JAERI 1131

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Fabrication of Thick Germanium Detectors

1967 年 3 月

日本原子力研究所

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JAERI 1131 UDC 539.1.074.8

Fabrication of Thick Germanium Detectors

Summary

Lithium-drifted germanium detectors of depletion depths up to 8 mm and diameter about 19 mm have been fabricated from pulled, indium-doped, p-type single crystals. The detectors have an energy resolution of 4∼5 keV (FWHM) for gamma rays from ^{60}Co, when used with a conventional low-noise preamplifier. The procedure for fabricating the thick germanium detectors is described in detail.

November, 1966

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厚いゲルマニウム検出器の製作

要旨

リチウム・ドリフト・ゲルマニウム検出器を，引上法によるインジウム添加のp型単結晶から製作した．検出器の大きさは空乏層の厚さが約 8 mm，直径が約 19 mm である．大半の検出器は通常の低雑音前置増幅器と組合せてもちいると，^{60}Co のガンマ線に対して 4 ないし 5 keV の半値幅の分解能をしめす．この報告で，厚いゲルマニウム検出器の製作に関する手順を詳しく述べた．

1966年11月

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原子核物理第1研究室　石井三彦
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1. Introduction

Semiconductors[1,2] have great advantages as materials of nuclear radiation detectors[3,4]. Firstly, the fact that they are in solid state makes it feasible to detect long-range particles such as electrons, high-energy protons, and gamma rays. Secondly, the average energy needed to produce an ion-pair by impact ionization in a semicnoductor is low. It is 2.9 eV in germanium, and 3.6 eV in silicon compared with the average value of about 30 eV for gases, or 300 eV per photoelectron in a scintillation counter. Such a low value gives a low ultimate limit to the energy resolution. At present germanium and silicon are the most suitable materials for the radiation detection. They are commercially available as single crystal of a suitably large size with low density of imperfections, comparatively long carrier lifetimes and high carrier mobilities ; these properties are necessary for efficient charge collection for a short time.

Pell discovered that acceptor levels in silicon can be compensated by lithium-ion drift in a reverse-biased p-n junction and that an intrinsic semiconductor region with high resistivity can be produced between the n- and p-type region[5,6]. The ion drift has since been used for the fabrication of large sensitive-volume silicon detectors. Recently, lithium-drifted germanium detectors, based upon this method, have also been developed in several laboratories[7–10]. These detectors are superior in the detection efficiency for gamma rays to silicon ones. This is because the absorption coefficients due to the photoelectric effect and pair production are proportional to the fifth and second powers of the atomic number respectively, while the Compton absorption coefficient depends linearly uopn it. In gamma-ray spectroscopy, good energy resolution and detection efficiency of the germanium detector are worth the inconvenience of cooling it to liquid nitrogen temperature in vacuum.

This report describes a detailed procedure for fabricating a type of thick germanium detector which has been used at JAERI. The general manner of detector fabrication is similar to that of Hansen and Jarrett[10].

2. Specification of germanium single crystal

Germanium single crystals used for the fabrication are in the form of pulled, indium-doped, p-type crystals, grown in (1 1 1) orientation, of about 24 mm in diameter ; resistivity is in the range of 8 to 12 ohm-cm, dislocation density 1800 to 2800 per cm^2, and minority carrier lifetime 200 to 900 microseconds*. About 4 ohm-cm, zone-levelled, gallium-doped crystals were also used with success in the early stage of the present study**.

3. Preparation of p-n junction***

A crystal is cut with a diamond saw or an ultrasonic cutter into slices which are 3 or 4 mm

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* Tokyo Denshiyakin Kenkyusho, in Japan

** Sylvania Electric Company

*** See the references 11) on mechanical shaping of crystals ; 11) and 12) on etching ; 2) and 13) on diffusion and solubility of lithium in semiconductors.

thicker than the desired thickness of the compensated region. All the damage due to the cutting is removed by lapping with 600-mesh polishing powder. Furthermore, the front face onto which lithium will be evaporated is finished with a finer grade, about 1000 mesh, of polishing powder. For the purpose of grease removal, all the surfaces of the slice are polished on cloth with 2000 to 4000 mesh powder, and washed in water. After this, the slice should never be touched with fingers. Plastic tweezers and beakers should be used for washing and etching to avoid grease marks from fingers, and should be as clean as the final product is intended to be.

