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Semiconductor Nuclear Radiation Detector Studies - A Final Report

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NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

SEMICONDUCTOR NUCLEAR RADIATION DETECTOR STUDIES - A FINAL REPORT*

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In response to a problem that arose with regard to the availability of germanium for lithium-drifted germanium detectors [Ge(Li) detectors], a comprehensive program was undertaken aimed toward the development of a method for the rapid specification of germanium quality for nuclear radiation detector use, and the determination of factors affecting germanium quality. Measurements on a large number of germanium crystals, most of which had been rejected for detector use, and intercomparison of these measurements and the methods employed led to significant developments in the measurement of lithium mobility and driftability, carrier trapping, and semiconductor defect and impurity determination via an improved infrared response (IRR) technique. The present improvement of the infrared response technique resulted in the observation of a number of discrete energy levels lying within the forbidden gap of germanium unobserved in previous studies. It was possible to assign the proper position of energy levels detected by IRR in the upper or lower half of the energy gap. It was thus possible, in some instances, to determine the nature of the defects responsible for the observed energy level from results reported in the literature. The goal of developing a method for the rapid specification of germanium quality was achieved.

Key Words: Carrier trapping; gamma-ray detector; germanium; Ge(Li) detector; infrared response; silicon.

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1. INTRODUCTION

The situation with regard to germanium for high resolution, lithium-drifted gamma-ray spectrometers [Ge(Li) detectors] was of particular concern to the scientific community involved in making, studying, and using these devices in late 1965. At that time serious difficulties in attempting to fabricate germanium gamma-ray detectors were encountered at many laboratories. The origin of these difficulties was traced to the germanium supplied by a domestic source used in the fabrication of the detector, but the exact causes could not be determined. Subsequently, suitable material became available, primarily from foreign suppliers, but selection was based ultimately on the characteristics of detectors fabricated from specimens of the crystals. Many of the crystals had to be rejected after this selection process, which might take up to two months, because satisfactory means to identify detector-grade germanium prior to the start of the lithium-drift process were not available.

In 1964, the NBS Electronic Instrumentation Division (currently the Electronic Technology Division) undertook for the AEC a comprehensive research program which had as its overall objective the identification of those parameters that would be most useful in specifying detector-grade germanium and silicon. Because of the immediate problem in 1965, the NBS program emphasized the study of germanium. The specific objectives of this program were the development of a method for the rapid specification of germanium quality for nuclear radiation detector use, and the determination of factors affecting germanium quality.

During the course of the program, the character and use of Ge(Li) detectors changed markedly. Detectors with larger sensitive volumes than those used in nuclear physics, the initial application, were required for an increasing number of different uses, including nuclear medicine, analytical applications, environmental pollution monitoring, and reactor fuel monitoring and safeguarding. The rapid determination of starting crystal suitability was especially critical in regard to the large-volume Ge(Li) detectors. Where once the cost of the crystal made up perhaps one-tenth the selling price of the finished detector, it was not uncommon for large-volume detectors that the cost of the starting material was one-third or more of the selling price. With a large investment in the starting material, the device producer expended considerable effort in reworking a crystal in order to obtain a saleable detector. Often, because of material loss during such reprocessing, the final sensitive volume of the detector would be less than that anticipated. Also, the fact that the sources of germanium for commercial detector fabrication were exclusively foreign was of concern to several government agencies.

The NBS study proceeded on two fronts, characterization of germanium and evaluation of detector performance. Specification of parameters customarily used to characterize semiconductors for devices such as transistors or rectifiers appeared to be insufficient for the purpose of insuring the fabrication of high quality Ge(Li) detectors. A series of isolated experiments at various laboratories had suggested that some other parameters such as lithium precipitation rate [1] or low-temperature electron drift mobility [2] might be correlated with

material quality. The approach adopted at NBS [3] was to collect and characterize a sizable group of germanium crystals as fully as possible with respect to the standard parameters such as resistivity, etch pit density, and lifetime, as well as other parameters such as Hall mobility at various temperatures, electron drift mobility at 77 K, infrared absorption due to interstitial oxygen, and lithium precipitation and drift rates. After a detector was fabricated from the characterized crystal by means of a standardized procedure, its performance was determined by measuring a number of device characteristics such as leakage current, noise, capacitance, energy resolution, and charge collection efficiency, in order to determine whether correlations existed between detector quality and initial material properties. In all, 85 germanium crystals were collected, most of which had previously been rejected for detector use by the contributors.

