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Remote Optical Interrogation of Radiation Sensitive Infrared Polarizers

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ABSTRACT

Remote detection of radiation is a difficult problem due to the $1/r^2$ fall-off. Recent advances in polymer research and nanoscale fabrication methods along with advances in optical polarimetric remote sensing systems suggest a solution. The basic device uses a micro-wiregrid infrared polarizer fabricated in conductive polymer. When the polymer is exposed to hard radiation, its conductivity will be affected and the polarization properties of the device will change in a corresponding manner. This change in polarization properties can be determined by optically interrogating the device, possibly from a remote location. We will report on the development of a radiation-sensitive passive dosimeter polymer with very low optical visibility. Progress on material development, lithographic fabrication and optical characterization will be presented.

Keywords: Conductive polymer, subwavelength grating, polarization, infrared, microstructure devices

1. INTRODUCTION

The detection and monitoring of ionizing radiation from a remote location or large standoff distance is an important, albeit difficult, application. This project endeavors to solve this problem using an optical polarizer based on conducting polymer whose extinction ratio between orthogonal polarizations is dependent on the device's received dose of ionizing radiation. The main difficulty with detecting ionizing radiation from a distance is the rapid decrease in signal as the range from the source increases. Assuming the source is radiating in an isotropic fashion, the available signal will decrease as the square of the distance. A dosimeter that actively relays its information (e.g. electronically) would provide a remote monitoring method, but for many applications this device is too bulky, dependent on an adequate power source and easily defeated. A passive device like an optical polarizer is much more innocuous and can be interrogated either passively or actively from a large distance.

A well focused laser beam can be used to determine the extinction ratio of the polarizer from a large distance. Rotating the polarization of the laser with a half waveplate provides a modulated return signal dependent on this extinction ratio. The extinction ratio and corresponding signal modulation can be made to depend on the received dose of ionizing radiation. Alternatively, the device can be monitored passively using an imaging polarimeter. This approach would use the ambient illumination and take several images with polarization filters included in the imaging optics to determine the polarization content of the scene. The degree of polarization provided by the polarizer would again be dependent on its extinction ratio and would correspond to a received dose. The following section the background of the device itself. Section 3 will then discuss the development of the conducting polymer material with the subsequent section detailing the lithographic fabrication of the optical polarizer. Section 5 presents experimental results of initial devices and the final section discusses the radiation sensitivity of the polymer material.

2. DEVICE BACKGROUND

The key to these applications is a polarizer with an extinction ratio dependent on the absorbed dose of ionizing radiation. A brief review of wire grid polarizers will help illustrate the use of conducting polymers and the development of the device. In the most basic sense, a wire grid polarizer is a set of conducting lines that absorbs incident radiation that is oriented along the lines while passing radiation that is polarized in a perpendicular orientation[1-3]. Figure 1 shows the details of a wire grid device previously fabricated for the MWIR (2-5 µm) spectral range[1]. This device used gold as the conducting material and a subwavelength grating period to provide an extinction ratio greater than 100 with high transmission. The approach for this project is to replace the gold with a conductive polymer.

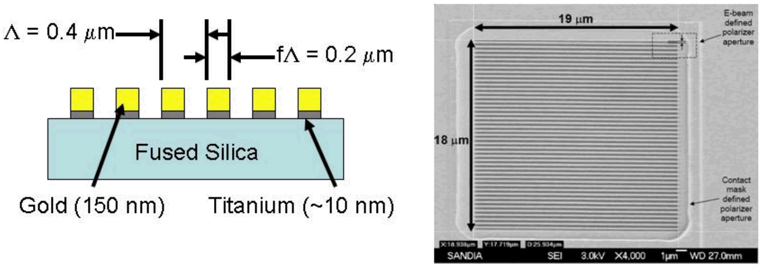


Figure 1. Design and scanning electron micrograph of gold based wiregrid polarizer.

