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Development of an optically interrogated chemical tag

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ABSTRACT

We report on the progress of an optical tag designed to indicate the presence of HF. The approach we followed uses a high spatial frequency grating consisting of lines of conductive polymer. The conductive polymer has been designed to be sensitive to HF; changing its conductivity upon exposure. This material change results in a change in the polarization response of the grating which can be read out remotely using optical techniques. The use of a polarization response makes the signal more robust to intensity fluctuations in the background or interrogation system. Additionally, the use of optical interrogation allows for standoff detection in instances where hazardous conditions may be present. A review of the material development work will be presented as well as the device fabrication efforts. Examples of material and device responses will be shown and directions for further investigation discussed.

Keywords: Conductive polymer, chemical sensing, HF sensing, subwavelength, polarization

1. INTRODUCTION

Hydrofluoric acid (HF) is used in many industrial processes; however, its high level of toxicity and adverse environmental impact has prompted considerable efforts to properly monitor its presence and concentrations. Successfully sensing HF in a compact form has proven difficult for several reasons including the existence of other reactive species, e.g. chlorine, in the same vicinity. It would also be useful to have a monitoring technique that provides a persistent and cumulative sensing of HF levels providing the equivalent of an integrated exposure level. Additionally, a sensor that can be read remotely would allow the use of the device within hazardous areas or equipment. Finally, a passive device removes the difficulties associated with providing power to the device.

This project will develop an optical device with a polarization signature susceptible to HF to allow for practical measurement at a standoff distance. The approach uses a classic wiregrid polarizer design with the lines comprised of conductive polymer composite. The polarization signatures are directly related to the conductivity of the polymer composite. This conductivity is altered by the introduction of HF leading to a measurable change in the response of the device. This change can be read from a distance by actively interrogating the device with a laser or by imaging with a polarimetric imaging system. The successful demonstration of an HF specific polarization tag could be leveraged to realize devices sensitive to other industrial materials; ultimately providing a suite of sensors.

The development of our HF sensitive tag began with intensive material development efforts that will be detailed in the following section. The development of a device fabrication process utilizing the polymer is discussed in Section 3 with measurements of the devices presented in Section 4. Section 5 briefly outlines the system model developed to simulate the use of the tag and help frame requirements for the various steps of development. Finally, conclusions and directions for further research will be discussed in Section 6.

2. MATERIAL DEVELOPMENT

When work began on the polymer development, three basic requirements were set forth. First, the polymer had to provide a high enough conductivity to result in an optical device with a measurable polarization signature. The figure of

50 S/cm was used as the preliminary goal for the conductivity level. Second, the polymer had to be sensitive to the target species, fluorine, or more specifically, fluoride ions. Third, the polymer had to demonstrate selectivity to minimize false readings due to the presence of materials other than the specific target. The choice of fluoride as the target species led to three material approaches: boron and silicon containing polymers [1] as well as capped nanoparticles.

2.1 Alternative polymer development

The final polymer blend that was determined to be the most promising was a silicon containing formulation (silane); however, two alternatives that were also investigated warrant further research and are discussed briefly here. The first is boron containing polymer or borane. Polymers and oligomers that utilize the Lewis-acidic nature of boron (as the recognition element) combined with the signal amplification of a semi-conducting polymeric-network (i.e. molecular wire) have shown significant promise for F^- detection. In general, π-conjugation is extended though the vacant p-orbital of the boron atom with this class of polymers. Coordination of a fluoride ion disrupts this conjugation; this can be read as an electronic, colorimetric, fluorescent or conductive signal depending on the exact system being examined. F^- binding also changes the polymer from a neutral-uncharged species to a zwitterionic-neutral species. This effect would be expected to change the physical properties of the polymer (such as swelling, hydrophobicity etc.) and might contribute to sensing. Here we aimed to utilize these phenomena to develop new sensors for HF/F^- binding. A change in conductivity will impact the optical polarization signature of the device. From the onset it was realized that semi-conducting polymers such as this would likely not have sufficient conductivity; however, doping with conductive materials such as fullerenes, e.g. C60, carbon nanotubes, e.g. multi-walled nanotubes (MWNTs), or graphene based materials, e.g. reduced graphene oxide (RGO), would provide a p-n type composite/blend with enhanced conductivity while retaining the F- detection capability.

