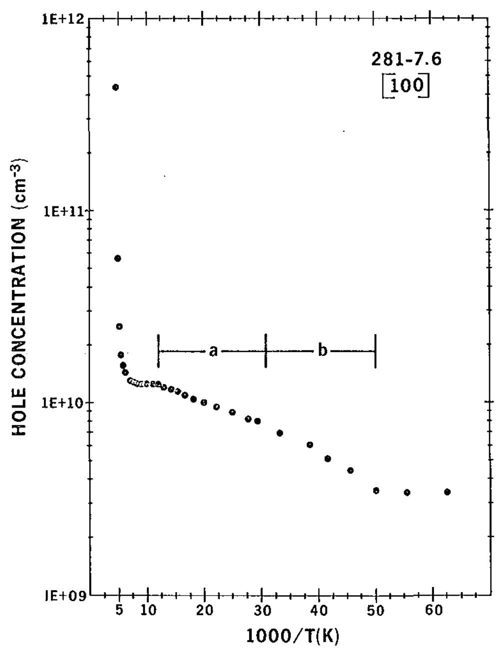

Fig. 3. Hole concentration (N_A-N_D) in sample 281-7.6 was measured by Hall effect and plotted as a function of 1000/Temperature (K). Region -a- represents distributed levels correlated with high dislocation density. -b- is a level at E_V + 0.02 - 0.04 eV and is copper or copper hydrogen. Sample size was 1 cm x 1 cm x 0.3 cm with indium contacts in a van der Pauw geometry.

Deionizing from 77 K to 30 K (-a- in Fig. 3) appear to be distributed levels with a total concentration (N_A-N_D) ~5.0 x 10^9 cm^{-3}. We were not successful in applying either graphic or curve fitting techniques to determine the activation energy (ies) of these levels. However, from the temperature at which 50% of the distributed levels are deionized, we estimate a "mean" energy of E_V + 0.08 eV. This is in rough agreement with energy measurements for dislocations in deformed germanium.[8] By examining nearby samples which had lower EPD, we determined that the distributed levels represent acceptors which are correlated with high dislocation density. Level -b- [(N_A-N_D) ~4.1 x 10^9] has an energy of E_V + 0.02 - 0.04 eV, depending on the technique used for determination. We believe the level is one of those associated with Cu (E_V + 0.044 eV) or Cu H (E_V + 0.017, 0.0175 eV) but its energy measurement may be distorted by the dislocation levels.[15]

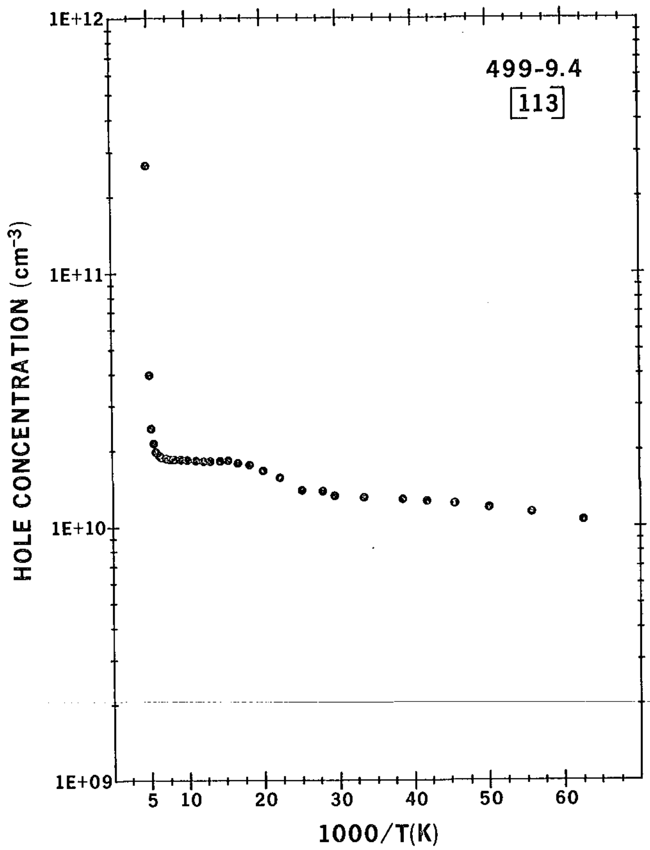

Fig. 4. Hole concentration (N_A-N_D) in sample 499-9.4 was measured by Hall effect and plotted as a function of 1000/Temperature (K). The single obvious deep level has an energy of about E_V + 0.07 eV. Sample size was 1 cm x 1 cm x 0.3 cm. Indium contacts were applied to corners in a van der Pauw geometry.

In Fig. 4, a [113] germanium sample containing lineage with an EPD comparable to the defect in the [100] sample shows no distributed levels. The single level clearly seen in 499-9.4 has a concentration (N_A-N_D)~5 x 10^9 cm^{-3} and an activation energy of E_V + 0.07 eV. At present we believe the level may be copper-related. It is interesting to note that although the concentration of moderately deep levels is comparable in both samples, the detector performance is quite different.

Deep Level Transient Spectroscopy (DLTS) Measurements

A new technique especially useful for examining deep levels in semiconductors has recently been applied to germanium.[16,17]

The power of DLTS is evident in Fig. 5, where diodes made from the same (or nearby) material as that used in Figs. 1 through 4 show markedly different response to heavily dislocated [100] and [113] crystals. A very large broad acceptor peak (labeled 3) is seen to dominate the spectrum of the [100] sample (281-7.6). Unfortunately, our apparatus did not permit us to get to a low enough temperature to see the peak of this level or "band" of levels. Thus, no calculation of an energy level was possible. Since other samples with lower EPD did not show this broad peak it appears the feature is correlated with high dislocation density. The temperature range over which the peak is visible suggests that this band of levels is the same as "-a-" in the Hall effect plot (Fig. 3).