The conductivity of gold is still several orders of magnitude higher than the best conductive polymers and this leads to several important design considerations. First, a comparison of the simulated performance of the gold based polarizer from Figure 1 and the same grating using a conductive polymer is shown in Figure 2. The gold based wire grid needs a small thickness to achieve a large extinction ratio while also providing a high transmission of the passed polarization. In contrast, the conductive polymer (σ = 100 S/cm) requires a much higher thickness to achieve a good extinction ratio. Unfortunately, the transmission of the polymer based polarizer is adversely effected by the thicker material. This result highlights the need to provide a polymer with as high a conductivity as possible. Additionally, the device fabrication must not reduce this conductivity while producing a grating with much higher aspect ratios (height versus width of line) than the gold based device.

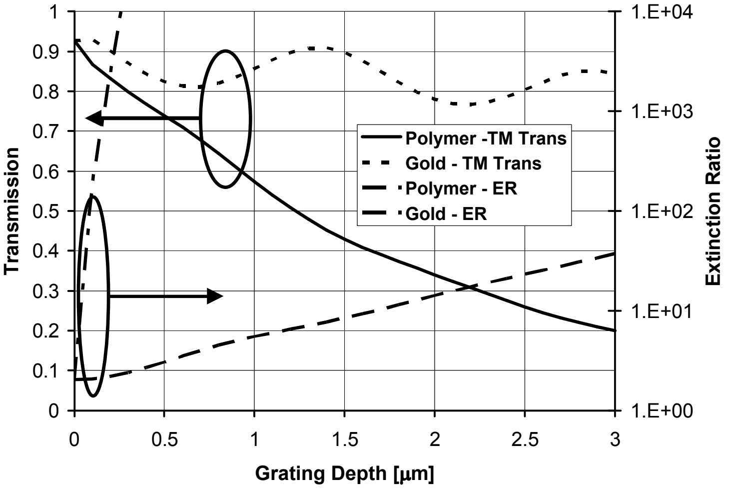


Figure 2. TM transmission and extinction ratio (ER) of gold and conductive polymer based IR polarizers versus grating depth. The polarizers were modeled with a fused silica substrate, Λ = 0.4 µm, f = 0.5 and λ = 3.39 µm.

Once a polarizer is successfully fabricated, its sensitivity to radiation determines its performance. The dependence of the polarizer extinction ratio to the conductivity of the material is shown in Figure 3. As the conductivity of the material decreases, the extinction ratio also declines rapidly. This change in extinction ratio is the measured parameter that is used to determine the radiation dose the device has received.

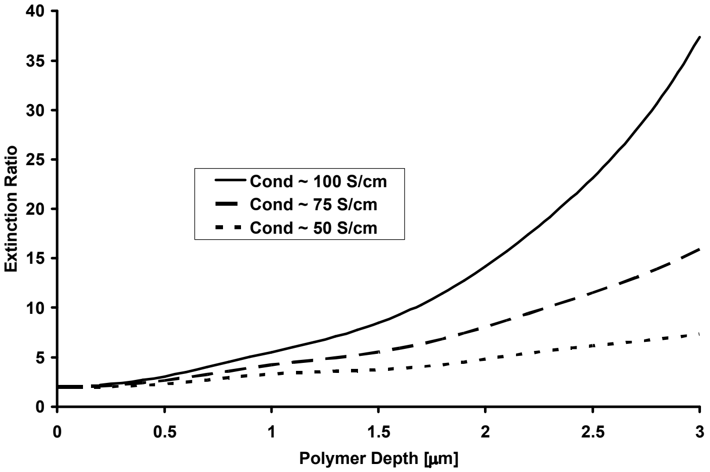


Figure 3. The importance of the polymer conductivity and depth on the extinction ratio of the polarizer.