Several versions of the borane were synthesized and two versions were found to be sensitive to HF as well as other acidic solutions. The addition of conductive dopants and other materials to the blend; unfortunately, reduced (or eliminated) the HF sensitivity. In contrast, in both cases, the eventual blends were found to still be sensitive to nitric acid (HNO_3) and may provide a base for future work on a tag for this material.

A second approach for HF sensing started with conductive material, gold nanoparticles, and attempted to add sensitivity to HF. Electronic transport between electrodes filled with organic capped nanoparticles is dominated by tunneling and activated tunneling. The likelihood that an electron will tunnel between two nanoparticles is related to the interparticle spacing exponentially. Consequently, electronic transport in metal nanoparticle films is very sensitive to interparticle spacing. This has been the basis of many nanoparticle sensor devices. Metal nanoparticle films can be used as sensors based on resistance changes. Metal nanoparticle films can swell on exposure to a variety of different vapors and have large changes in resistance. In order to generate a nanoparticle network that would be sensitive to HF, initial work involved the synthesis of gold nanoparticles coated with a ligand that would change shape and lose mass when exposed to HF. The general scheme is shown in Figure 1.

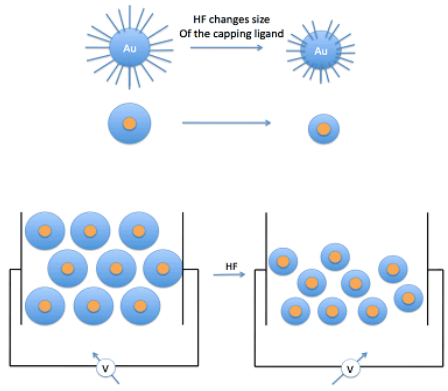


Figure 1. Capped nanoparticle scheme for sensing.

The capped gold nanoparticles provided the high conductivity the optical devices required and the proper choice of ligand led to good sensitivity and specificity to HF. The main difficulty with these films was poor environmental stability. While the boranes and silanes were fairly stable, the capped nanoparticle formulations had a shelf life less than a month long. Unfortunately, further development of this approach was not pursued, in part due to the success of the silane development, but the promise of this technique makes it a good candidate for future work.

2.2 Silane development and synthesis

Previously conjugated polymers containing silicon have found much use in light emitting diode devices as they tend to emit in the blue range.[2-7] The same conjugated polymers containing silicon are potentially useful for the detection of fluoride. It is well know that silicon forms a very strong bond with fluorine and has a value of

552.7±2.1 kJ/mol at room temperature.[8]

Conjugated polymers containing silicon should react to form smaller conjugated polymers and in the process decrease the conductivity and light emission of the resultant smaller oligomers and polymers. A sensing scheme is depicted in Figure 2 where the silicon in the backbone of polymer **1** forms a strong bond with silicon breaking a carbon-silicon bond which has a value of 451.5 kJ/mol.[14] The resulting products are lower in molecular weight forming olefin terminated and silicon terminated products **2** and **3** respectively.

