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TECHNICAL REPORT

Silicon-Based Examination of Gamma-Ray and Neutron Interactions with Solid State Materials

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14. ABSTRACT The objective of the research was to develop a fundamental understanding of the processes by which charge carriers interact in semiconductor materials in order to aid in the development of advanced radiation detection materials. During the first three years of the research, our focus was primarily on silicon, using a relatively well-behaved semiconductor as a material basis from which we can understand those physical principles that can impair the contact behavior and affect the charge transport. That information has been applied to single-crystal cadmium-zinc-telluride (CZT) and lead chalcogenide (PbS, PbSe, PbTe) nanocrystalline solids, with particular focus on the nanostructured materials during the latter two Phases of the work. During the research, we endeavored to develop general techniques by which charge creation is maximized and impediments to its transit are minimized, and to apply those techniques to the most favorable material systems.					
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UNIT CONVERSION TABLE

U.S. customary units to and from international units of measurement *

U.S. Customary Units	Multiply by Divide by[†]	International Units
Length/Area/Volume		
inch (in)	2.54 $\times 10^{-2}$	meter (m)
foot (ft)	3.048 $\times 10^{-1}$	meter (m)
yard (yd)	9.144 $\times 10^{-1}$	meter (m)
mile (mi, international)	1.609 344 $\times 10^3$	meter (m)
mile (nmi, nautical, U.S.)	1.852 $\times 10^3$	meter (m)
barn (b)	1 $\times 10^{-28}$	square meter (m ²)
gallon (gal, U.S. liquid)	3.785 412 $\times 10^{-3}$	cubic meter (m ³)
cubic foot (ft ³)	2.831 685 $\times 10^{-2}$	cubic meter (m ³)
Mass/Density		
pound (lb)	4.535 924 $\times 10^{-1}$	kilogram (kg)
unified atomic mass unit (amu)	1.660 539 $\times 10^{-27}$	kilogram (kg)
pound-mass per cubic foot (lb ft ⁻³)	1.601 846 $\times 10^1$	kilogram per cubic meter (kg m ⁻³)
pound-force (lbf avoirdupois)	4.448 222	newton (N)
Energy/Work/Power		
electron volt (eV)	1.602 177 $\times 10^{-19}$	joule (J)
erg	1 $\times 10^{-7}$	joule (J)
kiloton (kt) (TNT equivalent)	4.184 $\times 10^{12}$	joule (J)
British thermal unit (Btu) (thermochemical)	1.054 350 $\times 10^3$	joule (J)
foot-pound-force (ft lbf)	1.355 818	joule (J)
calorie (cal) (thermochemical)	4.184	joule (J)
Pressure		
atmosphere (atm)	1.013 250 $\times 10^5$	pascal (Pa)
pound force per square inch (psi)	6.984 757 $\times 10^3$	pascal (Pa)
Temperature		
degree Fahrenheit (°F)	[T(°F) – 32]/1.8	degree Celsius (°C)
degree Fahrenheit (°F)	[T(°F) + 459.67]/1.8	kelvin (K)
Radiation		
curie (Ci) [activity of radionuclides]	3.7 $\times 10^{10}$	per second (s ⁻¹) [becquerel (Bq)]
roentgen (R) [air exposure]	2.579 760 $\times 10^{-4}$	coulomb per kilogram (C kg ⁻¹)
rad [absorbed dose]	1 $\times 10^{-2}$	joule per kilogram (J kg ⁻¹) [gray (Gy)]
rem [equivalent and effective dose]	1 $\times 10^{-2}$	joule per kilogram (J kg ⁻¹) [sievert (Sv)]

* Specific details regarding the implementation of SI units may be viewed at <http://www.bipm.org/en/si/>.

[†] Multiply the U.S. customary unit by the factor to get the international unit. Divide the international unit by the factor to get the U.S. customary unit.

ii) Objectives:

The objective of the research was to develop a fundamental understanding of the processes by which charge carriers interact in semiconductor materials in order to aid in the development of advanced radiation detection materials. During the first three years of the research, our focus was primarily on silicon, using a relatively well-behaved semiconductor as a material basis from which we can understand those physical principles that can impair the contact behavior and affect the charge transport. That information has been applied to single-crystal cadmium-zinc-telluride (CZT) and lead chalcogenide (PbS, PbSe, PbTe) nanocrystalline solids, with particular focus on the nanostructured materials during the latter two Phases of the work. During the research, we endeavored to develop general techniques by which charge creation is maximized and impediments to its transit are minimized, and to apply those techniques to the most favorable material systems.

If the electrons and holes can be tracked during their drift through the bulk of the materials, then their passage can be used as a metric to gauge the effect of various material features, such as inclusions, dislocations, and other trapping centers. For CZT, this ability allows one to quantify the relationship between the size and density of defects- such as Te inclusions- and their effect on the charge transport, in terms of the length and strength of the trapping. For quantum-dot solids, the technology allows one to quantify the degree of charge trapping as the size, dispersion, and coordination of the matrix is varied. For silicon, the understanding allows us to develop robust, low leakage current contacts which are suitable for high charge-sensitivity applications.

In principle, nanocrystalline (NC) semiconductor materials provide an attractive material basis because they present a means of: 1) decreasing the underlying material cost by utilizing a solution-based fabrication methodology, 2) increasing the range of candidate materials by including the narrow-gap semiconductors, and 3) increasing the exciton multiplicity upon the impingement of radiation by utilizing multi-exciton generation, qualities that can potentially be utilized to revolutionize the capabilities of radiation imaging instruments.

The research was therefore designed to develop a robust silicon-based detector, aid in the continued material optimization of current wide band-gap single crystal materials while also bringing the next-generation of semiconductor materials, in the form of nanocrystalline (NC) solids, closer to fruition. Higher CZT yields in the short term and large-area high performance PbSe NC sheets in the intermediate term can facilitate the goal of providing inexpensive, high efficiency radiation imagers that can be widely deployed to sense radiological materials.

iii) Status

This Basic Research Project has delivered a radiation detection medium with the world's best room-temperature energy-resolution performance, which fortuitously, is accomplished with a highly efficient medium that can be manufactured cheaply and in large volumes, using solution-based self-assembly techniques.

During the course of the research, we have sought to optimize the charge transport behavior by gaining design control over the electronic structure of the surrounding condensed matter. For silicon, we have reduced the surface leakage current by five orders of magnitude during the research through five different processes, the two most important being: (a) the proper termination at the silicon interface, and (b) the development of an effective gettering recipe. The latter point should be emphasized in order to expedite the development of other semiconductor systems. The difference between a robust, low-noise device recipe and one with poor noise characteristics and variable performance from run-to-run is the degree to which one can getter the defects in the solids that are inherent following material growth. Working with III-V, II-VI, and single crystal solids on various projects, we now investigate gettering near the beginning of the projects rather than after the surface-control procedures because of the importance of the processing step.

In the case of the silicon detectors, the resulting devices, with nanoampere-scale leakage current are presently being commercialized. We have formed a company from the outgrowth of

the DTRA work, have delivered a prototype silicon detector to a potential customer working on rare-isotope beam characterization for nuclear physics studies, and we expect to begin selling the position-sensitive detectors during the middle of 2012.

The experience gained in processing robust, high performance contacts on silicon was applied to CZT, on which low-leakage contact recipes were developed, using Au, In, and Zn. With that processing knowledge, we fabricated position-sensitive CZT-based detectors using the novel serpentine electrode geometry.

Despite these studies into the optimization of single-crystal materials, we previously identified nanocrystalline (NC) methods by which the charge creation can be maximized and the uncertainty in that conversion can be quenched. Focusing primarily on the high density, high Z lead chalcogenide materials, PbSe, PbTe, and core-shell PbSe/PbTe structures, during the last Phase of the project, we were able to increase the monodispersity of the colloidal dispersions, form them into close-packed colloidal solids through either drop-casting or spin-casting, couple the solids to electrode structures, and measure the electrical responses of the devices.

Rather than searching through the universe of possible semiconductor compounds in order to realize favorable behavior, as governed by the atomic number and density, the charge mobility and trapping, as well as the band-gap, each of these properties can be controlled via the geometric design of the colloidal solid, both through the particle size and its spatial distribution. In particular, the band-gap of PbSe can be varied from its value in the bulk state, at 0.26 eV, to over 2 eV, as the particle diameter is reduced below 5 nm; thus, one can realize low-noise room-temperature operation with small particle size. Furthermore, the enhancement of the quantum confinement effect can be used to modulate the phonon-electron coupling, and the information loss due to heat can therefore be controlled; thus, particularly high resolution detectors are physically possible.

For composite materials, the realization of that performance is usually hampered by charge-trapping at the innumerable interfaces that the charge encounters during its drift through the solid. However, we successfully coordinated the colloidal ensemble with a conductive polymer, with which we not only realized good charge transport, but the low-Z coordinating molecules didn't substantially participate in the energy-to-charge conversion, as the high-energy recoil electrons traversed the assembly. As a result, we measured an energy resolution of 0.42 % at a gamma-ray energy of 356 keV (from ^{133}Ba).

During the last few months of the project, we also investigated the solution-based fabrication of CdTe nanowires using a novel technique: vacuum filtration, which allows the rapid, large volume fabrication of active volume (square meters in lateral extent, millimeters to centimeters of thickness). Our initial charge transport and spectroscopic experiments were not as promising as the other methods employed during the research, but the investigation is ongoing.

We completed the development of a delay-line electrode structure, which allows fine position sensing with a minimal number of readouts. We validated the performance of the novel technology on both silicon and CZT in demonstrating that one can propagate the information through 100's and potentially 1000's of (interconnected) strip-line segments, reading out the position information at the ends of the lines. For the delay-line, the actual measurements were far superior to the analytical predictions because the latter didn't consider the slow-mode propagation along the surface of the line, which is induced when a metal-insulator-semiconductor geometry is employed. The effect of the design is that the conductive losses and propagation speeds are low enough that large areas can be deployed in which charge collections on neighboring strips can be readily achieved.

Finally, during the last part of the work, we designed a CMOS-based low-noise current amplifier which uses novel noise cancellation methodologies, the effect of which is to reduce the noise by nearly a factor of ten, compared with the best commercial devices. We are currently in the process of evaluating the patentability of the design.

iv) Accomplishments/ Findings:

In the following sections, we will summarize the results of the work, focusing on the final state of the developments. In Sections 1 and 2, we will summarize the nanocrystalline results because the material system was our focus during the last two Phases. The silicon based work and the CZT process optimization will be summarized in Section 3, and the demonstration of the effectiveness of the delay-line method will be presented in Section 4.

1. Fine Spectroscopy of Ionizing Radiation via a Colloidal Array of Blended PbSe Nanosemiconductors

Abstract

Nanocrystalline semiconductor materials provide an attractive material basis upon which to develop advanced optoelectronic devices because they present a means of: (1) decreasing the underlying material cost by utilizing a solution-based fabrication methodology, (2) controlling the charge and phonon dynamics via geometric control of the colloidal solid, and (3) increasing the exciton multiplicity upon the impingement of radiation by utilizing multi-exciton generation. Lead chalcogenide materials (PbS, PbSe, and PbTe) in particular have favorable properties for their use in NC applications because the large bulk Bohr radii of their excitons (e.g. 46 nm for PbSe) enables strong quantum confinement in relatively large NC structures, and they possess nearly identical and small effective masses of the electrons and holes, advantages which are fortuitous if one extends their applicability beyond optical radiation to highly penetrating ionizing radiation because the high atomic number and mass densities yield a highly efficient detection medium. In this report, we show that an assembly of conductive polymers and PbSe nanocrystals can yield energy resolving behavior, at room temperature, which is comparable to that produced by high purity germanium cooled to liquid nitrogen temperatures. Specifically, an energy resolution of 0.42 % (1.5 keV) was measured at a deposited energy of 356 keV. Furthermore, an evaluation of W , the energy consumed per electron-hole pair created, indicates that the charge-conversion efficiency of the colloidal solid comprised of strongly confined nanostructures is superior to single-crystal materials, which can be attributed to a greater suppression of intraband relaxation processes relative to the exciton creation probability.

1.1. Introduction

Although ionizing radiation can be measured by its conversion into momentum (1), heat (2,3), or scintillation photons (4), converting the impinging quanta directly into charge-carriers offers simple device architectures and, in the case of semiconductor-based detection media, solid-state densities. If one wishes to gauge the precision with which a semiconductor estimates the energy deposited during its interaction with an incident quantum, Fig. 1.1 shows that the energy consumed during the creation of an electron-hole pair, W , is equal to approximately 3 times the band-gap, E_g , the extra energy lost during phonon exchange as the excited carrier de-excites to the band-edge, as illustrated in Fig. 1.2a. For instance, the W value in silicon is 3.66 eV (5,6), compared with a band-gap of 1.12 (7). In fact, the most common materials used to detect ionizing radiation- silicon, germanium, and cadmium-zinc-telluride (CZT)- all fall near the $W = 3 E_g$ line, while the n-VIIB materials, where $n = \text{II, III, or IV}$ (e.g. TlBr and HgI₂) follow the same slope but exhibit better charge-creation statistics, as shown in the green line of Fig. 1.1 (8).

One would prefer that W be reduced to one times the band-gap, as shown by the blue line in Fig. 1.1; that is, to be limited only by energy conservation, resulting in more charge carriers, which can not only enhance the size of the signal but it can reduce the statistical counting noise because more of the incident energy is converted into information which participates in the signal formation. If the variance in the charge population can be reduced by making the charge-creation

process more efficient, then the statistical counting noise can be quenched. For nuclear radiation detectors, the realization of a uniform multi-exciton response would allow one to tolerate relatively large band-gaps because the uncertainty in the energy determination would be more dependent on non-uniformities in the fabrication rather than on simple counting statistics.

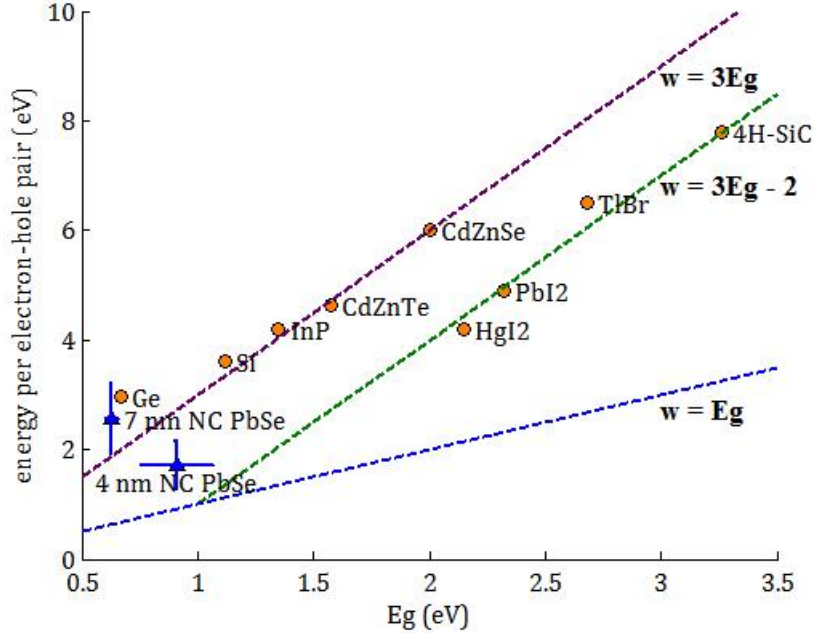


Fig. 1.1. Relationship between the energy consumed per electron-hole pair created, W , and the band-gap E_g for a variety of semiconductor materials used in ionizing radiation detectors (in maroon and green), in relation to the limit imposed by energy conservation (in blue). The data for the common materials is taken from (8) and the references therein, and the measurement of the NC data is described in this report.

These possibilities have been investigated for solar energy conversion, in which impact ionization (II) is used for carrier multiplication (CM) in semiconductor nanocrystals, with the goal of achieving quantum efficiencies limited only by energy conservation. That is, as illustrated in Fig. 1.2b, if the impact ionization rate can be made to exceed the phonon-assisted intraband relaxation rate, then multi-excitons can result.

Initial results, which were reported starting in 2004, by Schaller *et al.* (9-11) and Ellingson *et al.* (12) implied that this could be achieved with PbSe NCs. More recent results have clarified the fact that extrinsic contributions to carrier relaxation contribute to the apparent “multi-exciton signal”, and their removal has resulted in lowered quantum efficiency estimates (13-15). For instance, Klimov’s group at Los Alamos National Laboratory initially reported a best quantum efficiency (QE) of 218 %, for an impinging photon source with energies equal to $3.8 E_g$, where the quantum efficiency is the number of excitons created per impinging photon (9). When they mitigated effects such as degradation of the surface passivation and NC photoionization, both of which can potentially contribute to the CM signature, their group measured a QE of 140 %, for a photon source energy equal to $4.8 E_g$ (13). This reduction may delay or prevent the adoption of multi-exciton-generation (MEG) colloidal solids as solar cells, but more importantly from a research perspective, it points to the need to better understand the CM enhancement mechanism, including the degree to which CM variation is linked to defects and the details of the surface coordination. In fact, as argued by Nair *et al.* (14,15), there remains an inadequate theoretical and experimental understanding of the physics of highly energetic carriers in NCs, so that the relative

rate of impact ionization versus other intraband relaxation mechanisms can be quantified. The data in this report supports the supposition that impact ionization processes become more probable, relative to thermal losses, as the degree of strong confinement is increased.

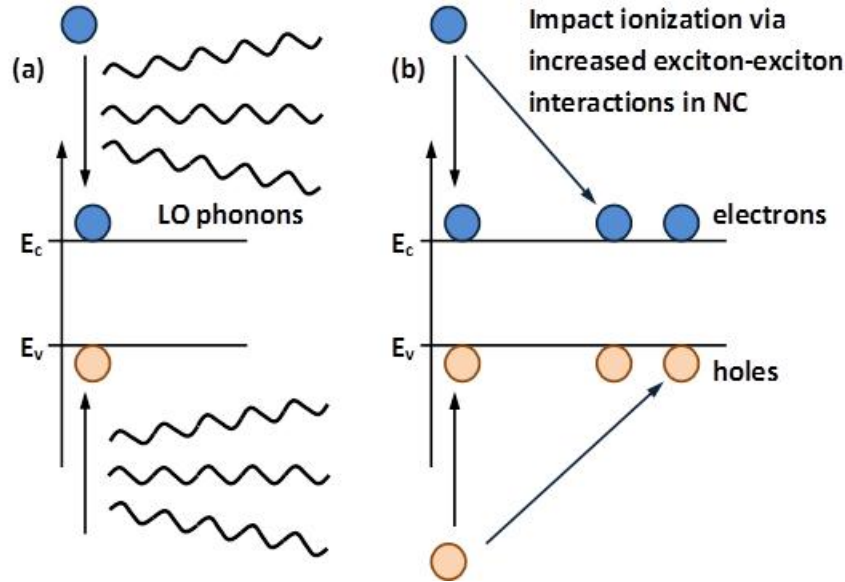


Fig. 1.2. Schematic diagrams of exciton relaxation processes: (A) without CM in bulk PbSe and (B) with CM in PbSe NCs. In bulk semiconductor materials, the excess kinetic energy of the carriers is transferred to lattice vibrations (longitudinal optical (LO) phonon emission); however, in NC solids, multiexcitons can be generated with higher probability via II from a single high energy absorption.

From the perspective of one wishing to apply NC-semiconductors to nuclear radiation detection, this uncertainty in the details which govern the magnitude of CM is not problematic because *even absent CM*, nanosemiconductors provide the means, in principle, to produce high Z , high energy-resolution materials using relatively inexpensive wet-chemical processing techniques. Specifically, Fig. 1.3A shows that when one compares various common single-crystal detection media and the lead chalcogenides under study, PbSe and PbTe in both single-crystal and nanocrystalline form are superior in terms of their combined mass densities and atomic numbers, Z , both of which combine to yield a higher specific detection efficiency.

The nanocrystalline forms of PbSe and PbTe are consistent with some of our current colloidal solids, in which spherical 10 nm PbSe nanoparticles or spherical 5 nm PbTe dots are spun cast into a face-centered-cubic (FCC) nanocrystalline solid with an interstitial para-MEH-PPV (poly[(*p*-phenylenevinylene)-*alt*-(2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene)]) polymer of order 1. In realized detectors, we vary the relative blending of the polymer and NCs such that higher polymer orders are typically employed, and we grow rods and cubes, as well as spheres. Furthermore, the geometry of the solid deviates from a perfect FCC structure to a degree depending on the size dispersion of the colloidal solution; nevertheless, the reduction in densities between the single-crystal lead chalcogenides and the nanocrystalline forms reflects the values that are achieved when the ordering and spacing are optimized for spherical NCs. As shown in the figure, even in nanocrystalline form, the lead chalcogenides maximize the probability of interacting with impinging high-energy photons, and more generally, they exhibit superior characteristics for the efficient stopping of primary or secondary charged particles.

As an example, Fig. 1.3B shows the photonic mean free path, as derived from the density and the macroscopic *photoelectric-absorption* linear attenuation coefficient at a photon energy of 662 keV, which is consistent with the gamma-ray emission from ^{137}Cs . A comparison of PbSe or PbTe with CZT- the most common room-temperature gamma-ray detection medium- shows that the mean free path in CZT is 1.85 times longer than that of either lead salt. On a path-length normalized basis therefore, the lead chalcogenides can form a highly efficient gamma-ray detection medium. Nevertheless, the question is: in a field in which device thicknesses are measured in nanometers to hundreds of nanometers, can the solid be formed into electronic structures with enough active thickness and lateral extent to take advantage of the inherently high interaction probabilities and stop charged particles that may range over hundred of micrometers? As described in Section 2, the drop-, dip- and spun-cast solids can be formed into thicknesses which yield highly efficient detector configurations.

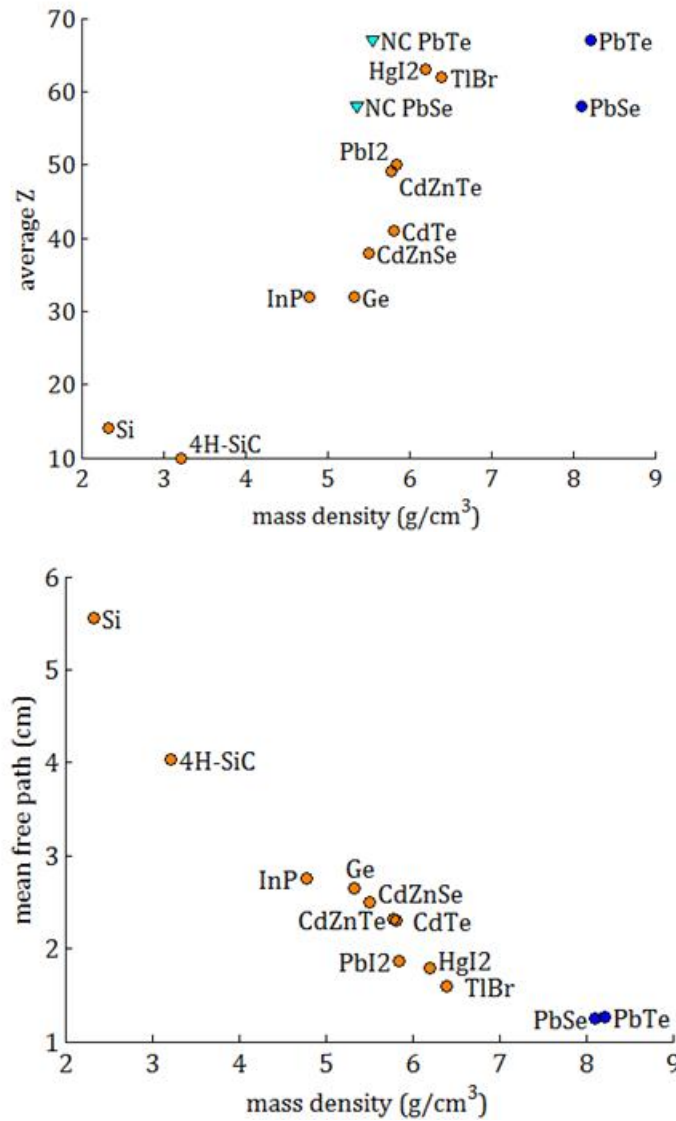


Fig. 1.3. (A) Relationship between the average atomic number Z and the mass density for various semiconducting materials. (B) The mean free path for a 662 keV photon interacting with single-crystal forms of the semiconducting media.

One not only desires high probabilities of interaction with the incident quanta, but the multiplicity of the subsequent charge-creation should be maximized and the trapping of the charge-ensemble should be minimized so that the information conversion is optimized. As shown in Section 1.3, even with a colloidal solid that is not optimized from a charge-separation and transport perspective, the resulting energy-resolving behavior is comparable to or better than state-of-the-art single-crystal semiconductors- Si, CZT, and high-purity germanium operated at liquid nitrogen temperatures- which reflects the promise of the nanostructured approach to semiconductor device design, extending beyond the sensing application reported.

1.2. NC PbSe/Conductive Polymer Composite Assembly

We have synthesized aqueous dispersions of the thioglycolic-acid (TGA)-stabilized CdTe, which were then formed into colloidal solids using the layer-by-layer (LBL) method, as detailed in (16). This route is a promising method of yielding high-performance sensors because layers that are ~100 nm thick can produce measurable responses to alpha particle passage as shown in (16). However, the cadmium chalcogenides have lower stopping power than the lead salts and less favorable charge-multiplication properties, as described in (16) and the references therein. We will therefore present results from PbSe nanoparticles, synthesized via the high-temperature solution-phase route (17), which is briefly described because our thick-detector approach differs from some of the thin-film studies focusing on less penetrating radiation.

The fabrication recipe used to form the colloidal dispersion, the subsequent characterization of the nanoparticles, and their formation into solid assemblies is described in (16) and (18). In order to form the PbSe NC dispersion, comprised of either spherical or star-shaped particles, lead oleate and selenide-dissolved trioctylphosphine (TOP-Se) were used as organo-metallic precursors and diphenyl ether (DPE) served as the high-temperature organic solvent. The synthesis of the star-shaped NC particles was described in (18). By alternating the relative concentration of acetate (Ac) from the $\text{Pb}(\text{Ac})_2$ precursor reagents, one can alter the reactivity of the precursor diffused on to the specific crystal plane, which concomitantly alters the growth speed (19).

The dispersions went through a post-growth NC clean-up process, in which the colloidal dispersion was first mixed with an incompatible agent- the short-chained alcohol ethanol- to precipitate the NC particles from the chemically diverse solution over a period of six hours. After decanting the supernatant, the NC particles were then re-mixed into ethanol, and the precipitation/re-dispersion process was repeated three times and finally re-dispersed in chloroform (20).

