Radiation resistant polymer-based photonics for space applications

E. W. Taylor\textsuperscript{a}, J. Nichter\textsuperscript{b}, F. Nash\textsuperscript{b}, F. Haas\textsuperscript{b}, A. A. Szep\textsuperscript{b}, R. J. Michalak\textsuperscript{b}, B. M. Flusche\textsuperscript{b}, P. Repak\textsuperscript{b}, G. Brost\textsuperscript{b}, A. Pirich\textsuperscript{b}, D. Craig\textsuperscript{c}, D. Le\textsuperscript{d}, D. Cardimona\textsuperscript{d}, H. R. Fetterman\textsuperscript{e}, B. Tsap\textsuperscript{e}, C. Castaneda\textsuperscript{f}, R. Barto\textsuperscript{g}, T. Zeng\textsuperscript{b}, D. Wood\textsuperscript{b}, R. O. Claus\textsuperscript{b}

\textsuperscript{a}International Photonics Consultants Inc., 30 Tierra Monte NE, Albuquerque, NM 87122
\textsuperscript{b}Air Force Research Laboratory, Rome, AFRL/SNDP, NY 13341-4515
\textsuperscript{c}Air Force Research Laboratory, AFRL/VSSSE, Kirtland AFB, NM 87117-5776
\textsuperscript{d}Air Force Research Laboratory, AFRL/VSSS, Kirtland AFB, NM 87117-5776
\textsuperscript{e}Pacific Wave Industries, El Segundo, CA 90245
\textsuperscript{f}Crocker Nuclear Laboratory, Univ. California, Davis, CA 95606-8569
\textsuperscript{g}Lockheed Martin Advanced Technology Center, Palo Alto, CA 94304-1191
\textsuperscript{h}Nanosonic Inc., Blacksburg, VA 24060

ABSTRACT

Empirical data regarding the radiation induced responses of Mach Zehnder interferometric electro-optic polymer based modulators (PBMs) operating at 1310 and 1550 nm and broadband InP quantum dot (QD) polymer photodetectors (PPDs) operating into the near infrared (NIR) are reported. Modulators composed of spun-on materials and hybrid electrostatically self assembled (ESA) and spun-on NLO materials are examined for changes to their half-wave voltage and insertion losses following a gamma-ray total dose of 163 krad(Si) and irradiation by 25.6 MeV protons at a fluence of \( \sim 10^{11} \) cm\(^{-2}\). Pre- and post- irradiation responses of ESA grown polymer detectors using InP QDs are examined for photovoltage degradation and aging effects. The data indicates an excellent potential for developing polymer based photonic (PBP) devices with increased radiation resistance suitable for transition to photonic space applications.

Keywords: Nonlinear Optics, Polymer Modulators, Polymer Detectors, Radiation Resistance, Space Environments, Polymer Photonics

1. INTRODUCTION

Emerging polymer modulators and detectors were investigated to determine their suitability for application in space environments. NLO polymer modulator technology is rapidly advancing with devices having bandwidths exceeding 100 GHz and half-wave voltages \( (V_\lambda) \) less than 1 V reported by various sources\textsuperscript{1,2}. However, unlike their inorganic counterparts, little is known of the stability of these devices to operate in adverse ionizing environments such as those found in space\textsuperscript{3,4}. Similarly, the ability of state-of-the-art polymer photodetectors (PPDs) to operate in ionizing environments has only recently been investigated and empirical data is presented indicating a high potential for realizing QD PPDs suitable for space applications. Within this paper the relative radiation resistance of emerging and leading polymer based modulators and polymer photodetectors is reported showing a potential for transition of the technology to microwave applications that are required to operate in ionizing radiation environments. As such, we focus on the measured radiation resistance of a much studied guest–host polymer modulator device incorporating phenyltetraene bridging (CLD) and amorphous polycarbonate (APC) and operating at \( \lambda = 1550 \) nm\textsuperscript{2}. Similarly, we briefly report on advances made in developing a radiation resistant InP QD- based PPD.

