LBL-9759
Preprint

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Engineering & Technical Services Division

CONF-791037--16

Presented at the IEEE Nuclear Science Symposium, San Francisco, CA., October 17-19, 1979, and submitted to IEEE Transactions in Nuclear Science

PROTECTIVE SURFACE COATINGS ON SEMICONDUCTOR NUCLEAR RADIATION DETECTORS

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October 1979

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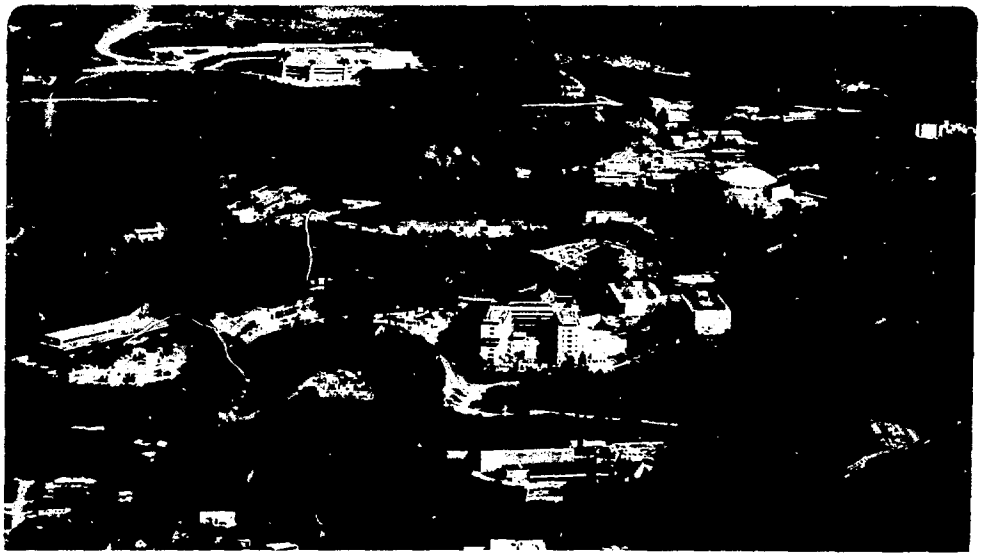

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

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PROTECTIVE SURFACE COATINGS ON SEMICONDUCTOR NUCLEAR RADIATION DETECTORS*

W. L. Hansen, E. E. Haller and G. S. Hubbard

ABSTRACT

Surface states on germanium p-i-n junctions have been investigated using deep level transient spectroscopy (DLTS) and collimated beams of 60 keV gamma-rays. The DLTS spectra have a characteristic signature for each surface treatment but the spectra are complex and not readily interpretable as to suitability for radiation detectors. Collimated gamma-ray beams give a direct measure of surface channel effects and typeness. Hydrogenated amorphous germanium (a-Ge:H) was explored as a surface layer to adjust the electrical state and passivate the surface. Our measurements show that these layers produce flat band conditions, introduce no additional noise and appear to be stable against a variety of ambients.

INTRODUCTION

The wide application of germanium devices has always been limited, in part, by the lack of a stable, passivating native oxide. Since the days of the very first transistors, various surface treatment and encapsulation methods were used in an effort to achieve long term stability of operating characteristics. Ultimately none of these methods proved satisfactory and germanium devices have been relegated to a tiny nitch in the semiconductor industry where some special characteristic of germanium makes the lack of stability tolerable.

For the use of germanium nuclear radiation detectors, a new set of priorities is imposed in order to achieve satisfactory surface stabilization. Because of the high cost of each detector, very careful handling, storing and mounting can be tolerated and the demand for good passivation is generally relaxed. However, the very large depletion widths and the extremely low electric fields in operating detectors mean that surface charge must be very small if surface channels are to be avoided. To be truly satisfactory, the surface passivation must be adjustable to produce flat band condition.

