IMPROVING GERMANIUM DETECTOR RESOLUTION AND RELIABILITY

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ABSTRACT

High purity germanium (HPGe) detectors used in radionuclide assay systems such as Radionuclide Aerosol Sampler/Analyzer (RASA) systems must be in operation for long periods of time without maintenance. To meet this critical need, HPGe detector reliability and resolution performance should be improved through the development of new surface passivation techniques to passivate and protect the surface area between electrical contacts. The goal of this research is to develop two surface film techniques for passivating detector intercontact surfaces: wet chemically grown oxide (WCO) films and sputtered films. Each film will be characterized to determine its surface chemistry and coating quality. Qualification will be carried out by examining the detector performance under various experimental conditions.

To evaluate these new passivation techniques, a set of baseline data was established for HPGe detectors using the current standard silicon oxide passivation technique at CANBERRA. Two 100% relative efficiency Standard Electrode Germanium (SEGe) detectors were fabricated using silicon oxide as the passivant. The performance evaluation of the standard SEGe detectors has been completed. This evaluation included CANBERRA standard product test procedures, as well as the temperature dependence test, rapid thermal cycle test, and pump/bake test. These data will be referenced to evaluate the performance for detectors fabricated using new passivation techniques.

A unique WCO technique has been developed to grow native germanium oxides directly on HPGe detector surfaces. The oxides are expected to be good passivants for detector interelectrode surfaces because they natively saturate the dangling bonds and result in a low density of surface charge states. These states lead to surface channels which can be a direct cause of leakage current. A HPGe detector was successfully fabricated using the WCO technique. Test results demonstrate the effectiveness of the new WCO technique in producing SEGe detectors with the following important characteristics: very low leakage current, excellent noise properties, ability to withstand thermal stress and maintain physical integrity, and stability over a long period of operation. Further evaluation of the natively grown oxides using the new WCO technique is underway on larger SEGe detectors to analyze the inherent noise contribution from the surface and compare it with that of silicon oxide surfaces. A sputtered film technique will be developed later in this project.

OBJECTIVES

HPGe detectors used in radionuclide assay systems such as RASA systems must operate unattended for long periods of time. Current commercially available germanium detectors using the SiOx (x~2) passivation technique have shown excellent performance and reliability which fulfill the needs of most laboratory applications in radiation detection and measurement. However, for remote systems such as RASA designed for nuclear detonation detection and analysis, this critical need for long term operation requires research to further improve detector performance and reliability.

One of the key factors affecting germanium detector performance and reliability is the passivation of the intercontact area between the electrical contacts. The contacts create the diode structure and, under reverse bias, collect charge produced by photon interactions with the germanium material. The intercontact surface has to be passivated to electrically separate the detector contacts. A successful intercontact surface must allow very little reverse leakage current under the stress of as much as 5000 volts of reverse bias. In addition, the intercontact surface must create little electrical noise. Both surface leakage noise and passivant dielectric noise must remain low to achieve excellent signal-to-noise ratio. For germanium detectors, a SiOx coating created by a well-controlled evaporation of silicon monoxide is traditionally used to passivate germanium surfaces (Holland, 1970). Although SiOx passivations have been an acceptable solution for many commercial detector products, some variability in reverse leakage currents as well as field-line distortion effects associated with intercontact surfaces have been observed. Some deleterious surface effects resulting from the evaporated silicon monoxide on germanium have been previously investigated (Dinger, 1976). The existence of weak-field regions and surface channels responsible for leakage current results from both fast electronic states (germanium surface) and slow electronic states (SiOx film, adsorbed gases) (Bardeen et al., 1956). On the other hand, uncontrolled growth of native oxide layers, which contain empty states with energy levels in the germanium band gap, can cause accretion of electrons on the germanium surface region, creating an inversion layer in P-type material or an accumulation layer in N-type material. Such effects in P-type germanium have been described by Brown (1953). Therefore, in order to further improve detector resolution and reliability, development of passivation techniques by improving or replacing the present SiOx passivation has become necessary to achieve a more consistently neutral intercontact surface (Martin et al., 2008).