3. MATERIAL DEVELOPMENT

There has been a great deal of interest in conducting polymers for optical applications ranging from photodetectors[4] and photovoltaic cells[5] to light emitting diodes[6-8]. Most work has used one of three material systems: aniline[9-11], thiophene[12-14] or pyrrole[15-19]. Our work has used electrochemically deposited polypyrrole, doped to provide high conductivity. This approach provided material with high conductivity that was environmentally stable and also able to be processed lithographically.

Polypyrrole films were grown on fused silica substrates that had a thin titanium (25 nm) / gold (30 nm) coating. The substrates were first prepared using a silver substitution in a three-electrode electrochemical cell to help adhesion of the polymer film[20]. The deposition and gold oxidation phase take place on the auxiliary electrode while the working electrode has repeated use for each additional substrate used for preparation on the auxiliary electrode. Subsequent film adhesion was greatly improved with the addition of this silver substitution.

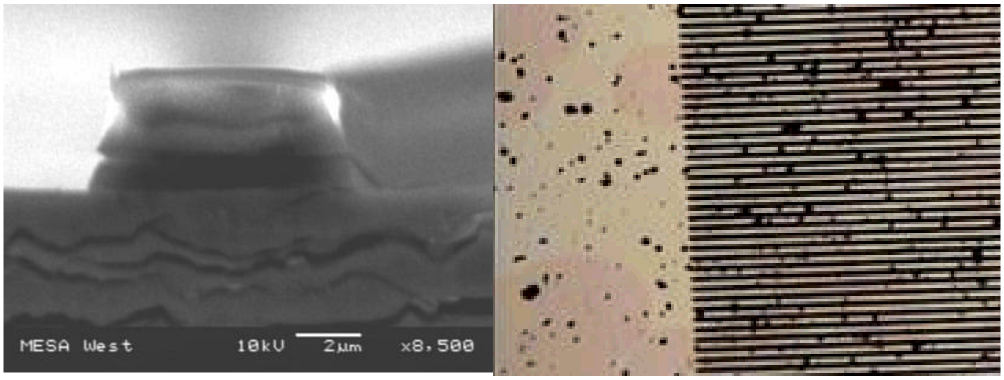
The polypyrrole film was then grown using a solution comprised of anhydrous acentonitrile, tetrabutylammonium tetraflouroborate electrolyte and pyrrole from solution. Previous work has used both potentiostatic[17,18] and galvanostatic[19,21] methods to control the growth of polypyrrole films. Samples were grown using both voltage and current control and it was determined that current control provided higher quality films. The oxidation-reduction potential required a steady square wave using 275 $\mu A/cm^2$ current density for 20 minutes on each side in an ambient atmosphere/room temperature setting. The use of 12 cycles provides a 1.2-1.4 µm black smooth film. A current density of less than 200 $\mu A/cm^2$ did not initiate the oxidation cycle of the pyrrole, while current densities greater than 400 $\mu A/cm^2$ resulted in heavy nucleation on the surface forming polymer growth that was dendritic with high surface roughness, and varying in thickness.

Conductivities measured on the PPy films ranged from 10-100 S/cm. The adhesion of the film to the substrate was adequate for subsequent processing, but the film could be removed with tape. Also, the film was not removed by photoresist developer allowing for the application and patterning of photoresist without the need for a protective overcoat.

4. LITHOGRAPHIC FABRICATION

In addition to the need for high conductivity, the device analysis shown in the Section 2 highlighted the thickness and grating dimension that was required for a polarizer with a good extinction ratio. That analysis assumed the grating period used for the gold device (to provide a direct comparison); however, subsequent analysis showed that much larger grating periods could also be used. Assuming a wavelength of 3.39 µm, grating periods as large as 1.6 µm could be used to provide an effective polarizer. This reduced the aspect ratio of the required polymer lines in the final grating and allowed for the use of contact print lithography to pattern the polymer. Additionally, the thickness requirement would necessitate the use of a hard etch mask, so initial efforts were made to process and pattern thinner polymer films of approximately 1 µm thickness.