The only passivant for germanium nuclear radiation detectors to appear in the literature is SiO as proposed by Dinger.[1] However, experience has shown that SiO can be unsatisfactory for the following reasons: (1) the surface compensation is sensitive to the initial state of the surface, (2) the surface compensation is not adjustable to flat band condition, (3) the passivated devices have a higher leakage current, (4) an additional 1/f noise is often observed and (5) the method of application (thermal evaporation) limits the application to simple geometries.

In a survey of materials which could prove useful for passivating the surfaces of germanium nuclear radiation detectors we found that some sputtered semiconductor coatings had the desired properties. In particular, a detailed examination of sputtered hydrogenated amorphous germanium (a-Ge:H) shows that this material shows so far none of the detrimental effects of SiO coatings.

EXPERIMENTS

1) Deep Level Transient Spectroscopy (DLTS)

Studies of germanium p-i-n devices by the DLTS technique have shown that the spectra are sensitive to surface treatment.[2] This observation led t the idea of using DLTS to survey materials use for stabilizing germanium surfaces. Also by us ng light to change the charge-state of traps, it is possible to selectively observe traps in the surface states.

After accumulating a large number of DLTS spe tra on a variety of devices and surface treatments it was found that this technique lacks the specificity needed to characterize different surface treatments. The spectra are complicated by two temperature-dependent RC time constants--one due to the R of the undepleted detector material and the C of the depleted region and the other due to the R of the surface channel and the C of the depleted region. In general, we were not able to determine whether a given spectral feature is due an n- or a p-channel from DLTS alone.

Although DLTS spectra were not adequate to enable selection between different detector surface treatments, some conclusions about surface treatments could be made from these spectra. When compared to the spectra of a neutral surface, suitable for detector use*, each surface treatment on a detector produces a characteristic DLTS signature. No surface treatment produced traps which had finite emission rates below 100°K except for the surface resulting after HF quenching which exhibited significant DLTS signals all the way to carrier freeze out (8°K). Regardless of prior surface treatment, surface coatings of sputtered germanium or silicon always returned the DLTS spectra near to that of the "standard" surface. Extreme surface conditions were produced by quenching in anhydrous ethanol saturated with iodine after etching (strong p channel) and by quenching in 48% HF (strong n-channel).

2) Collimated Gamma-Ray Measurements on Detectors

Collimated beams of charged particles or gamma-rays entering the sides of depleted detectors provide very sensitive probes of surface channels and have been widely used for surface channel studies.[3,4] If the detector surface deviates from the flat band condition, the field lines near the surface do not reach from the n^+ to the p^+ contact. Collection of the charge produced by the short-range radiation

*This work was supported by the Office of Health and Environmental Research of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

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*Etching in 4:1: = HNO_3:HF, quenching with methanol and blowing dry with N_2.

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takes place in part via the surface layer. This results in very slow signal components and a ballistic deficit in the filter networks. Many of the events which should appear in the photopeak are moved to lower energies. Recording the gamma-ray spectra along the side from the p^+ to the n^+ contact gives a measure of both the strength and type of a surface channel.

In the experiments reported here, a 60 keV, 1.5 mm diameter gamma-ray beam from a ^{241}Am source was directed normal to the surface and scanned between the contacts. All surface coatings discussed here were approximately 3000 Å thick although the range of thicknesses from 300 to 30,000 Å showed no apparent difference in properties. In the case of amorphous germanium, the layers were sputtered in pure argon or with the addition of hydrogen in the concentrations indicated. Details of the sputtering process are given in the Appendix.

Figs. 1-3 show gamma-ray scans for detectors with a range of net impurity concentrations. The curve labeled CH_3OH is for our "standard" surface treatment of 4:1 etch followed by CH_3OH quench and the other curves are for germanium sputtered in argon with the indicated additions of hydrogen to the argon. It is clear that there is an optimum hydrogen concentration to achieve exact flat band condition for each bulk net impurity concentration and that the appropriate concentration is readily predictable and non-critical. The "standard" surface treatment gives relatively weak surface channels only for a net-bulk concentration $> 10^{10}$ cm^3 and is poor for very pure crystals.