Although drop-, dip-, and spin casting can each be employed to produce responsive detectors, we achieve greater device reproducibility via *slow* (60, 90, 150 rpm) spin-casting, in which the PbSe NC solution is mixed with a conductive polymer, para-MEH-PPV, which is used as a hole transporting agent by connecting the highest occupied molecular orbital- lowest unoccupied molecular orbital (HOMO-LUMO) potentials between the two molecules (19). Depending on the batch of the solution, the concentration of the conductive polymer in the composite solution was varied from 1 - 3 weight percent of the overall solution. For instance, for the detector comprised of star-shaped particles, 30 mg of para-MEH-PPV was dissolved in 1 ml of chloroform, which was combined with 1 ml of the PbSe dispersed in chloroform, from which the colloidal solids were cast. As shown in Fig. 1.4, as the relative concentration of PbSe increases, the solids change from yellow to black. The molds from the thinner silicon and glass substrates were formed using wet and dry etching techniques (16, 18), while the mold for the several mm-thick detector shown in Fig. 1.4C was formed using mechanical milling techniques.

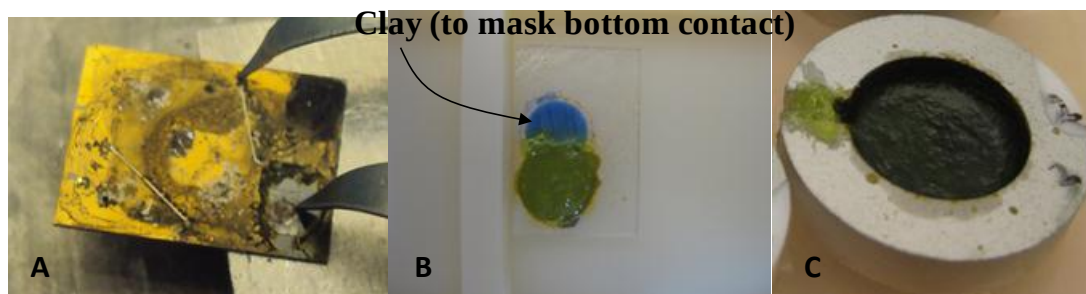


Fig. 1.4. p-MEH-PPV/PbSe NC composite assemblies deposited on (A) 550 μm thick silicon, (B) 500 μm thick glass, and (C) 3 mm thick plastic substrates. The mustard-colored or black solid comprises the blended NC assembly overlaying an indium or gold bottom electrode, and the thin (~ 10 's of micrometers) detector used to derive the gamma-ray spectra shown in Figs. 1.7, 1.8, and 1.10 is shown in (A), with a top gold contact and bottom indium contact.

One should particularly note that manner in which the fabrication recipe differs from those employed to sense quanta with short interaction lengths, such as optical photons. First, although the dispersion is nucleated and grown in either argon or vacuum environments, the casting of the colloidal solid is done in air, and one can therefore anticipate the rapid oxidation of any exposed PbSe surfaces (21). Note that although oxidation of the NC can potentially suppress recombination via increased band-gap due to the reduction of the size of the PbSe core, one generally desires to avoid surface oxidation because of carrier trapping (21).

In fact, the spectral results shown in the next section were derived from detectors that had remained in an ambient environment for one and a half years, exposed to both air and light. Specifically, the colloidal dispersion was grown in September of 2009, and the colloidal solids were initially tested in April 2010 and re-tested in May 2011, in order to observe their performance relative to more refined detectors made in the interim, as well as to observe any performance variation over time. With regard to the latter, no substantial variation in the detector's response nor its thermal properties were observed. Note that the detectors were bounded by 300 nm of evaporated gold or indium; however, we have previously observed that silicon Schottky detectors with similar metal electrodes suffer from diffused oxygen-based leakage-current degradation over the time-period of months; thus, the gold is not a hermetic seal against oxygen diffusion.

Second, although blends of conductive polymers and NCs have lost favor for solar-cell applications because of relatively poor charge-transport characteristics, we find acceptable mobility, as indicated in the relatively rapid pulse rise of the NC PbSe detector of Fig. 1.5, and more importantly, negligible trapping effects. Trapping can reveal itself either in: (1) the induced-charge pulse shape- through slope variations that correspond to the removal of charges from the drift stream (22, 23), or (2) via low-energy tailing of the gamma-ray peaks due to diminished charge collection at increasing interaction depths. As indicated in the pulse shapes and in the gamma-ray spectra in Section 3, neither manifestation of charge trapping is evident.

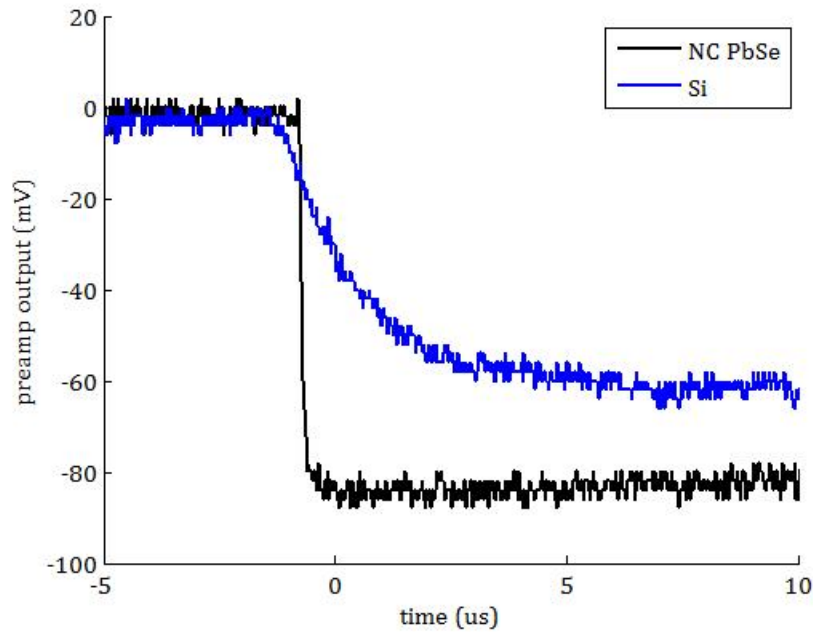


Fig. 1.5. The pulse shape derived from the charge-sensitive preamplifier (Ortec 142a) when an alpha particle from ^{241}Am is impinging upon a silicon PIN or NC PbSe detector, both operated at 0 V applied bias. The PbSe nanoparticles are spherical with a mean diameter of 7.4 nm (± 0.5 nm).

The most important fabrication variation relative to thin-film detectors is that, although we have made sensors based on spin-cast *monolayers* using the layer-by-layer method, for the detectors reported in this paper, the colloidal solution was allowed to self-assemble in thick layers, and the spinner was used mainly as a tool to increase the uniformity of the detector, relative to pure drop-casting. That is, the solid, which can vary from 10's of micrometers to several millimeters, was generally formed from the casting of 10 layers, and each layer can therefore vary in thickness from 2 μm to ~ 100 μm , the thickness depending on the quantity of NCs cast in the single-layer drop.

Finally, one should note that we have made PbSe/PbTe core-shell nanoparticles that exhibit superior charge conversion behavior to those reported here, perhaps exhibiting enhanced electron-hole charge separation due to suppressed Auger recombination (24). Thus, although the fabrication recipe is not optimized from a charge transport nor charge creation standpoint, the promise of the nanocrystalline approach is revealed in the fact that the results are comparable to or better than state-of-the-art single crystal detectors, as will be shown next.

1.3. Responses to Ionizing Radiation

1.3.1 Pulse Height Distribution derived from Alpha Particles and Gamma-rays

Fig. 1.6A shows the general configuration of a 1 cm x 1 cm detector, in which a colloidal dispersion of spherical 7.4 nm PbSe nanoparticles are cast with an interstitial polymer. Note that although the isolating oxide is only 30 μm thick, the active PbSe colloidal solid was several hundred micrometers thick. The pulse height distributions, or energy spectra that result are shown in Fig. 1.6C. As reflected in the black pulse trace of Fig. 1.5, the signals are sharp and clean above the background, yielding the black energy distribution in Fig. 1.6C, which is collected with the detector is exposed to alpha particles from an ^{241}Am source, which emits a 5.485 MeV alpha particle (85 % yield) as well as a 5.443 MeV alpha particle (13 % yield). Thus, the peak corresponds principally to the deposition of 5.49 MeV of energy in the detector,

broadened not by the detector characteristics but by the thickness and nonuniformity of the button *alpha-source*. In fact, in comparing the shape with that derived from a silicon surface barrier detector, the resolution is comparable to or superior, which implies that the conductive polymers are not only accomplishing the goal of realizing good charge transport through the device, but they are not substantially participating in the charge loss of the recoil electrons.

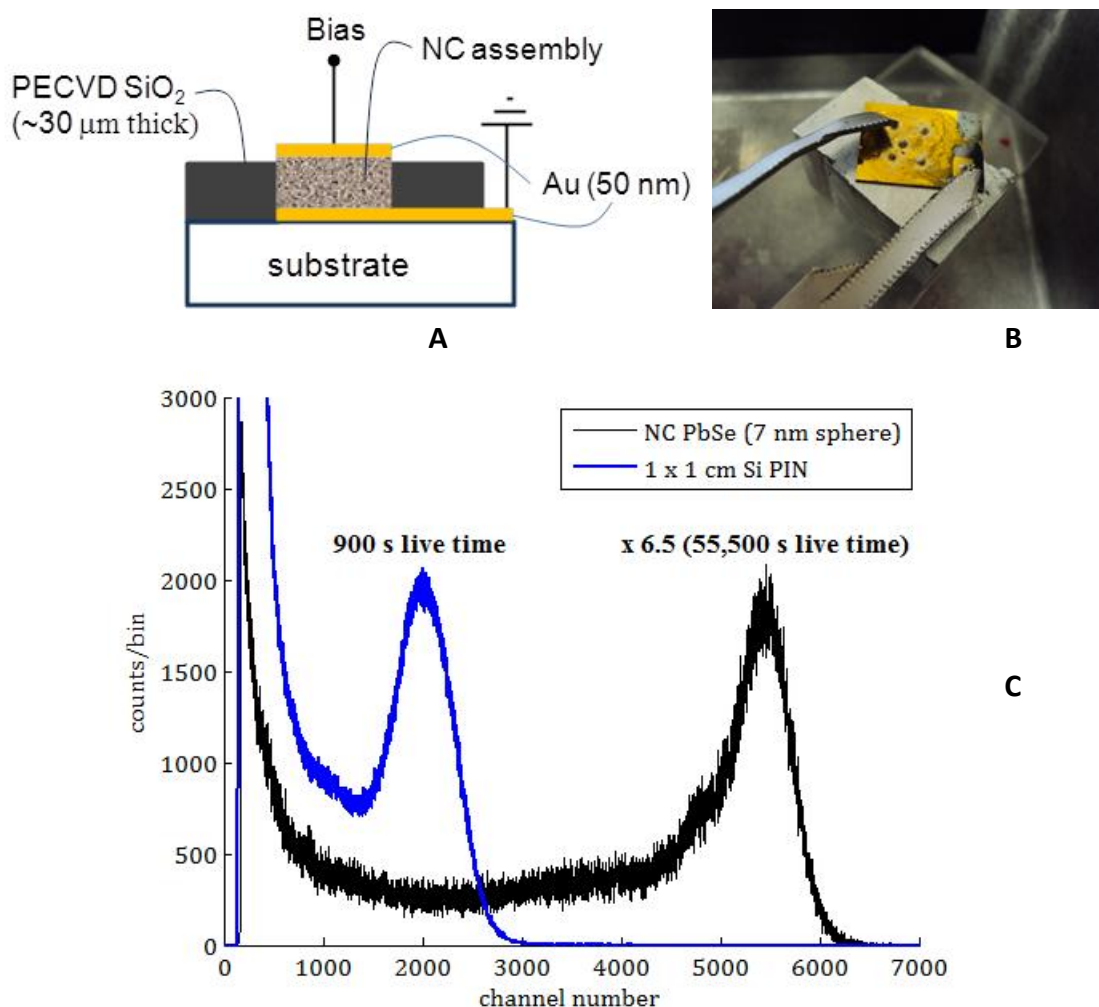


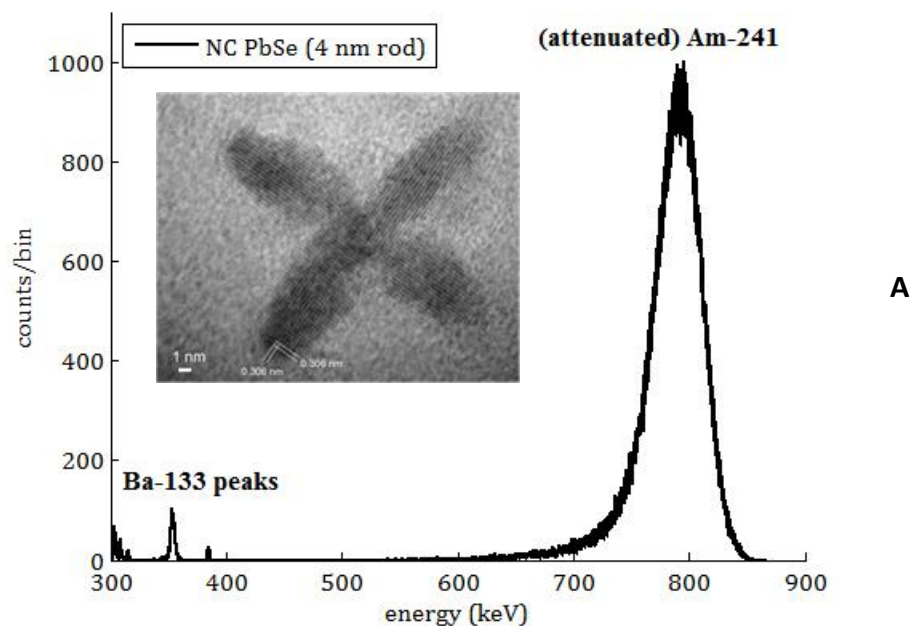
Fig. 1.6. (A) Schematic diagram of radiation-detector device geometry, in which NC assembly is sandwiched between metal contacts (Au on both anode and cathode sides in this case). (B) The realized device, in which the NC solid thickness was several hundred micrometers. (C) Comparison of the pulse height distributions from the PbSe NC assembly and a 1 x 1 cm silicon surface-barrier detector. The counts per bin from the NC PbSe distribution are multiplied by 6.5 in order to facilitate shape comparisons. The duration of the silicon measurement was 900s and that of the NC PbSe was 55,500 s (15.4 h), reflecting the small effective area of the detector.

That is, it isn't particularly surprising that the inherent energy resolution of the PbSe nanoparticles is fine, since the mean band-gap is 0.63 eV (± 0.03 eV); however, the fact that the conductive polymer does not substantially induce deterioration in the charge creation and transport behavior implies that the colloidal PbSe-solid is comparable to or superior to existing single-crystal materials. The two remaining challenge can be gleaned from Fig. 6C, which

shows: (1) that greater measurement periods were needed to accumulate the NC spectrum due to the relatively small size of the active area, and (2) the thermal noise was large enough that the measurement of the small energy depositions that accompany gamma-ray interactions were partially obscured. As shown in Fig. 1.7, we were able to overcome these challenges by utilizing smaller confinement structures and more uniform deposition conditions.

Fig. 1.7A corresponds to a mixed spectrum derived from alpha particles- emerging from a *thin-film* ^{241}Am alpha particle source and ^{133}Ba gamma-rays impinging upon the 1 x 1 cm detector shown in Fig. 1.4A. The alpha source, placed 3.7 cm away from the detector surface, attenuates the 5.49 MeV particles to the energy range shown, and the ^{133}Ba source was placed external to the box housing the detector, 5 cm distant. If one focuses on those spectral features whose appearance correlates to the presence of the ^{133}Ba source, then we can identify the features using both the pulse amplitude and the frequency of occurrence as follows.

Although the material need not be linear, the pulse amplitudes of the three full-energy gamma-ray peaks were linearly related to the energies identified in Fig. 1.7B. Second, the areas under the spectral features correspond to the expected values. For instance, if one takes the gamma-ray emission yield as well as the photoelectric absorption probabilities into account, the area of the 383.85 keV peak should be 12 % of that under the 356.02 keV peak, compared with a measured value of 11 %. The sizes of the x-ray escape features diminish for thicker detectors; however, the thin detector was utilized to characterize the charge-creation characteristics, minimally adulterated by charge-loss considerations, so that W and the inherent energy resolution can be better estimated.



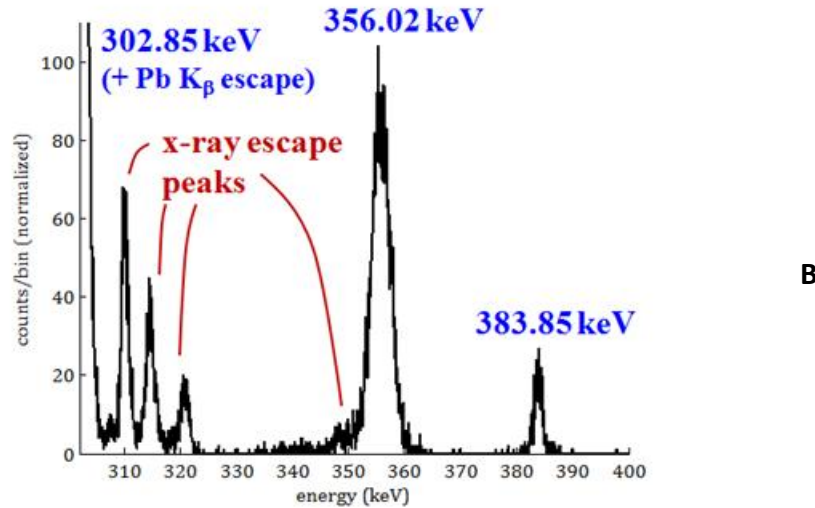
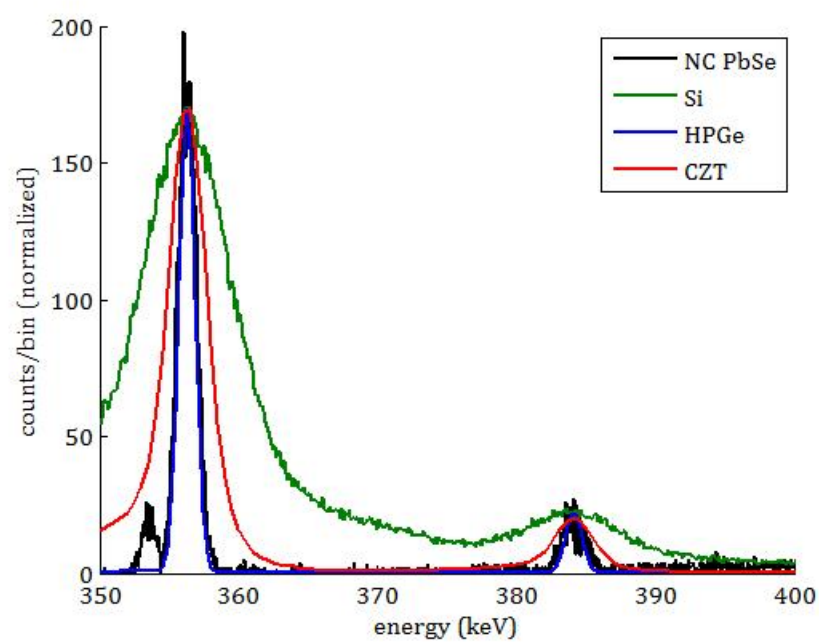
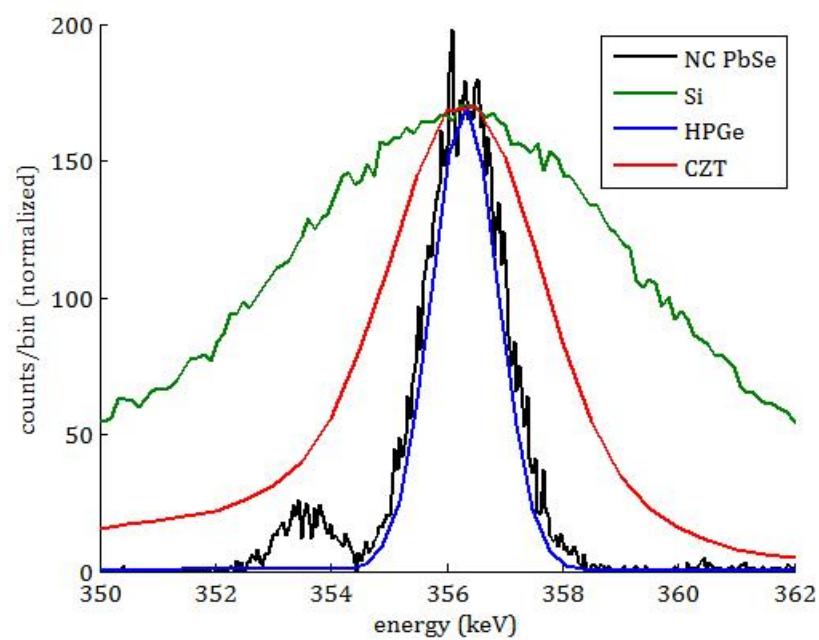


Fig. 1.7. (A) Energy spectrum derived from ^{133}Ba gamma-rays and ^{241}Am alpha particles, attenuated through 3.7 cm of air, impinging upon a 1 x 1 cm detector comprised of a 22 μm thick composite assembly of para-MEH-PPV and star-shaped PbSe nanoparticles, accumulated for a duration of 900 s. The inset shows a TEM micrograph of a typical PbSe NC in the assembly. (B) Typical ^{133}Ba spectrum derived from a thin detector, in which the Pb and Se x-ray escape peaks are prominent.

Fig. 1.8 shows the spectral widths compared with three state-of-art detectors, all operated at room temperature except for the high purity germanium (HPGe) detector, which was cooled with liquid nitrogen, noting that although they are state-of-the art detectors of typical volumes, the Si and CZT comparison-spectra don't represent the ultimate *material limit*- one can cool the silicon and use a smaller volume of high-quality CZT, for instance. The fabrication and characterization of the silicon PIN detector is described in (26). The 1 x 1 cm detector was fully depleted across the 550 μm thickness and biased at +100 V. The coaxial HPGe detector (GEMPM45P4-108: 84.7 mm diameter x 32.8 mm length) was operated at a bias of +3800 V, and the spectrum was accumulated over a 24 hour period, thus accounting for the relative smoothness of the curve compared to the PbSe-equivalent. The 2 x 2 x 1.5 cm $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ (CZT) detector uses a gridded array of 11 x 11 pixels to realize single-polarity charge sensing via the small pixel effect, and depth correction is used to compensate for non-uniform electron trapping (29). As shown in Fig. 6 above, nanostructured detectors can yield a sizable built-in voltage due to the metal-semiconductor interface alone and be operated at low bias voltages; however, the particular NC PbSe detector used in Fig. 8 was resistive and operated at a bias of +320.3 V.

As shown in Figs. 1.8A and 1.8B, the energy resolution of the PbSe nanocomposite is superior to silicon and CZT and comparable to HPGe, yielding an energy resolution of 0.42 % (1.5 keV) at 356 keV, compared with a resolution of 0.96 % (3.4 keV) for CZT and 0.39 % (1.4 keV) for HPGe. Fig. 8C shows an equivalent comparison between the detectors when impinged upon by 661.7 keV gamma-rays from ^{137}Cs . The ^{137}Cs source was more than one hundred times less intense than the ^{133}Ba source and the peak was therefore less well sampled. More importantly, the slight gain drift in the detector, as described in Section 3.3, dominated the peak width shown in the figure. Nevertheless, the ^{137}Cs results buttress those derived from ^{133}Ba gamma-rays; namely, the nanocomposite detector provides an energy estimate with similar fidelity to that produced by HPGe. Given the higher electronic noise associated with the preamplifier readout (Ortec 142a for the NC PbSe compared with a cooled A257P for the HPGe), the intrinsic Fano noise of the nanostructured detector is thus superior to all of the single-crystal semiconductor detector media shown.

**A****B**

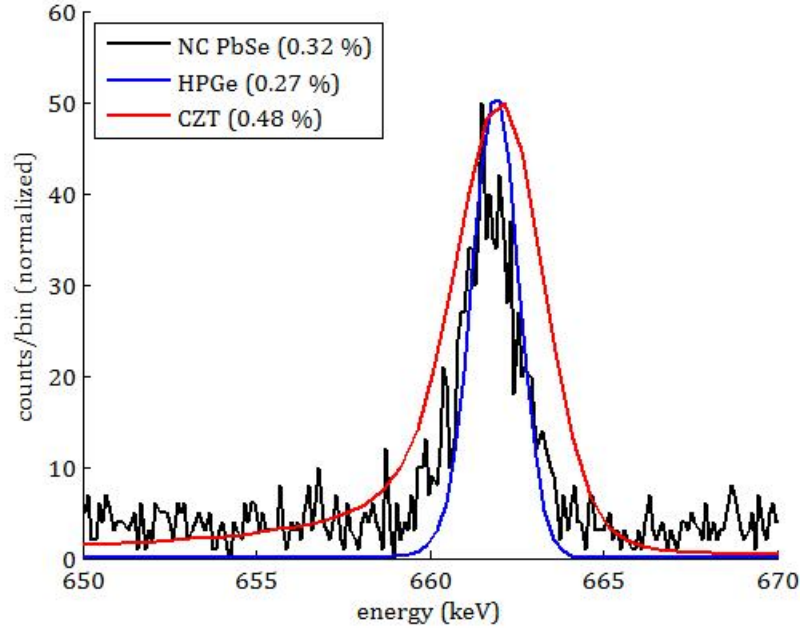


Fig. 1.8. (A) Spectral comparison between high-resistivity silicon (green), CZT (red), HPGe (blue), and the PbSe nanocomposite (black), when exposed to gamma-rays emitted from ^{133}Ba . The different measurement periods (e.g. 21.2 min for NC PbSe, 24 hr for HPGe) account for the differences in curve smoothness, and the curves were normalized to the number of counts in the PbSe peak. Note that the HPGe and NC PbSe traces largely overlap except for the x-ray escape peak from the NC PbSe detector. (B) Close-up of the 356.02 keV peak. (C) Spectral comparison between CZT (red), HPGe (blue), and the PbSe nanocomposite (black), when impinged upon by gamma-rays emitted from ^{137}Cs . The energy resolutions are shown in the legend. The measurement period for the NC PbSe spectrum was 46.4 min.

1.3.2 Measurement of the W-value

The blended-PbSe detectors thus exhibit charge-creation statistics comparable to a material with small band-gap, but their thermal noise properties are consistent with a wider band-gap semiconductor, noting that the leakage current measured at +320.3 V was 1.6 nA. In order to determine whether the spectra indicate more efficient charge conversion or greater noise suppression, one can compare the band-gap to the *W-value*.

The band-gap is measured by taking the average and the standard deviation of the nanocrystalline size, as extracted from an ensemble of NCs, such as those shown in Fig. 1.9 in the TEM micrograph. The band-gap is then calculated from the relationship between E_g and size shown in (28), yielding 0.9 eV (± 0.2 eV) for the rods which comprise the star-shaped particles shown in Fig. 1.9 and 0.63 eV (± 0.03 eV) for spherical NC's with a mean diameter of 7.4 nm. Note that the dispersions were not monodisperse, but the uncertainty in the band-gap for the star-shaped particles is governed by the limits to which one can extract accurate size estimates in fore-shortened particles in a TEM grid.

