

DOE/NV/25946--330

STL-20: Conducting Polymers for Neutron Detection

Principal Investigator: Clare Kimblin

Contributors: Kirk Miller, Bob Vogel, Bill Quam, Harry McHugh, Glen Anthony, Steve Jones, Mike Grover

Abstract

Conjugated polymers have emerged as an attractive technology for large-area electronic applications. As organic semiconductors, they can be used to make large-area arrays of diodes or transistors using fabrication techniques developed for polymer coatings, such as spraying and screen-printing. We have demonstrated both neutron and alpha detection using diodes made from conjugated polymers and have done preliminary work to integrate a boron carbide layer into the conventional polymer device structure to capture thermal neutrons. The polymer devices appear to be insensitive to gamma rays, due to their small physical thickness and low atomic number.

Background

Solid-state neutron detectors would provide a compact, low-power replacement for ^3He tubes typically used for neutron detection. While quite reliable and accurate, ^3He tubes are very expensive and relatively large. The cost of ^3He tubes is the principal reason that they are not widely employed in portal detectors. The cost of a ^3He detector is approximately \$40 per square inch. Conductive polymers can be applied to inexpensive substrates such as plastic or metal using simple techniques such as spin coating or spraying. Detectors fabricated from multi-layer conductive polymers offer the promise of less expensive, more versatile neutron detectors than the present ^3He tubes with low gamma sensitivity.

Project

Energy Deposition and Electrical Charge Generation/Collection

To make the solid-state detector being proposed, ^{10}B was used to capture thermal neutrons, resulting in emission of an alpha particle that can then generate electron-hole pairs to be detected by the polymer diode. Calculations show that a ^{10}B layer thickness of 1.5 μm presents an optimum thickness for capture of the neutron while ensuring a significant chance of an alpha escape with substantial energy intact. For a layer of this thickness, there is approximately a 3% probability of capturing a thermal neutron. See Figure 1 for a theoretical plot of alpha energy vs. boron thickness.

For this discussion, we shall analyze a 30- μm -thick polymer detector. At this thickness, almost all of the 1.5 MeV alpha energy will be trapped in the polymer. The ionization energy of this polymer is approximately 5 eV, leading to one electron-hole pair created for each 15 eV deposited (Radiation Measurement, 2007). In the case of a 1.5-MeV alpha, this equates to the creation of approximately 100,000 pairs, carrying a charge of 1.6×10^{-14} coulombs. If all the electron-hole pairs generated by the alpha particles could

be collected, the single-event pulses from the 30- μm polymer detector should be about 80 mV, well above the peak noise.

Figure 2 shows a display of the waveform obtained from an alpha capture in a 30- μm -thick polymer detector. The peak of the waveform is only about 15 mV (negative direction). The baseline noise peaks can be seen to be less than 7 mV. The low value of the peak voltage implies that only about 20% of the charge generated from the alpha capture reaches the detector. The cause of the charge loss is not known at this time, but further optimization of the materials and device structure may lead to improvements.

Experiment and data

Polymer Devices

The polymer devices used for this work were derived from the solar cell designs being widely developed for power generation (Brabec, 2001). The solar cell design uses a blend of a conjugated polymer, poly-3-hexyl-thiophene (P3HT), and a sensitizer, [6,6]-phenyl- C_{61} butyric acid methyl ester (PCBM) — a soluble derivative of buckminsterfullerene, C_{60} . Upon photoexcitation of the P3HT, the electron transfers to the PCBM, while the hole resides on the P3HT. The internal electric field (the sum of any externally applied bias and the mismatch of electrode work functions) then sweeps out the charges to their respective electrodes. The device architecture is typically a glass substrate coated with indium tin oxide (ITO, a transparent conductor), a thin layer of poly-ethylene-dioxy-thiophene, a spin-coated layer of the active material, then an aluminum electrode vacuum-evaporated on top.

We determined that the active layer of conventional polymer solar cells, approximately 100 nm thick, would be too thin and the capacitance too high for radiation detection. Therefore, our first intensive alpha-irradiation testing was done with a series of devices from 1 to 30 microns thick, and small-area electrodes. With this first generation, we discovered that static charge dissipation in the nitrogen glove box was crucial to having data that can be interpreted accurately.