* Electronic Mail: INTPHOTON@aol.com
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Empirical data regarding the radiation-induced responses of Mach Zehnder interferometric electro-optic polymer-based modulators (PBMs) operating at 1310 and 1550 nm and broadband InP quantum dot (QD) polymer photodetectors (PPDs) operating into the near infrared (NIR) are reported. Modulators composed of spun-on materials and hybrid electrostatically self-assembled (ESA) and spun-on NLO materials are examined for changes to their half-wave voltage and insertion losses following a gamma-ray total dose of 63 krad(Si) and irradiation by 25.6 MeV protons at a fluence of ~ 10^11 cm^-2. Pre- and post-irradiation responses of ESA grown polymer detectors using InP QDs are examined for photovoltage degradation and aging effects. The data indicates an excellent potential for developing polymer based photonic (PBP) devices with increased radiation resistance suitable for transition to photonic space applications.

Nonlinear Optics, Polymer Modulators, Polymer Detectors, Radiation Resistance, Space Environments, Polymer Photonics
2. PBM DESIGNS AND CHARACTERIZATIONS

The design, structure and processing of the chromophoric core, application of the conductive cladding materials and the assembly of CPW-1/APC modulators by the Air Force Research Laboratory followed techniques and approaches previously described for fabricating CLD-1/APC modulators \(^4\). Figure 1 shows a cross-section of the AFRL SNDP device \(^6\).

![Cross-section of the AFRL SNDP device](image)

Pre- and post- irradiation measurements were accomplished using a laser providing 2 mW polarized light at 1550 nm butt coupled into the modulator device via an optical fiber and lens system. A detailed description of the measurement techniques are described elsewhere \(^6\). CLD-75/APC modulators consisting of devices with waveguides 4 μm in width approximately 2.2 cm in length were also gamma-ray irradiated. The CLD-75/APC devices were fabricated with spun-on polymer layers and ridge waveguides formed by RIE and wet etching. The thickness of the device core region was 2.5 μm while the top cladding was composed of 3.7 μm of UFC-170 and the bottom clad was composed of 1.5 μm of UV-15. Typical half-wave voltages for these devices ranged from 7.18 - 7.65 V and the average EO coefficient was calculated at \(r_{33} \approx 22.9\) pm/V. The third irradiated PBM device was provided by Nanosonic (NS) and consisted of a hybrid combination of NS Poly S-119 hybridized with a Lockheed Martin NLO polymer [46M (modified) FTC-2/APC] \(^8\). The device was operated at \(\lambda = 1310\) nm, having an interaction length of 2 cm and measured to have a pre-irradiation half-wave voltage of \(V_e = 2.2\) V (although the modulation signal was near detection limits).

3. POST-IRRADIATION RESPONSES OF PBMs

Gamma-ray irradiations of all devices were conducted at the Sandia National Laboratory Gamma-Ray Irradiation Facility, Albuquerque, NM, while the proton irradiations were conducted at the Crocker Nuclear Laboratory at the University of California, Davis, CA. The gamma-ray irradiations resulted in a total dose \(D_g = 163\) krad(Si) for some PBMs while the maximum proton total dose received by CPW-1/APC devices was \(D_p = 100\) krad(Si). The devices were exposed to an average gamma-ray dose rate of \(D_g(t) = 2.02\) krad(Si)sec\(^{-1}\) while the proton irradiations were conducted at a proton energy of 25.6 MeV and fluence of 1.84-3.68 x 10\(^{11}\) cm\(^{-2}\). The proton energy was determined using the SRIM Computer Program to insure that the ions completely traversed the polymer modulator thin film claddings and active EO-core regions thereby being deposited well into the device substrate, or, passed through the device substrate region \(^9\). Using CaF thermoluminescent dosimeters, the uncertainty in the gamma-ray dose (Si) readings was estimated at 10\%, while the integrated current from a foil emitting electrons, calibrated by a Faraday cup was used to measure the proton beam fluence for determining the dose (Si) with an accuracy of ~ 5% \(^{10}\).

Shown in Figure 2 are the CPW-1/APC, CLD-75/APC and NS device half-wave voltage (\(V_e\)) responses following irradiation by gamma-rays. The uncertainty in measuring \(V_e\) was ~ 3\% for the SNDP devices and \(\pm 0.05\) V for the NS device. The range of pre-irradiated \(V_e\) values for the modulators was 4.8 -12.4 V and 7.3-
7.5 V for CPW-1/APC and CLD-75/APC devices, respectively. Prior to irradiation, the NS modulator had an initial weak signal response of $V_e = 2.2$ V. Figure 2 shows that for the CPW-1/APC devices the gamma-ray irradiation caused $V_e$ to first increase and eventually decrease at $D \geq 100$ krad(Si), while $V_e$ in CLD-75/APC devices immediately decreased at low dose. The NS device showed a small increase ($\Delta V_e = 4.55\%$) in $V_e$ for irradiation to a total dose of 109 krad(Si) in good agreement with the corresponding SNDP response. The degradation rates for the gamma-ray and proton irradiations of the CPW-1/APC and CLD-75/APC were determined by the slope values $m$ and $m_p$ of their fitted curves providing a gauge for comparing their relative radiation resistance. The data shown in Figure 2 agrees well with data previously reported asserting that polymer modulator devices possessing low $V_e$ values are less likely to undergo large changes to $V_e$ when irradiated by gamma-rays to a dose of ~100 krad(Si) 