W is calculated from the pulse height measured from the charge-sensitive preamp pulses, such as those shown in Fig. 1.5, as governed by:

$$V = \frac{E_\gamma / W - Q_{\text{loss}}}{C_{\text{det}} - C_{\text{fixed}}} \quad (1)$$

where E_γ is the energy deposited by the impinging quanta, Q_{loss} accounts for all of the charge-loss mechanisms, such as trapping, C_{det} is the detector capacitance, which can vary as with the applied voltage if the detector is partially depleted, and the fixed capacitance, C_{fixed} , is the circuit capacitance. We used a thin detector in order to ensure that the trapping contribution to Q_{loss} was negligible, noting that we can drift the charges through millisecond time frames at sufficiently low fields, thus buttressing the pulse shape and spectral measurements which indicate that charge trapping over the 100's of nanoseconds required to collect the charges can be neglected. As shown in the pulses of Fig. 1.5, the decay constant of the circuit is sufficiently short that the ballistic deficit in the silicon pulse-height is greater than that yielded by the faster-integrating NC PbSe detectors *at 0 V applied bias*. This difference in charge-loss characteristics is mitigated by operating the detectors such that the pulse rise-times are roughly comparable, which occurs when ~ 100 V is applied to the silicon PIN detector.

We also designed the experiments such that the detector capacitance was negligible compared to the fixed capacitance by: (1) employing a packaging arrangement with large parasitic capacitance, (2) utilizing small detector lateral areas for the NC PbSe detectors, and (3) applying enough bias to the control silicon detector such that the varying capacitance did not impact the measured pulse amplitude. If Q_{loss} and C_{det} are therefore both negligible, one can correlate a spectral feature- we used the peak of the alpha particle distribution- with a pulse amplitude, and calculate the NC PbSe value based on a comparison with the silicon equivalent.

The resulting values are shown in Fig. 1 for ease of comparison with single-crystal materials. The 7.4 nm spheres, with a W of 2.55 eV fall roughly on the $3 E_g$ single-crystal line ($W = 4.1 E_g$), but more importantly, W is lower than all other materials shown; in particular, smaller than the 2.96 eV plotted for HPGe. More interestingly, the W for the more strongly confined rods, with mean rod widths of 4 nm, indicates that a greater portion of the alpha particle's energy is transferred into charge carriers, yielding a W of 1.71 eV, which is 1.87 times the mean band-gap. Thus, an enhancement of the charge-creation probability, relative to non-exciting relaxation processes, is observed, which is consistent with charge multiplication. The results thus show that first, nanostructured detectors of ionizing radiation can be profitably employed to produce high resolution measurements of the energy deposited in the colloidal solid, and second, one can employ strong-confinement physics to realize charge-conversion characteristics that are superior to single-crystalline semiconductors.

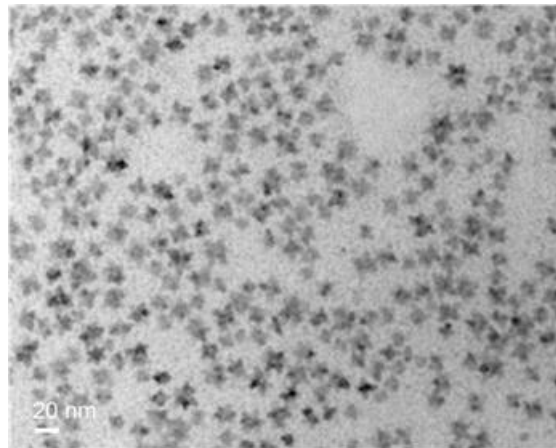


Fig. 1.9. TEM micrograph of field of PbSe star-shaped particles that are composed of the rod-structures of Fig. 1.7A.

1.3.3 Non-idealities of the Material

In order to fully realize the potential of lead-salt nanomaterials, one must optimize the design and synthesis of both the NC's and the overall solid and furthermore, gain a greater understanding of the non-idealities of the material shown below; namely, non-linearity and gain-instability.

One might expect *a priori* that a nanostructured detector might exhibit non-linearity due to an energy-dependent variance in the charge multiplicity. For instance, if the charge multiplication probability is enhanced relative to phonon-assisted relaxation processes at higher (secondary) electron energies, then the calibration between induced-charge and energy might exhibit positive curvature. However, if a higher multiplicity of excitons is created in a NC at higher deposition energies, then negative curvature might result since the effective band-gap may increase as the lower-energy states are filled. Experimentally, we don't observe a significant curvature in the charge-to-energy conversion ($R^2 = 0.99996$).

The detectors can exhibit drift, which manifests itself as gain instability, as indicated in Fig. 1.10, in which the gap between the full-energy peak and the x-ray escape peak is filled in as the peak shifts as a function of time. Although the exact source of the instability is unknown, phenomenologically the shift is consistent with a variation in the detector capacitance because for those small ($< 1 \text{ mm}^2$) detectors which have a negligible capacitance compared to the circuit capacitance (cf. Eq. (1)), the spectral features are highly stable. For instance, the alpha particle spectrum of Fig. 1.6 could be collected indefinitely, and repeated months later and still exhibit reproducible behavior. Furthermore, variations in the capacitive area and width are not expected; thus, the observations imply that the gain instability is caused by variations in the effective permittivity of the medium. Although one can design the preamplifier to be insensitive to modulations in the dielectric properties of the detector medium, one would prefer a highly stable medium and the source of variation should therefore be controlled.

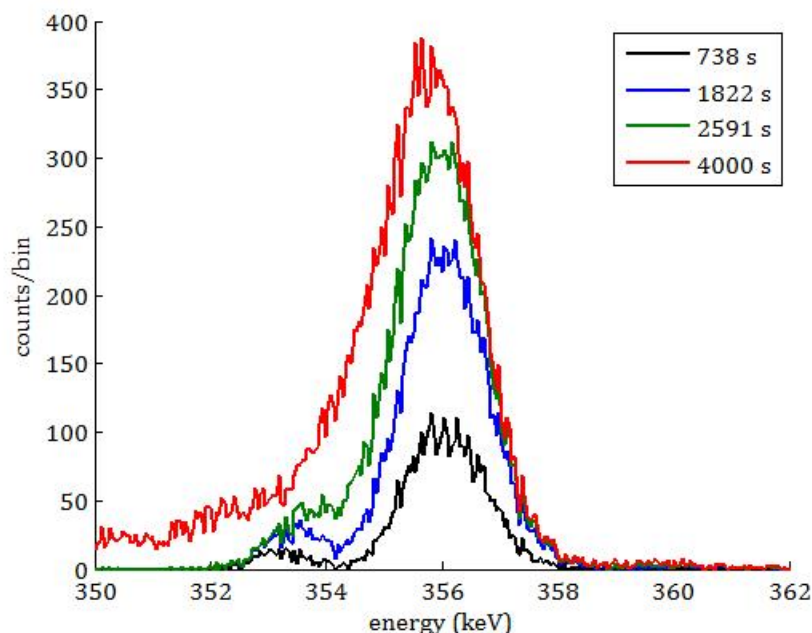


Fig. 1.10. Temporal variation in the 356.02 keV peak derived from ^{133}Ba , for the star-shaped NC PbSe detector of Fig. 4A. The legend indicates the measurement period (live-time) for the various traces.

1.4. Summary

Nanostructured cadmium and lead salts have been extensively studied as advanced media for optoelectronic devices. The sensitivity of their charge-transport properties to the surface conditioning of the nanoparticles and their degradation under ambient conditions has discouraged their use in a semiconductor configuration; rather, most of the efforts geared toward nuclear radiation detection have concentrated on nanostructured *scintillation* materials. Furthermore, the slight thicknesses that accompany the traditional spin-, dip-, and drop-casting methods have argued against their use as sensors of more highly-penetrating radiation.

However, we have shown that detectors with deep depletion regions can be constructed such that the deposited charge can be effectively drifted and the energy of the interacting quanta can therefore be measured. Furthermore, the accuracy of that measurement is comparable to those estimates provided by the best single-crystalline semiconducting materials, providing evidence for enhanced charge multiplication as the degree of strong confinement is increased.

2. Simulated Nuclear Radiation Responses Derived from Nanocrystalline Semiconductor Assemblies

2.1 Introduction

As discussed in Section 1, in a nanostructured material, the transport of the charge following its excitation in the solid can be hampered by trapping at the enumerable interfaces that the charge encounters during its drift to the bounding electrodes. Furthermore, even if the trapping is negligible, the drift through the energy states provided by the composite matrix can be slow enough that extraction of the initial charge number is hampered by the intrinsic noise of the sensor.

We found solutions to both the charge creation and transport challenges during the research, part of which was described above. CdTe, PbSe, and PbSe/PbTe (core-shell) nanoparticles all exhibit excellent charge creation and fast transport, the result from which is that a PbSe NC assembly detector exhibits energy resolution comparable to HPGe, but operated at room temperature. Compared with HPGe, the detectors responses vary because the lead-chalcogenide colloidal solid is comprised of higher atomic-number constituents, from which high-energy x-rays are emitted during the relaxation of the orbital electrons to low-lying energy states. X-ray escape peaks can therefore feature prominently in the gamma-ray spectra, particularly if the particular radiation-detector is thin relative to the mean free path of the secondary photon.

In order to better understand the empirical peaks that arise from the impingement of gamma-radiation upon the NC PbSe detectors, we simulated the spectral responses of the detectors as a function of various fabrication parameters, using MCNPX-Polimi for the Monte Carlo simulations, the results from which are presented in Section 2.3. The simulation results buttress the measurements which indicate that nanostructured lead-salts can yield low-cost, large area, high-performance radiation detectors.

2.2 Experimental Motivation

Nanocrystalline CdTe in a Layer-by-Layer Composite

Cadmium telluride (CdTe) is a II-VI semiconductor material that has been extensively investigated as a single-crystal semiconductor radiation detector. NCs of the cadmium chalcogenides are also widely studied for the detection of optical photons. In fact, the fabrication methods are geared toward thin films consistent with the stopping of non-ionizing poorly-penetrating radiation. Although less favorable than the lead chalcogenides for the intended application, the synthesis processes are more fully characterized, and we have therefore investigated both systems.

One method to produce monodisperse NCs involves the mixing of all the reaction precursors in a vessel at a low temperature and then moderately heating the solution to grow the particles. An accelerated chemical reaction induced by increasing the temperature of the solution gives rise to supersaturation, which is relieved by the nucleation burst. The subsequent control of the solution temperature will induce further growing of NCs (29).

For instance, NCs in the ~3 nm range can be grown in 20 minutes, whereas larger particles can take 24 hours or more, the size judged during growth via the UV-photoluminescence. According to the chemistry of the synthetic process, the resulting dispersion contains NCs with a CdTe crystalline core surrounded by deprotonated -OH and -COOH groups of the thioglycolic acid; thus, the NCs have negative charge (30).

For electronic testing, assemblies composed of ~4 nm NCs were prepared by two methods: the layer-by-layer (LBL) method and via drop-casting the NC dispersion on aluminum and gold-

metalized glass substrates. The LBL method is a well-known method for efficiently depositing NC colloidal dispersions into high quality and stable thin-film layers on the substrate, while preserving the distinctive optoelectrical and magnetic properties of the size-quantized states of the NCs. For the LBL deposition, poly(diallyl dimethyl ammonium chloride) (PDAA), was induced as a polycation used for adsorbing nanoparticles. Thioglycolic-acid (TGA)-stabilized CdTe nanocrystal solution was spread on the PDAA layer and adsorbed. By an alternatively adsorbing procedure, a bilayer consisting of a polymer/nanocrystal composite was developed and the cycle was repeated from 1 to 30 times, to obtain a multilayer film of the desired thickness.

Unfortunately, in order to stop the high-energy charged particles associated with ionizing radiation one desires a thickness of at least 10's of micrometers if not several centimeters, which requires repetitive and lengthy casting procedures; for instance, roughly 80 hours of aqueous layer-by-layer deposition is required to achieve 10's of micrometers thickness. This can be enabled by robotic dipping tools, but for characterization studies, one can utilize sub-micrometer layers to evaluate the material.

The result of spin-casting the NC assembly onto a glass 4" diameter wafer is shown in Fig. 2.1a. The varying color reflects the non-uniform thickness deposited towards the outside of the wafer. If the uniform, inner-section of the assembly is diced and bounded by metallic electrodes, then $1 \times 1 \text{ cm}^2$ detectors can be realized, as shown in Fig. 2.1b. In order to determine the thickness of the resulting NC assembly, we examine the cross-section of the layer and utilize energy dispersive x-ray spectroscopy to identify the constituent layers, as shown in Fig. 2.2. Note that the gold, indium, and cadmium signals overlap but a careful examination of the various structures reveals that the layer is only 130 nm thick, achieved after 48 drops of the LBL process was repeated (cf. Fig. 2.2c).

A priori, one expects only slight energy depositions within a 130 nm layer, particularly for weakly ionizing electrons. Even if one exposes the assembly to 5.485 MeV alpha particles (from ^{241}Am), the energy deposited from the transmission of the ion through the layer is less than 30 keV. This is enough energy to produce a measurable signal, as shown in Fig. 2.3, which is very promising because gamma-rays, for instance, can produce energy depositions that are 10 times as big if there is enough volume to fully stop the products of the interaction.

Thus, even though the cadmium salts may not be as favorable as their lead equivalents- at least in their physics properties (30)- they represent a promising material upon which nanostructured ionizing radiation detectors can be developed. Furthermore, detectors fabricated using the LBL method are more reproducible in their behavior than those that are solidified using gross drop- or spin-casting methods.

As mentioned in the Status Section, starting this month (Dec. 2011), we began to investigate vacuum filtration of CdTe nanowires as a means to rapidly deposit thick detector volumes. The resulting detectors are not the typical hard, brittle single-crystal devices commonly used but are flexible and have the mechanical characteristics of thick paper. One can therefore envision large-area detectors conforming to the shape of choice, the realization of which depends on excellent electrical characteristics. Unfortunately and perhaps expectedly, the first generation of detectors did not produce as good of a charge-conversion and transport response as either the CdTe LBL devices nor the PbCh detectors. Nevertheless, there is no fundamental reason why the charge transport and conversion cannot be excellent and we will therefore continue to investigate the technique beyond the project period.

Nanocrystalline PbSe in a Blended Composite

As an alternative the LBL in which one uses dozens of hours to grow detectors with good intrinsic detection efficiency, one can produce exceptional detector behavior using chemistry

based on fast-drying organic solvents and through deposition procedures that result in detectors that can be realized in minutes instead of hours. Furthermore, the lead salts, with their higher atomic numbers and densities, have inherently higher stopping power to either charged or neutral ionizing radiation.

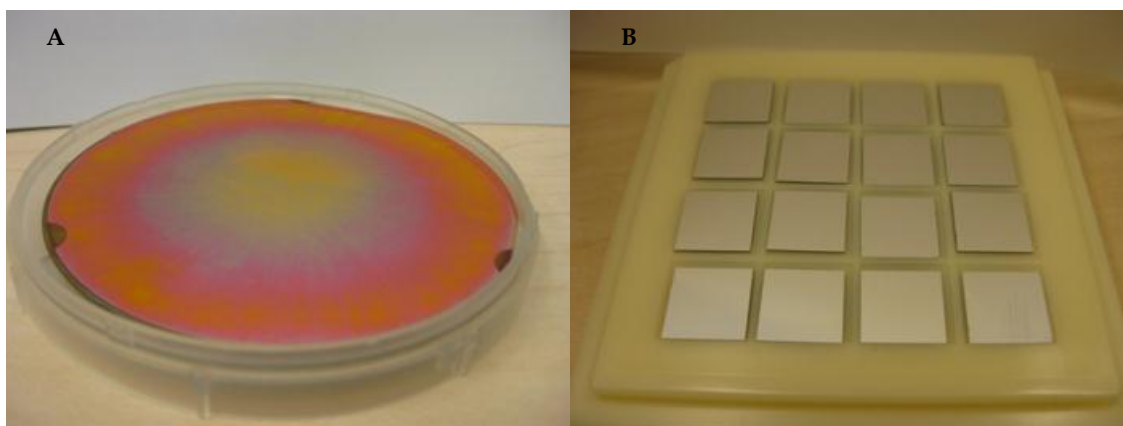


Fig. 2.1. (A) Gold-metalized glass wafer upon which a colloidal dispersion of CdTe NCs is deposited via the LBL method utilizing spin-casting. (B) The $1 \times 1 \text{ cm}^2$ detectors after indium evaporation and dicing.

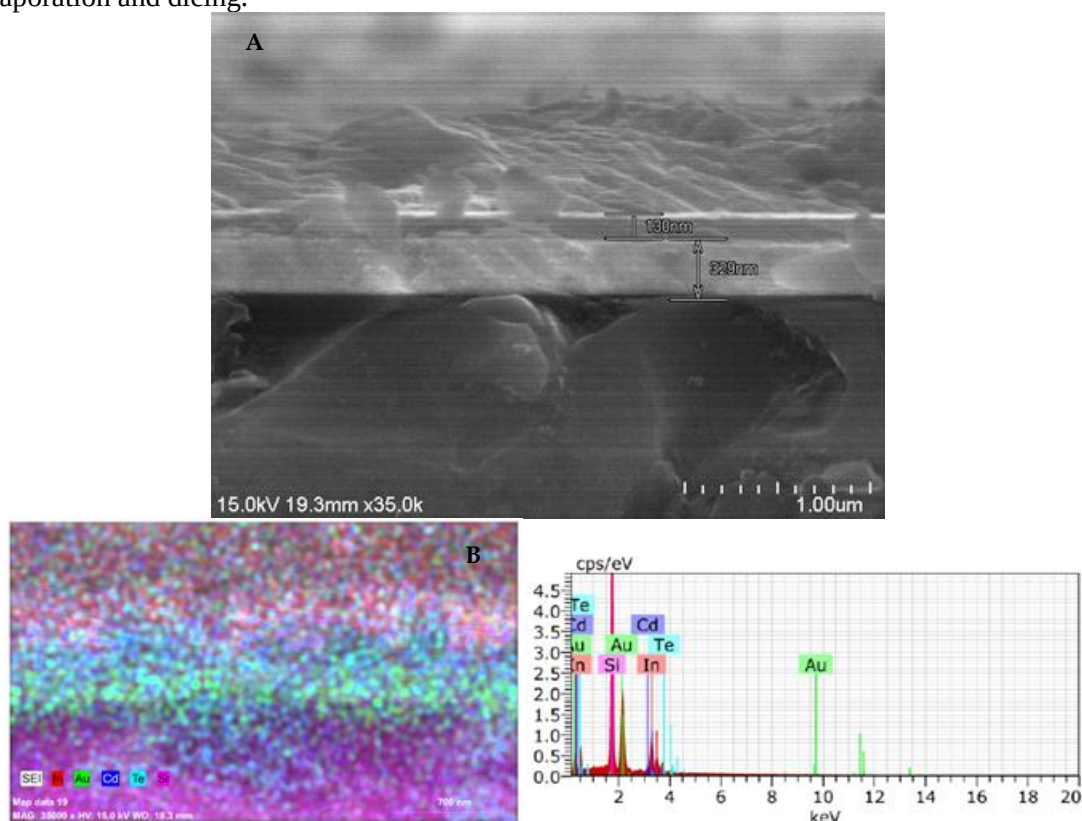


Fig. 2.2. (A) SEM micrograph of a cross-section of the NC CdTe detectors, showing the 329 nm gold layer and 130 nm CdTe assembly, assignments verified using energy dispersive x-ray spectroscopic mappings of (B) and (C).

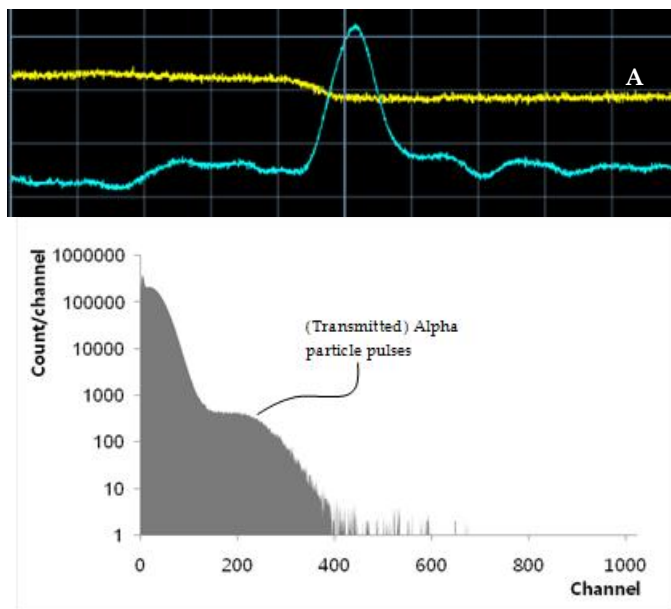


Fig. 2.3. (A) Preamp (yellow) and shaped (blue) signals derived from the passage of a 5.485 MeV alpha particle through a 130 nm CdTe nanocomposite detector, in which the induced charge signal is measured with a Ortec 142A preamp. The time per division is 10 μ s and the volts per division are 200 mV for the preamp and 5 V for the shaped pulse. (B) An example alpha particle spectrum in which the alpha pulses are shown as a hump above the noise.

As shown in Section 1, we have fabricated detectors comprised of PbSe, PbTe, and PbSe/PbTe core-shell nanoparticles coordinated in a matrix of MEH-PPV, and have yielded excellent charge creation and transport from both the PbSe and core-shell devices.

For this Section, the main point of gamma-ray spectra such as that shown in Fig. 2.4 is that the spectrum contains features that not only correlate with the emission spectrum from the gamma-ray source, but many other peaks proliferate, the intensity of which correlates with the detector size, which can include the thickness as well as the lateral extent. The goal of this section is to simulate the nuclear interaction processes, so that the various spectral features can be confidently identified, the results from which are shown next. For instance, the results indicate that the x-ray escape peaks identified in Fig. 2.4 are due to single, and more importantly, double x-ray escape events.

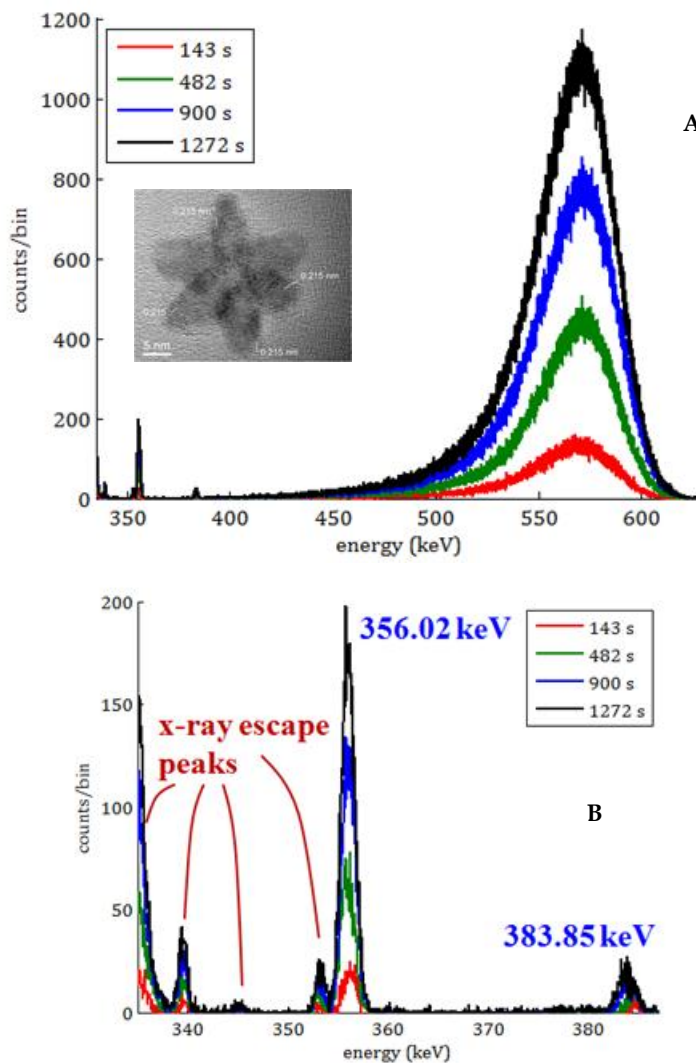


Fig. 2.4. (a) Energy spectrum derived from ^{133}Ba gamma-rays and ^{241}Am alpha particles, attenuated through 3.7 cm of air, impinging upon a 1 x 1 cm thin (10's of micrometers) composite assembly of para-MEH-PPV and star-shaped PbSe nanoparticles, accumulated for various durations shown in the legend. The inset shows a TEM micrograph of a typical PbSe NC in the assembly. (B) Typical ^{133}Ba spectrum derived from a thin detector, in which the Pb and Se x-ray escape peaks are prominent.

Modeling of PbSe NC/MEH-PPV composite assembly detector

The Simulation Parameters

The fabrication methods used to produce a self-assembled colloidal solid, comprised of either spherical, star-shaped, or polygonal NCs, are detailed in (16,18). The degree of NC-lattice ordering is dependent upon the size and shape dispersion, with monodisperse ($< 5\%$ variation in the lateral extent of the NCs) particles resulting in close-packed, regularly-spaced solids, while dispersions with greater than $\sim 10\%$ size-uncertainty result in random-packing.

For the physical detectors, the NC size dispersion was generally greater than 10% , but we hypothesize that those detector regions with the finest energy-resolution performance correspond to a high degree of NC ordering, because the charge mobilities are generally higher than those found in poorly order solids in which the conductive polymers retard the drift velocity. For the

sake of gauging the energy-deposited by impinging radiation, we simulated both superlattice structures as well as homogenized detectors, both producing comparable results because the range of the secondary reactants far exceeds the size dimension of the NCs.

If one assumes a uniform size distribution of the PbSe NCs, the packing of the quantum dots in a superlattice structure governed by cubic unit cells can arrange via either simple cubic (sc), body centered cubic (bcc) or face centered cubic (fcc). The face centered cubic and hexagonal close packed structure can form the most closely packed structure. The volumetric fraction occupied by the PbSe in each scheme is: 52% (sc), 68% (bcc), or 74% (fcc and hcp) respectively, in the case of the closest packing.

In the physical detectors, the NCs are separated by the capping ligands, which impose a finite separation between particles, as illustrated in Fig. 2.5, in which a polymer order of 1 is assumed for the organic polymer, MEH-PPV. In reality, we have experimentally sampled the parameter space in which the relative volumetric blend between the NC volume and the polymer volume can vary; however, the best detectors generally have a high concentration of NCs, and we will therefore simulate a typical separation. For example, making a simple assumption of 1 nm (20 % of the size of the particle) interparticle distance between the 5 nm PbSe NCs shown in Fig. 2.5, the packing fractions reduce to: 39% (sc), 51% (bcc), and 56% (fcc and hcp), respectively. If the size of each particle is not uniform, even higher packing ratios than 74% in volume are possible, because interstitials of smaller NCs can be packed between bigger NCs.