Contact printing patterned the polymer film with grating periods as small as 1.2 µm (0.6 µm lines). Photoresist was spin coated directly over the polymer film. A standard soft bake, exposure and develop process was used to pattern the photoresist. A UV cure was then substituted for the hard bake typically done after development. This process alteration avoided problems encountered with the polymer reflowing and provided a functional etch selectivity (approximately 1:1). A reactive ion etch (RIE) was then used to transfer the pattern into the polymer[17] using an oxygen based etch recipe, see Figure 4.



(a) (b)

Figure 4. Successfully patterned PPy films. (a) Test etch of a relatively large feature (8 µm) using thick photoresist. (b) Image of patterned 0.6 µm lines in polymer.

The final fabrication process is the removal of the polymer grating from the seed metal. As mentioned earlier, the polymer film could be removed from the substrate with tape. Patterned polymer was also easily removed using tape so a transfer process was investigated for lifting the polymer lines off the original substrate. In order for the device to be practical at the design wavelength of 3.39 µm, the material used to lift off the polymer had to be transmissive. Most tapes and adhesives do not transmit well in the IR, but we found that Norland 61™ optical adhesive would allow a substantial amount of transmission if spin coated. The Norland adhesive was spin coated directly on to the patterned polymer and cured. Using samples grown on Ti/Au, a diluted HF etch lifted off the adhesive layer and polymer. Similarly, a BOE etch also successfully lifted off the adhesive backed polymer from the original substrate. These flexible devices could then be put on a hard substrate to facilitate optical testing. A SEM image of a transferred grating is shown in Figure 5.

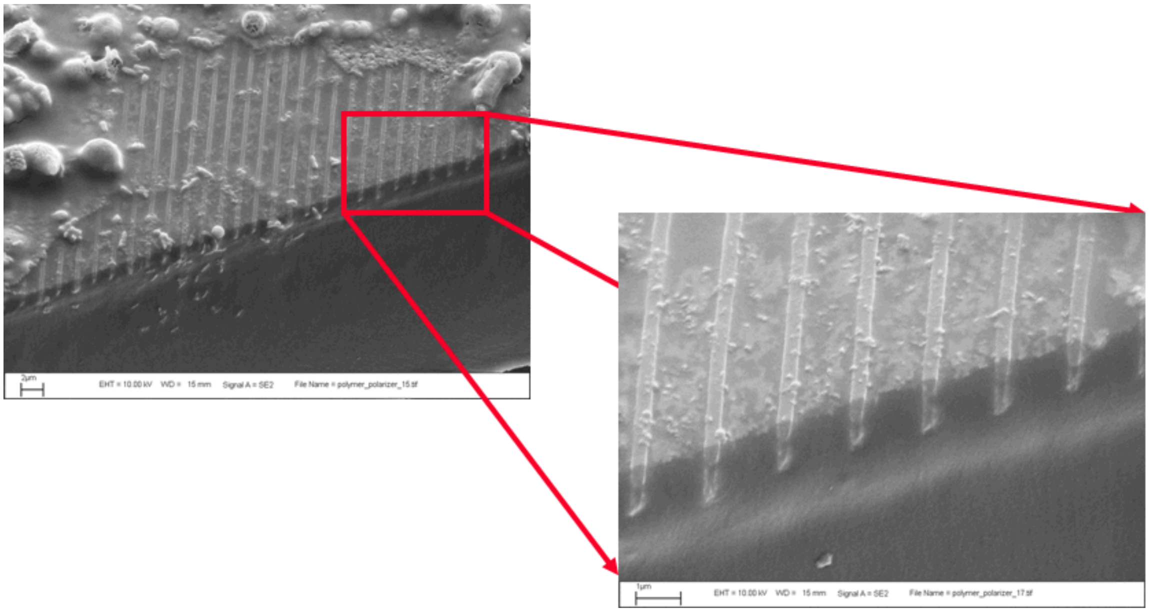


Figure 5. SEM image of transferred polymer grating embedded in Norland 61™. Grating period is 1.6 μm