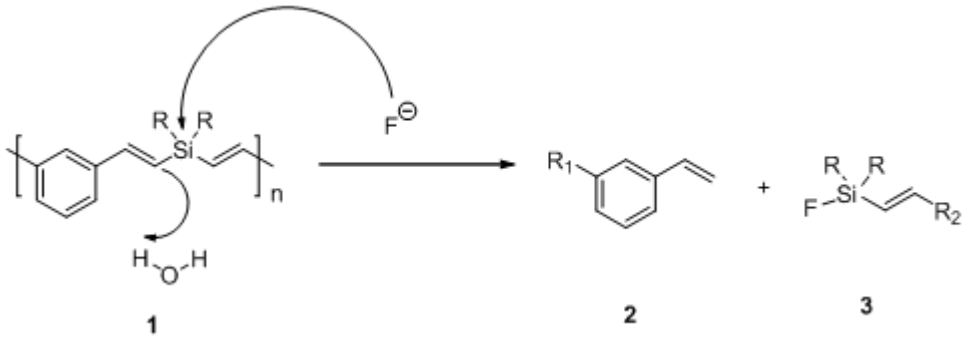


Figure 2. The sensing mechanism for the detection of fluorine or fluoride involves breaking carbon-silicon bonds to form smaller conjugated segments.

A platinum catalyzed hydrosilylation reaction was used to create a series of polymers containing silicon.[9] Polymer **4** was formed from the reaction of 1,3-diethynylbenzene (**5**) with diphenylsilane (**6**) using Karstedt's catalyst as shown in Figure 3. The reaction was run at a concentration of 1 M which resulted in the formation of a gel and resulted in the isolation of only 11% of the desired polymer. The remaining material was probably cross-linked due to hydroxilylation reactions with the resulting double bonds formed after the initial hydrosilylation step. When the reaction was run at 0.5 M the theoretical yield increased greatly to 57-58% for several reactions. Polymer **7** was synthesized from the hydrosilylation of **5** with 1,4-bis(dimethylsilyl)benzene (**8**) according to Figure 4.

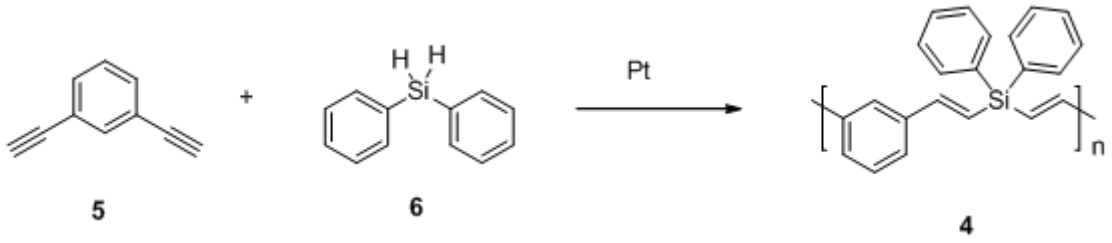


Figure 3. Synthesis of polymer 4.

All reactions were carried out under a dry atmosphere unless noted. ^{1}H nuclear magnetic resonance (NMR) was carried out on a 400 MHz Bruker DRX-AVANCE. Proton chemical shifts (δ) are reported as shifts from the internal standard tetramethylsilane (TMS). Infrared Spectroscopy (IR) was carried out on a Nicolet 6700 FTIR. Gel Permeation Chromatography (GPC) molecular weight determinations were performed by GPC using a Polymer Labs 220 PL-GPC equipped with a UV-Vis detector. Two columns (PLgel 5 μm MiniMIC-C, 250 × 4.6 mm) and a guard column (PLgel 5

μm MiniMIX-C, 50 × 4.6 mm) were used in series with a flow rate of 0.4 mL/min and a run pressure of 6.0MPa . Chloroform was used as the eluent (0.4 mL/min), and measurements were performed at 35 °C. Calibration was performed using polystyrene standards with a narrow molecular weight distribution (Fluka ReadyCal 400-2,000,000). 1,3-Diethynylbenzene (**5**) was purchased from Aldrich. Diphenylsilane (**6**) (97%) was purchased from Acros. Platinum divinyltetramethyldisiloxane complex (Karstedt's catalyst) was purchased from Hüls. 1,4-bis(dimethylsilyl)benzene (**8**) was purchased from Gelest. Toluene (99.8%, anhydrous) was purchased from Sigma-Aldrich. All chemicals were used as received from suppliers.