In addition to this comprehensive in-house research effort at NBS, Committee F-1 on Electronics of the American Society for Testing and Materials was assisted by NBS in setting up a task force to study germanium properties and to develop standard methods for measuring pertinent crystal parameters. Staff members also cooperated with the Nuclear Instruments and Detectors Committee of the Institute for Electrical and Electronic Engineers in developing standards for Ge(Li) characterization.

Significant accomplishments of the NBS research effort were the development of a rapid test procedure for determining lithium-ion drift mobility in germanium and an improved infrared response technique for detecting defects and impurities in semiconductors. The purpose of this report is to describe and summarize the results of the NBS study and show the impact they had on the Ge(Li) detector situation. Major emphasis will be given to the infrared technique (detailed in the Appendix - NBS Spec. Publ. 400-13), both for its application to material qualification for radiation detector use and its broader potential for semiconductor material characterization.

2. EARLY ACCOMPLISHMENTS

In this section will be briefly described the results of NBS research carried out prior to the infrared response study. Almost all of these results were published separately in the open technical literature during the course of the study.

2.1 MATERIALS CHARACTERIZATION

Measurements of lithium-ion drift mobility in germanium, a primary materials acceptance criterion, were performed in the temperature region in which the lithium drift process was carried out, between room temperature and approximately 335 K [4]. Prior to this work, such values of lithium mobility had been obtained by extrapolating values measured at 425 K and above into this region [5]. It was found that in the temperature region of interest, the directly measured mobility values were higher than those obtained by extrapolation. This study also confirmed for germanium some theoretical predictions concerning the two regimes of lithium drift

rate [6] that led to NBS introduction of a very rapid technique, subsequently adopted by the American Society for Testing and Materials [7], for measuring lithium mobility and utilized in industrial practice. Use of this technique based on diode capacitance measurements early in the drifting period, cut the drift time required for the test by a factor of 33 over a previous method [6] based on measurements made in later phases of the drifting period.

A more realistic model of the lithium-ion drift process was developed [8]. This model postulated loss of mobile lithium ions during drift. Calculations made using this model were in good agreement with the experimentally-observed behavior of many germanium crystals during lithium drift.

Because of the importance of oxygen contamination in germanium as it affects driftability, three methods for measuring this impurity were investigated: infrared absorption [9], lithium precipitation [1], and lithium mobility [4]. It was determined that oxygen concentration measured by both infrared absorption and lithium precipitation agreed to within 10 percent with that determined from lithium mobility measurements [10]. Whereas infrared absorption measurements require apparatus that is not normally found in a detector fabrication facility, and the precipitation technique was essentially destructive so that the germanium specimen could not be used for detector purposes, the mobility measurement, carried out as part of the detector fabrication process, could be used to rapidly measure oxygen concentration between 0.2 and 20 parts per billion (1×10^{13} to 1×10^{15} cm^{-3}). This technique also had the best precision of the three methods, a relative sample standard deviation of 10 percent as determined in a multi-laboratory experiment [10].

In the course of the research program, it was determined that the semiconductor properties usually measured to characterize the material could not be used to qualify germanium for detector use. This became evident in scatter diagrams, 129 in all, of the possibly meaningful combination of 21 parameters under study (such as bulk resistivity, Hall resistivity, photoconductive decay lifetime, diode recovery lifetime, etch pit density, electron mobility at both 300 and 77 K, Hall mobility, lithium mobility, infrared absorption at both 300 and 20 K, and lithium precipitation rate) that were generated by computer using data on some or all, depending on the measurement, of the 65 specimens collected at that time [11].