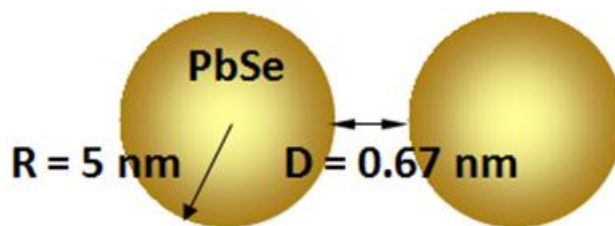


Fig. 2.5. Typical geometry for a PbSe quantum dot separated by a single link of the MEH-PPV (poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene]) polymer chain.

The high intrinsic efficiency of the lead chalcogenide materials to the sensing of ionizing radiation detection is discussed in Section 1. In comparison with competing detection media, lead chalcogenide materials can exhibit orders of magnitude higher stopping power, especially for high-energy gamma rays with energies exceeding 1 MeV. The Monte Carlo simulation was performed for a PbSe NC/p-MEH-PPV composite assembly, in which a conservative assumption on the particle packing in the assembly is assumed. As shown in the schematic of Fig. 2.6b, a single PbSe nanoparticle contained in a simple cubic unit cell (sc) with the distance between the nanoparticles of 20% of the PbSe NC particle size were assumed and the rest of the cell volume was filled with para-MEH-PPV. Therefore the volumetric fraction of the PbSe NC in the NC/polymer composite cell was only 39%. Amongst various types of MEH-PPVs, p-MEH-PPV ($(C_{25}H_{32}O_2)_n$, $\lambda_{ex} = 451$ nm, $\lambda_{em} = 517$ nm in chloroform) was used in the fabrication of the PbSe NC composite assembly samples, because: 1) it was characterized in chloroform, which is the solvent in which the PbSe NCs are dispersed, and 2) it has the longest excitation/emission wavelength so that it could be comparable in bandgap to the NCs.

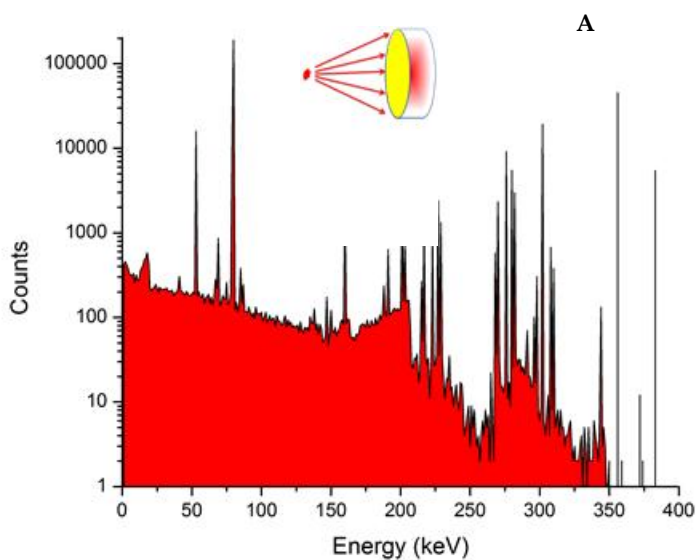
The simulation was performed for a Ba-133 source for which the branching ratio is illustrated in Table 2.1, to compare the expected spectral response of the PbSe bulk material with PbSe NC/conductive polymer composite assembly. The detector was cylindrical, with a 1 cm diameter and 1 mm thickness, and the detector was assumed to have a 300 nm gold contact on the front side, as shown in Fig. 2.6. Due to the complicated lattice structure geometry that is repeated hundreds of thousand times in a 1 mm thickness media, the computation time of the Monte Carlo simulation was substantial; therefore, 10^6 particles were simulated for both the composite

assembly and the single-crystalline equivalent., and peak broadening due the detector and electronics was not taken into the consideration for the following simulations.

The simulated spectra are illustrated in Fig. 2.6. The total intrinsic efficiency for 1 mm thick PbSe bulk crystal was calculated to be 35.5% and the total intrinsic efficiency for the 1 mm thick PbSe NC/p-MEH-PPV assembly was 6.28%; however, the packing fraction can be substantially improved by using shorter chain ligands, or by employing non-spherical particles. Qualitatively, the single-crystalline spectrum has a substantially higher Compton continuum as well as a greater density of x-ray escape peaks; however, the general peak structure is comparable. The extra organic materials used in the colloidal assembly do not muddy the peak structure at the energies of interest.

Table 2.1. Gammas emitted from Ba-133 (half life – 10.51 y)

Energy (keV)	Intensity (%)
53.161	2.199
79.6139	2.62
80.9971	34.06
160.613	0.645
223.234	0.45
276.398	7.164
302.853	18.33
356.017	62.05
383.851	8.94



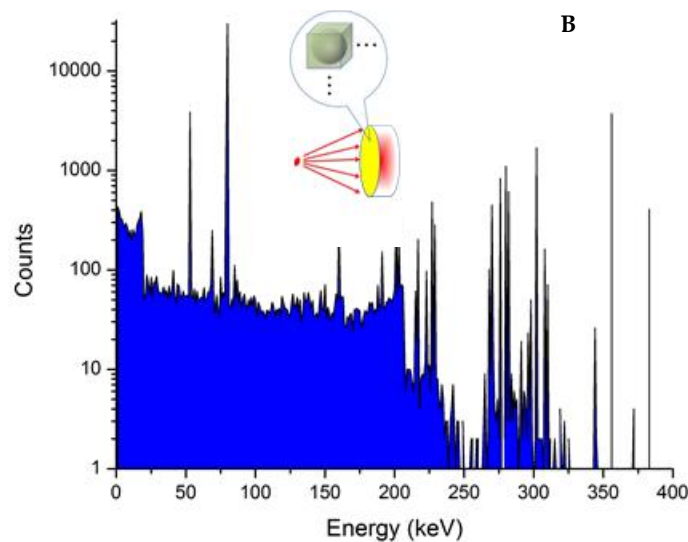


Fig. 2.6. Schematic of the simulation geometry and the simulated spectra of Ba-133 from (a) bulk PbSe medium and (b) PbSe NC/p-MEH-PPV composite assembly of 1 mm thickness.

Contributions of various event types to the spectra

The simulated spectrum shown in Fig. 2.6 exhibits many features, including x-ray escape peaks as well as the full energy absorption peak, and Compton continua from the scattering event either in PbSe NC or in p-MEH-PPV. Therefore, in order to correctly identify each specific feature in the spectra, every interaction that deposits energy in the assembly can be categorized by event type as well as the element with which the interaction occurred. The parsed spectra by event type and interacting element are shown in Fig. 2.7.

Fig. 2.7a shows the contributions from each event type (photoelectric capture, Compton scattering, single x-ray escape, and double x-ray escape). Even for the thin detector, the full-energy peaks are substantial compared to the Compton continuum, and the shape is dominated by photoelectric absorption, Compton scattering, and single x-ray escape peaks. In the physical spectra, peaks that are consistent with double x-ray escape are also observed, which indicates that the size is smaller than that simulated.

The x-ray escape peaks and the interaction with each element to the overall spectrum of ^{133}Ba in the PbSe NC/p-MEH-PPV assembly is displayed in Fig. 2.7b. The deposition of energy on selenium and lead is due to the interactions with PbSe nanoparticles, and the interactions with H, C, or O result in energy depositions due to the presence of p-MEH-PPV. Notably, most of the full energy absorption peak events are contributed by the PbSe NCs, whereas the Compton continuum, derived primarily from 356 keV and 384 keV gamma rays, is due to the carbon that accompanies the p-MEH-PPV. This is consistent with the experimental results, in which fully p-MEH-PPV sensors do not possess the full-energy peaks.

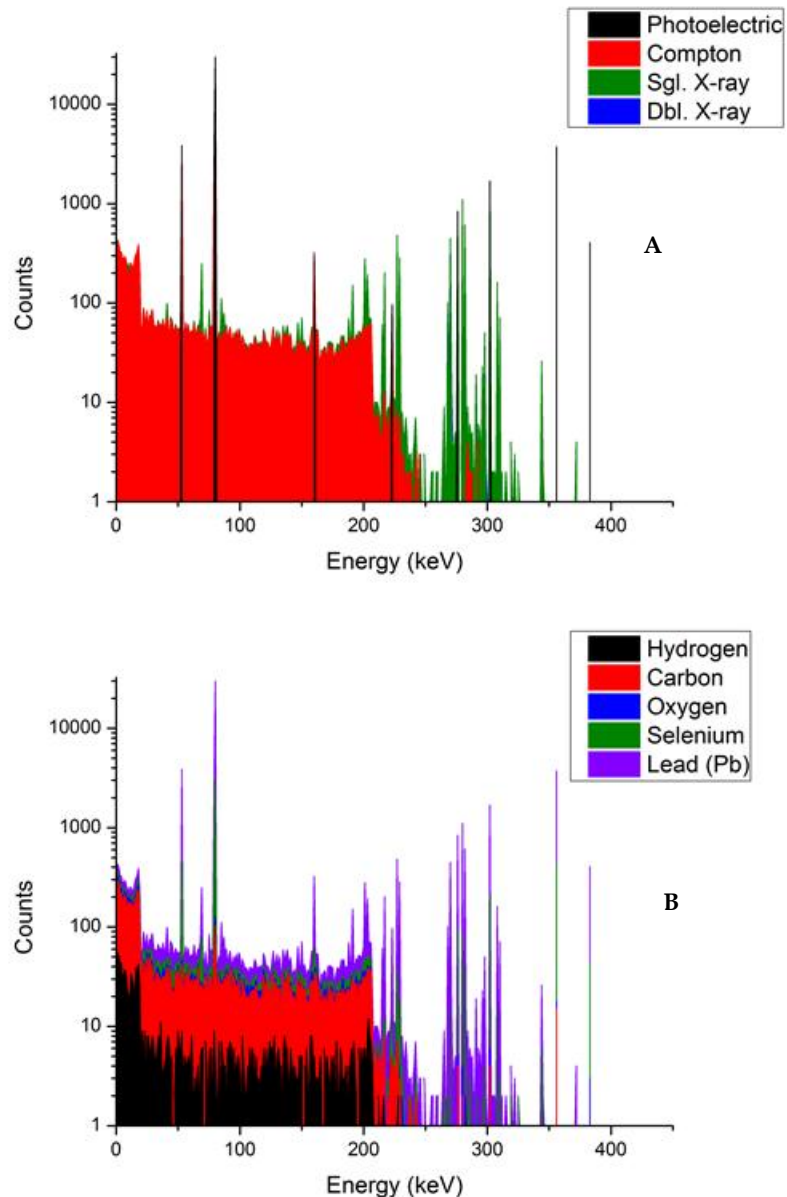


Fig. 2.7. Simulated spectra of Ba-133 from the PbSe NC/p-MEH-PPV assembly showing contributions from (a) each event type and (b) interactions with each element.

Since the photoelectric effect is an interaction of a photon with a bound electron, which is expelled from its orbit, x-ray fluorescence accompanies the interaction. If the detection medium is small enough, then those characteristic x-rays can escape from the active volume, resulting in an energy deposition reduced by the x-ray energy. One can identify from which element a specific x-ray escape peak is originated, an analysis which indicated that most of x-ray escape peaks are derived from Pb and Se atoms. Furthermore, Pb dominates the photoelectric events because the probability of photoelectric absorption scales with the 4-5th power of atomic number. Moreover, the energies of the characteristic x-rays from Pb are much higher and thus much more likely to escape from the NC assembly. Sometimes, two x-ray fluorescence events can occur in the interaction with Pb atom, and both x-rays can escape the medium. Single fluorescence events and double fluorescence events from the full energy deposition are shown in Fig. 2.7a with green and

blue bars respectively. The energy of the major peaks due to x-ray escape events are as follows : 1) single escape peaks at: 69 keV, 85 keV, 201-203 keV, 215-217 ke, 227-229 keV, 268-271 keV, 280-282 keV, 308-310 keV kev, and 2) double sacp peaks at 216, 269, 271 keV.

Gaussian Broadening of the Spectrum

The simulated spectra shown above did not include any broadening effects of the peak caused by the inherent statistical spread in number of charge carriers, variations in charge collection efficiency, and contributions of electronic noise, for example. The overall energy resolution of the radiation detector can be represented as follows :

$$W_T^2 (= (FWHM)^2) = W_D^2 + W_X^2 + W_E^2, \quad (1)$$

where W_D^2 represents the stochastic fluctuations in the number of charge carriers created, W_X^2 is due to incomplete charge collection, and W_E^2 accounts for the electronic noise. Considering the mechanism each component contributes to the energy uncertainty broadening, we can regard the first term as scaling with $\sqrt{E}$, the second term scaling linearly with the energy, and the last term a constant contribution to the energy broadening. Therefore, one can represent the empirical equation as follows:

$$FWHM = a + b\sqrt{E} + cE^2 \quad (2)$$

The three parameters can be determined empirically, by fitting the measured resolution in terms of the energy of the peak. If we assume a Gaussian broadening of the peak we can determine the relative contributions about a certain energy peak in count rate using the probability distribution function represented as follows,

$$f(E) = C e^{-\left(\frac{E-E_0}{A}\right)^2} \quad (3)$$

where E = the broadened energy

E_0 = the unbroadened energy deposited in the detector

C = a normalization constant

The Gaussian width A can be determined from FWHM:

$$A = \frac{FWHM}{2\sqrt{\ln 2}} = 0.6005612 \times FWHM. \quad (4)$$

Using experimental data for the peak energy resolution of 356 keV (0.42 %) and 662 keV (0.32%) gamma rays, the FWHM curve was fitted.

Variations in the Spectral Response with Thickness

Fig. 2.8 shows the Gaussian broadened energy spectrum simulated for the PbSe NC/p-MEH-PPV assembly of various thicknesses. The overall feature does not look remarkably different from the previous simulation results. Simulations performed for equivalent characteristic NC composite assemblies but with smaller thicknesses, exhibit a higher contribution from the x-ray escape peaks, as expected.

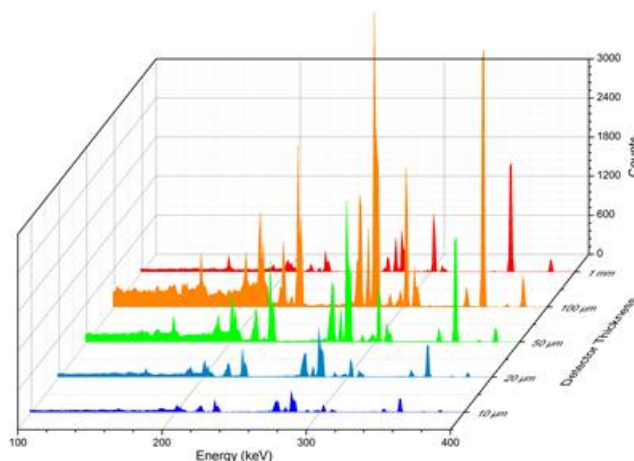


Fig. 2.8. Gaussian broadened energy spectra of Ba-133 simulated for PbSe NC/p-MEH-PPV assembly of various thicknesses. 1 mm thick assembly was simulated for 10^6 particles, whereas others were simulated for 5×10^7 particles, to qualitatively compare the relative peak area and x-ray escape peaks.

As the detector thickness increases, the probability of capturing the secondary x-rays increases, as reflected quantitatively in Fig. 2.10. Note that in the Fig. 2.10 and Fig. 2.11 results, the nanostructure of the detector was homogenized, because MCNPX cannot model geometries smaller than 50 nm, which prevents the precise modeling of the array comprised of 4 – 7 nm particles. The physical detector was approximated by homogenizing the PbSe nanoparticles and polymer, conserving mass. Nevertheless, the method is valid given that the structure of the PbSe varies throughout the volume of the detector, and that the size of the PbSe nanoparticles is not substantially larger than the size of a PbSe molecule (~ 0.1 nm). The PoliMi code was used to select only those events that deposit energy in Pb or Se, as this functionality is not available in the standard version of MCNPX when using a single homogenized material. It was also assumed that the entire NC region was active (i.e. there is no dead layer).

A two-dimensional diagram of the geometry used is shown in Fig. 2.9, and was designed to match the experimental setup as closely as possible.

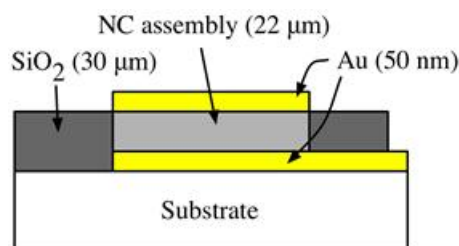


Fig. 2.9. Diagram of the detector geometry modeled. A 1x1 cm square of varying thicknesses (here shown as 22 μm thick) is sandwiched between two Au contacts.

The geometry shown in Fig. 2.9 was used in conjunction with a ^{133}Ba point source placed 5 cm above the detector region. The energy spectrum was tallied using 800 energy bins, each with a width of 0.25 keV. As shown in Fig. 2.10, the thickness of the detector increases the counts in the full energy peak relative to the x-ray escape peaks, where the ratio of the single x-ray escape

peak from Pb $L\alpha_1$ to the full energy peak is plotted against thickness for the 383.85 keV peak and the 356.02 keV peak from ^{133}Ba . As expected, the efficiency of the detector at counting the full energy peaks increases with thickness. More importantly, the complications associated with extracting full-energy peaks from a distribution adulterated by escape features can be avoided for detector with thicknesses greater than roughly 1 mm. The energy spectrum for ^{133}Ba using a thickness of 22 μm is shown in Fig. 2.11 with the main peaks identified.

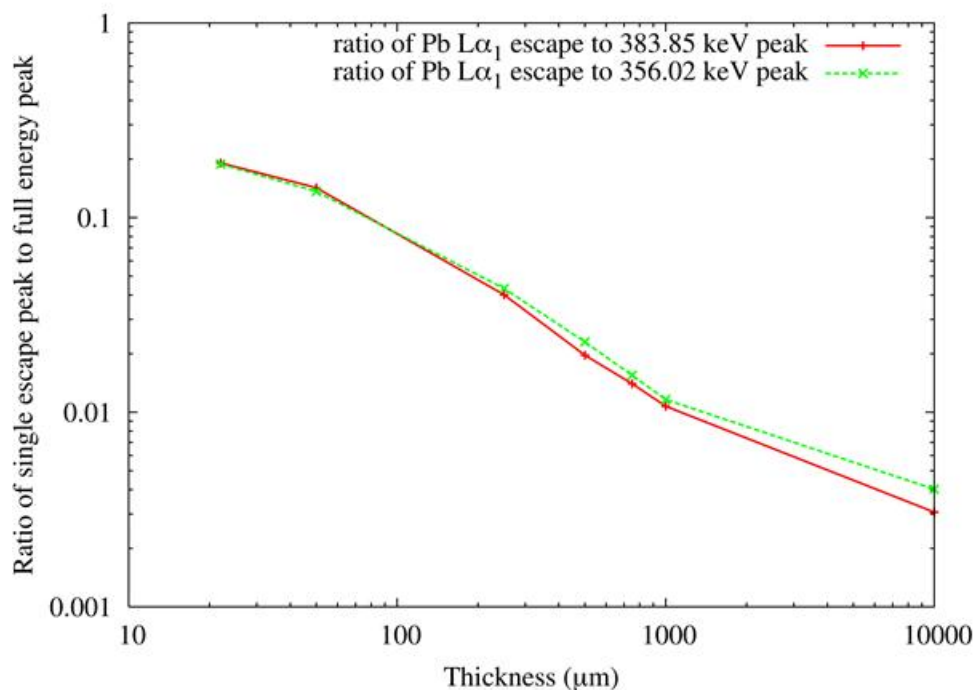


Fig. 2.10. A plot showing the ratio of the Pb $L\alpha_1$ single escape peak to its full energy peak for increasing thicknesses of the active region.

Modeling Conclusions

Nanostructured radiation sensors comprised of blended arrays of lead-chalcogenide nanoparticles provide exceptional energy resolution performance. However, if the detector is thinner than $\sim 100 \mu\text{m}$, then the high probability of photoelectric absorption, combined with the high energy of the x-rays emitted from lead, results in a spectrum within which single and double x-ray escape peaks proliferate. Using MCNPX-Polimi, we simulated the performance of the detectors as the thickness was varied and found that if the detector thickness exceeds 1 mm, then the full-energy peaks dominate the response. Furthermore, an event-by-event accounting of the interactions shows that the photopeaks are dominated by the PbSe NCs, but the Compton continuum intensity is governed by the amount of organic polymer used to coordinate the assembly. The simulated results support the experimental spectra, in which the photopeaks are accompanied by a distribution of single and double x-ray escape peaks.

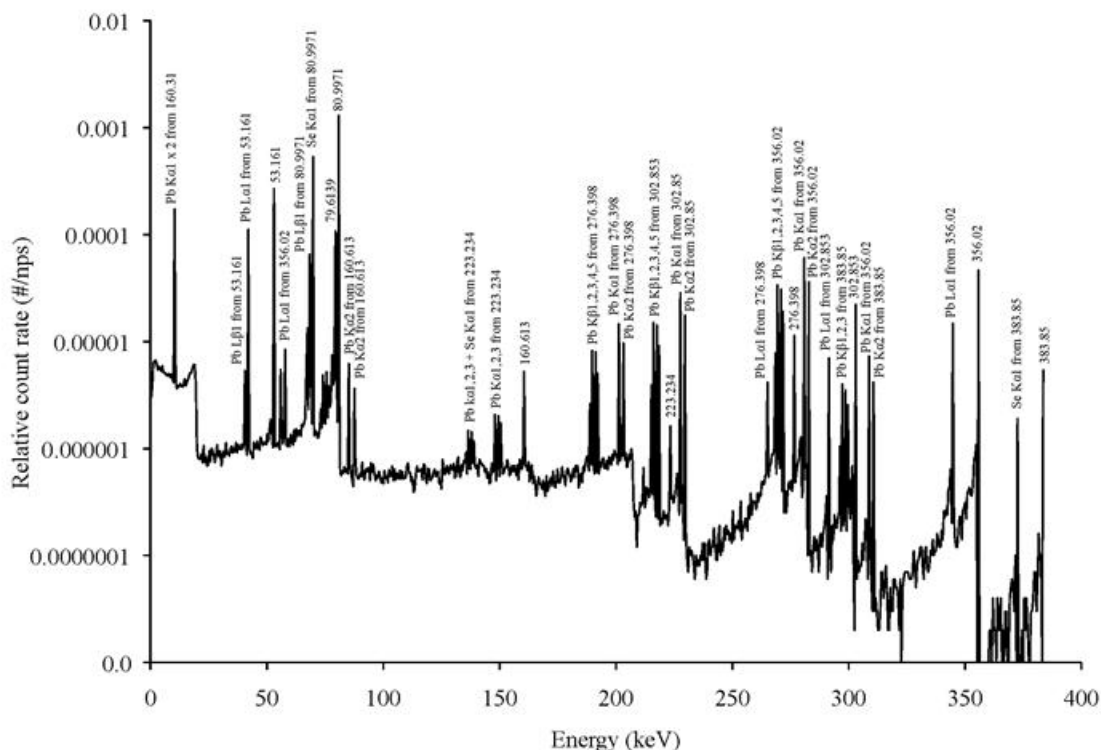


Fig. 2.11. The energy spectra of Ba-133 from simulation with the main peaks identified,

PbSe/PbTe Core-Shell Nanocrystals

Finally, consider the detectors that are closest to those that can be deployed in a practical device, in this case $\sim\text{cm}^2$ lateral area devices with mm-thicknesses. Core-shell structures nanoparticles were synthesized for these particular devices. Since PbTe is much more reactive than PbSe, it was expected to be easier to have PbSe core and PbTe shell structure, and this also matches our purpose since the PbTe has slightly larger band gap than PbSe, however, the bandgap matching can be always tuned by changing the size of the particle and thickness of the shell. First the PbSe core of the particle was synthesized through regular PbSe synthesis method. And then PbTe precursor prepared at the same time, was injected.

Evaluation

The PbSe/PbTe core-shell detectors, such as those shown in Fig 2.12, are of interest because they produce superior results to those single core (PbSe)-based detectors presented in Section 1. That is, the signal-to-noise ratios of the resulting charge-signals, such as those shown in Fig. 2.13, are significantly better than their single-core counterparts, which reflects a superior conversion of energy into charge carriers.

Furthermore, the detectors used to derive the signals are large (1.4 cm diameter) and thick. For instance, the signal in Fig. 2.13A was derived from a detector that is almost 1 mm thick (890 μm), and we have deposited detectors that are several millimeters thick, noting that we can deposit centimeter-thick detectors if desired by a simple repetition of the assembly chemistry. These preliminary results are highly promising and intriguing, for they reveal that further refinements of the nanosemiconductor approach can yield unsurpassed sensing devices.

As the project ends, we continue to study the PbSe/PbTe structures, including their material characterization, in which the sizes and dispersions of the nanoparticles are evaluated using

optical and TEM microscopic techniques, and the performance of the solids as detectors is tabulated.

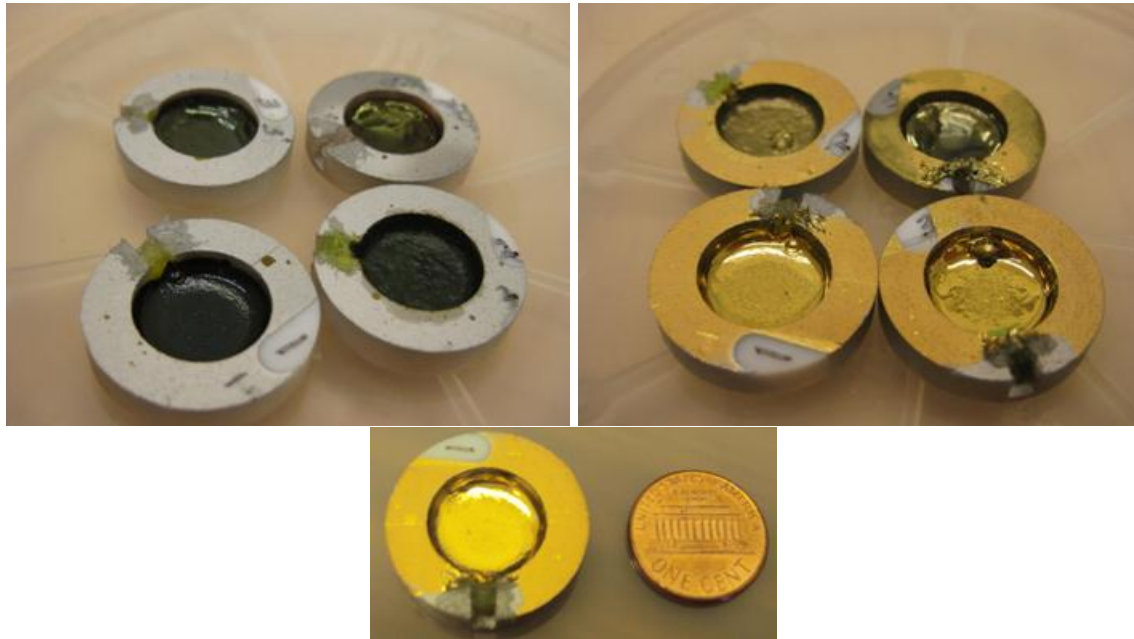


Fig. 2.12. Thick detectors deposited into a plastic mold in which a indium bottom contact is under the thick colloidal solid (upper left). The detectors after the gold is deposited on the top is shown in the upper right and the detector size relative to a penny is shown.

