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Wet chemical treatments of high purity Ge crystals for γ -ray detectors: Surface structure, passivation capabilities and air stability



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HIGHLIGHTS

- Different surface passivations were applied to HPGe by wet chemical methods.
- New chemical bonds were characterized by FTIR and XPS.
- Air stability: hydride and sulphide treatments display the best oxidation resistance.
- I-V measurements: all the treatments provided efficient passivation.

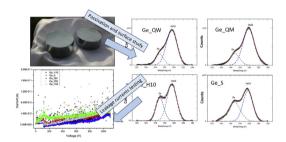
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G R A P H I C A L A B S T R A C T



ABSTRACT

Aiming at the production of HPGe diodes for γ-ray detection, surface passivation of the pristine Germanium surface is pursued by treatment of freshly etched, highly reactive Ge (100) surface by different chemicals, to obtain chemisorbed species with sufficient insulating properties for allowing high voltage application (up to 1100 V) with low leakage currents (lower than 30 pA). (100) surface termination of Ge crystal with hydride, methoxide, and sulphide is carried out by wet chemical treatments using suitable reactants. The chemical composition of the newly formed monolayers is investigated with regards to the nature of chemical bonding with Ge atop atoms. To this aim Fourier Transform Infrared Spectrometry (FTIR) and X-ray Photoelectron Spectroscopy (XPS) were used; the performance as dielectric layer of each native Ge compound/complex is measured directly from I-V measurements of a HPGe diode. Atomic stability of each surface layer is monitored detecting structural changes after air exposure by XPS and FTIR spectroscopies and by relevant leakage current variations.

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1. Introduction

The mature technology of Ge crystal-growth combines the donor/acceptor loading with precise doping levels and the extremely low net-impurity level reachable and it has been exploited since many decades for the fabrication of γ -ray detectors based on high purity Ge crystals (HPGe) with unsurpassed energy

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resolution with respect to scintillator detectors. For several years, this niche of application has been almost the only one where germanium was considered as leading material. Recently, the increasingly demanding miniaturization of electronic devices reached the intrinsic limit to the physical nature of silicon and a renewed interest in SiGe and Ge-based MOS-based devices can be perceived, as shown by literature appearing on this topic [1,2]. Ge displays higher mobility of carriers and lower bandgap than silicon, nevertheless has the remarkable disadvantage of a less efficient surface passivation. The GeO_{X} native oxide, composed of the unstable GeO and hydrosoluble GeO_{2} [3,4], does not compete with the high stability, ease of formation and thickness control of SiO₂.

In the specific field of γ -ray detectors, proprietary passivation layers are used, whose dielectric performance is especially suitable for charge collection from the full active volume of the detector. In spite of this, recent studies reported that remarkably thick dead layers, where charge collection is hampered by distortions of the electric field [5], were found in commercial HPGe detectors [6]. Thus, the research was oriented towards the topic of passivation layers with low surface resistance to inhibit leakage currents, but at the same time not inducing thick dead layers. Many authors performed important work devoted to Ge surface treatments and to structural and electrical characterization of as-grown top layers; treatments studies included sulphidation [7-9], controlled oxidation [10], and atomic layer deposition [11]. Nevertheless, it is still an open issue the application of surface passivation to improve the performances of HPGe detectors, like leakage currents reduction and energy resolution enhancement. In comparison with similar performances of Ge-based devices for microelectronics, this argument has scarcely been explored.

In this work, the results of different wet chemical treatments for the surface passivation of an HPGe γ -ray detector are reported, giving particular attention to surface chemical interactions with top Ge atoms and consequent modifications of the I–V characteristics of the diode itself. The structural evolution of top surface layers with focus on the originated chemical bonds is investigated by IR spectroscopy in Horizontal Attenuated Total Reflectance mode (HATR) and by X-ray Photoelectron Spectroscopy (XPS). The features of the newly generated bonds have been singled out by the electrical response of a working HPGe diode, in order to check the effectiveness of the applied chemical treatment to block charge carriers loss across the inter-electrodes surface of the diode. Moreover, aging tests for stability evaluation are carried out by exposing the samples to ambient air for one month.