The objective of this research is to investigate new passivation techniques that provide better resolution and reliability of performance than the current standard SiOx technique used in the detector industry. First, a set of baseline data for HPGe detectors will be established using the standard CANBERRA SiOx passivation technique. Two 100% SEGe detectors are to be manufactured following CANBERRA detector fabrication procedures. The performance of the SEGe detectors is to be evaluated, using CANBERRA product test procedures, as well as the temperature dependence test, rapid thermal cycle test, and pump/bake test. Then, two surface film techniques for passivating HPGe detector surfaces will be developed: WCO films and sputtered films. Future studies will focus on characterizing each coating to determine its surface chemistry and physical integrity. Passivation qualities and their inherent noise contribution to the overall system noise will be evaluated and analyzed under various experimental conditions. The goals in developing novel surface passivation techniques are the reduction of both surface leakage noise and passivant dielectric noise resulting in improved detector performance and reliability.

RESEARCH ACCOMPLISHED

Standard detector fabrication and characterization

Two 100% SEGe detectors were fabricated following the standard CANBERRA detector fabrication procedures to evaluate the detector resolution and reliability using the SiOx coating for passivating the intercontact surface. Two P-type HPGe coaxial detectors with a net active impurity level below 1.7×10^{10} cm^{-3} and a mass of ~2200 grams as the starting raw material were used as evaluation devices.

The detectors were manufactured by first mechanically polishing the surfaces to remove gross damage left from the machining process. Microscopic damage was removed by a concentrated nitric acid based etch followed by water and methanol rinses. Then the devices were immersed into a bath of lithium salt for lithium diffusion at an elevated temperature. A Li-doped layer with thickness approximately 1 mm was formed to achieve an n^+ electrical contact for each device. Following the diffusion, a drilled core hole was implanted with high energy boron to form a p^+

electrical contact. The intercontact surface was limited to a small annular region near the core by a unique wrap-around lithium contact. After the intercontact area was etched to ensure the surface was microscopically free of mechanical damage or scratches, the detectors were transferred into a vacuum chamber. A SiOx passivation film of 100–200 nm thickness was then deposited by physical vapor deposition (PVD).

Figure 1. CANBERRA CP-5® cryocooler, integrated electronics and cryostat. The two fabricated SEGe detectors were individually installed in the cryostat for evaluation of the detector performance.

Preliminary tests to check the detectors' leakage current showed that both detectors had very low leakage current under high voltage bias up to 5000 volts. This demonstrated the electrical contacts were non-injecting, and the passivated intercontact area did not exhibit high leakage current due to surface channel formation. As shown in Figure 1, the two fabricated detectors were mounted individually into a CANBERRA Cryo-Pulse® 5 (CP-5) cryocooler to cool the detector and preamplifier first stage field effect transistor. The CP-5 is an electrically powered cryocooler designed for use with germanium and silicon radiation detectors. It utilizes a pulse-tube cooler, which is a relatively new concept in cryogenic coolers as compared to Stirling coolers. The cooler not only keeps the detector at low temperatures down to 80 K without the need of liquid nitrogen, which requires daily maintenance, but also allows control of the detector temperature to study detector performance at different temperatures.

Resolution results of both detectors (serial numbers P3488B and P3489B) are shown in Table 1. Depletion voltage was determined by monitoring the peak shift of ^{57}Co energies when the detector is under increasing reverse biases. Above the depletion voltage of 4000 volts, the resolution represented by full width at half maximum (FWHM) and full width at tenth maximum (FWTM) for ^{60}Co (1.33 MeV) and ^{57}Co (122 keV) sources was measured. The electronic noise was also measured using a precision pulser. It was observed that increasing the reverse bias deteriorates the detector resolution, which is largely due to the increase of leakage current. The relative efficiencies of both detectors are around 100% which is in agreement with their dimensions and mass.

Table 1. Detector resolution for the two SEGe detectors fabricated with the standard SiOx passivation technique.