Figure 2. Reduction in $V_e$ responses of gamma-ray irradiated PBMs varying in interaction lengths.

SNDP PBMs having an interaction length $L = 2$ cm exhibited a linear regression curve fit and a slope value similar to PWI devices ($L = 1.5$ cm). The dotted curved line shows an alternative exponential fit to the $L = 2$ cm SNDP device responses (chi-square = 0.80). The $L = 1$ cm SNDP device shows the greatest reduction in $V_e$ following irradiation. The NS device $\Delta V_e$ response to proton irradiation [$D = 109$ krad(Si)] is slightly elevated in response above the SNDP device irradiated at $D = 100$ krad(Si). Figure 3 illustrates the proton-induced

Figure 3. PBM responses to protons and mixed proton-gamma-ray irradiations.
responses of the SNDP and NS PBMs. The irradiated SNDP devices showed an immediate increase in $V_s$ which scaled linearly to a total dose of 100 krad(Si) at a fluence of $-3 \times 10^{11}$ cm$^{-2}$. The previously irradiated NS device shown in Figure 2 also received a proton total dose of 100 krad(Si) causing its $V_s$ to increase from 2.3 V to $V_s = 2.5$ V (weak modulation signals in both cases) as indicated by the dotted curve in Figure 3.

The effects of protons and gamma-rays on the device material absorption and coupling losses are shown in Figure 4. Irradiated 4 µm and 6 µm width straight waveguides fabricated by SNDP were minimally affected by gamma-rays and protons at the dose levels investigated. The CPW-1/APC data reflects the normalized loss responses of 4 and 6 µm straight waveguides, while the CLD-75/APC responses represent losses through the entire device including waveguides, Y-branches and active-electrode regions. There was close agreement in the degradation rates of the 4 and 6 µm CPW-1/APC gamma-ray irradiated waveguides differing in slope by approximately the measurement resolution of the experiment. While the 4 and 6 µm width waveguide responses to protons were elevated in initial induced loss compared to the gamma-ray irradiations, their degradation rates were less amounting to $1.5 \times 10^4$ and $8.4 \times 10^4$ (dB·cm$^{-1}$·krad(Si)), respectively.

![Figure 4](image-url)

Figure 4. Responses of waveguide and device insertion losses following irradiation by protons and gamma rays. Insertion losses are initially decreased at low gamma-ray doses in normalized data of CPW-1/APC straight waveguides and in the CLD-75/APC devices. Proton irradiation is seen to minimally increase insertion losses in CPW-1/APC devices at low dose.

Of particular significance is the suppression of losses observed for gamma-ray irradiated devices following low dose gamma-irradiations. These reductions were attributed to trap-filling of inherent defects in the modulator device. As can be seen by the linear growth curve, any initial reduction in loss was soon offset by increasing loss as the dose was increased.

4. POST-IRRADIATION RESPONSES OF InP QD PPDS

The development of polymer-based detectors are very important to the space community since they potentially offer many advantages compared to their inorganic counterparts, including: reduced size and weight, very low...
manufacturing costs, high yields, robust structures, and most importantly, flexible plastic-like arrays that could have widespread potential for applications to next-generation DOD and commercial space systems. However, an understanding of the interaction physics caused by ionizing radiation in polymeric-based optical and electronic devices are virtually nonexistent. Recent investigations by AFRL/VSSS, IPC and NS have focused on incorporating nanocrystalline InP QDs varying in size between ~2-10 nm into a polymer matrix for the purpose of absorbing light over the range of 330 to ~1000 nm. QDs have been reported to increase the radiation resistance of inorganic lasers and photodetectors because of strong carrier confinement. Lifetimes in QD doped detectors are much less affected by nuclear radiation-induced ionization and dislocation effects compared to conventional QW detectors where the carriers have greater mobility.