2. Experimental

Germanium (100) wafers, 2" in diameter and 500 µm thick, were purchased from Umicore Ltd (Belgium, Olen) and preliminary polished by manual lapping with a slurry of bidistilled water (BDW) and alumina abrasive grains, with decreasing grain size from 30 µm to 3 µm. After each polishing step, the wafer was washed in ultrasonic bath with BDW to allow complete removal of alumina grains. The clean, mirror-like wafer was cut in small slabs, about $15 \times 15 \text{ mm}^2$, washed in BDW and ultrasonic bath, rinsed several times in BDW, acetone and isopropanol. These Ge samples were used for XPS measurements, while for HATR-IR measurements the Ge crystal plate (entry face 45°, 20 reflections) was used as dispersing element in HATR. FTIR measurements were performed using the spectrometer Jasco 660-plus. The spectra were recorded with 4 cm $^{-1}$ of resolution. For electrical measurements, an n-type HPGe diode, with planar geometry (thickness 21 mm, diameter 39 mm) was used (fabricated at the Laboratori Nazionali di Legnaro).

Chemicals (Carlo Erba Reagents, analytical grade) used for

treatments were hydrogen peroxide H_2O_2 at 30%, hydrofluoric acid HF at two concentrations 39.5% and 50.0%, nitric acid HNO₃ at 65%, ammonium sulphide (NH₄)₂S at 20% and methyl alcohol CH₃OH. A brief summary of the adopted treatments and methods is reported in Table 1.

For HATR measurements, the spectrum of the Ge crystal plate immersed in H_2O_2 30% for 2 min, rinsed thoroughly in BDW, then dried with N_2 is used as background and reference.

The reference sample for XPS was prepared by immersion in HF 10% for 2 min, rinsed in BDW and dried with N_2 blow (label: Ge_ref).

The treatment commonly adopted as a first step in the fabrication of HPGe γ -ray detectors was applied as follows: (i) etching in mixture of HF:HNO $_3$ 3:1 (volume ratio) for 3 min, (ii) etch quenching with excess BDW, (iii) final rinse in BDW and N $_2$ drying (Ge_QW). The approach used by Gurov [12] for treatment of HPGe detectors was also carried out by repeating the same etching in HF/HNO $_3$ but using methanol for quenching instead of BDW; the sample was blown with dry nitrogen (Ge_QM). The procedure for sulphur passivation was similar to previously reported ones [7,8,13,14]: the crystal was etched in HF 2% for 5 min, rinsed twice in BDW and immediately transferred in hot (NH $_4$) $_2$ S solution for 20 min at 60 °C; then it was rinsed three times in BDW and blown with N $_2$ (Ge_S).

For the H termination, two procedures were adopted [15–17]: the crystal was etched in HF 10% for 2 min and then rinsed in BDW. This operation was repeated five times; afterwards the crystal was blown with dry nitrogen, leading to low H termination (Ge_H10). The second procedure, called high H termination (Ge_H50), consisted in a single etching in HF 50% for 5 min, followed by thorough rinse in BDW and blowing. These two approaches were supposed to work with different effectiveness in originating surface Ge—H bonds; indeed previous papers pointed to a partial native oxide removal after HF treatment, irrespectively of the concentration, treatment time or number of repeated cycles [8,14,18].

Photoelectron spectroscopy measurements were performed using an Al K α unmonochromatized source (1486.7 eV) at a base pressure of 10^{-9} Torr. The photoelectrons were analysed by a cylindrical hemispherical analyser (CHA) operating at a pass energy of 58 eV or lower.

For the electrical measurements the HPGe diode was put in a cryostat after each chemical passivation treatment, pumped down to a pressure lower than 10^{-3} Pa, cooled down to the liquid nitrogen temperature and its p—n junction properties were tested by reverse-biasing the diode at increasing voltage up to 1100.0 V and measuring the reverse leakage current. The main contribution to the leakage current originated from surface conditions related to the different chemical treatments, while the bulk contribution was negligible. The measurements were carried out by means of a Keithley 237 source-measurement unit, which can measure dc currents as low as 0.01 pA. In order to minimize the effects of parasitic currents and capacities on the measured current, triaxial cables were used to connect the unit to the diode.