Detector number	Bias (kV)	RESOLUTION FWHM/FWTM (keV) ^{60}Co		^{57}Co		Pulser	P/C	Eff.
P3488B	4.0	2.05	3.93	1.29	2.33	1.18	72.9	110%
P3489B	4.0	2.12	4.08	1.27	2.35	1.18	73.1	99%

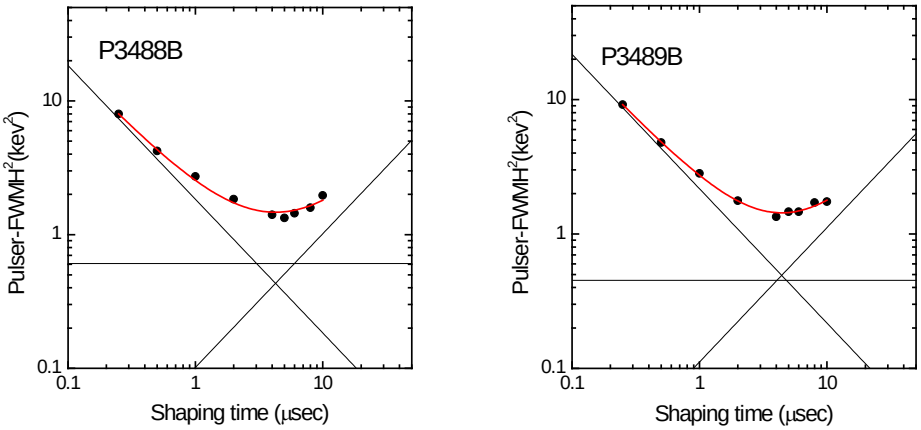

Figure 2. Noise analysis of the detectors (P3988B and P3989B) fabricated with the standard SiOx passivation technique. Detector noise (i.e., pulser FWHM) as a function of shaping time was measured at 93 K.

In radiation measurement it is a major challenge to reduce noise and amplify signal strength, thus improving the signal-to-noise ratio. The sources of electronic noise in spectroscopic measurements fall into three main categories: series noise, parallel noise, and *1/f* noise. The contribution of series noise as a fraction of the signal related to detector capacitance is inversely proportional to the square root of shaping time as defined by a semi-Gaussian shaper. Parallel noise associated with detector leakage current is proportional to the square root of shaping time. The *1/f* noise component is independent of shaping time (Knoll, 1999). The term *1/f* noise is a category of noise believed to be caused by many factors including electrical contacts and the intercontact surfaces. Although the physical mechanism of *1/f* noise is still an open question, an inversion layer across the intercontact surface can introduce a profound contribution to the *1/f* noise, which may affect detector resolution and introduce surface leakage current as well.

The above analysis gives us the three components of contribution to the noise FWHM. Squaring the measured pulser FWHM gives:

$$FWHM^2 = \frac{k_1}{\tau} + k_2\tau + k_3 \qquad (1)$$

Where k_1 k_2 and k_3 are fitting parameters, and τ is shaping time. The pulser FWHM was measured as a function of shaping time from 0.25 to 10 μsec for both detectors at several temperatures. The data (pulser-FWHM^2) were fitted with the above equation from a nonlinear least squares method. Typical results are shown in Figure 2 for both detectors at 93 K. The three components of the noise are also individually shown in the figure as direct lines. It was found that both detectors had similar noise characteristics at 93 K. The fitted parameters k_1, k_2 and k_3 were 1.83, 0.10, and 0.61, respectively, for the detector P3488B; the fitted k_1, k_2 and k_3 are 2.17, 0.11, and 0.45, respectively, for the detector P3489B. Therefore, the k_3 parameters representing the *1/f* noise contribution were between 0.4 and 0.6 for the detectors fabricated with the standard SiOx passivation technique. Further increase of detector temperature above 98 K would increase the detector leakage current, which would significantly increase the contribution of parallel noise, while the series noise and *1/f* noise would remain nearly unchanged.

