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**ENCAPSULATION OF HIGH-PURITY
GERMANIUM DETECTORS**

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Encapsulation of High-Purity Germanium Detectors*

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Abstract

The encapsulation of high purity germanium detectors is very desirable in order to increase their versatility and reliability. However, rapid and extensive degradation is seen for all detectors made from detector grade crystals which are encapsulated in a simple vacuum. Extensive studies have shown that the cause of this degradation is hydrogen adsorption on the detector surface. There it causes the formation of a strong p^+ inversion layer which in turn shunts the detector junction. Reliable encapsulation is shown to be achievable by the use of hydrogen-free germanium crystals.

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I. Introduction

The primary interest in high purity Ge detectors over Ge(Li) detectors is in their relative stability during storage at ambient temperatures. However, the surface of high purity Ge detectors (like Ge(Li) detectors) is extremely sensitive to contamination and thus either a controlled laboratory environment or a clean vacuum is required for their protection. Greater versatility in handling and use (either singly or in array applications) as well as greatly increased reliability would be anticipated for a properly vacuum encapsulated high purity detector. These advantages have provided the motivation to develop an adequate encapsulation technique.

Initially, it appeared that no significant problems would be encountered since the successful encapsulation of Ge(Li) detectors had been perfected a number of years earlier. On this basis, an encapsulating system based on the one used by R. J. Fox at ORNL was set up. The encapsulation is done using 1100 grade aluminum extruded into a cup. An OFHC copper lid, containing the electrical feedthrough, is then cold-welded to the aluminum can under vacuum ($\sim 10^{-4}$ torr) in a specially constructed sliding vacuum enclosure which allows a force of 20,000 pounds to be applied to the welding dies. The detector is held in place with indium foil pads and a phosphor-bronze spring.

Initial encapsulation attempts using high purity Ge detectors, however, revealed a very basic problem not encountered with the constantly cooled encapsulated Ge(Li) detectors. The detector V-I characteristics of all encapsulated high purity germanium detectors degraded drastically (reverse leakage currents of microamps to milliamps at only a few volts bias) in only

a matter of a few days even though the initially encapsulated detector had very good V-I characteristics. This problem provided the impetus for an extensive study to identify the cause of the degradation and to determine a way to achieve reliable encapsulation. It was subsequently shown that hydrogen diffusion from the crystal, resulting in the formation of a P-inversion layer, by adsorption of the hydrogen is the cause of the degradation. Successful encapsulation has now been achieved by using crystals grown in a hydrogen-free ambient or crystals from which the hydrogen was later removed.

In order to provide a better insight to the validity of this conclusion, we will consider the progress of the study from a historical point of view.

II. Search for the Problem

Our initial approach was to make sure that leaks or internal outgassing from the can didn't cause surface contamination. To do this, we took steps to improve the weld quality and to clean-up the equipment and encapsulating procedures. Integrity of the vacuum was subsequently verified and vacuum leaks were ruled out as the source of the problem. High vacuum cleaning procedures (including a 400°C vacuum bake-out of all encapsulating parts) were subsequently employed. All organics were eliminated from the processing steps. Special cans with gold-brazed ceramic feedthroughs were made and used. A number of different detectors were encapsulated a large number of times using increasingly stringent procedures. The net result, however, was no effect at all of these changes on the detector degradation characteristics--the detectors still degraded to the same extent at the same relative rate.

A number of additional studies were subsequently done in order to determine what the source of the degradation was. These studies included the effects of different surface treatments and surface protection and

subsequent pumping of detectors which had degraded following encapsulation.

One very interesting result was the rapid and almost complete recovery of the detector V-I characteristics after a small hole was cut in the can and the detector was pumped for only a few minutes at room temperature with a vacuum in the 10^{-3} - 10^{-4} torr range following detector degradation. This behavior is very suggestive of the role of a volatile surface contaminant. However, surface protection of the detector with an acrylic coating had no significant effect on the degradation characteristics. In addition, the presence of a N_2 atmosphere within the hermetically sealed can likewise had no effect. Both of these results are not expected if the problem is due to vacuum outgassing from the interior surface of the can.