The slice is etched in a 3 : 2 HNO_3/HF mixture until the front face becomes mirror-like. After quenching by diluting with deionized water of about 5 megohm-cm, the slice is rinsed in it, and dried on clean filter paper. The liquid reagents are at their normal commercial " concentrated " concentrations. Etching rate and time depend on resistivity of the crystal, temperature of the mixture, etchant composition, and, even, freshness of acids. The recipes of etchants given above and below are only illustrative. Fabricators should select etchants suitable for the crystal, they use, in each stage of device fabrication.

The slice is put in a graphite oven, as shown in Fig. 1. Graphite serves as a thermal shock absorber. The crystal is heated to a diffusion temperature in vacuum below 10^{-5} mmHg. Lithium is then evaporated onto the crystal and diffused into it for 5 to 8 minutes. Diffusion temperatures range from 400°C to 450°C, depending on acceptor concentrations of the crystals. Typically, 5-minute diffusion at 450°C is used for material of resistivity less than about 10 ohm-cm, with lower temperatures and longer periods for higher resistivities. As soon as possible after diffusion, the oven is taken out from the evaporator, and rapidly cooled on a cold plate. This

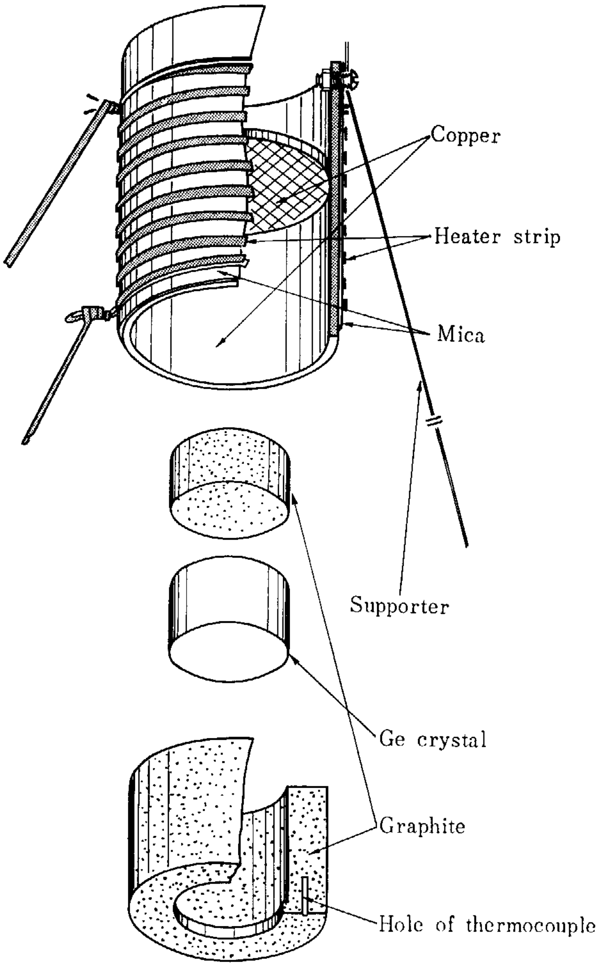

Fig. 1 Oven used for diffusion.

treatment introduces an n-type layer, highly doped with lithium and about 0.5 mm thick, into the surface region. Oxidation during the cooling process in air does not occur in such a deep surface region of the crystal as to affect the reverse characteristic of a diode.