To test the SiOx passivation method for ruggedness, three tests were performed on the detectors: rapid thermal cycles, atmospheric aging, and pump and bake. Plots of leakage current as a function of reverse bias at each stage of

tests for one of the devices P3489B are shown in Figure 3. The other device (P3488B) showed similar results but to a different degree. For the experiments, the device P3489B was removed from its CP-5 vacuum cryostat and five rapid thermal cycles from 87 K to approximately 300 K were performed. The leakage current worsened moderately after the five thermal cycles increased from 0.07 nA to 0.15 nA at 4000 volts reverse bias, suggesting that the passivant may be damaged to some extent by the fast thermal expansion and contraction processes. Then, the device was placed in a nitrogen-purged cabinet at room temperature for four weeks of aging. The subsequent measurement showed that the leakage current increased to a large degree, which made the device reinstallation for further resolution tests meaningless. Therefore, the intercontact surface was etched with nitric acid-based solution to remove the old passivant, and then repassivated using the standard technique to form a new SiOx film. The subsequent leakage measurement showed that the leakage current improved significantly. The device was then mounted into a CANBERRA 7500SL Slimline vacuum cryostat for a pump and bake test. After an overnight pump and bake at 100°C, the leakage current remained unchanged. These results led us to the conclusion that the standard SiOx passivant is susceptible to atmospheric treatments or contamination, which may cause an increase of leakage current through a surface channel, while the thermal variation for the device kept in a vacuum cryostat does not affect the performance of the device.

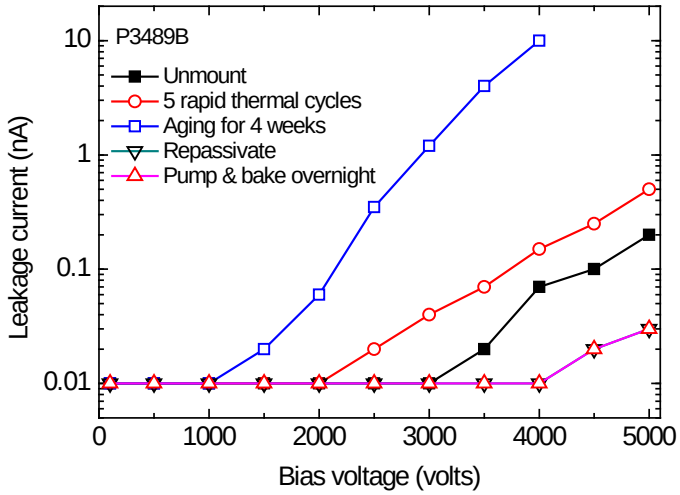

Figure 3. Leakage current as a function of reverse bias under various conditions investigating the passivation stability of the standard SiOx film.

Development of WCO passivation technique

In the next major phase of the research, the goal was to grow a native oxide passivation film directly on HPGe detector surfaces. By definition a native oxide is directly grown on the germanium surface with a resulting decrease in the density of unconsumed germanium bonds (dangling bonds) which act as charge generation sites. However, the literature suggests that the GeO_2 compound can have two phases, one is solvable in water/HF and the other is not (Valyocsik, 1967). It is imperative that only water-insolvable GeO_2 film is grown on detector surfaces so that it may withstand the environmental conditions in surrounding air. The newly developed WCO technique uses a hydrofluoric acid/oxidizer mixed solution. A miniscule amount of oxidizer is added into a large amount of HF acid solution, so that only a water/HF insoluble GeO_2 phase is grown on Ge surfaces, and the water soluble phase is prevented. Several experimental efforts were made to optimize the growth conditions for the native GeO_2 passivation. Different oxidizers with different concentrations mixed with HF acid at room temperature were considered and tested as the reaction solution. By optimizing the growth conditions, a technique was developed to produce natively grown passivation films on HPGe.