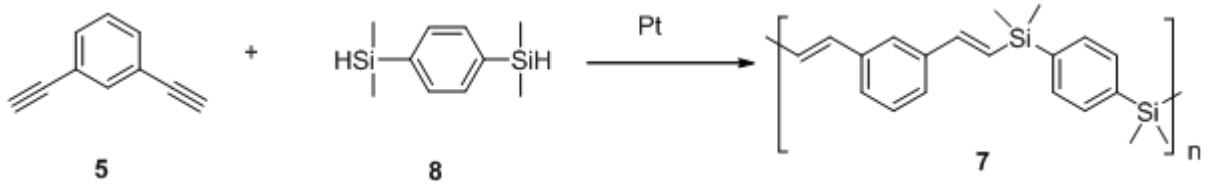


Figure 4. Synthesis of polymer 7.

The silicon containing polymer, poly(dimethylsilyene-*m*-phenylene-dimethylsilylene-vinylene-*m*-phenylene-vinylene) (**7**), was synthesized using the following procedure. To a 100 mL round bottom flask equipped with a reflux condenser was added **5** (0.63 g, 5.0 mmol) and the air was removed and replaced with nitrogen (3×). **8** (1.1 mL, 5.0 mmol) and toluene (10 mL) were added to the round bottom flask via syringe. The solution was brought to reflux and Karstedt's catalyst (5.0 uL) was added and the solution was held at reflux overnight. The solution was cooled the next day and precipitated into ice cold ethanol (100 mL) to yield a pale yellow polymer.

2.3 Initial material screening

It was essential to find a way to compare the materials being synthesized and quickly evaluate their potential as the material for a polarization based sensor. Several diagnostic approaches were attempted including fluorescence measurements, FTIR and UV-Vis spectroscopy; however, the method that provided the best screening tool was electrochemical impedance spectroscopy (EIS).

A number of electrochemical techniques have been used to study polymer films, the most common being EIS. Impedance spectroscopy examines factors in the polymer that resist the alternating flow of electrons generated from a small induced AC potential by comparing any lag from the resulting current. Using EIS measurements on polymer samples before and after exposure to HF, candidates with good sensitivity were quickly identified. These measurements could be done on undoped polymers with little or no conductivity and would still indicate the sensitivity of the material to HF. Multi-element, inter-digitated electrodes (IDEs) were used as the platform of the characterization process using EIS analysis. IDEs have been widely used and well established for chemical sensing techniques. The open circuit architecture enables continuity (i.e. capacitance or resistance) to be formed by conductive and non-conductive polymers by simply coating the material over the surface between the defined features. Each experimental film was drop coated and placed under vacuum, less than 1 torr pressure, to ensure no residual solvent interfered with polymer testing in solution. This particular step allowed the film to be inspected for any adhesion failure or excessive cracking of the polymer film.

Through the course of the material effort, eleven different polymers were synthesized and tested using EIS to find a subset for further development. The polymers with the highest admittance (lowest impedance) and/or largest change after HF exposure were chosen. The baseline criteria for initial sensitivity to the fluorine species was 100 ppm. After identifying the most promising candidates with HF sensitivity, the next step in the material development was the determination of a strategy for providing the necessary conductivity.

2.4 Doping schemes for conductivity and advanced characterization

To improve the conductivity of these polymers, various modifications of conductive nano-particles were blended with the parent polymers. Small concentrations of single wall carbon nanotubes (SWNT), multi-wall carbon nanotubes (MWNT), gold nano-particles, reduced graphene oxide (RGO), and titanium dioxide (TiO_2) nano-particles of various combinations were added to the parent polymers. A combination of literature references and previous explored work in silica and gold nano-particle loaded sensor films indicated a maximum of 60% by weight for metal nano-particles and a maximum of 25% by weight for carbon based material choices.[10] The loading of nano-particles is based dominantly on the principle of electron percolation path and threshold within the polymer matrix.[10] Therefore, blending materials into a polymer conductive material in excess of greater than 50% by weight, has potential to yield inconclusive results because of competition for surface sites towards the reacting species. It was recognized that every combination of base polymer and dopant could not be tried. Fortunately, the polymer compositions were similar enough that if a dopant composition worked well with one polymer, it was very likely to work well with another. Combinations were attempted with SWNT, RGO, carbon black and MWNT. Ultimately, the best results were obtained using the MWNT. Several experiments were also attempted using metal nano-particles. Unfortunately, it was quickly determined that the level of loading required to obtain useful conductivities was so high that the response of the composite material was no longer dominated by the original polymer. Thus the usefulness of the polymer as an HF sensing material was lost.