All sides of the crystal are lapped off with 600-mesh polishing powder to the depth enough to ensure even coverage of the whole face with the n^+-type layer and p-n junction line parallel to the face ; a simple method of junction location[11, 12) is to electroplate copper on a reverse-biased junction in a saturated solution of copper sulfate. Care is needed not to crack the junction and not to flake the n^+-type layer, because these troubles harm the diode characteristic. In order to prevent attack on the lithium-diffused layer by the etchant, it is necessary prior to chemical etching to coat the front face with a protective layer of etch proof meterial. This is done by masking the face with Sotch Brand plastic tape. The crystal is etched first in a 3 : 2 HNO_3/HF mixture until mirror-like surfaces are obtained. After the masking tape peeled off with tweezers, it is lightly etched in a 5 : 1 HNO_3/HF mixture to remove the black lithium-rich alloy and to clean all surfaces, rinsed in deionized water, and dried.

4. Drifting

Ion drift process should be taken in dry atomospheres to avoid exposition of the junction to moisture ; the condensation of moisture on the junction results in an increase of the surface leakage current[11). Silica gel is convenient and satisfactory for this task. **Fig. 2** illustrates an apparatus and a control circuit for drifting. The circuit controls the operation or release of a relay corresponding to the diode current under or over a desired value respectively. The contacts of this relay serve to turn a heater on and off. The heater supplies to the apparatus the heat which increases the diode current. The cooling of the apparatus is supplied by continually flowing water or a thermoelement. The thermal conductances of the germanium crystal and the heat sink limit the drift current and bias. In the apparatus used the power dissipated in the junction is at most 25 watts.

The front and back faces of the crystal are coated completely with gallium-indium eutectic alloy[14) for making ohmic and thermal contacts. The crystal is set on the apparatus, the n^+-type layer down. De-greased stainless steel tweezers are suitable for the handling of the dry and clean crystal, but should never come into contact with its surfaces except the front and back faces.

The reverse bias is then applied to the junction and raised slowly up to 500 volts at a temperature of about 30° C. The saturation current density of good diodes is less than 3 milli-amperes per cm^2 at 30° C. During the initial period of applying the bias across the junction, the reverse current density may be twice or more times as large as the value described above, but will decrease to it in half an hour. It sometimes happens that lapping cracks, poor surface treatment, and improper diffusion condition lower the breakdown voltage and the drift temperature. The excess leakage current due to the first two causes can be reduced simply by removing the cracks or cleaning the device by etching. In the case where the diffusion condition is improper, re-diffusion of lithium should be given to the device.

The ion drift process is carried out with current density ranging from 10 to 15 milli-amperes per cm^2 at a bias voltage of 400 to 500 volts at elevated temperatures between 70° C and 50° C. A compensated region of about 7 mm thick is obtained in one week under the above typical drifting conditions.