We also learned that device fabrication techniques needed improvement for such thick films, so a second generation (Gen-2) of devices was made using a “doctor blade” technique on glass/ITO substrates. With the Gen-2 devices, we sought to test various thicknesses, from 2.5 to 15 microns, and to control the experiment with devices of similar geometry, but using a non-conducting polymer, poly-vinyl-carbazole (PVK), instead of the P3HT/PCBM blend. These devices can be characterized by their light and dark currents, and we found that the 10-micron device had the highest ratio of light-to-dark current. Data presented here are from that device, with its matching control (PVK) device.

Based on these observations, and to test the integration of the polymer devices with a boron-rich substrate, The University of California, Santa Barbara, prepared a third generation (Gen-3) of samples with thicknesses of 10 and 25 microns, plus 10-micron-thick PVK devices, on both glass/ITO and aluminum substrates coated with boron carbide.

Circuit Configuration

The polymer detector was connected to a 3-V reverse bias through a 100-MOhm resistor. The junction of these devices was connected to a high-impedance, low-noise charge preamplifier with a junction gate field-effect transistor (JFET) front end and a gain of 5×10^{12} V/coulomb for an input capacitance of approximately 4–10 pf (dominated by the capacitance of the polymer device). The detector contacts were connected to the amplifier via a commercial IC clip that squeezed the detector contacts against flat copper pins. The entire assembly was mounted inside a sealed Faraday enclosure designed to reduce pickup of external electromagnetic interference. Extensive filtering was used on all of the power inputs, and all leads were shortened to a minimum.

In a low-count-rate, low-signal-level situation such as this, one must be careful not to confuse spurious electrical pulses with actual signals. The alpha-induced ionization of air near the preamp generated signal pulses. Also, static electric discharges in the dry air created spurious signals that tended to dissipate with time. It is essential to be able to either eliminate these spurious signals or distinguish between them and true signals. As one measure, we installed an ionizing air blower in the glovebox to more quickly dissipate static.

Alpha Irradiation Measurements

Since detection of the neutrons hinges on detection of alpha particles, we initially tested polymer devices under alpha-irradiation from a 5-MeV alpha source. Counting was initially done with a storage oscilloscope, but then a multi-channel analyzer (MCA), the Health Physics Rainbow, was implemented to better visualize the pulse heights being generated during data collection. The resolution of the Rainbow was approximately 0.25 mV/channel, with the low-level discriminator set to approximately channel 35. Data were typically collected for 5 minutes for alpha-irradiation experiments, and 20 minutes for neutron-irradiation experiments.

The alpha source, which consisted of a thin foil of metal, was placed approximately 5 mm above the detector surface. An aperture with a 1-cm diameter was used to collimate the alpha particles and reduce the volume of ionized nitrogen. The electronic chassis box, polymer device, and alpha source are shown in Figure 3.

We used the 5-MeV alpha-emitting source to irradiate the Gen-2 and Gen-3 devices, and sheets of mylar, 10-microns-thick, to slow the alpha particles and increase the energy deposited in the active layer. Using the National Institute of Standards and Technology ASTAR database (ASTAR, 2007), we estimate the stopping distance for the 5-MeV alphas and 1.5-MeV alphas to be 40 microns and 8.5 microns, respectively, in mylar; hence, we expect alphas generated by neutron capture in ^{10}B to be stopped by a single sheet of mylar, while the more energetic alphas from the alpha source will be slowed but not stopped by one sheet of mylar.

Data in Figure 4 are taken with the Gen-2 10-micron device and the Gen-2 control device under alpha irradiation. The structure in channels 0–35 is entirely due to imperfections in

the low-level discriminator (LLD) circuitry in the Rainbow MCA. The sensitivity to alpha particles can be seen in channels 50–90, where the heavy black curve rises above the background when using the 10-micron mylar film. While these data are encouraging, they raise some questions that we have not yet answered. For instance, what is the source of the large number of counts in both the active polymer and control devices when they are exposed directly to the alpha source? Why is the background count level so high, even with no source?