5. OPTICAL CHARACTERIZATION

Several devices were tested optically and even the relatively thin 1.0 μm polymer provided measurable modulation of a polarized beam. A HeNe laser emitting at 3.39 μm was used as the input source with a specified linear polarization of 500:1. A half wave plate provided a convenient means of rotating the input linear polarization to the device under test (DUT). The transmitted signal was then detected using a HgCdTe detector. A chopper placed at the laser was used to synchronize a lock-in amplifier and eliminate background noise providing a high signal to noise ratio (SNR). The signal was recorded as the half wave plate was rotated through one full rotation. A background measurement was also taken without the DUT in place to take into account any diattenuation and beam drift caused by the rotating wave plate. The data from these measurements was used in conjunction with the physical parameters of the grating to determine the complex refractive index of the conductive polymer. By iterating with RCWA, the polymer's material properties were found.

The first device measured had patterned polymer wiregrids on top of the metal seed layer. Despite the high loss associated with the metal layers, the high SNR of the test setup allowed for consistent data to be taken. A portion of the gold was removed during the RIE etch as depicted in Figure 6. Figure 6 shows the sample data from a device with a period of 1.2 μm as well as the fit determined from RCWA. The resulting refractive index for the polymer was 0.95 – 0.3i which corresponds to a conductivity of 28.1 S/cm.

The final device tested had polymer grown on a titanium/gold seed layer and was removed using diluted hydrofluoric acid that etched the titanium. As mentioned in the previous section, spin coated Norland adhesive was used to pull the gratings off of the original substrate. To ensure mechanical robustness of the adhesive layer, the spin coated layer was relatively thick, approximately 10 μm. The thick adhesive layer resulted in a large loss at the test wavelength of 3.39 μm, but this effect was measured separately and taken into account in the analysis of the DUT. This device also exhibited modulation similar to the original device and had overall higher transmission. Iterative analysis with RCWA showed the polymer to have a complex refractive index of 1.1 – 0.5i and a conductivity of 54.2 S/cm. Figure 7 shows the data and simulated fit.

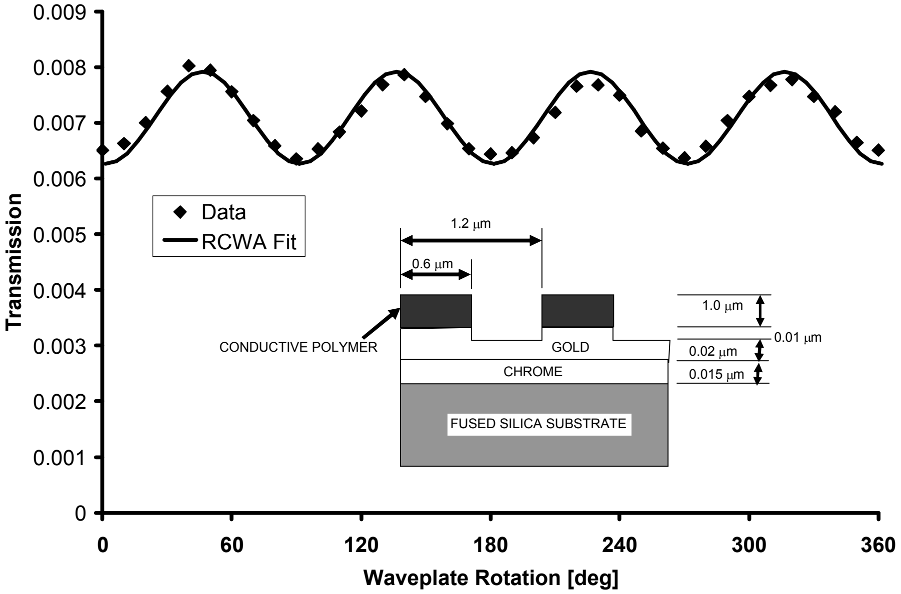


Figure 6. Measured transmission of conductive polymer wire grid (dots) and simulated fit (solid line). The physical parameters are shown on the included diagram.