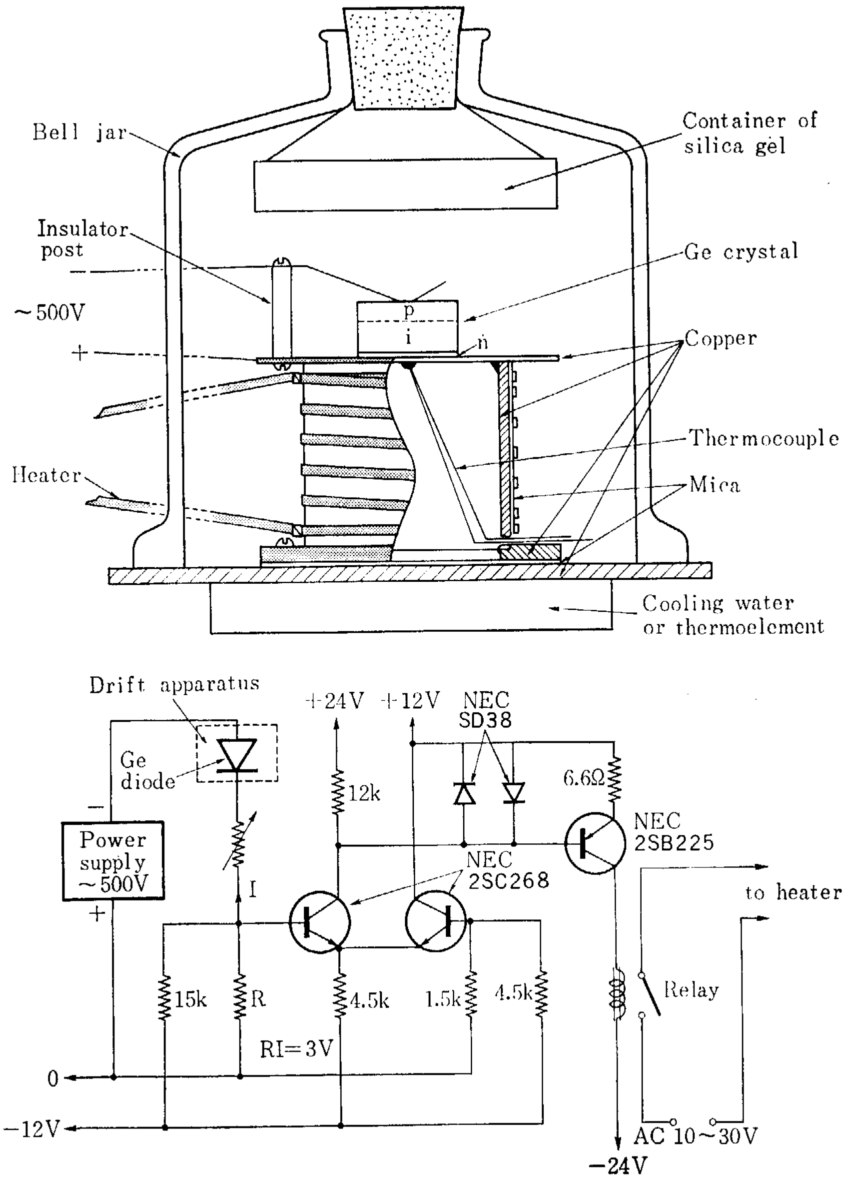

Fig. 2 Schematic diagram of apparatus and control circuit for drifting.

5. Re-diffusion of lithium

In order to obtain the good performance with the device of a thick depletion layer, it was necessary to make re-diffusion of lithium. The thick devices showed the poor reverse voltage-current characteristic; even some devices which gave the good diode characteristic had poor energy resolution.

The poor performance at this stage seems to have bearing on reduction of the depth of an n^+-type region by the ion drift in the following ways:

When a compensated region is extended to the neighborhood of the surface of the n^+-type region, the microcracks and other structural flaws of the surface can act as shortcircuiting paths to the compensated region.

A large amount of precipitated lithium[2] is contained in the compensated region* which is

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* The main part of the compensated region is, of course, produced on the p-type side by the rise of the lithium-ion concentration toward the acceptor doping level. Trapping and recombination of carriers also occur in this region. See Section 7.

produced on the n^+-type side by the fall of the lithium-ion concentration toward an acceptor doping level. Such lithium atoms may serve as trapping or recombination centers to cause the degradation of energy resolution.

The re-diffusion process will be probably unnecessary to the devices fabricated from the germanium crystal which contains few of acceptors to be compensated and sites of lithium precipitation. For instance, the crystal with resistivity higher than 20 ohm-cm and dislocation density less than 100 per/cm^2 may fulfil this reqirement.

The procedure for the re-diffusion and the subsequent treatment is the same as already described in Section 4, but the following cares should be taken :

(1) Before diffusion, 0.3 mm of meterial is carefully lapped off from the n^+-type layer with 1000-mesh polishing powder.

(2) After diffusion, material having reverted from the intrinsic one to the p-type during a heating cycle is removed from the side of the crystal. A removal of roughly twice the depth of lithium diffusion is considered adequate.

The device is subsequently given the ion drift process for a period up to two days necessary to restore the thermally agitated boundary of about 0.5 mm thick between the intrinsic and p-type regions.