The aluminum substrate devices demonstrated a great reduction in background counts, with almost no counts in channels above channel 45 when no radiation source was present. Data on the aluminum substrate device, 25-micron thickness, are shown in Figure 5. One important observation is the shift of the peak of the signal away from the LLD (channel 35) out to channel 45 with the insertion of the 10-micron mylar film. In addition, channels 50–80 show higher counts when the mylar film is added, in agreement with the data taken on the glass/ITO substrate devices.

Neutron Irradiation

To test the full sequence of neutron capture, alpha emission, and electronic detection, we used a neutron source moderated with polyethylene and a ^{10}B -carbide hemisphere placed close to the active polymer film. The distance from the ^{10}B -carbide to the active polymer layer was approximately 3 mm. Since the count rates are much lower than those for alpha irradiation, we chose to use the aluminum substrate devices, with their much lower noise floor. Data shown here are for the 25-micron-thick polymer device.

The data in Figure 6 show spectra taken with no neutron source present (background), with the neutron source present, and with the neutron source plus 10 microns of mylar between the ^{10}B -carbide and the polymer film. The stopping distance for the 1.5-MeV alpha particles is approximately 8.5 microns in mylar, so the addition of mylar blocks all of the alpha radiation from reaching the polymer film. The high ratio of signal-to-background strongly suggests that alpha particles from the ^{10}B disintegration are being detected by the polymer detector.

Conclusion

The successful detection of neutrons in this prototype configuration suggests that integration of the ^{10}B -carbide layer into the device structure would yield an all-solid-state neutron detector made primarily from conjugated polymers. Device geometry and material optimization may lead to improved charge collection. The origin of some spurious signals, such as the high background count rates for devices on glass/ITO substrates and the high count rates for control devices exposed to alpha irradiation, must be clarified but may be due to radio frequency pickup by the device, which would be shielded in a packaged detector.

References

Radiation measurement. Encyclopedia Britannica. 2007. Encyclopedia Britannica Online. Available at: www.britannica.com/eb/article-80706/radiation-measurement. [Accessed 9/28/2007]

For a review, see C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, "Plastic Solar Cells," *Advanced Functional Materials*, Volume 11, Issue 1, Pages 15 – 26, 2001.

ASTAR database, 2007. National Institute of Standards and Technology. Available at: <http://physics.nist.gov/PhysRefData/Star/Text/ASTAR.html> [Accessed February 1, 2007]

Acknowledgment

Polymer devices for this work were prepared in the laboratory of Dr. Guillermo Bazan at the University of California, Santa Barbara, by Corey Hoven, Dr. Je Jun, and Jeffrey Peet.

Copyright statement

This manuscript has been authored by National Security Technologies, LLC, under Contract No. DE-AC52-06NA25946 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