Another parameter, electron drift mobility, was studied as a candidate for a predictor of acceptable material. Based on measurements of oxygen concentration, electron drift mobility, and lithium mobility for germanium specimens with resistivity ranging from 4 to 40 Ω·cm, correlation was not observed between decreasing electron drift mobility and increasing oxygen concentration or between increasing electron drift mobility and increasing lithium mobility [12]. Thus electron drift mobility measurements did not appear to be useful in specifying suitability of germanium for detector fabrication.

2.2 DETECTOR CHARACTERIZATION

While measurements of lithium drift mobility and oxygen concentration gave information on the probability that a given germanium crystal could

be drifted to some desired depth, there was, as yet, no guarantee that the resulting detector would be of high quality. The performance parameter of concern was the trapping of charge carriers that reduced collection efficiency, degraded energy resolution, and made quantitative determinations using the detector (such as in activation analysis) difficult. Thus, to qualify germanium for fabrication of high-quality detectors; a detector still had to be fabricated from a specimen of the germanium crystal and its performance evaluated.

A series of planar Ge(Li) detectors was fabricated that had performance characteristics considered, at the time, to be typical of high performance devices [13]. These detectors served as the basis for comparison for subsequent test detectors and were also used in a series of measurements on trapping. One criterion used in judging the degree of carrier trapping in Ge(Li) detectors was the Fano factor, F. Prior experimental measurements of F using uncollimated radiation sources at NBS and other laboratories indicated that $F \simeq 0.13$. Since the true Fano factor, F, is associated only with the charge production process, corrections must be made to experimental data for additional statistical and loss contributions from the collection of charge in the detector as well as by factors contributed by the electronic components of the system. Because of the difficulty in sorting out these additional statistical and loss contributions, F cannot be measured directly. Therefore, the concept of an effective Fano factor, F', [14] was introduced. The effective Fano factor, which is measured using collimated gamma-radiation so that the effects of electron and hole collection can be separately assessed, represents an upper limit for the true Fano factor. Study of two Ge(Li) detectors showed that $F' \leq 0.11$. That the true Fano factor was less than or equal to 0.11 indicated that the performance, with regard to carrier trapping, of Ge(Li) detectors characterized by $F = 0.13$ was not the optimum as previously thought. This result was later experimentally confirmed at another laboratory where detectors were fabricated that had effective Fano factors of less than 0.10 [15].

Another criterion used to judge the degree of carrier trapping in Ge(Li) detectors was the shape of the gamma-ray photopeak obtained in a pulse-height vs energy spectrum. Trapping is usually manifested as a broadening on the low energy side of the ideal, symmetrical, gaussian-shaped peak. However, models of the trapping process proposed at the time could not satisfactorily reproduce experimentally-obtained gamma-ray photopeaks. A new model was developed [16] that could predict the variation in peak shape resulting from gamma-ray irradiation of planar Ge(Li) detectors using experimentally obtainable input parameters. The key to the success of the model was the incorporation of a variation of peak amplitude as a function of charge collection efficiency (shown to be responsible for the observed increase in tailing with a decrease in field) and of the variation of carrier lifetime, for both carriers, with applied field (responsible for the observed shift in peak positions with field).

In order to aid in the fabricating, testing, and use of Ge(Li) detectors, a series of six nomographs was produced and published covering calculations routinely used in fabricating detectors and measuring detector quality [17]. These nomographs found wide use; one thousand copies of

this document were sold through the Government Printing Office, and some 400 were distributed directly by the author.

Contributions were also made to efforts aimed at standardizing detector measurements. NBS staff members served as project leaders for the development of a voluntary standard test procedure for specifying Ge(Li) detectors at the buyer-seller interface [18]. Prepared in cooperation with the Nuclear Instruments and Detectors Committee of the Institute for Electrical and Electronic Engineers and later accepted by the American National Standards Institute, this standard included several test procedures developed at NBS.