6. Test

After the final drift process, 0.1 to 0.2 mm of material is removed from the side of the crystal by lapping. This is because the surface layer of the intrinsic region has reverted to slightly p-type material due to the diffusion of lithium to the surface during a period of drifting. The devices without this treatmemt have so high capacitances as to give output pulses of reduced amplitude when they are cooled to liquid nitrogen temperature.

The process of washing and de-greasing is carried out, and the n^+-type face is masked with a plastic tape. The device is then etched in a 3 : 2 HNO_3/HF mixture long enough to give a distinctly visible n-i junction line and a mirror-like surface. Adequate etching temperature is between 20°C and 25°C. After the masking tape is peeled off with the tweezer, once again, the device is lightly etched in a 5 : 1 HNO_3/HF mixture. When insufficient oxidizing agent, that is nitric acid in this case, is included in the etchant, a thin and yellow layer is established on the crystal, especially on an n^+-type layer ; such a layer tends to cause excess leakage current on cooling. After removal from the etch, the device is dipped in methyl alcohol, rinsed in it for a few minutes, and dried, the n^+-type face up, on clean filter paper. The "alcohol break" is a useful measure for cleanness of the surface ; a thin film of alcohol, when evaporating from clean surface, should contract to only one or two centers before it disappears.

Ohmic contacts are made to the front and back faces of the device by small and very thin coating with gallium-indium eutectic alloy. The device is then mounted, the p-type face down, on a cold finger of the cryostat. Silicon grease is used for the thermal connection between the device and the cold finger, The cryostat is evacuated below 10^{-5} mmHg and cooled to liquid nitrogen temperature. If the leakage current is not below 1 millimicro-ampere at the reverse voltage of 100 volts per 1 mm intrinsic layer, the device should be re-etched until the leakage falls below this value.

Incomplete removal of slightly p-type material on the intrinsic region prevents the fall of the leakage current sufficiently low to allow the detector performance. In this case the leakage current decreases with the cooling of the device, and reaches minimum at a temperature higher than liquid nitrogen temperature. The leakage current increases as the device is cooled beyond this temperature. Hysteresis is observed in the reverse voltage-current characteristic of the device cooled to liquid nitrogen temperature ; the current at any reverse voltage, measured in the descendent direction of bias, is smaller than that measured in the ascendent direction, and the former increases slowly toward the latter.

It often happens that devices are defective through corrosion damage to the n^+-type layer by attack by the etchant during repeated etching ; lithium concentration in the strongly etched n^+-type layer is not high enough to suppress unwanted minority carrier injection. Such devices require re-diffusion of lithium.

The cryostat on which the device is mounted is shown in **Fig. 3**. A Vac Ion pump of 8 liters per second is employed, since it is compact and can produce clean and high vacuum. A rotary pump with a cold trap is used as a fore pump. Careful vacuum tests of the cryostat are necessary, prior to mounting of the device, not only at room temperature but also at liquid nitrogen temparature. Moreover, even in a good vacuum, water vapor and other gases outgased within the container may condense on the cooled crystal and cause both immediate and gradual long-term degradation of the characteristics of the device. Therefore, special precaution must be