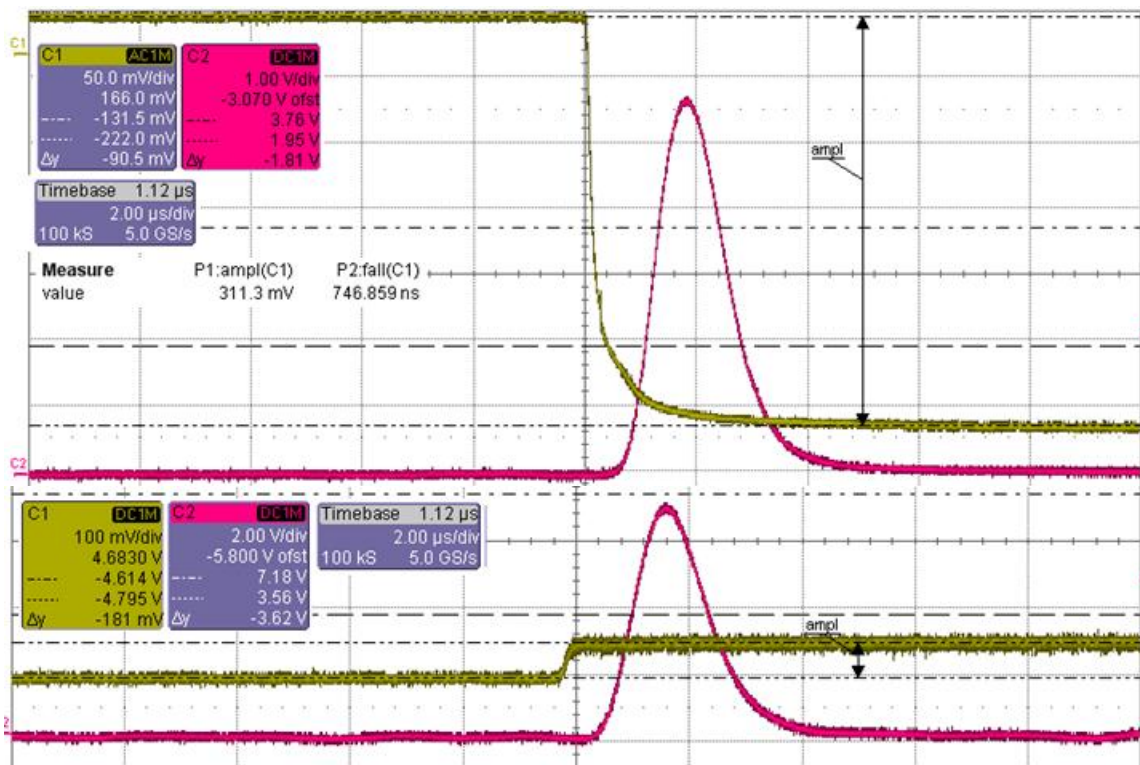


Fig. 2.13. (top) Typical pulse derived from a PbSe/PbTe thick detector is larger and cleaner than the equivalent from a PbSe detector (bottom), the results from which are presented in this report.

3. Achieving Low-Noise and Robust Contacts in Silicon and CZT

3.1 Abstract

Silicon PIN-type diodes with active areas of 1 cm^2 have been fabricated on n-type, high-resistivity ($>10 \text{ k}\Omega\text{-cm}$), $550 \text{ }\mu\text{m}$ thick 4" Float-Zone (FZ) silicon substrates. In order to reduce the leakage-current density, optimized metal field-plate and multiple guard-ring structures were included in the electrode design. In addition, both phosphorus-doped polysilicon and amorphous silicon gettering resulted in n-type PIN diodes with room-temperature leakage currents lower than 10 nA at -100 V reverse bias voltage. Several gamma-ray spectra, from isotopic sources ^{133}Ba and ^{57}Co , were acquired when the PIN-type detector was connected to various preamplifiers from Ortec, Amptek and Endicott Interconnect Technologies, Inc. (EITI). The eV-5093 produced the best noise performance, yielding a full width at half maximum (FWHM) energy resolution of 4.7% at 122 keV and 1.88% at 356 keV . Gettering methods by which the resolution is improved further are demonstrated.

3.2 Introduction

Recall that one doesn't simply collect the radiation by-products after creation and from their enumeration, derive the energy signal; instead, we measure the charge *induced* on the electrode by those in the bulk. Thus, just after charge-hole creation in the semiconductor bulk the charges feel the effect of the local electric field and begin to drift. A current is immediately induced on the bounding electrode in response to the changing electric field condition.

For planar detectors, or for interactions far from some surface partitioning, the drift velocity is constant as is the weighting field, and the current magnitude is therefore proportional to the initial charge number. After the initial step in the current pulse, the subsequent charge shape reflects the charge transport. Of concern to us is the case in which charges are lost, or delayed, during their motion through the bulk semiconductor. If the charges are trapped during transport, then the pulse shape exhibits a diminishing magnitude relative to an unaffected charge stream; however, as long as we extract the initial current peak, our energy measurement is not affected. The method is therefore insensitive, in principle, to loss during transport, and it therefore opens the door to exotic semiconductors with charge trapping as well as poorly conducting heavily trapping materials (although polarization can impact the field formation). The current peak measurement method therefore works in principle, but what about in practice?

For either charge-sensitive or current-sensitive measurements, the fluctuations in the baseline can limit the signal-to-noise ratio (SNR), rather than the desired case in which the statistical counting associated with the charge-carrier creation limits the energy resolution. One of the advantages of integrating the charge in the detector is that the high-frequency noise is filtered as a natural part of the signal formation. In either case however, the detector leakage current, or the readout circuitry noise can limit the SNR and the resolution. The key to effectively utilizing current sensing is to therefore quench both the leakage current and the electronic noise in the circuit, so that the current peak magnitude is effectively extracted.

In (23), we showed that if one does utilize a detector with a stable baseline, then fine energy discrimination is possible. In Sections 3.3 and 3.4, we show that the baseline noise has been made small for both silicon and CZT detectors. The main limitation of the method is thus the inherent limitations of the available readout electronics. As shown in (31) and (32), we have tested many different high-speed microwave transimpedance amplifiers (TIAs), some with bandwidths up to 10 GHz , and found that although they are suitable in extracting the fast current fluctuations in the signal, they are insensitive to the small fluctuations that accompany low-energy gamma-ray depositions.

Therefore, one can accept the current-sensitivity limitations of the existing readout chips and focus the applications on the imaging of *ion* tracks, for application in a neutron imager for

instance. However, we would prefer to have a solution for the lower energy depositions associated with gamma-ray interactions, the charge from which can be diminished by (1) (partial energy) Compton-scatter interactions, rather than full-energy photoelectric capture reactions, and (2) by charge sharing between multiple pixels or lines in a partitioned detector. Both of these limitations come to bear in a silicon-based detector, and since the charge mobility in CZT is lower than silicon (by roughly 50 % for electrons) current sensitivity is also at a premium for wider band-gap materials.

We have developed two innovations, which can be used to enhance the nuclear-radiation sensing capabilities of any semiconductor material. One innovation, the serpentine electrode pattern, is geared toward more precise *position sensing*, in which a time-sensitive delay-line allows one to readout micrometer-scale position resolution with only one or two readout channels per detector face (31,32). The second innovation is utilizing current sensing to enable fine *energy measurement* that is insensitive to the transport of the charges through the bulk of the active detection volume, by focusing the measurement on the initial peak in the induced current upon charge creation (23).

We have developed low-noise silicon and CZT detectors, with which ion and gamma-ray imaging instruments can be constructed, using conventional readout electronics. However, the power requirements and readout complexity are reduced because one utilizes two readouts per face of the detector, compared to the hundreds of readouts associated with pixellated or strip-line designs. In comparison with co-planar grid and Frisch collar electrodes- which are primarily used as a means to achieve single-polarity charge sensing- the meander-line electrode is position sensitive, which enables the angular imaging of the radiation field.

The degree to which one can improve the imaging (angular and energy) resolution for either neutrons or gamma-ray depends on the sensitivity with which one can extract the *initial* charge information, which can be muddled by detector and electronic noise, as well as by the inherent charge losses associated with transport through imperfect solids. We have successfully made both silicon and CZT detectors for which the detector noise is small compared with the electronic noise, and more importantly, small compared with the slight current fluctuations that accompany radiation interactions. The methods used to achieve low detector noise are described below.

In Section 3.3, we present the design and the fabrication process for a Si-based PIN diode with methods for the low leakage-current, and in Section 3.4, we will explain methods by which low leakage can be achieved in CdZnTe-based nuclear-radiation sensors.

3.3 Fabrication and Performance of the Si-PIN Detectors

In order to maximize the charge-sensitivity, and thus, the energy and position resolutions of the detector, the current fluctuations flowing over both the detector surface and through its bulk were reduced via multiple process steps. The *surface* leakage was mitigated below that provided by the bulk leakage via the inclusion of optimized metal field-plate and multiple guard-ring structures in the electrode design, as described in detail in the status reports and in (31). Once the surface leakage was quenched, the bulk leakage was reduced via the contamination-gettering with both phosphorus-doped polysilicon and amorphous silicon, the result of which are n-type PIN diodes with room-temperature leakage currents lower than 10 nA at -100V reverse bias voltage. The nuclear-radiation sensors are fabricated with a PIN structure on a substrate of high-resistivity ($\rho > 10 \text{ k}\Omega\text{-cm}$) double side polished <100> n-type 550 μm -thick 4" wafer, by using conventional microelectronic fabrication processes, which include oxidation, furnace doping, photolithography, dry/wet etching and sputtering. For the PIN detectors, the process sequence to fabricate the detectors is illustrated in Fig. 3.1.

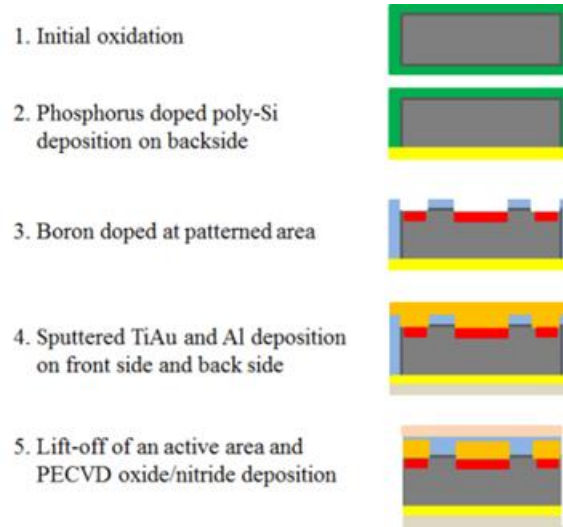


Fig. 3.1. Schematic of the important steps in the fabrication process.

An initial low temperature oxide (LTO) with a thickness of $0.5\ \mu\text{m}$ was grown at the temperature of $415\ ^\circ\text{C}$ (Step 1 in Fig. 3.1). After removal, via wet-etching, of the oxide on the backside of the wafer and the subsequent deposition of backside polycrystalline silicon, an n^+ layer was formed via phosphorous doping with a diffusion furnace at the temperature of 975°C (Step 2). In order to form a p^+ active region, boron was diffused at $1050\ ^\circ\text{C}$ for 20 minutes to make a shallow depth doping profile, after the patterning and removal of the initial oxide (Step 3). Thick gold (Au, $0.5\ \mu\text{m}$ thickness) electrodes, used to minimize the signal's conductive losses and increase the integrity of the wire-bond between the detector and the readout circuit, were sputtered to form the front-side metal anode. Aluminum (Al, $3000\ \text{\AA}$) was sputtered on the backside of the detector to form the cathode. Finally, sintering with forming gases, which are comprised of 95% nitrogen and 5% hydrogen, was carried out to optimize the ohmic contacts and saturate the silicon dangling bonds. A post-processing annealing with a furnace at $200\ ^\circ\text{C}$ for 10 minutes was also performed (Step 4). In order to: 1) prevent the diffusion of oxygen into the structure over long (weeks, months) periods, 2) passivate the surface, and 3) protect the detect surface from contamination, we deposited a sandwich of thin oxide ($1000\text{\AA}$) and nitride ($2000\text{\AA}$) on the front side of the detector, patterning a window only for the wire-bonding pad (Step 5). Fig. 3.2 shows the fabricated silicon PIN-type radiation detector.

Comparison of Gettering Methods

Gettering means the transfer of unwanted impurities from the active area of the device to an unimportant region. The goal for this process is to maintain or enhance the starting minority carrier diffusion length, which is achieved with phosphorous diffusion in microstructured silicon, whether polycrystalline silicon (poly-Si) or amorphous silicon (a-Si).



Fig. 3.2. Pictures of the fabricated silicon PIN-type radiation detector (right) and shielded module (left) for low energy gamma spectroscopy. The active area was 1cm^2 .

In order to deposit and condition the optimal material for gettering, we compared the current-voltage (I-V) characteristic as the backside material was varied, from low-stress poly-Si to a-Si, each layer with a thickness of $5000\text{\AA}$. In addition, we also compared the I-V characteristics with and without a $5000\text{\AA}$ thick passivation layer.

Fig. 3.33 shows the I-V characteristics as the gettering materials were varied. Leakage currents under reverse bias voltage were measured with a Keithley 4200-SCS (Semiconductor Characterization system). As shown in the figure, the detectors have low leakage current when one employs both a-Si and a passivation layer. A-Si is composed of uniform regions with larger grain size than those regions in low-stress poly-Si. The I-V results indicate that the microstructure of a-Si more effectively traps the impurities that generate minority carriers. Furthermore, the passivation layer can block leakage current paths near the surface and mitigate the contamination caused by dust and humidity, the protection from which was further enhanced with the oxide/nitride capping layer. The measured leakage current for the Si PIN-type radiation detector is shown in Fig. 3.4. The maximum leakage currents were observed to be 10nA at -100V , and no premature breakdown was observed.

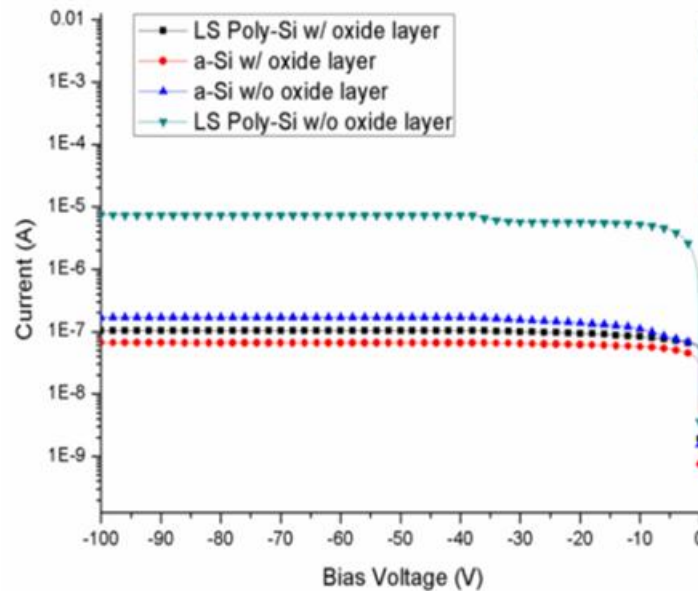


Fig. 3.3. Reverse bias I-V characteristics with different type of gettering materials.

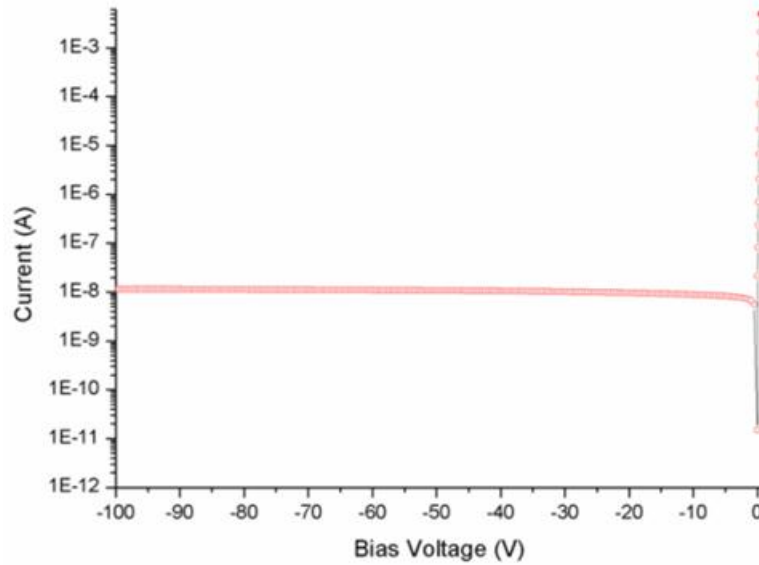


Fig. 3.4. Leakage current against reverse bias voltage with oxide/nitride capping.

Effect of Charge-Sensitive Preamplifier

We compared the spectroscopic effect of utilizing three different types of preamplifiers, from vendors Ortec (142A), AMTEK (A250NF), and Endicott Interconnect Technologies, Inc. (eV-5903). Fig. 3.5 shows the block diagram of the detection system with different kinds of preamplifiers.

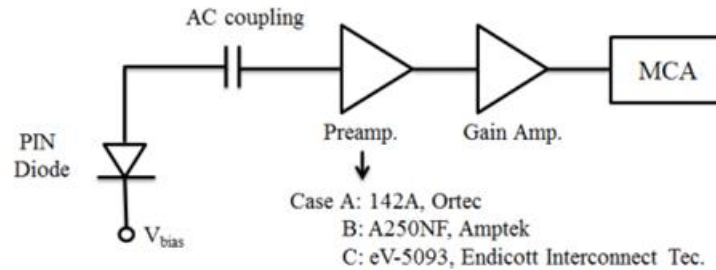


Fig. 3.5. Block diagram of the detection system with different kinds of preamplifiers.

Low energy gamma-ray emitters ^{57}Co and ^{133}Ba have their main photopeaks at 122 keV and 356 keV respectively. The relaxation of ^{57}Co following electron-capture (EC) yield photons of energies: 14keV, 122keV and 136keV, as shown in Fig. 3.6. The energy resolution of the 122 keV photopeak is 5.82%, 5.11% and 4.7% for the preamp cases of A, B and C, defined in Fig. 3.5, showing that there is a substantial difference between the effects of the preamps, as buttressed by the results in Fig. 3.7 and Table 3.1.

Specifically, Fig. 3.7 shows a comparison between the ^{133}Ba spectra in the upper energy range, where the 276.398 keV, 302.853 keV, 356.017 keV, and 383.851 keV full-energy peaks reside. The superior noise properties of the eV-5903 results in qualitative consequence, as shown by the enhanced clarity of the inter-peak dips and Compton edges of the black curve shown in Fig. 3.7. Quantitatively, the peak resolutions, as derived from the FWHM the 356 keV peak channel, are 2.22%, 2.25% and 1.88% for the A, B and C preamp cases, as detailed in Table 3.1.

The results show that the effects of the preamp design are thus non-negligible, relative to the detector noise produced by silicon operating at room temperature. That noise is highly sensitive

to the fabrication recipes employed as shown next.

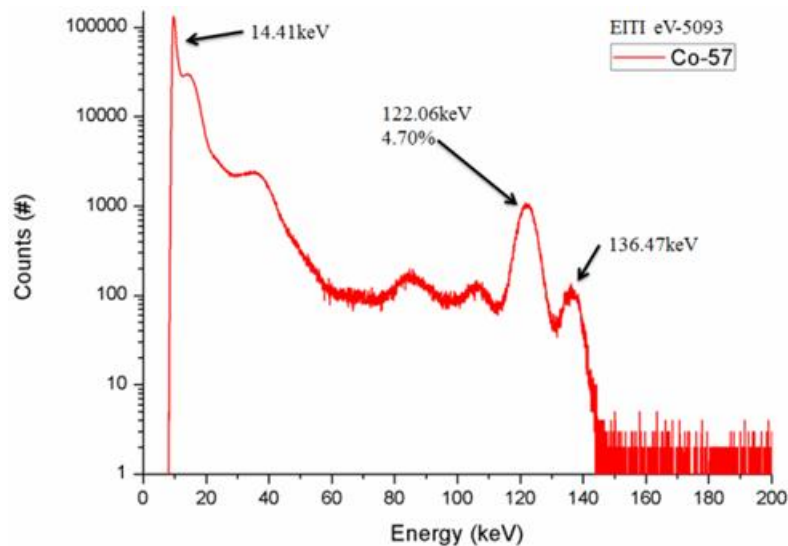


Fig. 3.6. Resolution of 4.70 % based on full width at half maximum (FWHM) were obtained for the 122 keV photopeak of Co-57 with eV-5093.

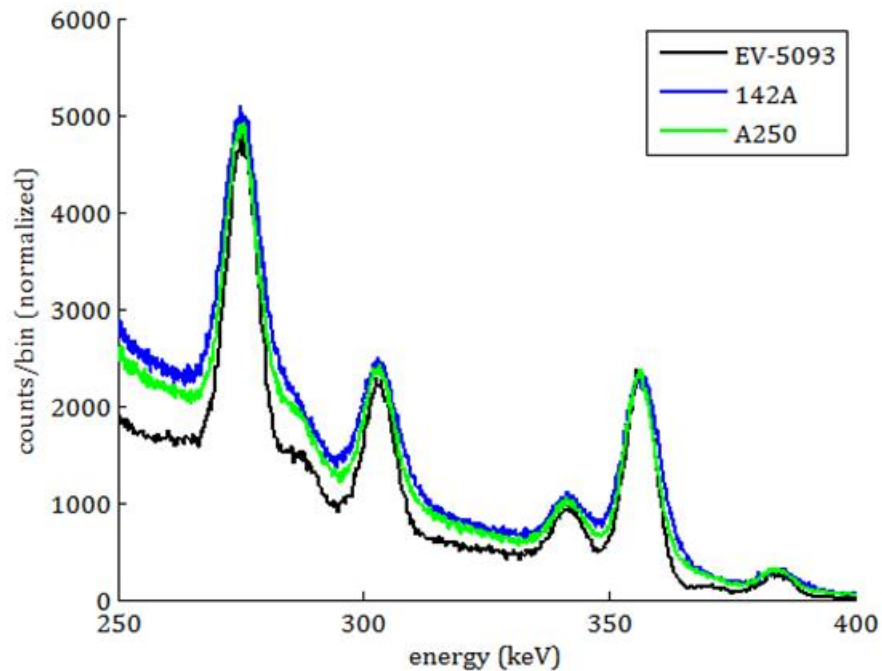


Fig. 3.7. The gamma-ray spectra derived from ^{133}Ba gamma-rays incident upon the detector described in Section IIA, when connected to three typical charge-sensitive preamps. The counts for the 142 A and A250 are normalized to match the counts in the 356 keV peak derived from the EV-5093 measurement.

Table 3.1. Peak resolution test results with three types of preamplifiers, for the detector operated at room temperature at -100V reverse bias (0.5 μ sec shaping times, gain = 100).

Preamplifiers	Source	Ba-133					Co-57	
	Energy(keV)	81	276	303	356	383	122.06	136.47
Ortec 142A	H	305.89	1047.34	1154.94	1358.79	1465.3	1133.19	1268.29
	FWHM	30.76	31.44	29.32	30.28	30.34	66	46.67
	R(%)	10.0559	3.001891	2.53866	2.228453	2.070566	5.824266	3.6797578
Amptek 250NF	H	767.16	2642.45	2912.04	3431.8	3703.15	2440.79	2717.76
	FWHM	73.68	78.11	64.34	77.39	58.88	124.82	91.73
	R(%)	9.604255	2.955969	2.209448	2.255085	1.589998	5.113918	3.3752061
EITI eV-5093	H	705.58	2417.56	2666.95	3135.61	3382.35	2217.77	2476.29
	FWHM	61.08	60.27	59.3	59.24	59.53	104.45	96.95
	R(%)	8.656708	2.493009	2.223514	1.889266	1.760019	4.7096859	3.9151311

Effect of Passivation and Annealing

The detector's noise properties are highly sensitive to both the passivation and gettering processes. By optimizing both, we are able to improve the leakage-current by roughly an order of magnitude by altering the oxide recipes and cleaning recipes as follows. For all of the processes, we first prepared starting wafers via a pre-furnace clean, which includes an organic cleaning step, oxide etching, and an ionic clean. For the organic clean, we used a 10 min dip of DI-H₂O + NH₄OH + H₂O₂, after which we removed the thin native oxide with 100:1 HF for 10 min. The 10 min ionic clean utilized DI-H₂O + HCL + H₂O₂.

An initial thermal oxide of 0.5 μ m was grown at a temperature of 1100 °C, in contrast to the LTO used in the higher noise detectors, described in Section IIA. After removal, via wet-etching, of the oxide on the backside of the wafer and the deposition of polycrystalline silicon (poly-Si, 0.5 μ m) with a CVD furnace at 585°C for 100 min., an n+ layer was formed via phosphorous doping with a diffusion furnace at the temperature of 950°C for 20 min diffusion time and 25 min drive-in time. For the protection of the poly-Si layer, we performed a thermal oxidation with 3000 Å thick wet oxide. In order to form a p+ active region, boron was implanted at 1000 °C for 45 minutes to make a shallow depth doping profile, after the removal of the initial oxide with wet etching (buffered HF). For the patterning, we used S1813 photoresist (4k-rpm spin coat makes 1.5 μ m thickness) which has good performance for the wet etching. Following each patterning process, the PIRANHA clean should be used in order to fully remove any organics- most topically, photoresist- from the wafer surfaces. In contrast to the gold/aluminum detectors, aluminum (Al, 3000 Å) was sputtered on the *front* and back-side of the detector to form contacts. Finally, sintering with forming gases at the furnace on 425°C for 15 min., which are comprised of 95% nitrogen and 5% hydrogen, was carried out to optimize the ohmic contacts and saturate the silicon dangling bonds. For passivation as well as device protection we deposited a thin oxide (2000Å) and nitride (3000Å) on the front side of the detector, and made a window just for the wire bonding pad side with plasma etching tool. Note that this capping layer was twice as thick as that described in the above section. Before dicing, we coated the wafers with photoresist which can protect the surface and keep it clean from tap water during dicing. Finally, we cleaned the diced detectors with IPA and acetone for 10 min. and anneal at 150 °C for 10 min. in order to dry the devices.