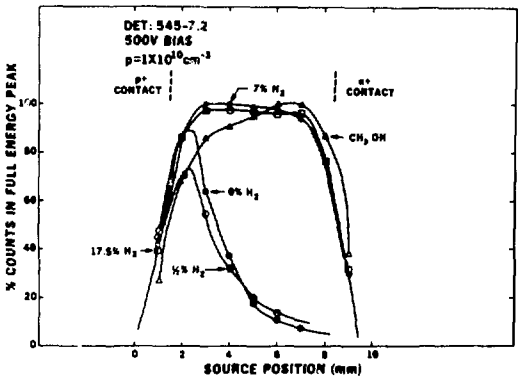

Fig. 2. Same surfaces as Fig. 1 but on detector made from 1 x 10^{10} cm^{-3} p-type germanium. Detector is fully depleted at 300 V.

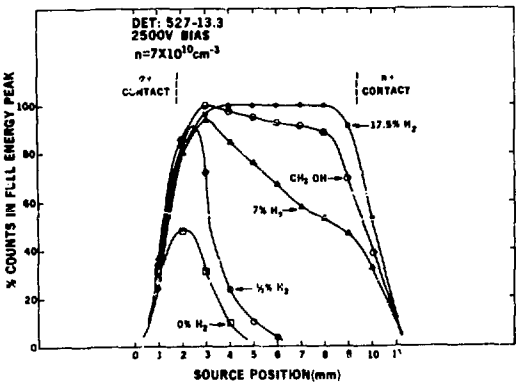

Fig. 1. ^{241}Am 60 keV scans on a detector fabricated from 7 x 10^{10} cm^{-3} n-type germanium. Detector is fully depleted at 2800 V. The beam diameter is 1.5 mm. The curve labelled CH_3OH is for 4:1 etch followed by CH_3OH quench while the other curves are for 3000Å layers of amorphous germanium (a-Ge) sputtered in argon with the indicated percent of H_2 added to the argon.

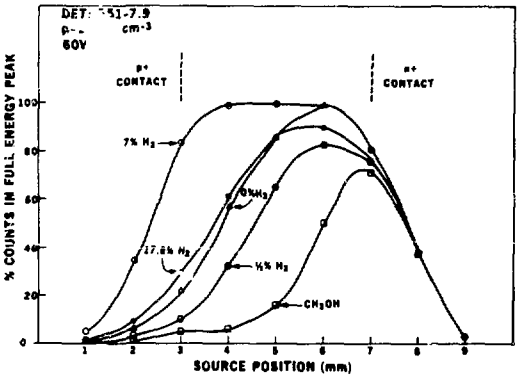

Fig. 3. Same surfaces as Fig. 1 but on detector made from 2 x 10^9 cm^{-3} p-type germanium. Detector is fully depleted at 20 V.

Figure 4 illustrates the insensitivity of the a-Ge:H passivation to the condition of the surface before sputtering. Only the H_2O quenched surface shows a slight n-channel, and even this could be accommodated by lowering the hydrogen concentration.

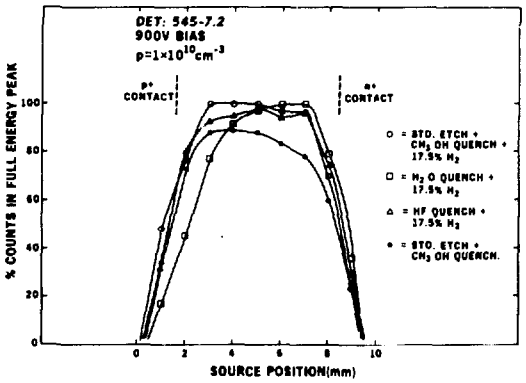

Fig. 4. Effect of surface treatment prior to sputtering.