PPDs were designed and fabricated by NS incorporating synthesized InP QDs as the photosensitizer, and using anatase TiO$_2$ nanocrystalline material as the electron collector layer. Tris(4-bromophenyl)ammonium hexachloroantimonate N(PhBr)$_3$SbCl$_6$ and N-lithiotrifluoromethane sulfonamide ([Li(CF$_3$SO$_2$)$_2$N]). N(PhBr)$_3$SbCl$_6$ were also used in processing the materials and acted as a dopant, introducing free charge carriers into the HTM by partial oxidation of the OMeTAD. Li[[CF$_3$SO$_2$)$_2$N]. provides a positive charge on the surface of the TiO$_2$ and produces an electrostatic field, thus aiding electron injection from the excited-InP QD to the conduction band of the TiO$_2$ semiconductor. The HTM film was coated onto the InP QD-stained TiO$_2$ film using the spin coating process. Figure 5 illustrates the sandwich-structure of the solid polymer HTM-based InP-TiO$_2$ QD PPD.

![Figure 5. InP QD TiO$_2$ nanocrystalline-HTM-polymer-based photodetector.](image)

In Figure 6, empirical data representing the radiation resistance exhibited by InP QD PPDs is shown. Gamma-ray irradiation of the PPDs resulted in a modest reduction in device photovoltage, scaling with increased dose. Linear and first order exponential curve fits to the PPD response data are represented by the solid and dashed lines, respectively. The horizontal dashed line depicts the reduction in photovoltage ($\Delta$PV) for the non-irradiated Control PPD resulting from the natural aging process over the two week period between pre-and post-irradiation measurements. As can be seen, the loss in the photovoltage output response of the control PPD is greater than the majority of the irradiated PPDs. As were the polymer modulators, the PPD device exposure to ambient light was minimized, in order to avoid acceleration of aging effects.

The photovoltage response data in Figure 6 includes the combined gamma-ray induced losses in the PPDs contributed by the active QD-polymer matrix material, ITO electrode and the glass (borosilicate) substrate.
Previous IPC and NS measurements of gamma-ray induced transmission loss through identical glass substrates at $\lambda \sim 532$ nm Figure 6. Gamma-ray induced loss in QD- polymer photodetector revealed that the incident light intensity incident on the active detector area is reduced by approximately: 2%, 4% and 6% at doses of ~50, 100 and 150 krad(Si), respectively. Thus, the light intensity reaching the PPD active area is reduced by radiation.

\[ \Delta PV = 366.3 \text{ mV} - 386.6 \left[ \exp \left( -\frac{D_{\gamma}}{134.5} \right) \right] \text{ mV} \]

\[ \Delta PV = 4.32298 \text{ mV} + 1.64139 \times D_{\gamma} \text{ mV} \]

Figure 6. Gamma-ray induced loss in QD- polymer photodetectors.

induced color centers in the glass substrate. Loss of light intensity attributed to radiation darkening in the 200 $\mu$m thick ITO electrode was determined to be minimal at the applied doses. The control sample exhibited a decrease of 184 mV over the two week period that separated the PPD pre- and post- irradiation measurements. This large decrease in photovoltage output for the control device indicated the presence of a complicated deterioration process believed attributable to the environment (e.g. effects of moisture, oxidation, photosensitivity, temperature and other unknown factors that could affect the photovoltage stability. The control PPD was kept in proximity to the pre- and post- irradiated devices except during the brief periods of gamma-ray irradiation where the control device was far removed from the devices under irradiation. Under these conditions, it is reasonable to assume that all devices experienced exposure to a common ambient environment. A further assumption made was that the non-irradiated control PPD was physically representative of the irradiated PPDs. Under this assumption it would not be unreasonable to expect that the Control PPD would experience less photovoltage degradation compared to the irradiated PPDs. Figure 6 clearly shows that five devices within three of the four irradiated PPD pairs appear to have experienced less post-irradiation PV degradation than the non-irradiated control PPD. This data strongly suggests three possibilities: 1) that in some manner, the irradiated PPDs benefited from the $\gamma$- ray irradiation; 2) the control PPD aged at a rate faster than the irradiated PPDs or 3) both processes may have occurred. One possible explanation for the responses of the irradiated PPD is that free carriers arising from the radiation process contributed to trap filling or removal of native defects within the polymer composition. Trap filling is known to occur in crystalline and amorphous optical and electro-optical materials that possess numerous defects. If defects existed within the PPDs, or within the QDs, trap filling may have provided a mechanism for reduction in optical scattering and propagation losses as exhibited by the low dose irradiated PPDs.