Fig. 3.8 shows the I-V curves before and after dicing and annealing. Note that the main goal is to preserve the behavior of the devices achieved before dicing, but the extra annealing step yields an improvement of roughly 10 times in the device leakage. Note that these values are all measured without guard ring bias, which can further quench the leakage current by an order-of-magnitude or more.

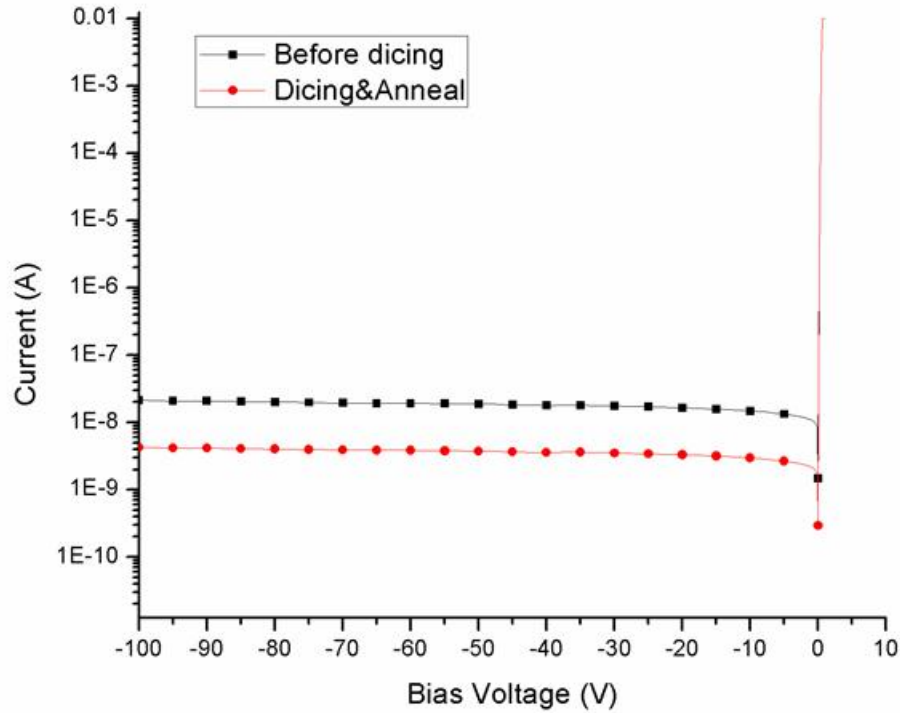


Fig. 3.8. The variation in the I-V characteristic which result from dicing and annealing the sensor..

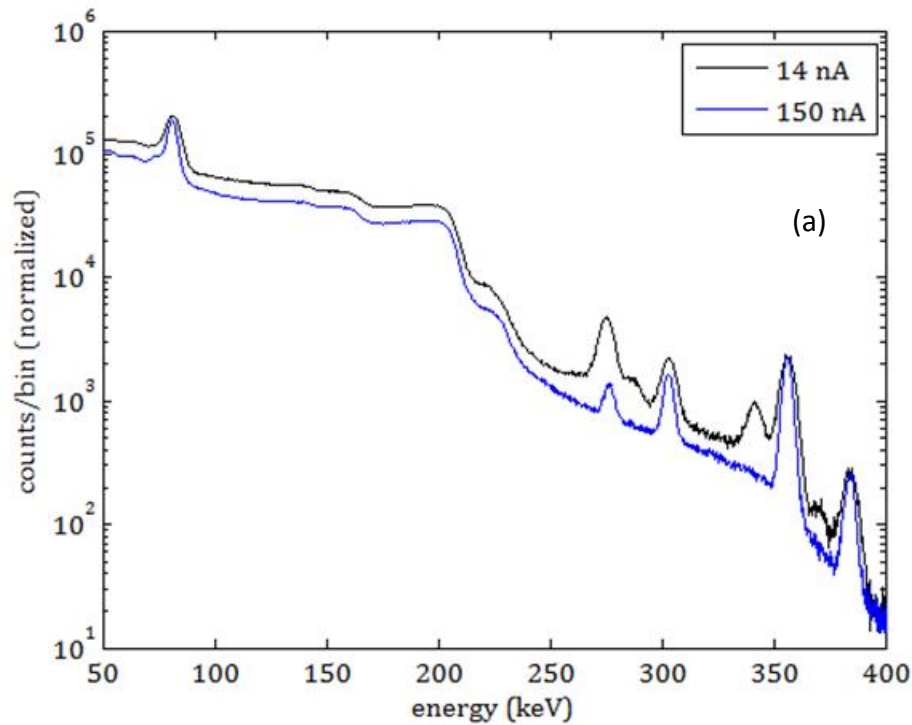
Fig. 3.9 shows the fabricated silicon PIN-type radiation detector, from which spectra were derived, such as that shown in Fig. 3.10. The blue distribution shows the spectrum derived from a detector fabricated using the refined recipe, and the black distribution was derived from a detector fabricated from devices with thinner, less close-packed oxide passivation layers. Note that the spectrum derived from the noisier detector is equal to that derived nine months earlier (not shown), soon after fabrication, and the detectors are therefore stable against long-duration performance variations; thus, the oxide/nitride capping layer is performing well in preventing any oxidation-induced degradation in the detector properties.

Most pertinently, the refined detectors have leakage currents that range from ~10 nA on the high end to 100 pA on the low end, the variation due to the non-uniform effectiveness of the getter layer as delivered by the doping furnaces. These values should be compared to the ~150 nA leakage current that characterizes the detectors derived from devices with nominally the same process. The results show that the microstructure and thickness of the oxide layer can substantially impact the performance of the devices, and deliver devices that don't require guard ring bias, which simplifies their packaging. In our goal to minimize both the detector and circuit noise in order to optimize the radiation-imaging performance, the silicon detectors do not constrain that performance.

Quantitatively, the *energy* resolution of the 356.15 keV peak is 4.58 keV (1.29 %), compared with 8.46 keV (2.38 %) for the un-refined detectors. Some of the spectral features appear to vary between the two devices; specifically, the satellite peaks in Fig. 3.10b that reside roughly 15 keV below the main peaks in the noisy detectors are absent in the refined devices. These features are not due to x-ray escape or other nuclear processes; rather, they are due to incomplete charge collection due to charge collection that is shared with an improperly designed guard ring.



Fig. 3.9. Picture of the enhanced-performance silicon PIN-type radiation detector, when bound by aluminum/aluminum contacts. The active area is 1 cm².



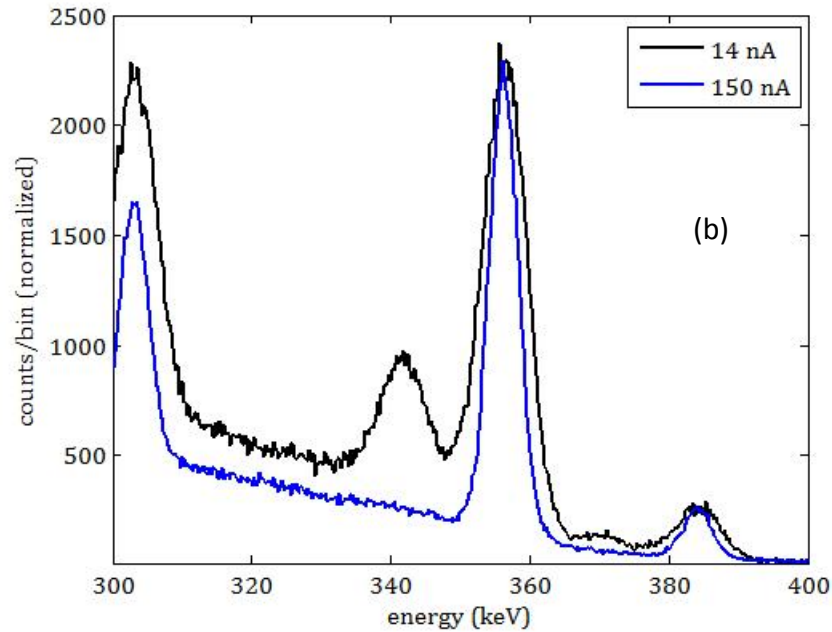


Fig. 3.10. Comparison of the spectroscopic performance of silicon PIN nuclear-radiation sensors, with different degrees of surface passivation in: (a) semilogarithmic form, and (b) linear form, focusing on the higher energy gamma-ray region. The counts from the 14 nA detector are normalized to match the 356 keV peak counts in the 150 nA detector.

3.4 Fabrication of Low-Noise CZT Detectors

For the efficient sensing of higher energy gamma-rays, one would prefer a higher Z, denser detection medium, such as nanostructured PbSe or, more conventionally, CdZnTe (CZT). We fabricate both: (a) planar-type CZT with multiple floating guard-rings, and (b) meander-line CZT devices, such as those shown in Fig. 3.14 below. Before the microelectronic processing, we lapped and polished the crystals with 10 μ m, 5 μ m and 0.5 μ m grain size of lapping and polishing papers. After polishing, we rinsed the bulk CZT with IPA and methanol for 5 min, after which we performed a Br-methanol (1%) etch for 1 minute. Fig. 3.11 shows microscopic pictures of the CZT surface after mechanical polishing and after Br-methanol etching, exhibiting the obvious improvement accrued from using chemical polishing.

Fig. 3.12 shows I-V curves of the bulk CZT derived from various vendors, provided by either Redlen or eV-product (via Orbitech). The “Redlen” sample corresponds to a re-processed pixellated device purchased directly from the vendor. The sample labeled “old GE” corresponds to mechanical-grade CZT, as provided by General Electric but originally supplied by Redlen, and “new GE” corresponds to spectroscopic grade Redlen material, manufactured in 2010.

As shown in the plots, the leakage current improves as the defect level of the material is reduced. The mechanical grade CZT (“old GE”) has the highest leakage, the spectroscopic grade Redlen material (“new GE”) has the lowest leakage, and the eV-product material is intermediate between the two. In absolute terms, the leakage current is quite good because at -100 V, the value is ~ 35 pA for the nominal 5 mm thick sample, which is much lower than that produced by the samples upon the receipt from the vendors and about 10 – 1000 times smaller than that produced by silicon, which is 10 times thinner. Thus, the imperfections in the crystal are not preventing us from taking advantage of the wide band-gap of the material. The consequence of this low leakage is that the signals are substantially above the noise for both ions and gamma-

rays, and one can therefore extract the charge information well, relative to the electronic noise. Of course, the poor hole transport and electron trapping still spreads the spectrum unless it is properly corrected.

With the polished CZT crystals, we deposited photoresist SPR-200 which has a maximum thickness of 3 μm , which requires a 6 s UV exposure time and 1 min development time. Before the metallization, we performed an ashing run for removing the remaining photoresist. We then used an indium (In) deposition of 3000 $\text{\AA}$ thick, which was patterned using lift-off, in which a 30 min acetone dip was used for PR removal. N_2 annealing for 10 min. at 150°C was used.

After metallization, we did a passivation with H_2O_2 and NH_4F (wt 1% each) for 10 min. to make an oxide on the CZT surface. Several different metallizations were investigated, including Au, In, Cr/Au, In/Ag, In/Au and Ti/Au, mainly to find the recipe that yielded the best adhesion, which facilitates the patterning of small features. When the evaporator was operated at the normal deposition rate (10 $\text{\AA}/\text{s}$), the entire metal was taken off; however, when we reduced the deposition rate to 3 or 5 $\text{\AA}/\text{second}$, finer grain structure was produced and adhesion between the CZT and the metal were good, and we can successfully pattern the meander, as the 20 and 25 μm width patterns of Fig. 3.13 show.

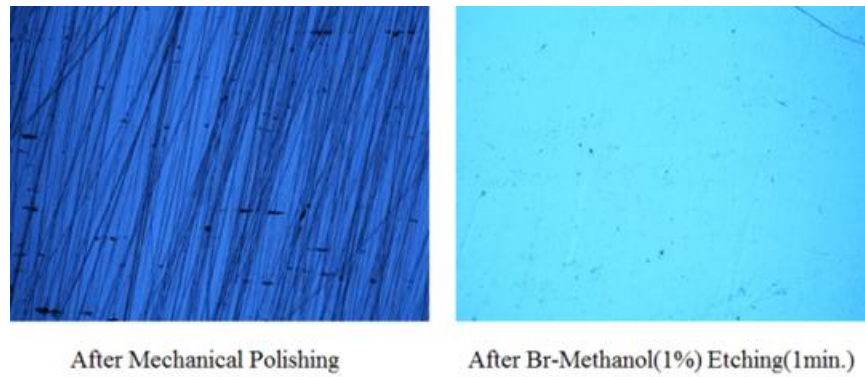


Fig. 3.11. Pictures of CZT surface after mechanical polishing(left) and Br-Methanol etching(right).

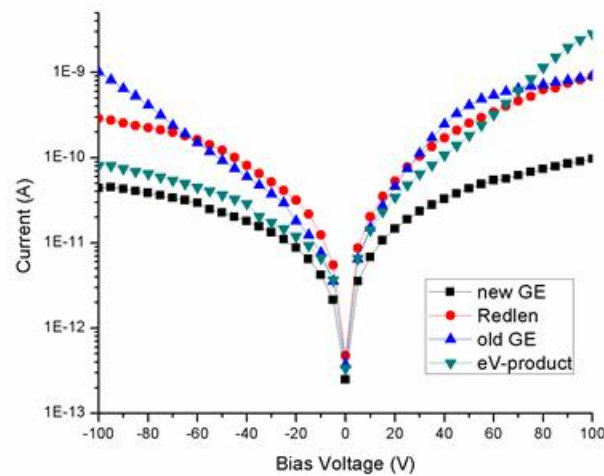


Fig. 3.12. Leakage current against reverse bias voltage with bare CZT from different vendors.

Polishing with 10 μ m, 5 μ m and 0.5 μ m lapper

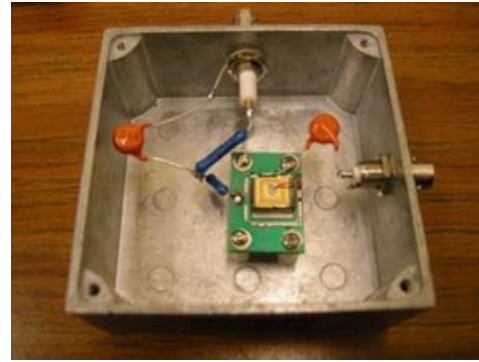
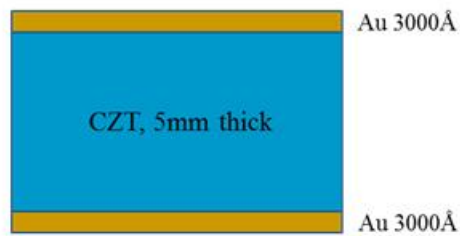
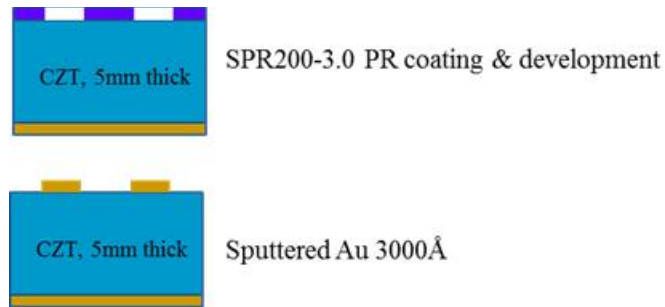
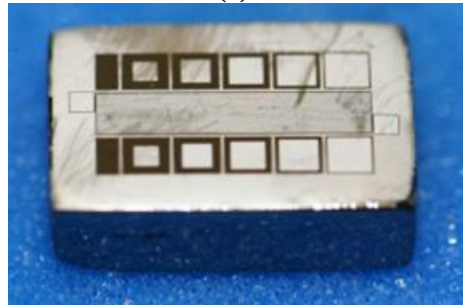


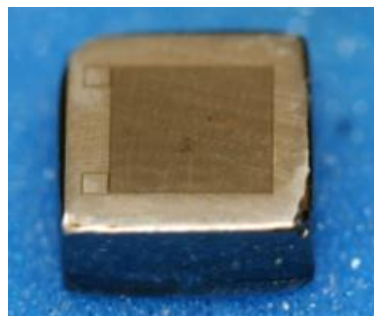
Fig. 3.13. Planar type CZT detector with multiple guard-rings.



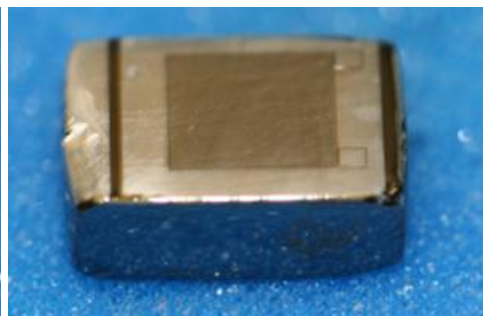
(a)



(b)



(c)



(d)

Fig. 3.14. (a) Simplified version of process used to fabricate meander-line CZT detectors. (b) Derived from spectroscopic-grade GE CZT, fabricated detector which has test-pixel pattern. (c) 20 μ m width meander, derived from eV-product CZT, and (d) 25 μ m width meander detector from GE mechanical grade CZT.

3.5 Conclusions

In the absence of perfect crystalline semiconductors, the intrinsic noise performance of the solid is governed by the efficacy with which one can segregate impurities in getter layers. For silicon, the optimization of the getter process depends on finding the optimal balance between the polycrystalline dimensions of the getter structure, the constituent chemistry of the composite materials, and the annealing conditions during which contaminants and defects are diffused and trapped into the inconsequential assembly.

In order to observe the effectiveness of the gettering, the ease of charge transport over the surface must be stiffened, which can be achieved with: (1) thick passivation layers of multiple microstructural components, (2) chemical passivation which ties off the dangling bonds of the cleaved solid, and (3) guard ring and metal-field plate electrode designs.

We have successfully made both silicon and CZT detectors for which the detector noise is small compared with the electronic noise, and more importantly, small compared with the slight *current* fluctuations that accompany radiation interactions, and one can therefore maximize the energy and angular resolutions following nuclear radiation interactions, limited by the inherent uncertainties in the charge-creation process.

4. Position sensing with the meander line detector

We have previously described in great detail the manner in which a meander-line detector can be used to enhance the capabilities of nuclear-radiation imaging devices. We will summarize the final performance of the innovation in this section without repeating all of the technical details which govern the device performance.

Position sensing can be elicited via either timing or amplitude variations. The main physical mechanism through which we ascertain the position via *amplitude*-based methods is through the phase-velocity dispersion and RC stretching of the pulse-shape. Recall that one can use an asymmetric strip-line to preserve the pulse shape, and one then extracts the position from the pulse timing and the energy from the steps in the signal, the advantage of which is that longer lines can be employed and more detailed information can be extracted.

However, if one wishes to simply use the detector as an energy and position measurement instrument, then one can eschew the overlay and permit pulse shaping. The degree of pulse shaping then provides a measure of the position-of-interaction along the transmission line. Practically speaking, the current step is elongated and thus diminished in amplitude as the pulse traverses the electrode, the consequence of which is that the *slope* in the charge-integrated signal is reduced as the interaction position increases. We measure that slope by taking the derivative of the preamp signal and use that as a measure of the position. In the following, we compare this phase-velocity distortion technique with a timing method, in order to gauge the resolution with which the position can be extracted with the most simple transmission-line design.

Although this pulse shaping is the main mechanism through which we gauge the position, for longer lines, the resistance of the conductor can also play some role. As shown in Fig. 4.1a, the general circuit configuration consists of a photodetector and a transimpedance amplifier (TIA) which converts the current from the photodetector into a voltage at the output node of the TIA. Fig. 4.1b is an equivalent circuit modeled by the photodetector. The special gamma ray photodetector has a meandering line which is presented as two resistors R_{m1} and R_{m2} . Those resistors are variable due to a position where the gamma ray comes in the photodetector. Ideally, by measuring the current flowing through R_{m1} and R_{m2} , one can determine the gamma-ray interaction position.

Let V_x be the voltage across R_{m1} and R_{m2} .

$$\frac{V_x}{R_{m1}} + \frac{V_x}{R_{m2}} = I_p \quad (4.1)$$

I_p is a photocurrent generated by the incident gamma ray into the photodetector. If a current I_1 flows to TIA₁, then we can obtain the I_1 as follows:

$$\frac{V_x}{R_{m1}} = I_1 \quad (4.2)$$

Substituting Eq. 4.2 into Eq. 4.1,

$$I_1 = I_p \left(\frac{R_{m2}}{R_{m1} + R_{m2}} \right) \quad I_2 = I_p \left(\frac{R_{m1}}{R_{m1} + R_{m2}} \right)$$

I_2 follows similarly. By comparing the amount of these current values, one can find the position of incident gamma ray in the. The resistance method is more applicable for a balanced transmission-line because its effect is negligible compared with the shaping inherent to a standard micro-strip line.

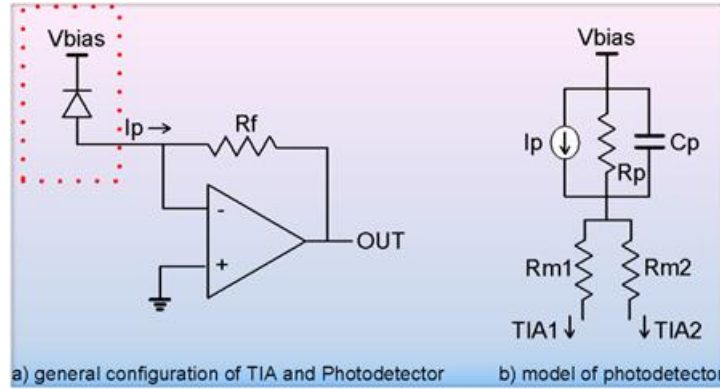


Fig. 4.1. The general configuration of TIA and photo detector (a) and the model of photodetector (b).

With 5nA leakage at 100V reverse bias voltage and the Am-241 alpha source collimated at one side of the 50 μm width meander lines, the meander line Si detector was used to acquire the time difference and amplitude difference at both ends, using the charge sensitive amplifiers as shown at Fig. 4.2. The system has 3 outputs- from preamplifiers for the both ends of meander line as well as the back side cathode. The shaped and amplified signal from the cathode was used as the trigger signal.

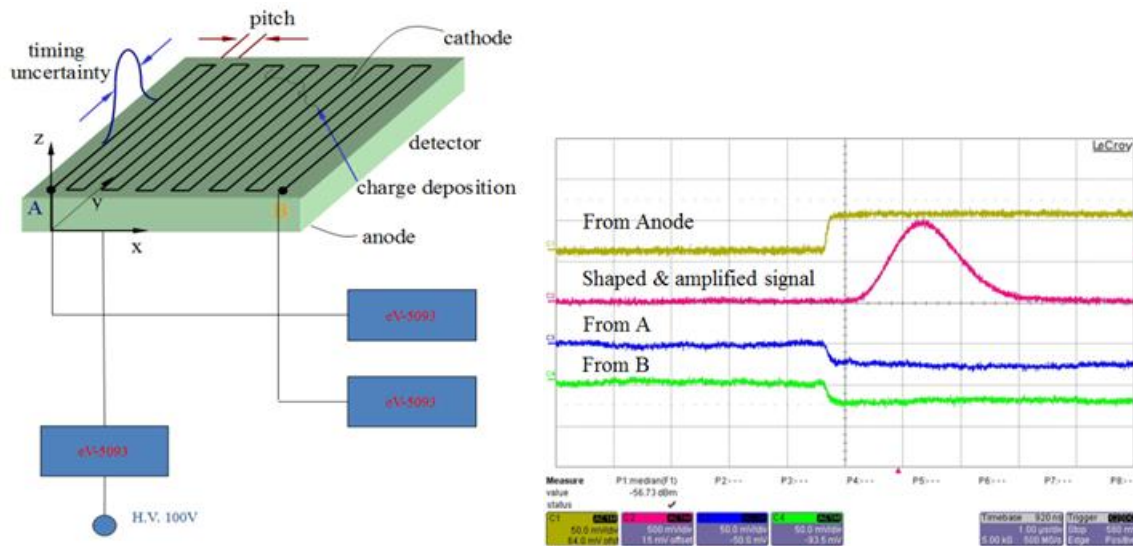


Fig. 4.2. The system configuration for the signal acquisition from anode and two ends of cathode with eV-5093 preamplifiers (left) and acquired signals (right).

For the signal acquisition, an oscilloscope (LeCroy) which has 2GHz bandwidth and 5Gs/s sampling rate was used. As shown in Fig. 4.3, outputs from the 3 preamplifiers (eV-5093) were acquired. The blue signal near the yellow signal (from the cathode) was calculated by signals of both meander ends (green and red). Fig. 4.4 shows the digital shaped signals from ends of meander line (thick green and red), cathode signal (blue) and sum with opposite from both ends of meander (black). A digital shaping amplifier was designed using CR-RC² shaping and implemented in a Matlab code. In order to calibrate the position of interaction, a collimator made of copper tape was arranged as shown in Fig. 4.6. Specifically, the top edge of corners was

exposed to the radiation; thus, the time or amplitude spectra should count the number of corners in the detector which is half of the number of lines in the meander-pattern.

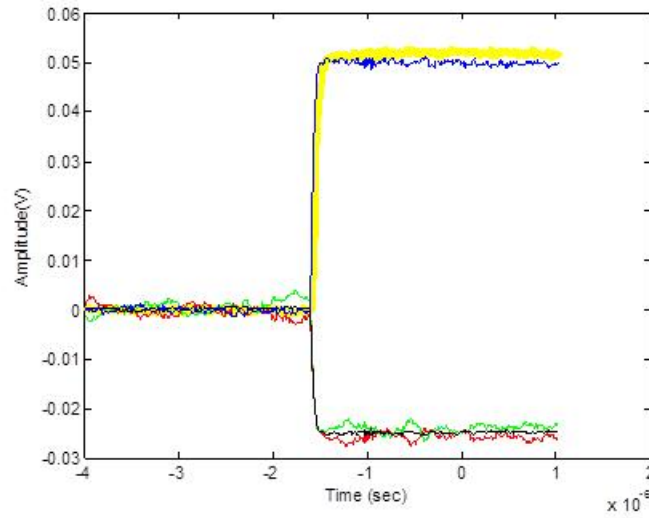


Fig. 4.3. Preamplifiers signals from both ends of meander line (green and red), their average signal (black), cathode signal (yellow) and sum with opposite from both ends of meander.