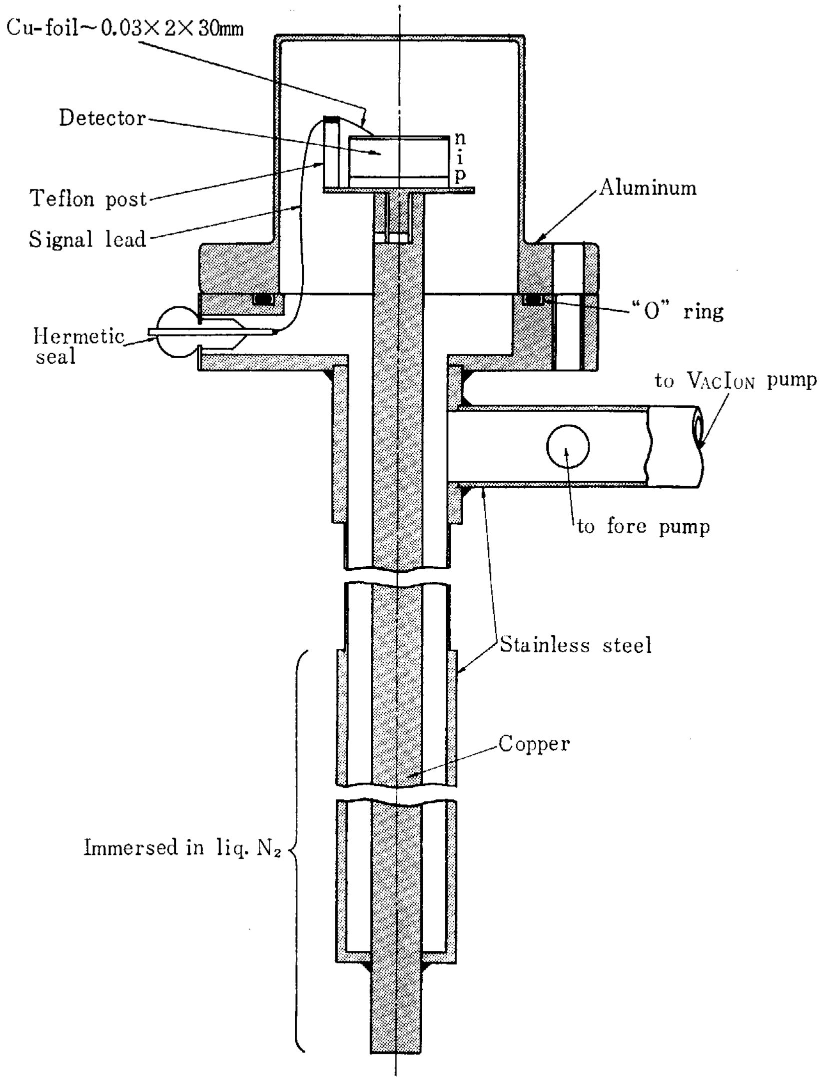

Fig. 3 Cross sectional view of cryostat.

taken to remove them by heating all parts of the cryostat for a few tens of hours to as high temperatures as possible with simultaneous absorption of the vapor with a liquid nitrogen trap.

7. Results

Most devices gave energy resolution of 4 to 5 keV (FWHM) for gamma rays from ^{60}Co, where electrical noise in an amplifier with device was about 3.5 keV (FWHM). **Fig. 4** and **5**

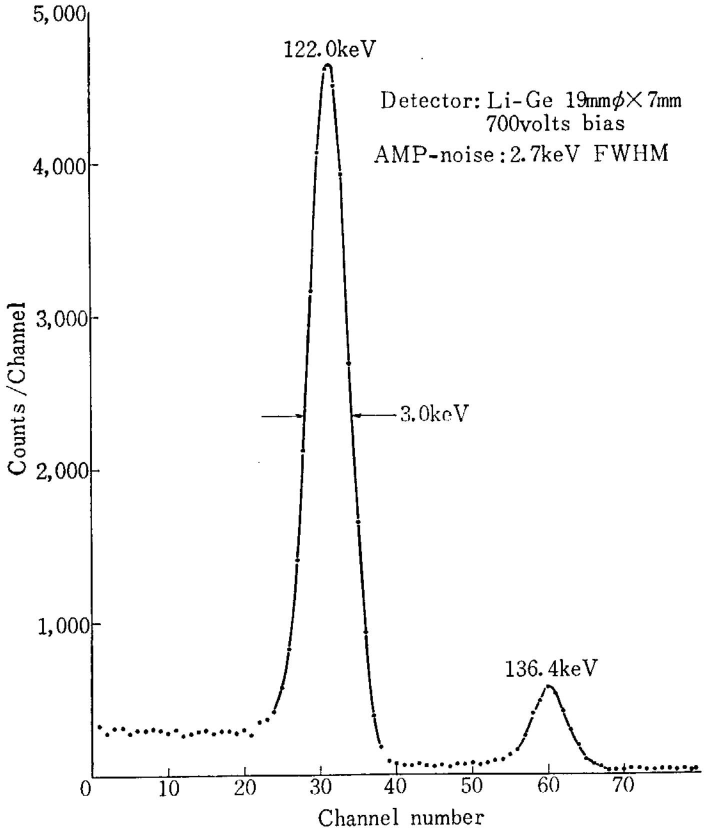

Fig. 4 A gamma-ray spectrum of ^{57}Co.