The two measured conductivities are consistent with measurements taken on the polymer films before photolithographic processing. Previous work[9,11] has shown that some processes can be detrimental to the level of conductivity in the polymer. In fact, a device grown on chrome/gold was tested after the metal layers in the grating trenches were wet-etched. This device exhibited no discernible modulation and our conclusion is that the highly oxidizing chrome etchant (a solution of perchloric acid and ceric ammonium nitrate) effectively destroyed the polymer's conductivity. In light of this type of difficulty, measuring conductivities higher than 50 S/cm in a final device is a very encouraging result.

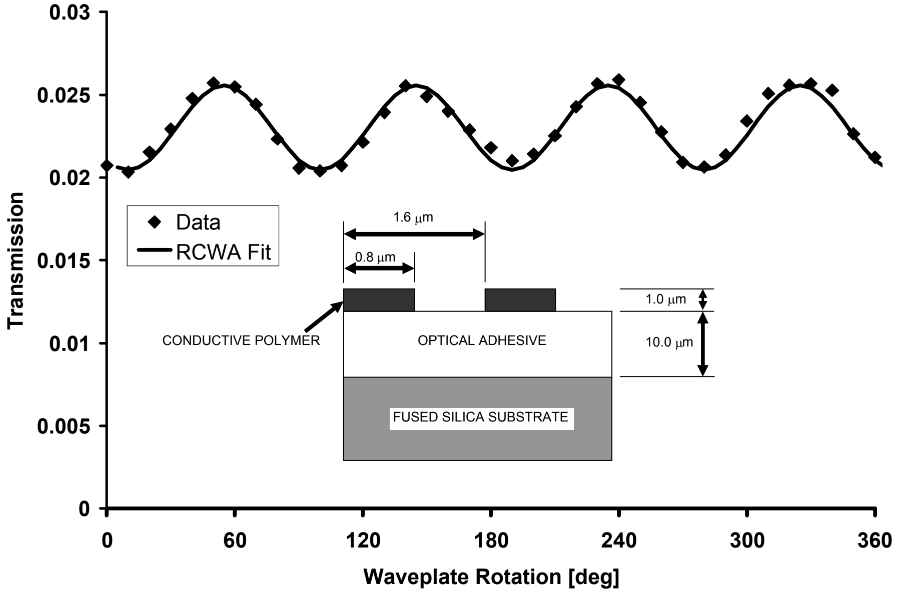


Figure 7. Measured data (dots) and simulated transmission (solid line) of polymer wire grid transferred via optical adhesive.

6. RADIATION SENSITIVITY

While the development of the optical polarizer has proceeded, the characterization of the conducting polymer's sensitivity to ionizing radiation has begun. The analysis shown earlier assumed that ionizing radiation would produce a decrease in the conductivity of the polymer. Previous work on polyaniline irradiated with both high and low energy protons did show a measurable decrease in conductivity[22,23]. Additionally, gamma ray and electron beam irradiation have produced conductivity decreases[24,25]. Unfortunately, there are also reports showing the opposite result. Gamma ray irradiation was shown to produce increased conductivity in polyaniline[26] as was heavy ion irradiation in conducting polypyrrole[27] and polythiophene[28]. In light of these apparently contradictory results, it is imperative that the material being used here be studied experimentally.

Fortunately, the direction of change in conductivity is not as important as the degree of change. A device that is non-polarizing and then becomes polarizing after being irradiated is still an effective device for this application. However, the magnitude of the conductivity change must be significant enough to produce a measurable change in the optical polarizer's performance. Again, this point highlights the need to experimentally characterize the material being developed.