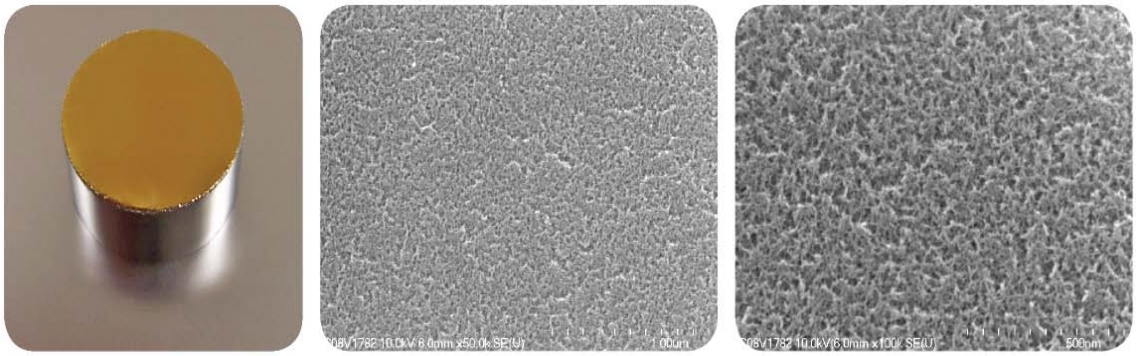

Figure 4. Passivation film grown on HPGe and its scanning electron micrographs. The film was created by a mixture of hydrofluoric acid and a specially formulated oxidizer using the WCO technique.

Figure 4 shows pictures of a germanium oxide film with gold-like color, which was natively grown on a HPGe surface by the WCO technique. The SEM (scanning electron microscope) topography of the film surface in high resolution demonstrates that the oxide films produced by this WCO technique are very dense, homogenous, and for the most part, defect-free. No porous or fissure structures are found on the passivated surface, which greatly helps to make detector surfaces impervious to ambient atmospheric conditions. Note that the naturally occurring native germanium oxide which results from exposure to atmospheric moisture and oxygen is an inferior compound, which is not only highly non-stoichiometric, but also contains the soluble form of oxides. Therefore, it is very important to form a stoichiometric and defect-free oxide film on HPGe surfaces for passivation. To determine the composition and chemistry of the oxide film, an X-ray Photoemission Spectroscopy (XPS) analysis was performed on the oxide samples. Figure 5 shows the spectrum of XPS analysis of the film. The deconvolution of the peak profile indicates two compositions in the data including metallic germanium and its oxides. The chemical shift of the oxide peak in binding energy with respect to the metallic germanium peak suggests that the oxide film is in the stoichiometric form of GeO_2. As the growth solution used contains a large amount of HF, the grown oxides are the stable HF-insoluable GeO_2 phase. The growth of the stable GeO_2 film suggests that the oxide film is of high quality and the expectation is that a successful detector passivation can be fabricated by the new WCO technique.

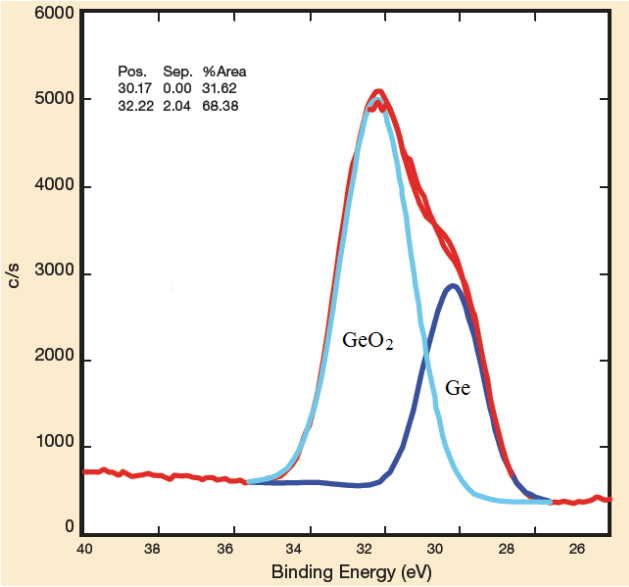

Figure 5. XPS analysis of the film indicating that the germanium oxide is of the form GeO_2 which is the desired stoichiometry.

Figure 6. Fabricated detector with the WCO passivant (left), and assembled cryostat and electronics (right).