In Fig. 5, various surface treatments are compared. The GeO_2 was produced by reactive sputtering in Ar + 10%O_2 and the SiO is the result of thermal evaporation. These results illustrate a basic difference between passivation by insulators and amorphous semiconductors. The case of GeO_2 is special insofar that the number of counts in the photopeak stays rather constant across the device, but is reduced from the maximum possible number. Such a dead layer of "constant" thickness can only be explained with a surface having a negative excess charge near the p^+- and a positive excess charge near the n^+-contact.

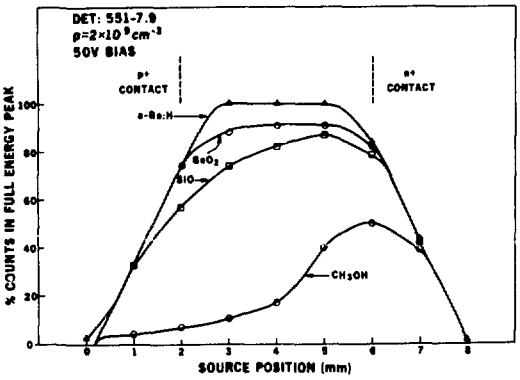

Fig. 5. Comparison of surface charge collection efficiency for various surface coatings. The GeO_2 was produced by reactive sputtering in Ar + 10%O_2 and the SiO was deposited by thermal evaporation.

Figure 6 is an attempt to illustrate the effect of H_2 concentration on charge collection as a function of the substrate. The curves are drawn to guide only. The collection efficiency is simply averaged over the whole scan. The reason why some of the curves turn up at zero H_2 concentration is due to the channel becoming so strongly conducting that the charge collected in the channel is transferred to the adjacent electrode in times shorter than the amplifier time constant and thus appears in the full energy peak. This observation is verified by the fact that as the detector bias is increased and the channel depleted, the counting efficiency decreases. This effect has been previously noted by Baertsch[3] on hemically treated surfaces.

3) Leakage Current, Noise and Detector Performance

Figure 7 shows the reverse leakage current as a function of temperature for several surface treatments. The standard detector (CH_3OH) shows a low leakage current even though the surface has a strong channel as can be seen in Fig. 3. The observation that the surface channel for one particular coating is unrelated to the leakage current has been found to be true for all the treatments tried. However, large differences exist between different coatings. Also for the a-Ge:H surface, the reverse leakage current is independent of the hydrogen concentration and thus of the band bending near the surface.

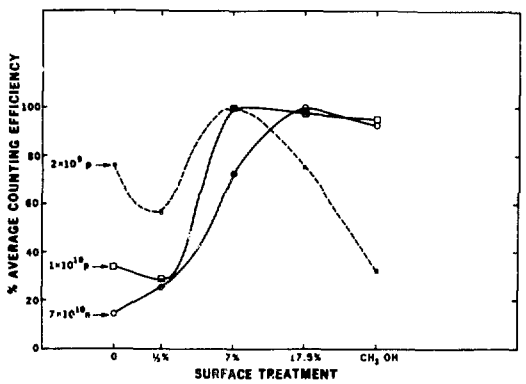

Fig. 6. Schematic representation of the effect of H_2 content in sputtering gas on surface charge collection efficiency for various substrates. Counting efficiency is averaged over the whole surface. Surface treatments have the same meaning as in Fig. 1.

The increased leakage current of the a-Ge:H coated device is not due to an ohmic shunt because ohmic behavior as a function of bias voltage is not observed at any temperature.

The leakage current-temperature dependence could be explained if the a-Ge:H acted as a semiconductor with a band gap smaller than the crystalline germanium. No explanation is offered for the leakage current of the SiO coated device.