3. Results and discussion

3.1. Infrared analyses

In Fig. 1 the spectra of the Ge crystal after immersion in HF 10% (Ge_H10) and 50% (Ge_H50) for different times, are shown. The components with negative absorption at about 3250 cm⁻¹ and 1480 cm⁻¹ can be ascribed to the removal of Ge-OH hydroxyl groups, which are formed during hydrogen peroxide immersion, according to literature data [19,20]. Other oxidation products are not detected: GeO₂ is highly soluble in water and dissolves as soon

Table 1Summary of applied chemical treatments.

Sample	Chemical treatment	Notes
Ge_ref	HF 10% (diluted)	2 min
Ge_QW	Etching 3:1 (vol) with HNO ₃ (65%):HF (39.5%)	3 min etching time, quenching in BDW
Ge_QM	Etching 3:1 (vol) with HNO ₃ (65%):HF (39.5%)	3 min etching time, quenching in CH ₃ OH
Ge_H10	HF 10% (diluted), BDW, 5 cycles	2 min dip time in HF
Ge_H50	HF 50% (concentrated)	5 min
Ge_S	HF 2%, (NH ₄) ₂ S 60 °C	2 min dip in HF, 20 min in (NH ₄) ₂ S

as it is produced. The more stable GeO, which should be observed at about 770 $\rm cm^{-1}$ [21,22], is not visible, probably because of the low detector sensitivity at this particular range of wavenumbers. Other components due to surface adsorbed water are visible as negative absorption at 3500 $\rm cm^{-1}$ and 1650 $\rm cm^{-1}$.

The sharp peak at about 2015 cm⁻¹ indicates the formation of germanium hydride [18] and its intensity increases with treatment times up to 3 min; the longer 5 min treatment does not induce further increase, suggesting that a saturation is reached in hydride termination of surface dangling bonds. On the contrary, diluted hydrofluoric acid (10%) does not apparently induce appreciable surface changes, even for repeated HF/H₂O immersions, thus indicating incomplete surface coverage of the Ge crystal, as already reported by Bodlaki in previous work [14], or difficult removal of Ge-OH bonds formed during immersion in H₂O₂ and of native GeO oxide, which hinder hydride surface modification. Interestingly, when the crystal is immersed in the HF 50% bath, after about 2 min it starts to change in colour and it appears dark reddish. As soon as it is plunged into BDW for rinsing, the red shade vanishes and the classic lustre, silvery glance reappears. In literature there is no evident trace of this red compound, but the intensive nature of the treatment and previous literature on HF etching of Ge points to the formation of a transient oxyfluoride germanate [23,24], that should be readily dissolved during the treatment but can remain as adsorbate species in case of absence of stirring, as in the present treatment.

Spectra of Ge crystal after etching in HNO₃/HF 3:1 mixture and quenched in BDW (Ge_QW) or CH₃OH (Ge_QM) are shown in Fig. 2. The signal of Ge—H is evident in both spectra at 2010–2015 cm⁻¹. It must be noticed that the low signal/noise ratio in other spectral regions hampers the observation of possible signals due to Ge–O, Ge–OCH₃ or Ge–OH. As a matter of fact, though etching time has

been purposely kept as short as possible (only 15 s), the crystal size and shape are significantly modified by the etching treatment, which removes about 20 µm/min in this concentration ratio [25]. Hence, possible spurious effects on the spectrum features are induced by imperfect background subtraction and only the unambiguous detection of the signal ascribed to Ge—H at about 2010 cm⁻¹ is discussed here. In the case of methanol quenching, previous results reported by Bae and co-workers [26] demonstrated the occurrence of dissociative adsorption of methanol as a result of exposure of clean Ge surface bearing highly reactive dangling bonds to methanol vapours; this fact may justify the weak component from Ge—H bonds. Though our method does not rely on vacuum annealed clean Ge surface, the freshly etched surface atoms are expected to have high chemical reactivity so that the mechanism proposed by Bae may likely be extended to our case.