Examination of the PPDs photovoltage responses over a range of wavelengths was of special interest since the purpose of incorporating the InP QDs into the polymer PPD matrix was to ascertain the viability of using InP QDs for shifting the PPD responses to longer wavelengths (i.e. $\lambda \sim 800 - 1000$ nm). A tunable broadband solar simulator was used to illuminate the PPDs from approximately 400-1100 nm and each sample was illuminated.
over an active area of 0.28 cm². A small percentage of InP QDs having above average particle size ≥ 6 nm, are responsible for the 600-920 nm responses shown in Figure 7a. The gradual increase in photovoltage with time

![Graph showing photovoltage response over time](image)

Figure 7. Aging of γ-ray irradiated InP QD PPDs. In (a) wavelength responses of device g7 over a two month period are shown while in (b), the response data for two devices irradiated at D ~ 150 krad(Si) are compared to the non-irradiated Control device response at λ = 500 nm

suggests interactions occurring between different components within the nanoparticle films, and that the Schottky barriers might be re-formed during or following illumination. These interactions would occur at the interfaces between TiO₂ nanocrystalline particles, InP QDs and within the HTM regions. Shown in Figure 7(b) is a plot of the λ = 500 nm response data shown in Figure 7(a) comparing the aging of the irradiated InP QD PPDs with the non-irradiated Control devices at λ = 500 nm. The data are typical of all gamma-irradiated device responses wherein all irradiated devices and the Control device exhibited a gradual recovery of photovoltage at the end of the aging study. Since the measurements were made at room temperatures, the data suggest that photo-bleaching by the solar simulator source was primarily responsible for the recovery of the photovoltage signal. It is clear that a complicated regeneration mechanism was responsible for the photovoltage aging behavior following the gamma-ray irradiation of PPDs and subsequent illumination by a broadband light source.

5. CONCLUSIONS

It is believed that the gamma-ray induced reductions in \( V_a \) at low dose are due to an increase in the device free volume predominantly resulting from the interaction of gamma-rays with the core materials which initially caused cross-linking and scission. However, changes to the refractive index in the core material and the differing top and bottom cladding materials used in the CPW-1/APC and CLD-75/APC devices may have also undergone refractive index changes. The trend shown for the CPW-1/APC gamma-irradiated devices suggests that the observed reduction in \( V_a \) may extend well beyond 163 krad(Si). The suppression of material and insertion losses observed for gamma-ray irradiated devices following low dose gamma-irradiations was attributed to trap-filling of inherent defects within the modulator device, causing an initial reduction in device loss and eventually offset by increasing loss as the dose was increased. Again, gamma-ray induced changes to the refractive index may also have contributed to this process, but was not directly confirmed by the data. Irradiation of the CPW-1/APC modulators by protons was observed to induce a moderate increase [(≤ 7.55%) in \( V_a \) in 2 cm devices at a total dose of 100 krad(Si), while an increase in \( V_a \) of 13.6 % was measured for the NS hybrid modulator irradiated to mixed-proton gamma-ray total dose of 209 krad(Si). The majority of the
irradiated InP QD PPDs devices experienced less post-irradiation PV degradation than the non-irradiated control PPD suggesting that 1) the irradiated PPDs benefited from the γ-ray irradiation; 2) the control PPD aged at a rate faster than the irradiated PPDs or 3) both processes may have occurred. One possible explanation for the responses of the irradiated PPDs is that free carriers arising from the radiation process contributed to trap filling or removal of native defects within the polymer composition. The gradual increase in photovoltage with time suggested that the interaction between different components within the nanoparticle films, and that the Schottky barriers might be re-formed during and following illumination indicating that photo-bleaching was primarily responsible for the recovery of the PPD photovoltage.

The data for both polymer-based modulators and photodetectors indicates that the devices appear to be intrinsically radiation resistant at moderate dose and have a high potential for applications such as micro-satellites operating under restricted power budgets, economic constraints and in harsh environments. However, in order to qualify polymer-based modulators and photodetectors for applications in space systems, additional studies at higher dose are required to address the issues presented in this paper.

References