Communications with R. J. Fox of ORNL indicated that they were observing exactly the same degradation behavior for their encapsulated high purity detectors. This fact removed the question of some peculiarity associated with our own laboratory procedures and established the phenomena as likely being basic to the encapsulation process.

Fox then suggested the possibility that hydrogen diffusing out of the germanium crystal might be the source of the problem. We subsequently exposed a detector to atmospheres of H_2 , N_2 , and He. The gases were slowly admitted to the cryostat, eventually attaining a pressure of 1 atmosphere, while the detector was kept at 77° K. The resulting effect on the V-I characteristics was then observed. No significant effects were noted for any of the gases. The detector was then cycled to room temperature and re-cooled to simulate ambient storage. Again, no change was noted for the N_2 and He atmospheres. However, the H_2 atmosphere caused a complete shorting of the detector. The detector was then re-warmed and the gases

were pumped out at 10^{-4} torr for about 5 minutes. Following recooling the detectors exposed to the N_2 and He atmospheres still showed no change. However, the detector that had been exposed to H_2 completely recovered. This was very significant because the behavior of the hydrogen exposed detectors essentially duplicated the observed behavior of all the encapsulated detectors thus far.

III. Verification of Hydrogen as the Problem

At this point, a series of experiments were performed to determine whether or not hydrogen from the germanium could be the cause of the observed degradation. These studies included encapsulation of N_2 and He grown crystals, studies of the effect of H_2 on germanium surfaces using surface barrier junctions and surface conduction studies, use of various catalysts and getters within the can, and calculations of possible H_2 contamination based on the known behavior of H_2 in germanium. (2-5)

The results obtained thus far are conclusive and bear out the hypothesis of internally generated hydrogen contamination of the detector surface. The following results are pertinent.

- A. Nitrogen and helium grown crystals were obtained from Lawrence Berkeley Laboratory and General Electric and detectors made from these crystals were encapsulated. A-1 of these detectors do not show the normally observed degradation following encapsulation in a hydrogen-free can. Conversely, all encapsulated detectors made from hydrogen grown crystals show the expected degradation characteristics with a time constant varying from a few hours to a few days.
- B. The use of a platinum black catalyst in different combinations with vacuum sieve materials within the sealed can dramatically affects

the degradation characteristics of detectors made from hydrogen grown crystals. The objective of this combination is to reduce the partial pressure of hydrogen within the can by catalytic oxidation and then pump the water vapor with the vacuum getter. While the stability of such encapsulated detectors hasn't been as good as those which are hydrogen free, the effect of the catalyst and getter is to effectively extend the "life" from hours to months of the encapsulated detector. One detector, in fact, has shown very good stability for a four month period.

- C. A successful cold-weld depends on a properly annealed copper lid. The standard technique had been to hydrogen fire the lids at 700°C for several hours. However, hydrogen-free detectors encapsulated with freshly fired lids showed rapid degradation characteristics identical to those of detectors made from hydrogen grown crystal. Subsequent encapsulation of these detectors using vacuum annealed copper lids did not show any degradation. However, the use of vacuum fired copper or aluminum lids had no effect on the degradation effect of hydrogen grown detectors. Solubility and diffusion rate data for hydrogen in copper⁽⁶⁾ indicate that the copper could act as an effective hydrogen source since the solubility, while not high, is quite temperature dependent and has a relatively slow diffusion rate at lower temperatures which would favor the slow release of small quantities of hydrogen over a period of time.
- D. Our surface barrier and surface conduction studies indicate the formation of a p+ inversion on germanium by adsorbed hydrogen. Studies reported in the literature^(2,3) indicate that atomic

hydrogen (the specie diffusing out of the detector) adsorbs very strongly on the germanium surface. This adsorbed layer apparently mixes with the surface germanium atoms (as opposed to simple surface adsorption) and creates a high density of surface acceptor states, thus imparting strong surface p-type conductivity. The formation of this surface layer would likely involve an activation energy since it is not due to simple surface adsorption and this correlates well with our observations of the need for ambient temperature contact with hydrogen in order to see any significant effect.