Unexpectedly, in case of BDW quenching, Ge—H bonds are clearly detected, in spite of low peak intensity due to background subtraction. Indeed, only Ge—OH and Ge—O species resulting from hydroxylation or simple oxidation of surface Ge atoms are expected. A possible interpretation arises from the pioneering work of Harvey and Gatos on the reaction of germanium with aqueous solutions [27]. They considered water dissolved oxygen as electron acceptor, thus behaving as follows:

$$O_2 + H^+ + e^- \rightarrow -O-OH$$
 (cathodic)

$$Ge + H_2O \rightarrow Ge-OH + H^+ + e^-$$
 (anodic)

The -O-OH moiety represents the surface $\equiv Ge-O-OH$ intermediate which can evolve to soluble metagermanic acid. The presence of vicinal Ge radicals may concurrently lead to hydride and hydrosoluble GeO_2 through the reaction:

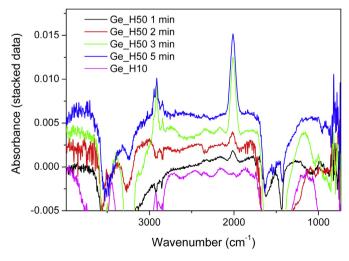


Fig. 1. HATR-IR spectra collected from Ge crystal treated with HF 10% (Ge_H10) and 50% (Ge_H50) for different times. Data are stacked on the vertical axis.

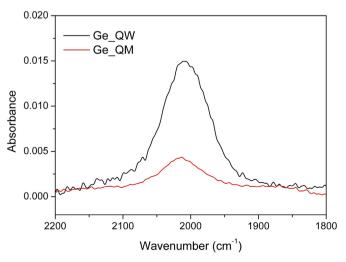


Fig. 2. HATR-IR spectra of samples Ge_QW and Ge_QM.

 $Ge + Ge-O-OH \rightarrow Ge-H + GeO_2$

More recently, Steinert and co-workers [28] studied in detail the mechanism of silicon dissolution in HNO₃ rich HF/HNO₃ mixtures, as the one used in the present case, and using XPS analyses they revealed a surface termination with Si–H bonds, without Si–O nor Si–F bonds. This behaviour is explained in terms of divalent electrochemical dissolution, where nitric acid injects holes on the silicon surface atoms (oxidant action) thus making it susceptible of nucleophilic attack from HF or HF₂ species. Consequently, a persistent hydride termination is present on silicon surface and hydrogen is released as reduction product. The proposed mechanism may apply also to the case of germanium etching in nitric/hydrofluoric acids mixtures, though remarkable differences in the etching behaviour of the two elements are known since long time [23].

The spectrum (not reported) of the sample treated with ammonium sulphide Ge_S does not show specific features with respect to the reference sample immersed in H_2O_2 30% for 2 min, rinsed thoroughly in BDW.

3.2. XPS measurements

We collected XPS measurements at the Ge 2p and 3d core level photoemission spectra l region. The Ge(2p) region of the XPS spectrum is more surface sensitive than Ge(3d) band owing to the smaller mean free path pertaining to Ge(2p) core level photoelectrons. Hence, possible changes in oxidation states of Ge top atoms should be better evidenced by the Ge(2p) band structure evolution. In the reference sample, Ge_ref, the Ge 2p peak is at 1217.2 eV, in good agreement with previous assignments [14,22,29]. However, the peak cannot be fitted with a single contribution and a second, weaker component, which can be ascribed to GeO, is found at 1218.6 eV [18,29]. Also in the Ge_H10, Ge_QW and Ge_QM samples two components are present, as shown in Fig. 3, where the Ge 2p regions are reported, with relevant peaks deconvolution. The presence of GeO suboxide, even after repeated cycles of HF/H₂O, was detected by several authors and discussed by Bodlaki [14]; clean Ge surfaces for subsequent thin films deposition or epitaxial growth require UHV flash annealing of the Ge wafer at temperatures as high as 1000 K [4]. The relative amount of this residual suboxide or, conversely, the surface coverage with Ge-H bonds evaluated by different authors are not in agreement, in spite of applying the same procedure to remove the native oxide layer. This fact was attributed to different grades in the used reactants, either semiconductor grade or analytical grade, and also traced back to the brief lapse of time between the exposure to ambient air and the insertion in the analysis chamber, though much care has been devoted to blow inert gas over the sample during this operation.

As for the relative amount of GeO with respect to elemental Ge, it can be observed that for samples Ge_ref (data not reported) and Ge_QM the ratio between the integrals of the two components Ge:GeO is quite similar (about 7.1). The relative experimental error on the peak amplitude has been evaluated from the peak to baseline ratio and is about 10%, hence the error on the ratio between integrals of each component is in the same order of magnitude. The ratio Ge:GeO further increases up to 8.4 in the sample Ge_H10, thus evidencing a higher efficiency in the suboxide removal, resulting from repeated cycles HF/H₂O, proposed by Deegan [17], instead of a single dip in HF as done in the case of Ge_ref.