During this second phase of polymer development, a parallel investigation into inorganic titanium dioxide nano-particles as a gettering dopant for fluorine was undertaken.[11] The reactivity of titanium dioxide with hydrofluoric acid is known; however, the mechanism is not entirely understood. It is speculated the fluorine affinity towards titanium is significantly higher than the oxygen binding, and at only 0.01% impurity in the nano-particles the potential reaction of other species is quite low (i.e. silicon dioxide, alumina). Therefore, a fluorotitanic acid is generated at the surface and was leveraged with a silicon containing polymer to enhance the gettering effect.

At this point of the development, the materials need to provide the three original requirements; conductivity, sensitivity and selectivity as well as other criteria that became evident during the initial screening tests. These other requirements included water and water vapor stability, physical stability and ease of manufacturing. The characterization of the doped polymers and capped gold nanoparticles was again done with EIS and a second in-situ measurement using an LCR meter. Initial testing with the LCR meter used an aqueous exposure using 100 ppm and materials were tested against HF as well as HNO_3, HCl, H_2SO_4 and deionized water. A composition with MWNT and TiO_2 nanoparticles added to the silane polymer demonstrated conductivity levels just short of the 50 S/cm goal, and the HF sensitivity was greatly enhanced by the addition of the TiO_2, see Figure 5. Additionally, this material exhibited the best stability in the presence of water and was determined to be the best candidate for a polarimetric fluorine sensor.

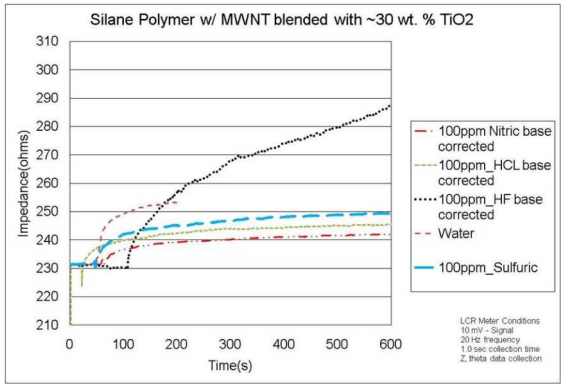


Figure 5. Silane response to aqueous exposure.

After the initial success with the silane/MWNT/TiO_2 composite, an experiment was performed to begin to understand the lower limits of sensitivity and selectivity. The use of 100ppm HCL and deionized water was used as a reference indicator to determine the signal generated from the HF solutions of 100ppm, 10ppm, and 1ppm. At 1 ppm of HF in solution, the device is near the sensing limitations for a definable measurement above the deionized water and HCL concentrations. In Table 1, the percent change of resistance is established for each of the devices tested.

2.5 Iterations on polymer blend design

One area of concern from the characterization work was the lack of repeatability in many of the results. jAbsolute conductivity measurement includes errors due to the application process of the film on to the IDE's, the error due to non-uniformity of the nano-particle distribution (the blending process), and errors due to film reproduction (batch-to-batch processing). Polymers that were highly conductive and reposed well to HF exposure, were not very reproducible. To address the consistency and optimization of the silane blend, a rigorous design of experiments (DOE) was constructed. The approach was arranged in two phases. The first ANOVA phase (ANalysis Of VAriation) was intended to discover

the level of variation in the polymer blend and its material response. Assuming the level of variation was limited, the second phase would help determine the optimal mixture of each of the blend components with the final blend providing the best tradeoff between conductivity, sensitivity and selectivity.