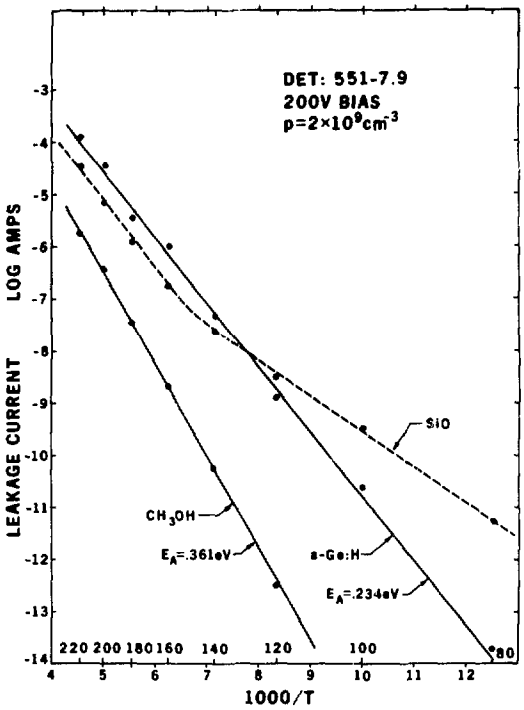

Fig. 7. Detector leakage current as a function of temperature for bare, a-Ge:H and SiO coated surfaces.

The noise behavior of devices coated with a-Ge:H is comparable to the very best devices with standard surfaces. Fig. 8 shows the noise behavior of a very high quality large planar device both before and after coating with a-Ge:H in which the square of the FWHM of an electronic test peak (i.e., resolution^2) is plotted versus amplifier peaking time. The curve is drawn with a slope one, which is the theoretical noise behavior in the absence of 1/f noise. A silicon detector of nearly equal capacitance is shown for comparison. The lower noise for the germanium device is due to the smaller energy per electron-hole pair for germanium than for silicon. The deviation at longer time constants from the straight line is due to FET gate leakage (FET = TIS75).

Gamma-ray spectra obtained using detectors with a-Ge:H treated surfaces show photopeaks with FWHM in accord with the test results. In addition, the flat band condition leads to an very "clean" spectra with no low energy "ghost" peaks or background counts.

4) Surface Stability

No scheme has been devised to test the limits of passivation of these surfaces and only experience will demonstrate their ultimate usefulness. However, as an indication of the surface stability, treatments which have been found not to affect the surface are listed: (1) wash in CH_3OH, (2) wash in H_2O, (3) Three month storage in laboratory air and (4) heat to 300°C in argon for 10 min.

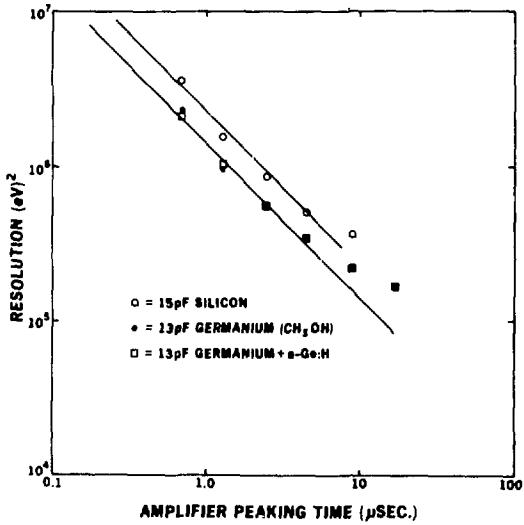

Fig. 8. Square of the FWHM of an electronic test pulse versus amplifier peaking time for a very high quality germanium detector before and after coating with a-Ge:H. Curve is drawn with a slope of one. The deviation from ideal behavior at long time constants for both silicon and germanium devices is due to FET gate leakage current.