A different behaviour is found for the sample Ge_QW, which displays a much higher amount of the component ascribed to GeO or GeOH species, as shown by the remarkable Ge:GeO ratio reduction down to 2.6. In this case, the etching mechanism proposed for discussing the FTIR results may be recalled: the atop Ge

surface, as-etched, is abruptly exposed to flushing water, thus promoting the partial saturation of surface radical sites by hydroxyl groups or bridging oxygen, though also Ge—H surface bonds are present as revealed by FTIR measurements. In the case of methanol quenching, the reactive surface promotes dissociative adsorption, as previously proposed [26], leading to Ge—H and Ge-O-CH₃ covalent linkages, which provide effective shielding against oxidation, according to the low content of GeO shown by XPS measurements in the sample Ge_QM (Ge:GeO ratio about 7).

The assignment of the component at higher binding energies is more difficult for the sample Ge_S and a superposition of signals from residual oxide, GeO, and GeS_2 , resulting from sulphur bridging groups, can be envisaged. Maeda and co-workers [30] proposed that saturation of surface sites of Ge(100) is achieved by coverage of one sulphur atom per surface Ge atom GeS component at about GeS about GeS component at about GeS component at about GeS component at about GeS and GeS by the appearance of GeS peak (inset of GeS by with a single spin-orbit doublet with energy separation of 1.2 eV [13,30].

Some interesting observations can be derived from C1s spectra reported in Fig. 4, which can provide indirect confirmation of previous description of differently passivated surfaces. The sample Ge_ref displays the more intense carbon peak, as it was expected on the basis of the absence of any applied degreasing procedure and of the relatively weak treatment in diluted HF, so that the presence of adventitious carbon is relevant. However, the repeated cycles of HF/ H₂O applied for the preparation of Ge_H10 sample do not seem to be effective in complete removal of carbonaceous species, as proved by the still intense C1s signal. On one hand, this behaviour is in agreement with the results of Rivillon and co-workers [18], who ascribed this contribution to the higher hydrophobicity and, in turn, higher affinity towards adventitious hydrocarbons of the H-terminated surface. On the other hand, very recently Seo and co-workers cast doubts on this interpretation [31] and they suggested that the surface carbon species are so tightly bound to Ge atop atoms that the repeated dip cycles in HF are not enough to fully remove carbon contamination. On the basis of Auger spectroscopy data, Seo claims that the treatment of Ge in solution of ammonium hydroxide (NH₄OH) can indeed drastically reduce carbon contamination owing to best solubility of the reaction by-products induced by complexation with ammonia. This reasoning can indeed be supported by our XPS data collected on Ge_S sample, which displays the lowest content of surface carbon, indicating a possible contribution to effective Ge cleaning due to the presence of traces of ammonium hydroxide in equilibrium with un-buffered ammonium sulphide during the Ge_S sample preparation. Moreover, the highly polar nature of the newly formed Ge-S bond (dipole moment is as high as 1.3 Debye vs 0.2 Debye of Ge-H bond [7]) accounts for the lower affinity towards almost apolar carbonaceous species, so that post-contamination with carbonaceous species is inhibited. Carbon is still present in the case of Ge_QM, where surface grafting of Ge-OCH₃ methoxy groups can account for C presence, besides residual contamination from ambient air. The case of Ge-QW, where about the same carbon content is found, is more difficult to interpret. However, the possibility that the as-etched surface, bearing reactive Ge radicals, can react with CO₂ dissolved in water or that GeO/Ge-OH terminal groups undergo carbonation from reaction with CO₂ in ambient air cannot be ruled out. It is also worth to remember that FTIR revealed the presence of Ge-H bonds, which have high affinity with carbonaceous species.