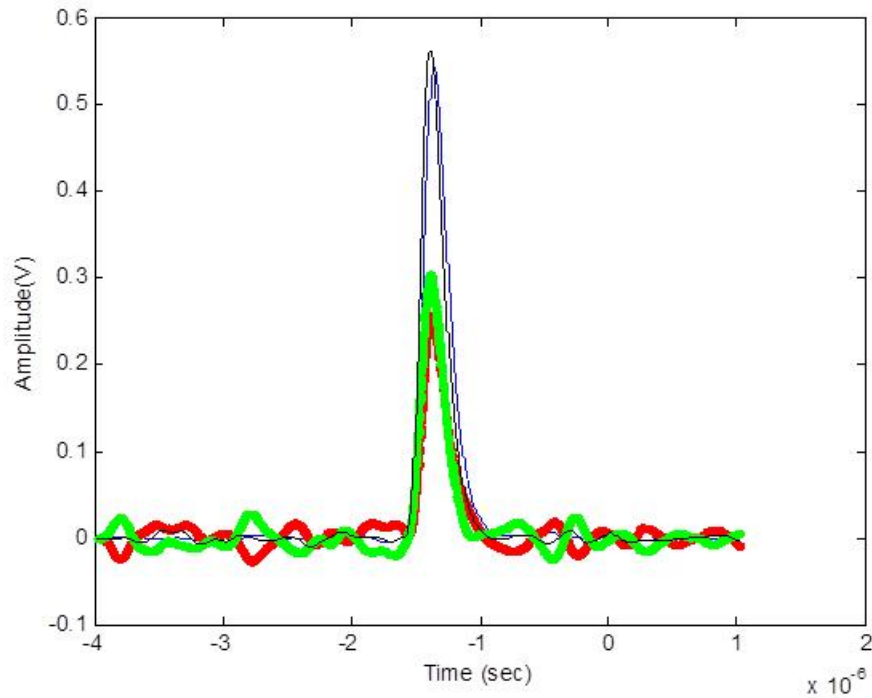


Fig. 4.4. Digital shaped signals from both ends of meander line (green and red), cathode signal (blue) and sum with opposite from both ends of meander (black).

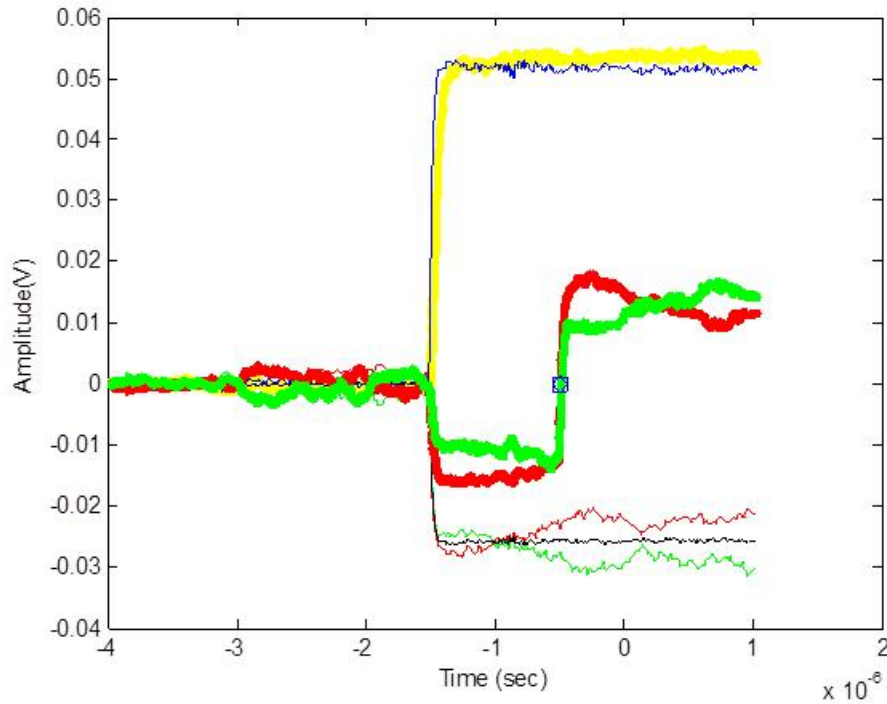


Fig. 4.5. Signals after applying the Constant Time Fraction (CFT) methods for both ends of meander (black). Note that small rectangular marks correspond to each t_0 .

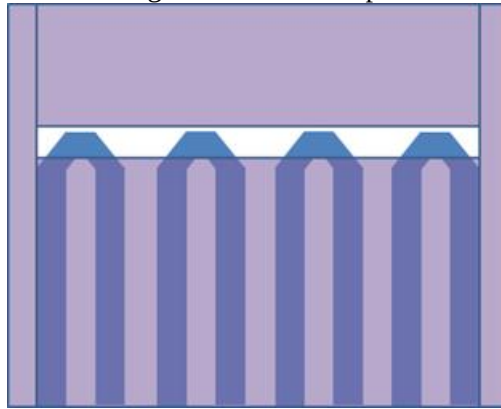


Fig. 4.6. The collimation at the each corner of 50 μm width and 8 lines meander. Note the blue line is the meander line and purple block is the copper collimator.

Fig. 4.7 shows examples of signals for the different interaction position at both meander ends. When the interactions occur at the extreme ends there are amplitude differences and time delays between the two signals, as shown in Fig. 4.7. In order to use the time difference between the signals at the meander ends for the position determination, the constant time fraction method is applied as shown in Fig. 4.5. With these acquired signals, amplitude differences between the meander ends are calculated for the position sensing as shown Fig. 4.8.

The time spectra in Fig. 4.8 from the four-turn meander, indeed shows four peaks, in which the outer peaks are larger, in area, because of greater effective detection volume associated with the edge strips. Also note that the time difference between the two middle peaks is greater than the two outer features, which reflects the fact that signal propagation is more shaped by the increased capacitance and inductance of interior lines. The Fig. 4.9 amplitude distribution

reflects the feature that the central peaks are generally sharper than the edge peaks because of superior SNR due to the higher signals amplitudes. That is, nearer the edge of meander line, the far pulse experiences a greater degree of pulse shaping, and the resulting signal is more adulterated by the electronic and thermal noise.

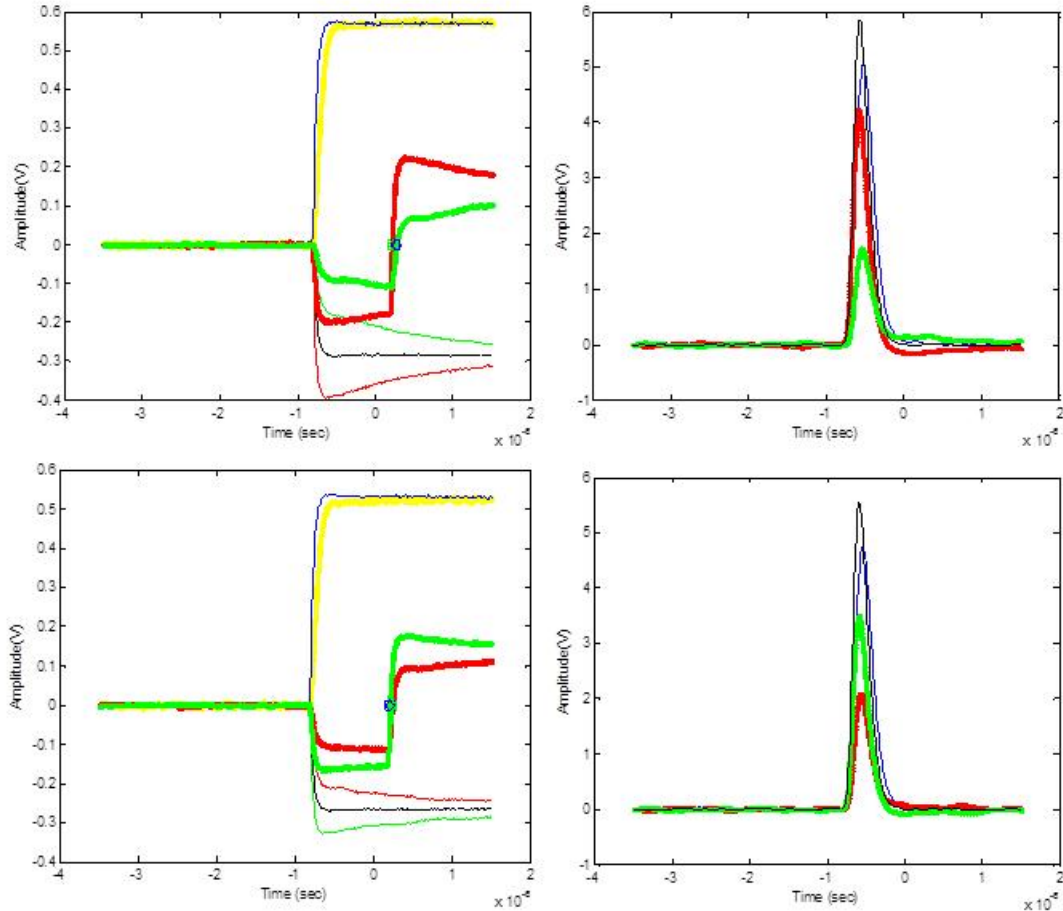


Fig. 4.7. Signals acquisitions when the interaction happens at left meander end (top) and when it happen the opposite site (bottom). Note that the pulses of right side are corresponding to their amplitude comparison.

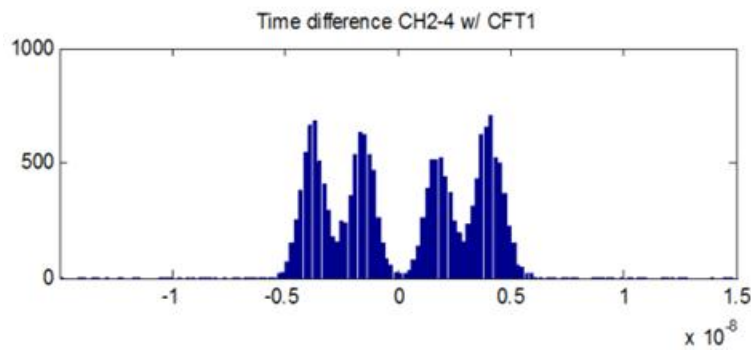


Fig. 4.8. Time difference histogram from the signals at both meander ends for the 50 μm width, 4 turns.

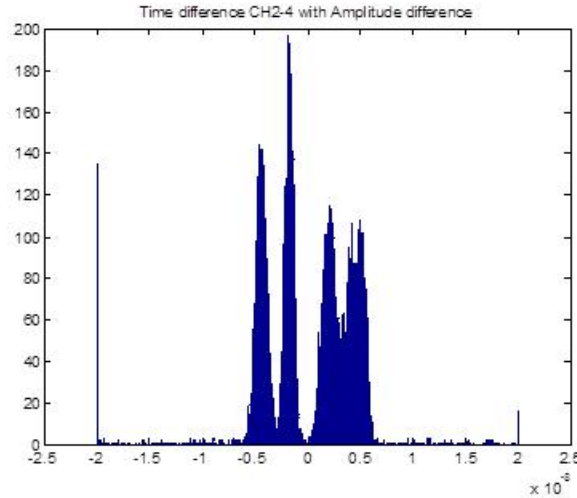


Fig. 4.9. Amplitude difference histogram from the signals at both meander ends for the 50 μm width, 4 turns.

This trend is reflected in Fig. 4.10, in which the edge lines reach further down than the central line. That is, Fig. 4.10 shows the distribution of interaction positions corresponding to the time difference spectrum in Fig. 4.8, and Fig. 4.11 shows the alpha source image with collimation as shown at Fig. 4.60. The broadness in the horizontal direction is due to the line-collimation (rather than hole collimation), and the uncertainty in the vertical direction reflects the uncertainty in the position determination along a given line. According to the result of the time spectrum in Fig. 4.8, the transition time of the current between two lines was 2.032 ns, which means that the propagation speed is a rather slow 1.016 ns per 1 cm. However, this transition time is increased by increasing the number of turns because of increasing the inductance. Also, when the width of meander is decreased the transition time is increased.

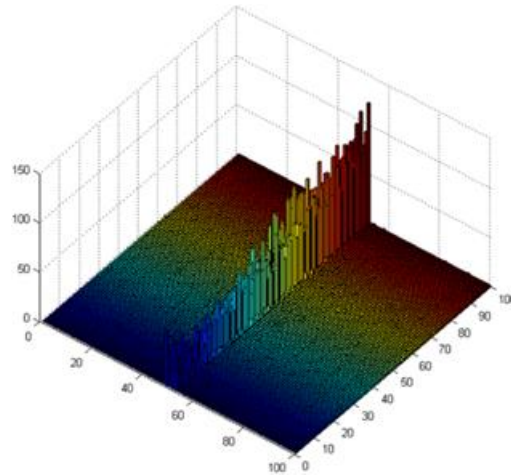


Fig. 4.10. Probability of the interaction position at the 50 μm width 4 turns meander line detector.

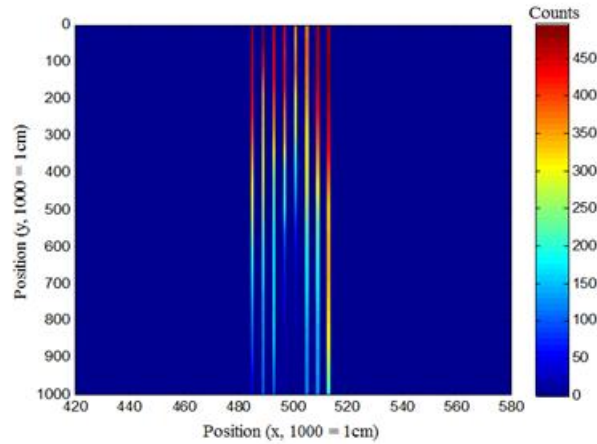


Fig. 4.11. Alpha source image with collimation like Fig. 4.6 for the 50 μm width 4 turns meander line detector.

For the purpose of evaluating the meander line detector, several detectors which have different number of turns were used, and time-difference and amplitude-difference spectra were measured, as shown in Figs 4.12 and 4.13. With these acquired data the alpha source collimated images were acquired as shown in Fig. 4.14. As shown in the figures, the total time difference and amplitude difference are increased by increasing the turn number. For the 4 turns, 6 turns and 12 turns, total time differences were 8 ns, 12 ns and 24 ns, respectively.

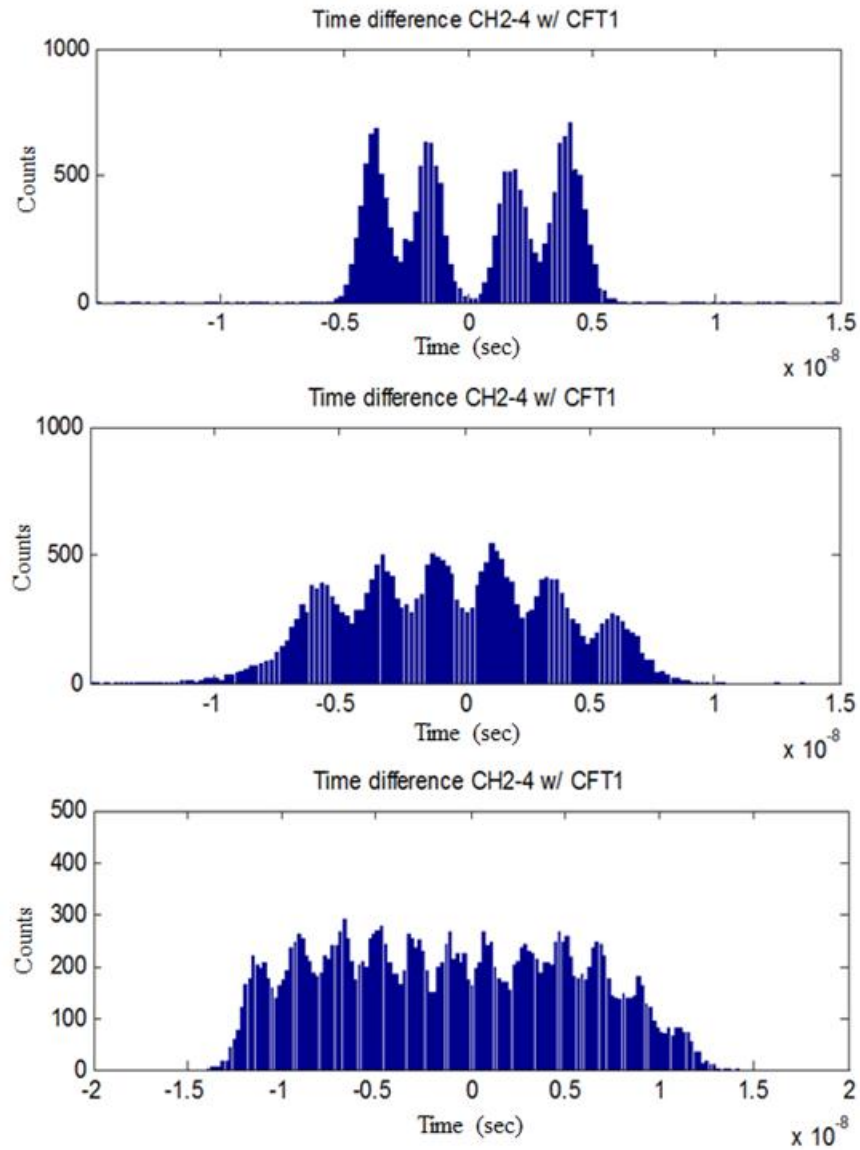


Fig. 4.12. Time difference histogram from the signals at both meander ends for the 50 μm width 4, 6 and 12 turn.

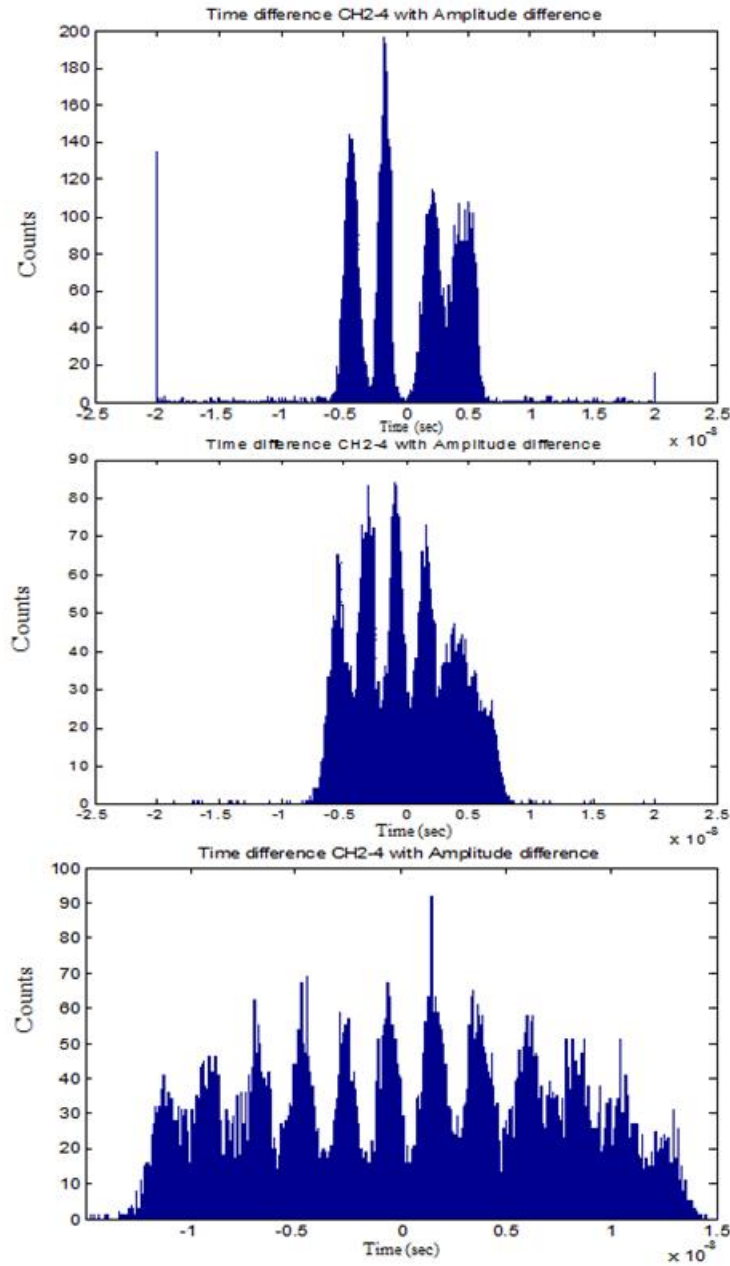


Fig. 4.13. Amplitude difference histogram from the signals at both meander ends which have 4, 6, 12 turns of the 50 μm width.

For the sake of further demonstrating position sensing with the meander line detector, the source was collimated to the upper half of the 24 line detector, resulting in the time spectrum of Fig. 5.79. With this information, the alpha source image with half collimation can be acquired, as shown in Fig. 4.16.

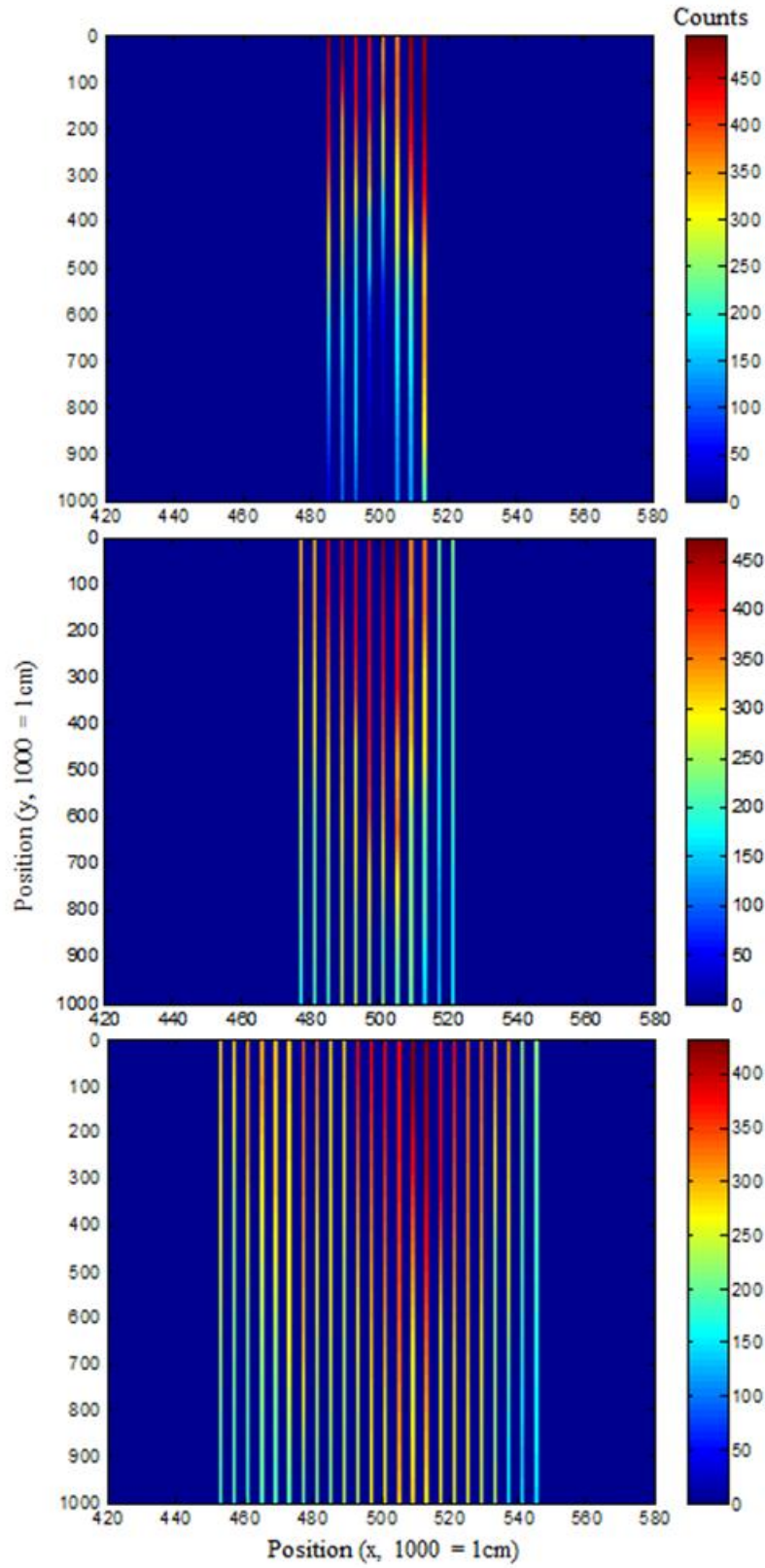


Fig. 4.14. Alpha source image based on amplitude variation with meander detectors which have 4, 6, 12 turns of 50 μm width.

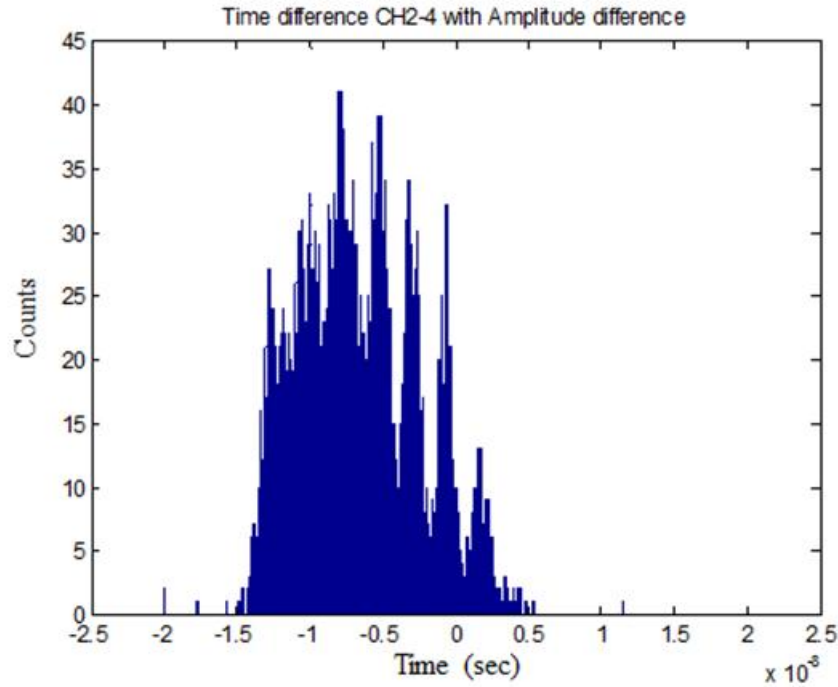


Fig. 4.15. Time difference histogram from the signals at both meander ends for the 50 μm width 12 turn with half collimation.