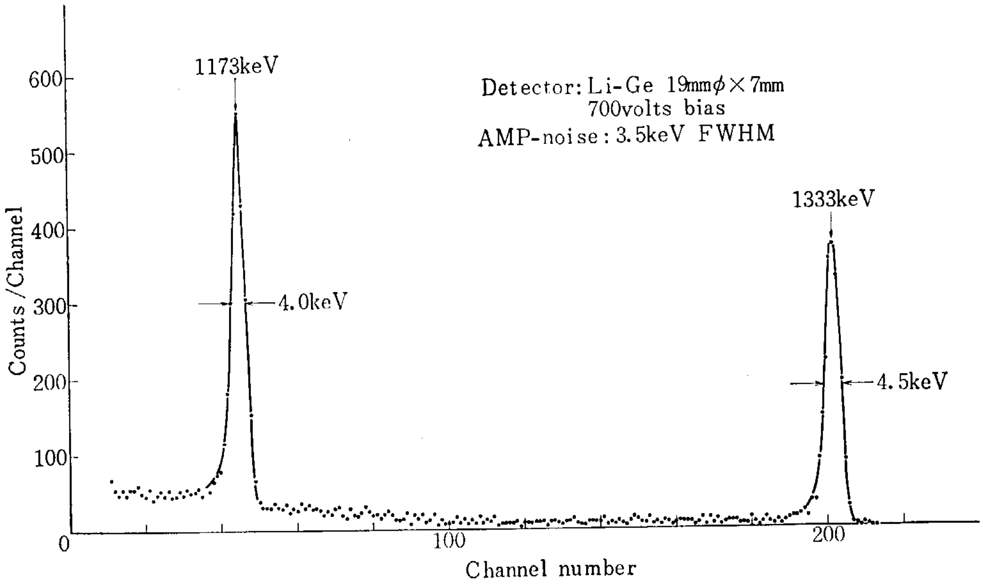

Fig. 5 A gamma-ray spectrum of ^{60}Co.

show gamma-ray spectra of ^{57}Co and ^{60}Co respectively. Carrier trapping and recombination in the bulk of the compensated region appear to be responsible for somewhat broader line widths for the photopeaks than those reported by HEATH, BLACK and CLINE[15]. If germanium crystal with low dislocation density is used, the effect of trapping and recombination centers will be reduced and the energy resolution improved.

Any short circuit of the diode will usually cause the detector performance to fail. Causes of short circuits are summarized as follows :

(1) Surface contaminations due to incomplete de-greaseing, deposit left by an etchant, or mishandling after etching.
(2) Inadequate etching treatment.
(3) Incomplete removal of the surface layer of the intrinsic region having reverted to p-type material.
(4) Damaged surfaces, such as lapping cracks, not completely etched away.
(5) Cracks on the n^+-type layer due to the different coefficients of expansion between n^+-type germanium and gallium-indium alloy. The reverse voltage-current characteristic of the device with a damaged n^+-type layer is much more abrupt than those affected by other causes.
(6) Repeated attacks on the n^+-type layer by the etchant, which result in a displacement of the diode characteristic toward higher and higher current.

Acknowledgements

The authors wish to thank Professor HIDETSUGU IKEGAMI and Mr. TACHISHIGE HIROSE of Tokyo Institute of Technology, and Dr. TOKIHIRO KUROYANAGI of JAERI for their advice and help in this work. They are also grateful to Mr. TERUO MOMOTA ; Head, Division of Research, Dr. KINEO TSUKADA and Dr. EIKO TAKEKOSHI of JAERI for the generous support and encouragement.

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