3.3. Ambient air stability: XPS study

The Ge2p spectra of samples collected after 1 month of ambient air exposure (relative humidity about 55%) are shown in Fig. 5. The

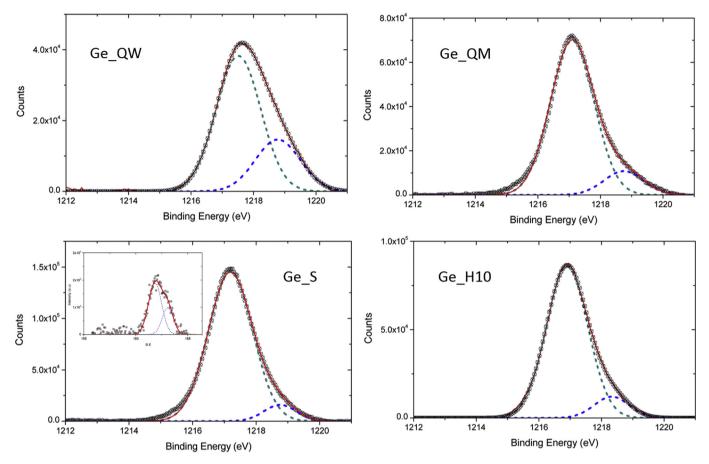


Fig. 3. XPS spectra of Ge2p peak, with corresponding peak deconvolution, for different wet treatments of the Ge surface.

growth of a quite intense component at +2.5-3.0 eV higher binding energy can be observed. This feature can be ascribed to GeO_2 layer formation, in agreement with previously reported data [14,21,22,29]; air exposure firstly gives GeO_x mixed oxides, but after few hours the structure GeO_2 becomes dominant. The GeO_2/Ge ratio is about 1.8 for the reference sample $Ge_ref - single$ HF dip — while for repeated cycles the value is about 2.0 (sample $Ge_ref - single$ HI). In the sample $Ge_ref - single$ HP dip — while $Ge_ref - single$ HP dip — while $Ge_ref - single$ HF dip — wh

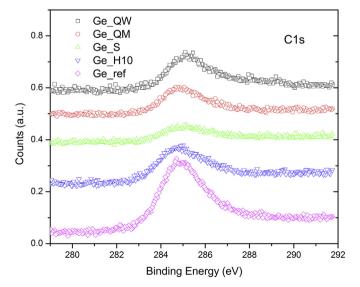


Fig. 4. XPS spectra of C1s region for different wet treatments of the Ge surface.

the highest one and reaches 4.1, leading to the conclusion that the presence of GeO/Ge-OH surface sites is less effective in hampering further oxidation than Ge—H bonds, though a limited amount of H-terminations has been revealed by FTIR analyses.

Quenching in methanol (sample Ge_QM) appears as more "oxidation-proof", since the ratio decreases to 3.7 but still insufficient for our purposes. In case of dissociative adsorption of methanol, the presence on the surface of low polar and hydrophobic Ge methoxide, with methyl external groups, and Ge—H bonds, which can contribute to oxidation resistance in humid air, as evidenced by the low contribution of GeO₂ in the sample Ge_H10, accounts for this behaviour.

The most interesting result concerns the Ge_S sample, which displays the lowest ratio between dioxide and elemental germanium (GeO_2/Ge about 1.3). This could be expected on the basis of the results of Lee and co-workers [22], who explained the stronger stability of S-terminated Ge surface, as compared to H-termination, on the basis of several factors, such as bonding of S with two Ge surface atoms in a (2×1) structure, or formation of a glassy layer of GeS_x . Moreover, recalling the discussion above on the presence of residual adventitious carbon, it can be inferred that a greater surface coverage is achieved in the case of Ge_s sample, owing to the almost complete removal of contamination carbon in alkaline medium, which leads to the maximum exposed area of Ge_s surface sites towards the sulphide reactant. Therefore, a better shielding against oxidation can be offered by the almost continuous layer of Ge_s surface bonds.

3.4. I-V measurements on HPGe diode

In order to test the effectiveness of the surface passivation by the

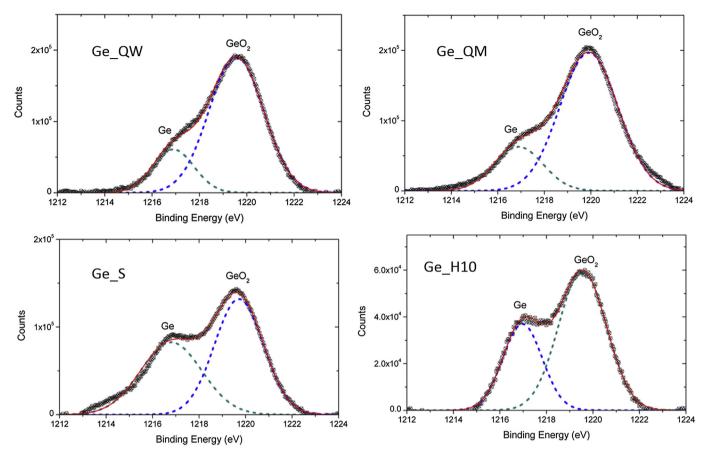


Fig. 5. Ge 2p core-level photoemission spectra with peak deconvolution for each chemical treatment, collected after 1 month of air exposure (RH about 55%).