The other peaks labeled 1 and 2 have been seen in many crystals. Peak 1 at energy $E_V + 0.175$ eV is some form of CuH complex and accompanies the level at $E_V + 0.02 - 0.04$ eV seen in Fig. 3. The origin of peak 2 is unknown at this time. By contrast, the [113] diode (499-9.4), shows an almost flat profile despite the fact that the gain setting was ~ 6 times more sensitive than for 281-7.6. One small peak at about 50 K may be the same as that identified at energy $E_V + 0.07$ eV in Fig. 4, although for some reason the peak is not as large as expected from the Hall data.

Discussion

It seems clear that any attempt to correlate dislocations with detector performance must specify the average dislocation density in the area being irradiated by a given source. As we have shown, a device made from [100] germanium such as 463-6.3 can have small areas of very high dislocation density and still give quite good ^{60}Co gamma-photopeak resolution. We suggest that since such a small volume of the device is above the critical EPD of 10^4 cm^{-2} the degradation in resolution is slight. Put another way, one could say that since the ^{60}Co gamma-rays probe the whole volume of the detector they encounter an average density of much less than 10^4 cm^{-2}. If one takes a source which can be collimated, such as ^{241}Am, and then probes a very small area, such as the defect in 281-8.8, the average EPD encountered by the radiation is of course much higher and the spectrometer performance suffers.

An exception to this pattern is shown by crystals grown in the [113] direction. Whether one uses ^{60}Co or scans with a collimated 59.6 keV ^{241}Am source, detectors with average EPD > 10^4 cm^{-2} and lineages where the EPD is $\sim 10^5$ cm^{-2} show little nor no degradation in resolution.

Electrical measurements indicate that the high density of defects in [100] germanium give rise to acceptor type levels similar to those found in deformed germanium. However, the [113] grown crystals with a high EPD do not show this phenomenon.

We believe that the fundamental cause of this difference in behavior may lie in the nature of the dislocation itself. As was mentioned earlier, the exact type of dislocation in our "as grown" crystals is unknown. In general, two broad classes of dislocations are possible, the edge type and screw type. The edge type is generally considered to have a dangling bond, as proposed by Read, while a screw dislocation involves a distortion of the lattice which would not have a site for accepting further electrons. Theoretical work by Hornstra[18], which describes most of the possible types of dislocations in a diamond lattice, demonstrates that many gradations between pure edge and pure screw type dislocations are possible. Among these is the so-called 60° dislocation, where the line of dislocations makes an angle of 60° with the lattice slip direction (known as the Burgers vector) and is hence, partly screw and partly edge type. Another possibility is an edge dislocation which by virtue of rearranging bonds contains no unpaired electrons.

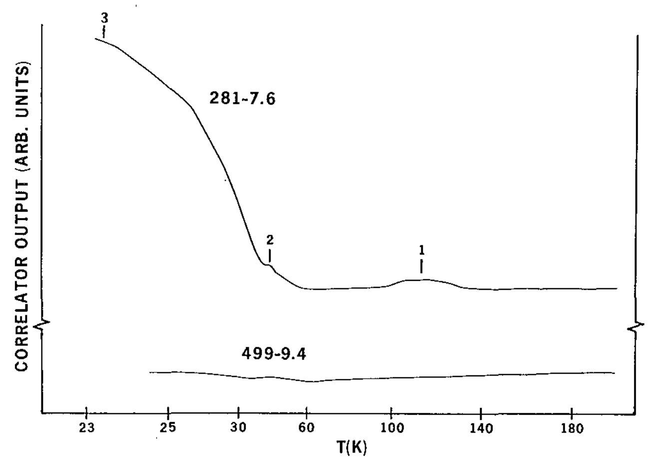

Fig. 5. Deep Level Transient Spectroscopy (DLTS) was used to examine [100] and [113] crystals with EPD $\sim 10^4$ cm^{-2} (281-7.6 and 499-9.4). Peak 3 in 281-7.6 appears to be correlated with high dislocation density. Peaks 1 and 2 appear to be Cu related. The small peak at 50 K in 499-9.4 may be correlated with the level at $E_V + 0.07$ eV in Fig. 4.

We suggest that dislocations in [113] oriented crystals may be of a type which do not have unpaired electrons and hence do not function as an electron trap. This idea can be tested to some extent by determining the Burgers vector of the dislocations in our crystals. When the dislocation line is at an angle of 90° to the Burgers vector (lattice slip), the dislocation is an edge type. An angle of 0° indicates that the dislocation is a screw type. Using an x-ray topography technique developed by Lang,[19] the Burgers vector in germanium can be determined and hence, the dislocation type. Work is currently under way to perform this measurement.

Conclusions

Hall effect, DLTS and chemical etching techniques have been used to correlate acceptor type traps due to dislocations with x-ray spectrometer performance in high-purity [100] germanium detectors. [113] grown germanium with EPD similar to the [100] material has been shown to be free from these levels, thereby making possible an increased yield of detector grade slices in as grown crystals. In addition, the comparison of [100] and [113] crystals has made it possible to begin to identify fundamental material parameters which affect detector performance. The application of x-ray techniques may make it possible to identify the type of dislocation and thereby explain the observed differences between different growth directions.

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