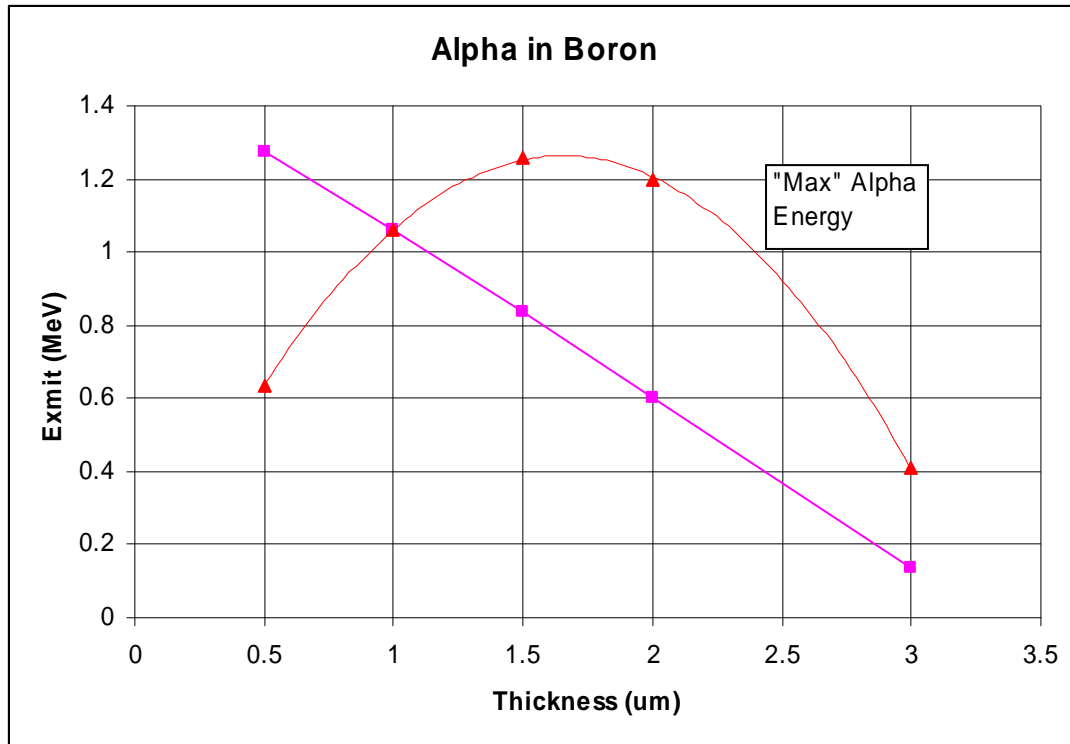


Figure 1: Escape energy of alpha-particles exiting boron.

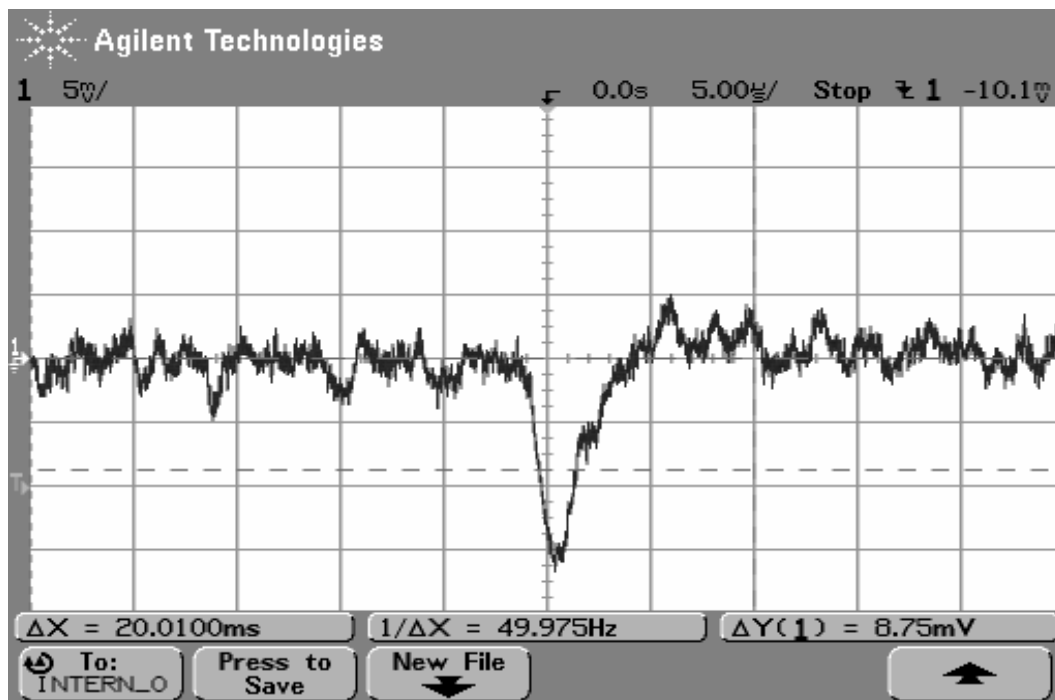


Figure 2: Waveform of Alpha Capture in a 30- μm Detector.