To investigate the performance of the GeO_2 passivant, a small SEGe detector was fabricated utilizing the WCO technique. A P-type HPGe crystal (detector No. P84648A) with a net impurity level below 2.00×10^{10} cm^{-3} and a mass of 547 grams was used as the starting raw material for the detector fabrication. After fabricating the inner boron implanted contact and outer lithium diffused contact, the intercontact surface in the groove region was exposed to the pre-mixed WCO growth solution. The groove presented a gold-colored GeO_2 film, which is insoluble in water and hydrofluoric acid as previously discussed. The completed detector along with the assembled electronics and a CANBERRA 7500SL dipstick cryostat where the detector is installed is shown in Figure 6. Figure 7 shows its leakage current and capacitance as a function of applied reverse bias for the detector at 87 K. The leakage current is below 0.01 nA and remains flat to the range of 5000 volts. The depletion voltage is about 2300 volts, and the capacitance after full depletion is about 23 pF. This result suggests that the new WCO passivation technique provides very low leakage current. The WCO passivant not only successfully blocks the current flow between electrical contacts, but also generates few or no surface states in the band gap which may otherwise facilitate thermal excitation of electrons and induce leakage current.

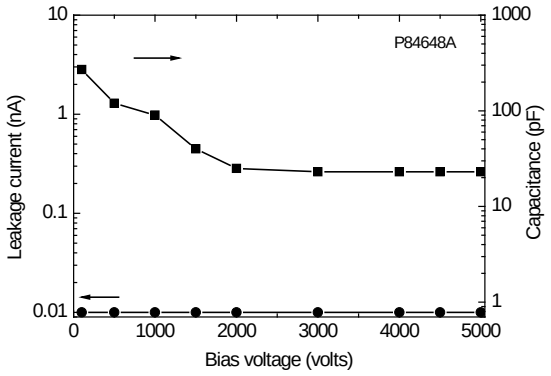

Figure 7. Leakage current and capacitance as a function of applied reverse bias from 0 to 5000 volts. The detector was fabricated with the developed WCO technique.

Table 2 shows test results of the detector (P84648A). Increasing the reverse bias appears to slightly improve the detector resolution. At 3 kV bias, the FWHM of ^{60}Co at 1.33 MeV and ^{57}Co at 122 keV are 1.72 keV and 0.88 keV, respectively. At 3 kV bias, the detector efficiency is 21%, which is a little less than what expected based on the dimensional size of the detector. This is possibly due to the thick Li layer (0.62 mm) for this detector, which decreases its active volume and thus slightly reduces its efficiency. Following the above tests, the detector was warmed up to room temperature for a thermal cycle test. This was done to determine the performance stability in case of a power failure or long term storage at room temperature. As shown in Table 3, the detector maintained its good resolution after the thermal cycle. To check stability under prolonged operation, a 4.5 kV bias was applied overnight. Subsequent measurements with ^{57}Co and ^{60}Co sources indicated that the detector resolution did not deteriorate, suggesting that the detector performance can remain stable for extended periods of operation. Finally,

the detector was kept in the cryostat at room temperature for three months; the next measurement at 3 kV reverse bias showed that the detector's resolution and efficiency was maintained.

Table 2. Detector evaluation for detector P84648A passivated with the developed WCO technique.

Bias (kV)	RESOLUTION (keV) ^{60}Co	^{57}Co	Pulser	P/C	Eff.
2.5	1.76 3.23	0.88 1.64	0.73	52.9	20.9
3.0	1.72 3.19	0.88 1.64	0.73	53.9	21.0
3.5	1.73 3.14	0.85 1.56	0.73	54.0	22.2
4.0	1.74 3.18				22.4
4.5	1.71 3.16				22.5
5.0	1.71 3.14				22.4
Thermal cycle					
4.5	1.70 3.13	0.88 1.62	0.76	55.3	23.9
Overnight bias					
4.5	1.71 3.16	0.90 1.68			
After 3 months for the cryostat at room temperature,					
3.0	1.74 3.24	0.89 1.72	0.77		21.6

With a collimated ^{241}Am source, measurements were made of the FWHM of the 59.5 keV peak at different locations along the side of the detector from the grooved end to its front window. The measured resolution at the back edge of the detector where the intercontact surface with the WCO passivant is located was comparable to those at other positions of the body and its front window. This result further confirms that there were no significant surface charge states or a surface inversion layer around the back end which would otherwise affect the device's charge collection process deteriorating the resolution.