chemical treatments studied in this work, the reverse leakage current of a planar HPGe diode was measured after each passivation. The resulting I—V data, as obtained by biasing the diode until a maximum applied voltage of 1100 V, are reported in Fig. 6. It can be observed that the reverse leakage current keeps very low in the whole measurement range, even at the highest applied voltage: at 1100 V the current is below 10 pA, for all the chemical treatments. This is an important premise for the application of these treatments

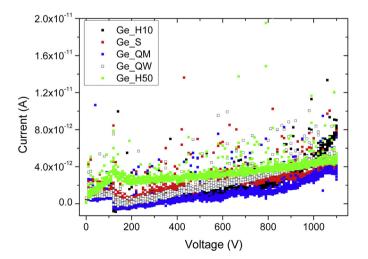


Fig. 6. I–V measurements obtained with HPGe diode after application of different passivation treatments. The kink in the current curves found at 110 V is an instrumental effect due to the change of the measurement range (and then of the measurement circuit) of the Keithley 237 source-measurement unit, occurring when the applied voltage goes beyond 110 V.

as passivation routes of HPGe detectors, wherein a low leakage current is particularly important to assure a good energy resolution in the detection of gamma radiation. These measurements also show that the breakdown voltage of the HPGe diode is well above 1100 V for all the tested passivations, thus assuring the complete charge depletion of the diode volume, necessary for using it as a totally-depleted detector [32].

A more careful look at the curves in Fig. 6 allows to find some small differences: at low voltage, the current of the Ge_H50 diode is the highest, while for the Ge_H10 diode a slightly steeper increase is found in the high voltage region. On the other hand, the diode treated as in Ge_S and Ge_QM shows optimal performance over the entire range, with negligible fluctuations and with a leakage current lower than 4.5 pA. The S-terminated diode was also exposed to ambient air for 30 h (temperature 22 °C, RH 66%) to test the stability of this passivation and the leakage current was measured again. Negligible changes were observed, thus confirming the durability of this passivation on this time scale [14]. These evidences are clues of the different electrical properties of the passivated surfaces, which affect the performance of the diode when used as γ -ray detector, especially energy resolution, efficiency, working voltage and dead layer thickness. The measurement campaign of this detector is still ongoing and the results will be published in a forthcoming paper [33].

4. Conclusions

Different wet chemical passivation methods have been applied to either Ge small samples or HPGe working diode, aiming at the evaluation of effectiveness in minimizing leakage currents and charge carriers loss during HPGe working as γ -ray detector. HATR analysis has been performed to investigate the formation of Ge-H chemical bonds, in case of treatment of freshly cleaned Ge shards in diluted and concentrated hydrofluoric acid. The appearance of Ge—H typical stretching mode occurs in case of dip in concentrated HF, demonstrating that the presence of mixed oxides, GeO and GeO₂, on the native surface can hamper full coverage with Hterminated sites. Treatment of a freshly etched Ge surface with methanol also leads to the appearance of Ge-H band, indicating that dissociative mechanism of the methanol molecule takes place as soon as CH₃OH reacts with highly reactive Ge surface radicals. XPS analyses confirm the results pointed out by HATR as regarding H-terminated Ge surface and allows to appreciate the effectiveness of S-termination and to follow the evolution in Ge surface changes as resulting from exposure to ambient air. Terminations with hydride and sulphide display the best oxidation resistance, suggesting successful inhibition of inter-electrodes leakage currents, which are detrimental for energy resolution of HPGe detector. Our surface treatments show optimal performances as passivating layers, as demonstrated by the ultra-low currents detected after application of voltage as high as 1100 V; this fact may enhance the performance of HPGe γ -ray detectors, as foreseen by preliminary tests ongoing at the LNL laboratories.

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