3. THE INFRARED RESPONSE TECHNIQUE

NBS efforts concerning two of the major germanium problems, driftability and carrier trapping, resulted in more meaningful measurements and procedures for characterizing material in terms of driftability and Ge(Li) detectors in terms of trapping. However, there was, as yet, no method that could be used to rapidly determine the suitability of a germanium crystal for detector use, particularly with regard to carrier trapping. Neither was there much information about the nature of the factors that affected germanium quality.

To proceed further, an infrared response (IRR) technique was evaluated for its utility in qualifying germanium for detector use. In this technique, the diode impurity photovoltage is measured as a function of energy of incident infrared radiation. Features in the resulting IRR spectra can be interpreted in terms of impurity and defect levels lying within the forbidden energy gap. Because of several improvements of the technique made during this evaluation, it was possible to observe because of increased sensitivity a number of discrete energy levels lying within the forbidden gap of germanium which had passed unobserved in previous studies. These levels were correlated with the type of defects and vacancies introduced by radiation damage into germanium as measured using such techniques as photoconductivity and Hall measurements after irradiation. Furthermore, the improved infrared response measurement method was used to identify impurities, such as copper, gold, and iron, and dislocations resulting from heat treatments in germanium.

A major advance was made when it was determined that the IRR spectra could be grouped into five distinct types on the basis of spectral features observed in the energy range from 0.6 to 0.7 eV. One of the spectrum types represented crystals from which good quality detectors could be fabricated; the other four represented crystals that yielded poorer quality detectors due to carrier trapping or crystals that presented problems in detector fabrication such as low lithium drift mobility. Three of the four spectrum types representative of poor crystal quality could be duplicated by suitably treating specimens of a good quality crystal (introducing neutron damage or lithium precipitation) so as to degrade them. The material and detector characteristics of crystals within each spectrum type were found to be similar. Of the 55 crystals studied that yielded usable IRR spectra, about 56 percent exhibited the two spectrum types that were found to be indicative of carrier trapping. It was possible to assign the proper position of energy levels detected

by IRR in the upper or lower half of the energy gap. It was thus possible, in some instances, to determine the nature of the defects responsible for the observed energy level from results reported in the literature. The results of this study are detailed in the Appendix (NBS Special Publication 400-13).

4. SIGNIFICANCE AND IMPACT

The objectives of the germanium study were: 1) the development of a method for the rapid specification of germanium quality for nuclear radiation detector use, and 2) the determination of factors affecting germanium quality. The method developed at NBS for measuring lithium-ion drift mobility [7] and the infrared response technique fulfill the first objective. The mobility is obtained in about three hours of drifting; less by a factor of about 50 than the time required for drifting a 5-mm-thick detector for evaluating crystal quality; the IRR technique can be applied to a planar diode after another 24 hours or so of drifting. In terms of the second objective, the results obtained from IRR spectrum types showing carrier trapping and subsequent linking to known energy levels seem to confirm the role of oxygen in the creation of trapping centers in germanium. In addition, the results of the work disclosed the inadequacy of numerous methods which had been employed in this field and led to the adoption of new standards which would promote more effective and efficient evaluation of crystals and detectors.

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NBS-SP-400-13 is the appendix to this report.

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

In response to a problem that arose with regard to the availability of germanium for lithium-drifted germanium detectors [Ge(Li) detectors], a comprehensive program was undertaken aimed toward the development of a method for the rapid specification of germanium quality for nuclear radiation detector use, and the determination of factors affecting germanium quality. Measurements on a large number of germanium crystals, most of which had been rejected for detector use, and intercomparison of these measurements and the methods employed, led to significant developments in the measurement of lithium mobility and driftability, carrier trapping, and semiconductor defect and impurity determination via an improved infrared response (IRR) technique. The present improvement of the infrared response technique resulted in the observation of a number of discrete energy levels lying within the forbidden gap of germanium unobserved in previous studies. It was possible to assign the proper position of energy levels detected by IRR in the upper or lower half of the energy gap. It was thus possible, in some instances, to determine the nature of the defects responsible for the observed energy level from results reported in the literature. The goal of developing a method for the rapid specification of germanium quality was achieved.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Carrier trapping; gamma-ray detector; germanium; Ge(Li) detector; infrared response; silicon.

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