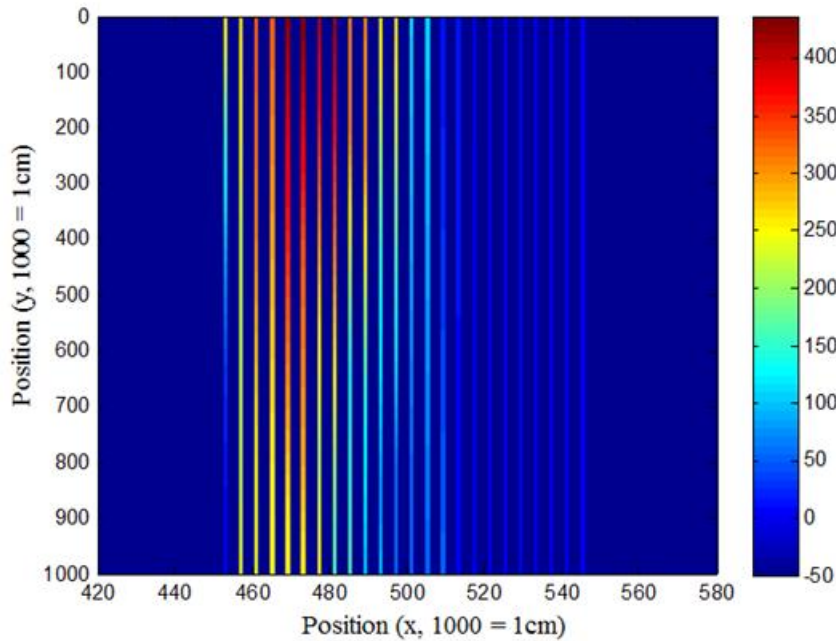


Fig. 4.16. Alpha source image of the meander detector which has 12 turns with half collimation.

In order to validate the effect of varying the width of the meander line, 8 turns of the 25 μm width meander line detector was used. Fig. 5.81 shows the time difference histogram and amplitude difference histogram. The transit times between each line are from 4.08ns to 4.58 ns, which implies a propagation speed of ~ 2.04 ns per cm, which is almost double that measured for

the 50 μm width meander (1.05ns). Favorably, smaller partitions result in lower propagation speeds and thus greater position clarity. With these acquired time difference and amplitude difference spectrum, the collimated alpha source images are acquired as shown at Fig. 4.18. As shown Fig. 4.17, the position uncertainty due to timing is poorer than that realized when one employs the amplitude difference histogram.

This is also reflected in the alpha source image, as shown in Fig. 4.18, in which the “reach-down” of the uncertainty in red is less for the amplitude-difference case. The spatial resolution is dependent on the meander’s pitch size. Using either time-differences or amplitude differences, the position of interaction can be isolated to a single line as shown.

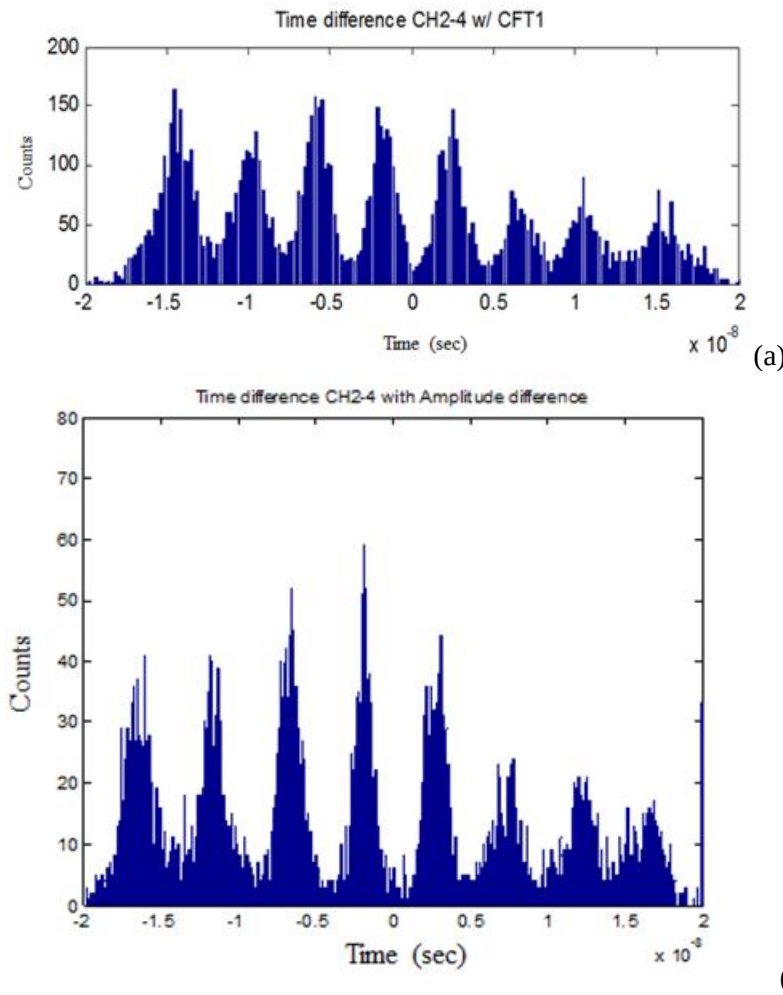
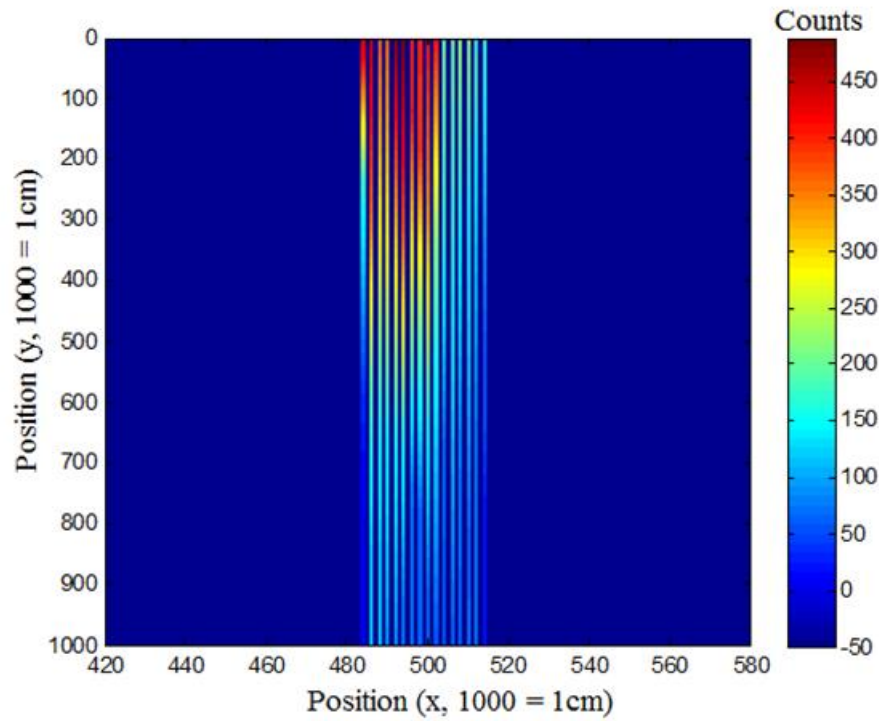
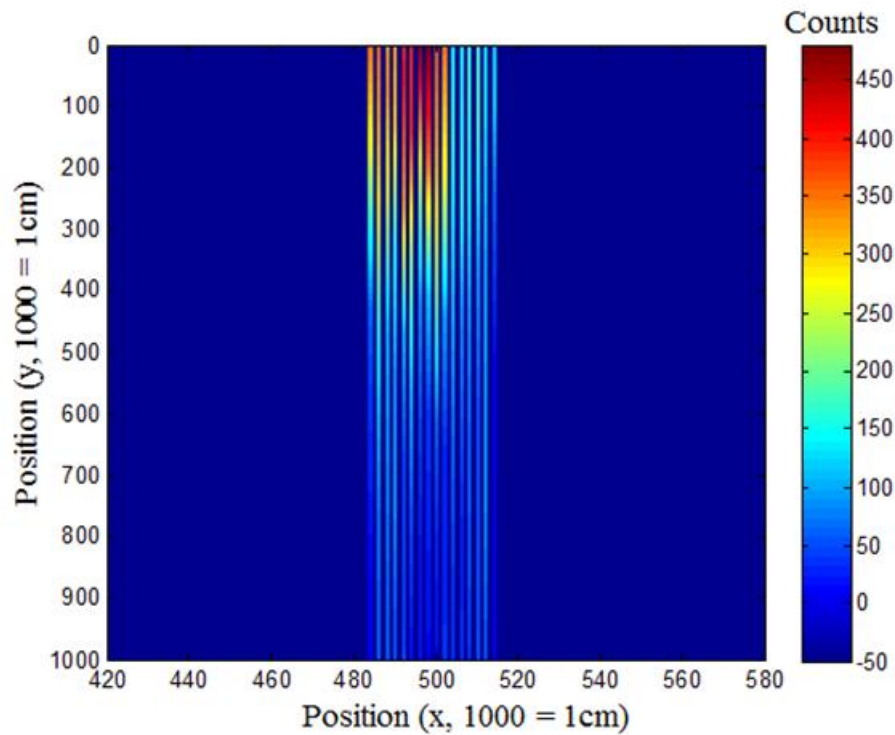


Fig. 4.17. Time difference histogram (a) and amplitude difference histogram (b) from the signals at meander’s both ends for the 25 μm width 8 turn.



(a)



(b)

Fig. 4.18. Alpha source image of the meander detector which has 8 turns with using the time difference method (a) and amplitude difference method (b).

v) *Personnel Supported:*

- 1) Mark Hammig, Ass. Research Scientist, Nuclear Engineering and Rad. Sciences (NERS), 30 % effort
- 2) Justin Sanders, Grad..Stud., Ph.D. Candidate, Electrical Eng. (January - April 2007)
- 3) Manhee Jeong, Grad. Stud., Ph. D. Candidate (NERS)
- 4) Geehyun Kim, Grad. Stud., Ph.D. Candidate (NERS), (August 2007-December 2011)
- 5) Derek Lax, Undergraduate Student, Junior (NERS), full-time in summer.
- 6) Ellen Dupler, Undergraduate Student, Junior (Chemical Engineering), part-time during school year.
- 7) Joseph Karbowski, Undergraduate Student, Senior (NERS), full-time in summer, part-time during school year.
- 8) Divya Kondapolli, Undergraduate Student, Junior (Chem. Eng.). part-time during school year.
- 9) Andrew Trumbo, Undergraduate, Freshman, full-time in summer, part-time during school year.

vi) Publications from Project (P = peer-reviewed, C = conference publication):

Referred Journal Articles

- [P1] M.D. Hammig and G. Kim and M.D. Hammig, "Fine Spectroscopy of Ionizing Radiation via a Colloidal Array of Blended PbSe Nanosemiconductors", Nucl. Instr. and Meth. in Phys. Res. A (submitted Dec 2011).
- [P2] M.D. Hammig and G. Kim and M.D. Hammig, "Simulated Nuclear Radiation Responses Derived from Nanocrystalline Semiconductor Assemblies", IEEE Transactions on Nuclear Science (submitted Dec 2011).
- [P3] M.D. Hammig and M. Jeong, "Fabrication of Si PIN-type Sensor for Gamma-Ray Spectroscopy", IEEE Transactions on Nuclear Science (submitted Dec 2011).
- [P4] M.D. Hammig and J. Noh, "The degree of enhancement in a gamma-ray image gleaned from recoil-electron tracking", IEEE Transactions on Nuclear Science (to be submitted January 2012).
- [P5] G. Kim, J. Karbowski, and M.D. Hammig, "Signal formation on a serpentine delay-line electrode patterned on the CdZnTe detector", Nucl. Instr. and Meth. in Phys. Res. A, vol. 652, p. 439-444 (Oct. 2011).
- [P6] M. Jeong, M.D. Hammig, and S. Ramadoss, "Optimizing the SNR from a radiation detector with delay-line position-sensing electrodes", Nucl. Instr. and Meth. in Phys. Res. A, vol. 652, p. 427-434 (Oct. 2011).
- [P7] G. Kim, J. Huang, and M.D. Hammig, "An Investigation of Nanocrystalline Semiconductor Assemblies as a Material Basis for Ionizing Radiation Detectors", IEEE Transactions on Nuclear Science, v 56, n 3, pt.2, p 841-8 (June 2009).
- [P8] M. Jeong and M.D. Hammig, "The Atomistic Simulation of Thermal Diffusion and Coulomb Drift in Semiconductor Detectors", IEEE Transactions on Nuclear Science, v 56, n 3, pt.2, p 1364-71 (June 2009).

Conference Publications

- [C1] G. Kim and M.D. Hammig, "An Investigation of Single-Crystal PbTe for Nuclear Radiation Detector Applications", 2011 IEEE NSS/MIC.
- [C2] M.D. Hammig and G. Kim and M.D. Hammig, "Simulated Nuclear Radiation Responses Derived from Nanocrystalline Semiconductor Assemblies", 2011 IEEE NSS/MIC.
- [C3] M.D. Hammig and M. Jeong, "Fabrication Methods by which the Intrinsic Noise is Reduced in Si and CZT Nuclear Radiation Detectors", 2011 IEEE NSS/MIC.
- [C4] G. Kim and M.D. Hammig, "Fabrication Methods by which the Intrinsic Noise is Reduced in Si and CZT Nuclear Radiation Detectors", 2011 Materials Science Symposium (**best physics poster presentation by student**).
- [C5] M. Jeong, M.D. Hammig, and S. Ramadoss, "Silicon-based Delay-Line 3D position Sensitive Radiation Detector", Symposium on Radiation Measurements and Applications (June 2010).

- [C6] G. Kim, J. Karbowski, and M.D. Hammig, "Signal formation on a serpentine delay-line electrode patterned on the CdZnTe detector", Symposium on Radiation Measurements and Applications (June 2010).
- [C7] G. Kim and M.D. Hammig, "Development of Lead Chalcogenide Nanocrystalline (NC) Semiconductor Detectors", 2009 IEEE Nuclear Science Symposium.
- [C8] B.T. Wells, R.C. Stevenson, J. Noh, S. Ramadoss, J. McElroy, and M.D. Hammig, "Defeating IEDs, SNM and Contraband Secreting via Long Range Gamma-Ray Imaging of Neutron Interrogated Materials", 2009 IEEE Nuclear Science Symposium and Medical Imaging Conference.
- [C9] J. Noh, R.C. Stevenson, and M.D. Hammig, "Statistical Methods for Chemical Compound Identification from Neutron-Induced Gamma-Ray Spectra", 2009 IEEE Nuclear Science Symposium and Medical Imaging Conference.
- [C10] M. Jeong, M.D. Hammig, and S. Ramadoss, "Fabrication and Signal Acquisition of the Silicon-based Delay-Line Radiation Detector", 2009 IEEE Nuclear Science Symposium and Medical Imaging Conference (accepted for presentation: October 2009).
- [C11] G. Kim and M.D. Hammig, "An Investigation of Single-Crystal PbTe for Nuclear Radiation Detector Applications", 11th European Symposium on Semiconductor Detectors (June 2009).
- [C12] M.D. Hammig, M. Jeong, D.K. Wehe, and S. Ramadoss, "Delay-line electrode partitioning as a means of simplified position sensing", 2008 IEEE Nuclear Science Symposium and Medical Imaging Conference Record (October 2008).
- [C13] M.D. Hammig and R.C. Stevenson, "The degree of enhancement in a gamma-ray image gleaned from recoil-electron tracking", 2008 IEEE Nuclear Science Symposium and Medical Imaging Conference Record (October 2008).
- [C14] G. Kim, J. Huang, and M.D. Hammig, "An Investigation of Nanocrystalline Semiconductor Assemblies as a Material Basis for Ionizing Radiation Detectors", Symposium on Radiation Measurements and Applications (June 2008).
- [C15] M. Jeong and M.D. Hammig, "The Atomistic Simulation of Thermal Diffusion and Coulomb Drift in Semiconductor Detectors", Symposium on Radiation Measurements and Applications (June 2008).
- [C16] M. Jeong, M.D. Hammig, and D. A. Lawlor, "Optimization of the position resolution in semiconductor detectors", 2007 IEEE Nuclear Science Symposium and Medical Imaging Conference Record, (Nov. 2007).

vii) Interactions/Transitions:

One of our existing projects is with the U.S. Army (2010 Phase II SBIR: *Increased Range Neutron Response High Explosives Detection*) in which the goal is to detect *conventional* explosives at intermediate to long ranges (10 – 100 m) by: a) interrogating the environment with 14 MeV neutrons, b) imaging the return gamma-ray flux, and c) making determinations about the chemical composition per voxel based on the spectrum recorded. The successful realization of this capability- for which feasibility has been determined and a scaled-prototype is under development- will also aid the DTRA mission. The imaging of conventional explosives is more challenging, in terms of the required neutron flux (or equivalently, in terms of the operational range), than the detection of SNM. Thus, the development of the imager is highly relevant to the DTRA mission. Upon evaluating both semiconductor and scintillator-based systems, one quickly realizes that currently existing materials and detector methodologies are inadequate if large volumes of detector systems are to be inexpensively deployable; thus, the materials research inherent to the Combating WMD Basic Research Program is vital.

As the developers of the detector, we coordinate with various neutron-source research firms (e.g. Michael Fuller at Adelphi Technologies, Michael McGuirk at Vusek in Natick, Mass.),

aiming to provide the high-intensity pulsed source. Through another program, we have already completed the initial design and characterization stages and are currently working to make a scaled prototype imager, based on inorganic scintillators.

The funded SBIR projects include, necessarily, the positive collaboration between the University and various commercial entities, including Galt LLC, Radiation Monitoring Devices (RMD), and Svaati Scientific LLC. Thus, a mechanism exists for transitioning the research results into applications of commercial interest. In general, the University-based research produces an optimized process or device which is then replicated and packaged by the industry collaborator.

For this work in particular, the low-noise surface-barrier detectors were optimized during the final two work periods, and a commercial collaborator developed a package solution, as shown in Fig. VII.1. One of the most important factors that required resolution for industry use was the degree of detector robustness, which was established by our finding that the multi-year spectroscopic performance did not vary, as enabled by suitable fabrication recipes that included a thick nitride/oxide layer that resulted in long-term low noise stability. As mentioned above, we are therefore coordinating with the first customer, who has a requirement for the detector technology as well as the current-sensing electronics that we developed during the research. The nuclear physicists plan to test the detector at a rare-isotope beam facility in the early fall.

The planar detector for ion sensing is the first in a series of technologies that are ready to be transitioned to commercial products. In general, we couple the detectors with a die-form current sensing amplifier, which can be either mounted on-chip or directly adjacent to the semiconductor. Since we are making the detector and preamp on the same detector substrate, we plan to market the combination as a high-performance position-sensing detector. A contact-deposition service, for silicon as well as CZT and HgI₂, may follow if the developments in that regard are sufficiently novel or if there is a market need; for instance, if someone wants a low leakage contact in the form of their own electrode geometry.

The other technology application that is targeted for transitioning to industry is a simplified readout design that allows position sensing. The goal has been to develop amplitude-based and/or time-based position sensing schemes that are applicable to all semiconductor technologies. However, the initial devices will be based on silicon, which can find applicability in x-ray imaging applications and gamma-ray imagers, perhaps as a front-end scatter layer or layers.

We are also in the process of commercializing the products of the nanocrystalline semiconductor research, given our success in generating excellent detectors during the past two years. Specifically, one of our commercial collaborators plans to sell the NC powders, the dispersions, and the colloidal solid, in that order. We have developed the fabrication recipes to the point where we can make CdTe, PbSe, and PbTe NCs to a desired size and shape, and we hope that the accrued knowledge will expedite the research of other groups developing this new class of electronic materials.

One of the greatest benefits of the nanocrystalline research is that we have formed close scientific collaborations with the leading nanotechnology research groups in the world. Geehyun Kim, the main funded graduate student during most of the work, is going to work as a visiting scholar in the spring with Dr. Victor Klimov's group, at Los Alamos National Laboratory. Victor Klimov is the Director of a large consortium of National Labs and Universities (the DOE's Center for Advanced Solar Photophysics) who are studying the fundamental physics of charge creation and transport in nanosemiconductor devices, driven primarily by an interest in solar cell devices. We hope to couple our experimental methods- and the exceptional devices that result- with more precise characterization of the underlying physics of the transport, capabilities delivered by the DOE consortium.

We have also formed a close collaboration with Nicholas Kotov, one of the most highly cited chemists during the last decade. He brings his chemical synthesis techniques with our expertise in electrical characterization and device fabrication, a marriage that we hope will yield large area,

high performance detectors. Our current investigation into CdTe nanowires synthesized via vacuum filtration is a result of the collaborations formed during the research.

The main conferences with which we participate are: (a) the annual IEEE Nuclear Science Symposium, (b) the biannual SORMA conference, held alternatively in Ann Arbor, MI and Berkeley, CA, and (c) the European Symposium on Semiconductor Detectors.

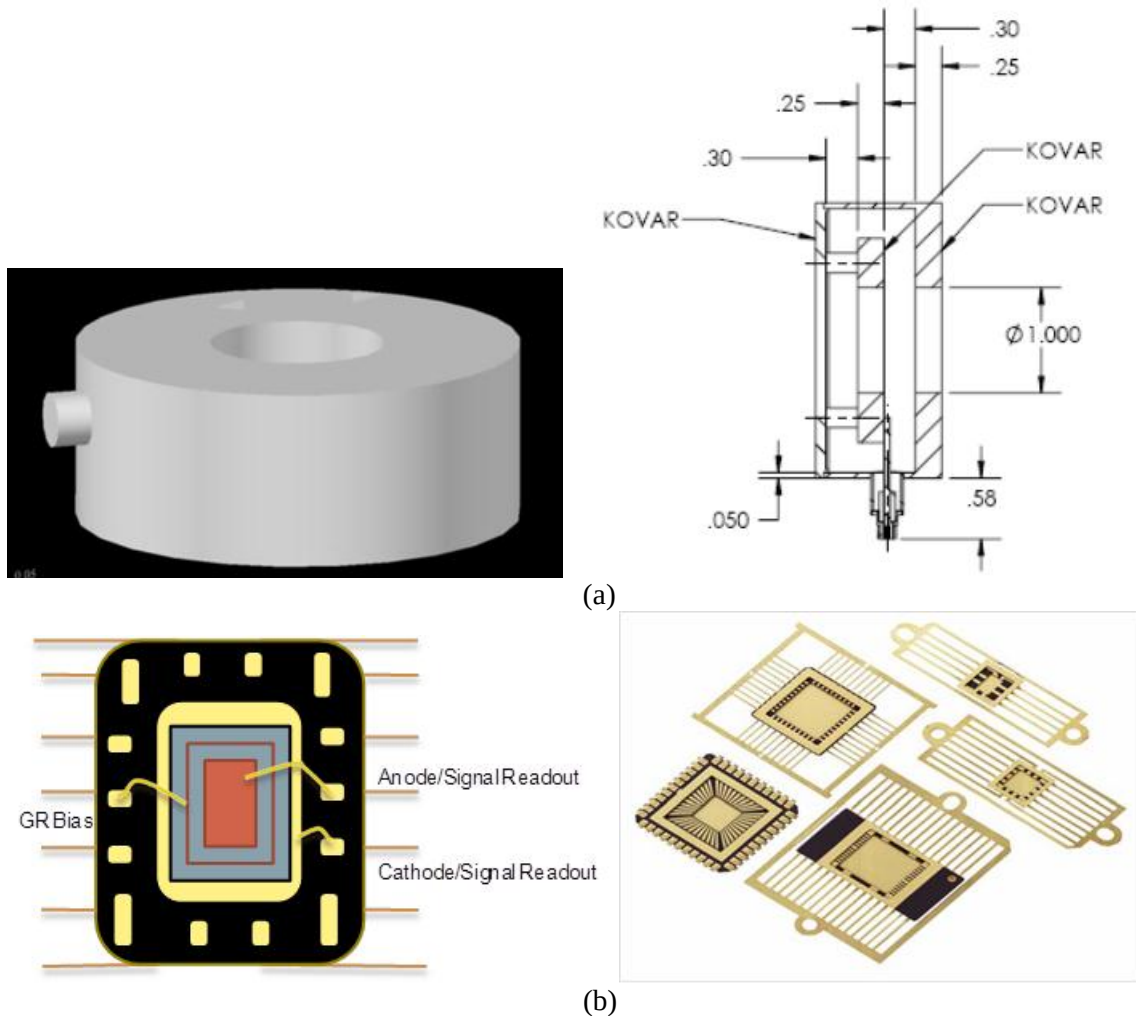


Fig. VII.1. (a) Cylindrical package used for surface-barrier detector with a microdot readout, used for standard charge-sensing applications. (b) Socket packaging for high-speed, current-sensing applications.

viii) New discoveries, inventions, or patent disclosures

Nanocrystalline Semiconductor Detectors

When we started the investigation into the application of colloidal solids for nuclear radiation applications during the latter part of Phase I, we were the only group considering that possibility to our knowledge, although there is significant activity in applying the material for optical photons (driven by solar cell efficiency concerns). Since then we see, through reviewing the proposals of others, that other groups also see the value in the material technology.

The successful fabrication of a colloidal solid that exhibits charge multiplication while maintaining subsequent charge transport has particular relevance beyond the nuclear radiation detection application. Such a development can impact the efficiency of solar cells because the quantum efficiency is governed solely by energy conservation concerns; for example, calculations

have shown that a quantum dot solar cell can, in principle, achieve 65 % efficiency, compared to the “ultimate” Shockley-Queisser limit of 44 %, and roughly 20 % for good silicon solar cells. The University of Michigan is evaluating the patentability of the processing methods and devices that we have developed.

Time-based Single-Contact Lateral Position-Sensing Scheme

As discussed in previous reports, upon investigating various methods by which one can discern the lateral position of a drifting charge-carrier, we considered one based on pulse-timing. Since one (or two) contacts per detector surface can be used to provide fine three-dimensional tracking of the charge carrier, then the hardware multiplicity and complexity that currently accompanies the deployment of sizable gamma-ray and neutron imagers can be avoided. The realization of this capability can thus substantially enhance the DTRA mission by making the deployment of ubiquitous detectors for the detection of SNM more economically feasible. We disclosed this invention to the University in 2009 and via publication at the IEEE conference in Dresden, Germany. The technology transfer office at the University is currently pursuing potential licensees for the technology.

Note that although developed for nuclear radiation detection, this development is not confined to high-energy charge depositions, but rather, can be used for single photon sensing (IR, optical, or UV) or x-ray applications, for which charged coupled devices (CCD) and controlled drift detectors (CDD) are currently used. The meander design provides a clearer path to extending the position sensitivity to higher degrees of partitioning without the concomitant increase in hardware multiplicity. Thus, this DTRA project in particular is an important driver of this technology since we desire single carrier sensitivity for the trapping investigations, a capability that can then be applied to optical photon imaging, for instance.

ix) Honors/Awards:

- Best Student Poster Award in Physical Sciences in 2011, *Microscopy and Microanalysis Meeting*. “Microscopic Analysis of Lead Chalcogenide Nanoparticles for Ionizing Radiation Detectors.”
- 2011 Rackham Pre-doctoral Fellowship (all expenses paid for one year) for Grad. Student Geehyun Kim based on DTRA work.
- 2nd place best paper presentation- IEEE SE Michigan Nanotechnology Conf. Fall 2010

x) quad chart (at end)

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