Subsequent desorption of the hydrogen is possible if the partial pressure of hydrogen above the surface is sufficiently low. This allows the recovery of diodes by pumping and explains why detectors mounted in either large volume or actively pumped systems have demonstrated much better stability than those encapsulated in a small can.

The degradation mechanism is apparently due to the formation of a p-type inversion layer on the surface of the detector. This inversion layer then acts as a shunt conductive path between the electrodes and accounts for the very large shunt conductances which are observed for degraded detectors.

Hydrogen is relatively soluble in germanium at the growth temperature ($\sim 1 \times 10^{15}/\text{cm}^3$) and crystals grown in atmospheric hydrogen likely retain an appreciable fraction of this.⁽⁵⁾ Solubility at 20°C is very low, however, and creates a strong driving

force for hydrogen diffusion to the surface where it forms a p+ inversion layer unless it can be pumped from the surface. A simple calculation based on a reasonable hydrogen concentration gradient of $10^{14}/\text{cm}^3/\text{cm}$ and the ambient temperature diffusion constant of $1 \times 10^9 \text{ cm}^2/\text{sec}^{(4)}$ indicates that a surface concentration of $10^{10}/\text{cm}^2$ can easily build-up during a 24-hour period. Since a $10^{10}/\text{cm}^2$ surface concentration is equivalent to $10^{15}/\text{cm}^3$ bulk concentration, it is easy to see why an inversion layer can be formed over the lithium junction whose ambient temperature equilibrium solubility at the surface is less than $10^{14}/\text{cm}^3$.

Diffusion from the crystal at this rate would correspond to a constant source of hydrogen for over 25 years. Of course, the rate of diffusion would change slowly over a period of years, just as there is a variation from one crystal to the next due to variations in hydrogen concentration and distribution in the crystal, but the net effect for all practical purposes is that of a never-ending source.

- E. Initial attempts at hydrogen removal from a hydrogen grown crystal have been successful in terms of achieving stable encapsulation. Detectors made from crystals which had been heated at 360°C for several weeks show good stability characteristics. In addition, we have removed hydrogen from a crystal by heating it in a closed evacuated quartz tube containing titanium strips for 72 hours at 325°C . A detector made from this crystal has proven stable when encapsulated as compared to earlier detectors made from the same ingot which showed the normal degradation curve.

IV. Conclusions

Based on the measurements performed thus far, hydrogen has been shown to cause the observed degradation behavior of encapsulated high purity germanium detectors. Control studies involving hydrogen containing versus hydrogen free crystals are definitive in terms of showing the role of hydrogen out-diffusion as the source of the degradation. Computations based on hydrogen solubility and diffusion characteristics in germanium, coupled with the known surface behavior of adsorbed hydrogen, verify the results obtained on the encapsulated detector studies.

The encapsulation of high purity germanium detectors is still a desirable goal. However, this is complicated by the fact that all currently available detector grade high purity germanium has been grown in hydrogen at atmospheric pressure and detectors made from these crystals will degrade when encapsulated in a simple vacuum can.

The most reliable solution we have found thus far is to grow the high-purity germanium in a hydrogen-free atmosphere. At present, hard vacuum represents the only reasonable alternative due to the oxide inclusion problem.

Two possible alternatives to vacuum growth have also been tried and show promise. The first involves inclusion in the can of a means to remove the hydrogen. A rare-earth gettering compound was tried without success. Vacuum getters are only partially successful. Best results thus far have been obtained for a mixture of a hydrogen catalyst (platinum black) and a vacuum getter.

The second alternative involved removal of the hydrogen from the crystal following growth. This can be done by heating the crystal for long periods of time at temperatures in excess of 300°C while maintaining a low partial pressure of hydrogen above the surface of the germanium.

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