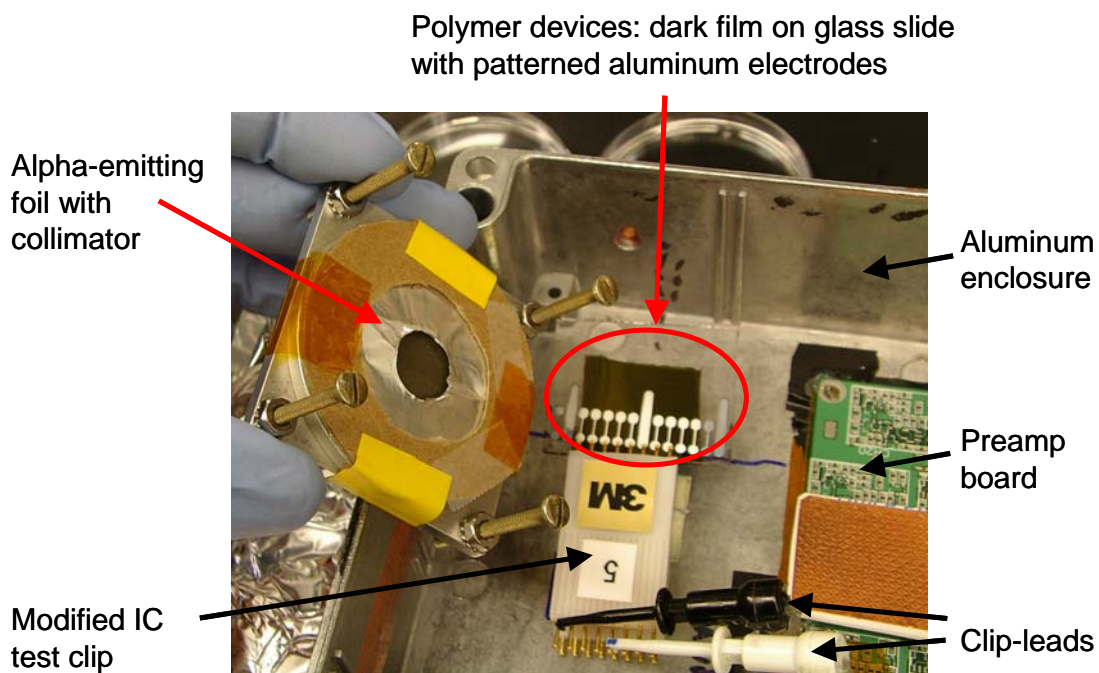


Figure 3: View of electronic chassis box with polymer devices and alpha-emitting foil.

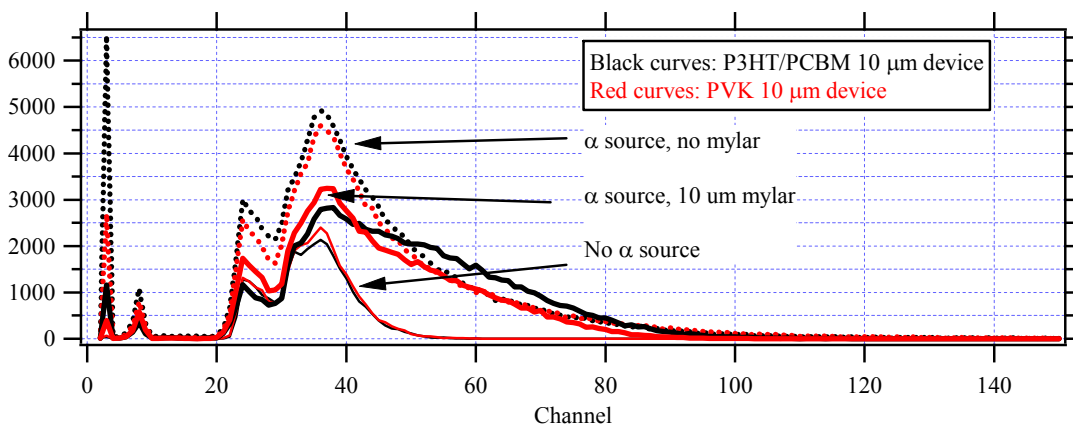


Figure 4: Alpha-irradiation spectra of conducting polymer and control devices, 10 μm thick, for 5 minutes. The bulge in the heavy black curve demonstrates the detection of alpha particles above the background.