Our first experiments have used protons with an energy of 250 keV in an evacuated chamber. Figure 8 shows the effect of this irradiation on the conductivity of the polymer. The measured changes are always positive, i.e. we observed an increase in conductivity. The amount of increase asymptotically approaches zero with larger doses. An earlier experiment done with higher energy protons and a much higher dose resulted in the complete loss of conductivity. This qualitative result indicates that further increases in the dosage will eventually lead to another transition to negative. In addition, on the lower dose side, there must also be another transition since the change in conductivity with no dose is by definition zero.

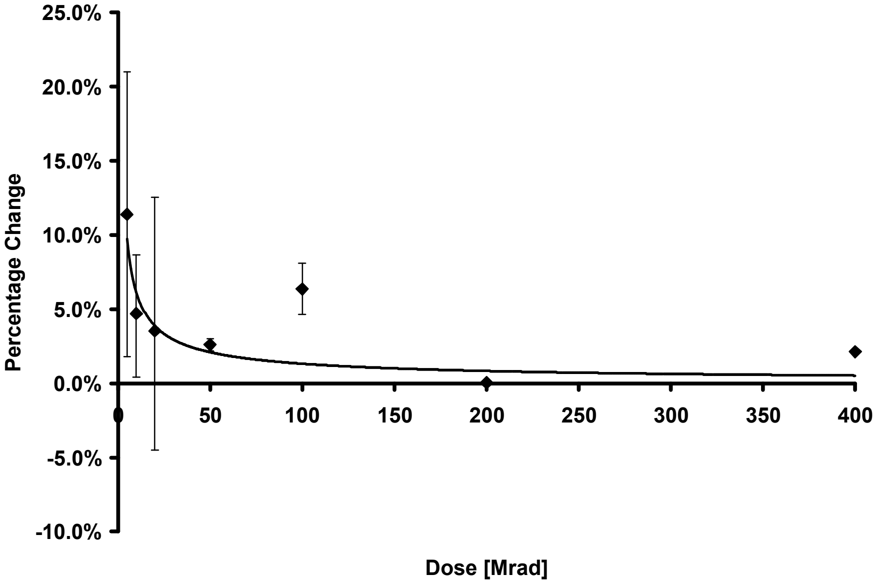


Figure 8. Effect of proton irradiation on polymer conductivity. Error bars indicate maximum and minimum observed changes in conductivity. Note: the data at 200 and 400 Mrad is comprised of a single data point; therefore, there are no error bars shown.

7. CONCLUSIONS

The concept of an optical polarizer susceptible to ionizing radiation as a passive dosimeter has been presented. The background of optical wiregrid polarizers and the use of conducting polymers in their design has been reviewed with the tradeoff of device extinction ratio and transmission highlighted. Our progress in both the development of conducting polypyrrole has led to the demonstration of uniform film thicknesses greater than 1.0 μm with conductivities reaching 100 S/cm. The fabrication of a wiregrid devices using this material has successfully produced gratings with features as small as 600 nm and these devices have been characterized optically. Finally, the results from the first tests of the polymer's sensitivity to proton irradiation have been shown to have a positive effect on the conductivity of the material.

There are several tasks that are now being pursued as part of this program. First, thicker polymer films are being deposited to provide optical polarizers with usable extinction ratios. Film thicknesses of greater than 2.0 μm have already been made. The inclusion of a hard mask in the fabrication process is being pursued to enable the anisotropic etching of the thicker polymer. A nickel mask has been successfully patterned on polymer films and we a currently developing the etch process. The characterization of the polymer to ionizing radiation is also continuing as we experimentally verify the other transitions expected in material behavior as discussed in the previous section. We will also be characterizing the material with other types of radiation to see if radiation type and / or dose rate are also factors in the effects on conductivity. Finally, we will ultimately test the radiation sensitivity of polymer based polarizers.

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