In Figure 8, the results of a noise analysis of the detector are plotted. The FWHM of the pulser was measured for the detector as a function of shaping time from 0.5 to 10 μsec. The data were fitted with Equation (1) via a nonlinear least-squares method. The fitted parameters k_1, k_2 and k_3 were 0.65, 0.02, and 0.37, respectively. As discussed previously, these values of k_1, k_2 and k_3 are associated with detector's capacitance noise, leakage noise, and *1/f* noise, respectively. Although this detector has a relatively low capacitance because of its size as compared to the above two large (100% relative efficiency) detectors fabricated with the standard SiOx passivation technique, it showed a very low leakage current noise and *1/f* noise as well.

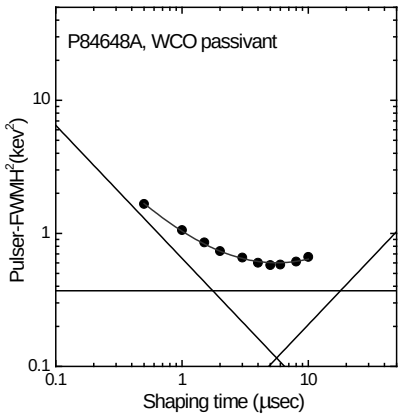

Figure 8. Noise analysis of the detector passivated with the WCO technique.

CONCLUSIONS AND RECOMMENDATIONS

Two large-volume (~100% relative efficiency) SEGe detectors have been manufactured using the standard SiOx passivation technique. Baseline data were established by characterizing each detector using CANBERRA standard test procedures which include the measurement of relative efficiency, electronic noise analysis, and resolution measurements. Testing the current SiOx method for ruggedness with thermal cycles, atmospheric aging, and pump/bake, suggest that SiOx film is subject to atmospheric treatments and contamination which may introduce a surface channel that results in increased leakage current. Since the surface characteristics of high-purity germanium can be influenced both by the net impurity concentration at the intercontact surface and by local crystallography, the same detector elements will be used throughout our development efforts to ensure a solid comparison between passivation techniques.

For a preliminary investigation, a small germanium detector (~25% relative efficiency) was successfully fabricated with the newly developed WCO passivation technique. The detector showed very low leakage current and excellent noise properties. The advantage of the WCO technique is that it involves only a wet-chemical process which is convenient for large-scale production. Immediately after etching the intercontact surface, an in-situ growth of the passivation film is easily accomplished with the surface exposed to a pre-mixed growth solution. Since the device is not transferred from wet to dry chemistry, this greatly minimizes the surface exposure to most contaminants including water vapor, oxygen, and organics that are present in the surrounding environment, Natively-grown oxides produce fewer electrical surface states by taking advantage of the natural tendency of native oxides to passivate the dangling bonds of surfaces better than other materials. The test results demonstrated the effectiveness of the new WCO technique in producing SEGe detectors with the following important characteristics: very low leakage current, excellent noise properties, ability to withstand thermal expansion and contraction while maintaining physical and chemical properties, maintenance of good measurement resolution after thermal cycling, stability over a long period of operation, and stability over long time storage in cryostat.

Current ongoing efforts in the research include studying the device performance for the WCO passivation technique being applied to large volume (~100 % relative efficiency) SEGe detectors. The compatibility of the WCO passivation with the geometry and configuration of electrical contacts will also be investigated to achieve the best detector performance and reliability. Further evaluation of the natively grown oxides using the WCO technique will be to analyze the inherent noise contribution from the surface and compare it with that of SiOx passivated surfaces. The sputtered film techniques will be developed later in this project.

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