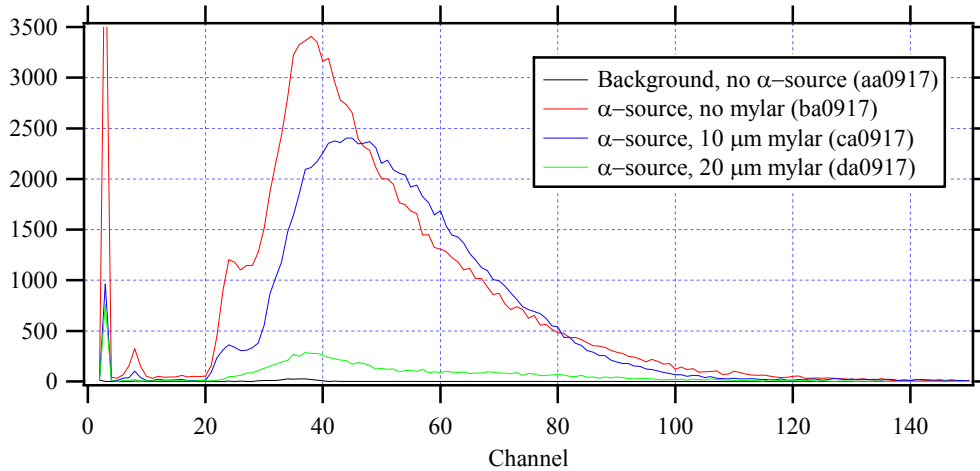


Figure 5: Spectra taken with aluminum-substrate device, 25 μm thick, with alpha irradiation using mylar to slow down the alpha particles. Integration time was 5 minutes.

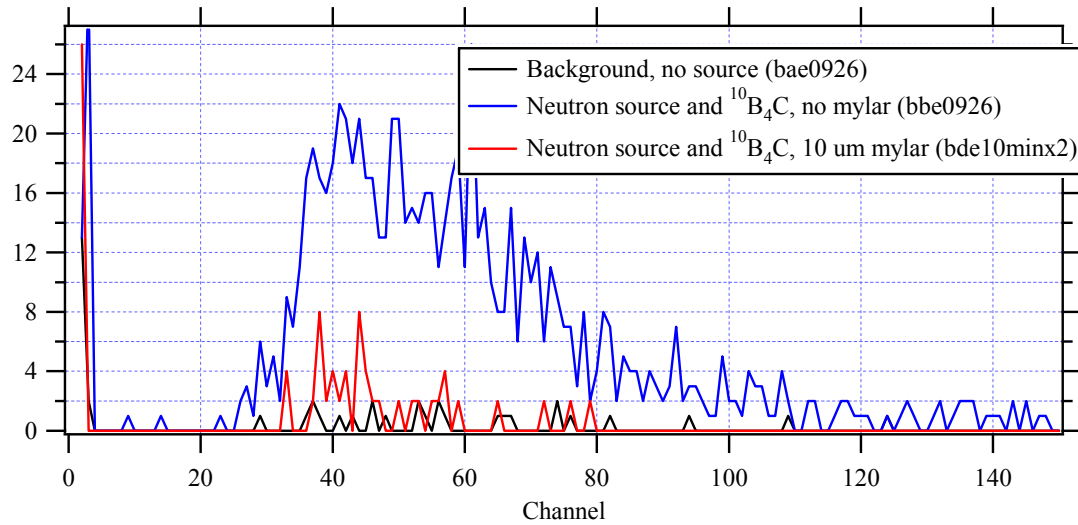


Figure 6: Spectra using 25 μm aluminum-substrate device, irradiated with the neutron source. The signal above the background demonstrates the detection of alpha particles emitted after neutron capture by ^{10}B . The mylar sheet blocks the alpha particles. Integration time was 20 minutes.