DISCUSSION

The ability to make passivated surfaces with flat band condition on germanium nuclear radiation detectors can extend the application of these devices. An important use for this technique is in making multi-detector arrays for which case the detectors can be fabricated and tested one-by-one without concern for any ambient degradation before mounting in the final system. Another important application will be for charged-particle telescopes where the freedom from entrance windows will allow the fabrication of detectors many centimeters deep using normal thick lithium contacts. The fact that a-Ge coatings more than 1 μm thick are opaque to visible light will allow detectors to be operated in conditions where such light cannot be avoided.

An important property of the a-Ge:H passivation is that it is unaffected by rather high-temperature (300°C) anneals. This means that radiation damaged detectors can be thoroughly annealed without any intermediate chemical treatment. Devices coated with a-Ge:H have higher leakage currents at high temperature than bare devices. Because of this effect, coated devices are limited to a maximum operating temperature of about 120° K (for 10^{-9} A leakage) for high-resolution gamma-ray spectroscopy, whereas a comparable bare device could operate at 160° K if surface contamination can be avoided.

Preliminary measurements show that a-Si:H acts very similar to a-Ge:H on germanium devices. The surface compensation can be adjusted to give flat

band condition over the compelete range of crystal impurity concentration of interest for fabricating nuclear radiation detectors by simply varying the hydrogen concentration in the sputtering gas. Since it is known that the group III and V impurities begin to be effective in amorphous semiconductors containing large hydrogen concentrations, it is likely that this passivation technique can be expanded to applicators involving a greater range of substrate impurity concentration by using doped sputtering targets along with hydrogen compensation.

The properties of amorphous semiconductors are remarkably unaffected by impurities so there need be little concern for target purity during sputtering or from inadvertant sputtering from metal parts of the apparatus. The only impurity of consequence is H_2O which provides an uncontrolled source of hydrogen. In order to achieve a reproducible hydrogen concentration in the a-Ge:H coating, it is necessary that the sputtering apparatus contains a shutter over the device so that the initial H_2O transient can be pumped away before coating begins.

APPENDIX

Sputtering Apparatus and Procedure

Both a simple D.C. and a more flexible A.C. sputtering apparatus have been used to produce surface coatings and each gave essentially similar results with respect to detector performance.

D.C. Sputtering

The D.C. sputtering apparatus consists of a 15 cm diameter chamber on a 10 cm diameter liquid nitrogen (LN) trapped diffusion pump. Pump throttling is on the pump itself so that the chamber sees the full bore of the LN trap during sputtering. The 9 cm diameter cathode and anode are water cooled and spaced 2.5 cm apart. The apparatus contains no anode shutter. The usual sputtering conditions are 15 μm gas pressure, 2000 V cathode voltage and 6 mA current. These conditions give a sputtering rate for germanium of about 170 Å/min. The detector coating sequence is as follows: the apparatus is evacuated and adjusted to the sputtering pressure and run for one hour under voltage to desorb water. Meanwhile, the detector to be coated is placed Li side down on an indium foil and the boron side is partially covered by a small piece of indium foil. The apparatus is then quickly vented to air, the device pressed against the anode, and quickly evacuated. The resulting coating is highly non-uniform due to the small cathode diameter and close spacing.

A.C. Apparatus

The A.C. apparatus consists of three 20 cm diameter water cooled cathodes and anodes in a 61 cm diameter chamber. Any cathode can deposit on any anode and the electrode spacing is adjustable during operation. An anode shutter is incorporated. The pumping system is 15 cm diameter with direct and adjustable throttling (Venetian blind) and the LN trap is 20 cm diameter Usual operating conditions are; 7 μm pressure, 300 W at 1.1 kV and 13.56 MHz, electrode spacing of 5 cm. Germanium sputtering rate under these conditions is 600 Å/min. Detector preparation is the same as the D.C. apparatus and water degassing is done for 5 min. with the detector present and the shutter closed. The deposits are highly uniform and will even coat negative relief surfaces.

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