HF Exposure (ppm)	Before (ohms)	After (ohms) at 1200s	Percent Change
100	69.4	82.1	18.30
10	69.4	75	8.07
1	69.4	73.9	6.48

Table 1. Describing the percent change of resistance in the silane polymer (23% MWNT blend) and ~10% titanium dioxide.

The results of the ANOVA revealed a level of variation in the polymer blend and measured responses that precluded performing the optimization DOE. A substantial effort was made to determine sources for the variations observed and three were identified. First, the size distribution of both the MWNT and the TiO_2 nanoparticles was critical. Vendor labeling was found to be inadequate and size distributions were measured empirically to ensure consistency from one lot to the next. The second source of variation was the agglomeration of particles within the blend, see Figure 6. As will be discussed later, this agglomeration was also a concern for the proper fabrication of the optical devices. Finally, it was determined that the molecular weight of the base silane also played a role in the sensitivity of the blend. Several lots of the silane have been synthesized and variations from one lot to another can lead to significant differences in the resulting molecular weights. Lots with the highest molecular weights did not perform nearly as well as lower weight versions. We hypothesize that the density of the polymer has an effect on the interaction with the fluorine species. We also know from previous work that if the molecular weight is too low, the polymer physical stability is affected; thus, there appears to be an optimal molecular weight for proper sensing.

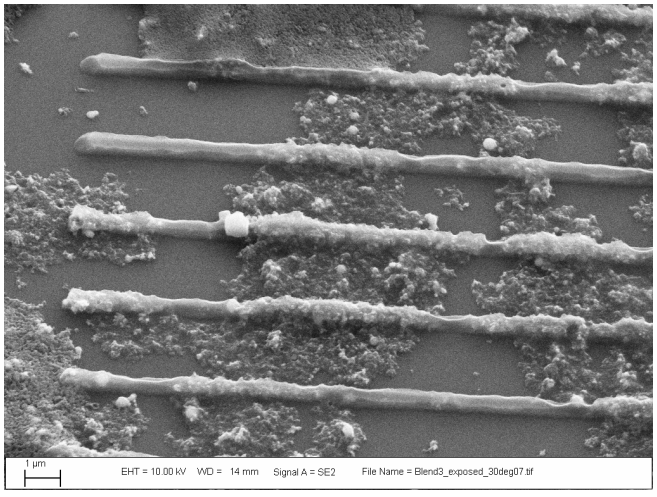


Figure 6. SEM of agglomerating particles during grating fabrication.

To address the agglomeration of the MWNT, the dispersal was improved by using dimethylformamide (DMF) as the solvent for the blend preparation and sonicating the mixture with a horn or finger. Alternatively, the MWNT could be combined with sodium dodecyl sulfate (SDS), a surfactant, in a water based solution. The TiO_2 did not readily disperse even with the use of sonication during blend preparation so the use of surfactants was examined. While initial results were promising, difficulties with the device fabrication led to a new approach for the TiO_2 inclusion.

The level of TiO_2 loading and the size distribution of the nano-particles resulted in a colloidal mixture that was not adaptable to optical device fabrication methods. To alleviate this difficulty, the latest version of the polymer blend uses liquid precursors to the TiO_2 with a precipitation reaction initiated at the proper stage of device fabrication. The blend reformulation has been tested using the LCR meter and the HF sensitivity has been confirmed. Currently, we are examining the sensitivity of the precipitation reaction to the moisture content in the solvent and associated temporal dependencies.

3. OPTICAL DEVICE FABRICATION

Analytical work was done to provide quantitative requirements for the device fabrication effort. These requirements included conductivity greater than 20 S/cm, a grating period of 2.3 μm or less, grating depth of 1.0 μm or more and a

target duty cycle of 50%. In addition to these device requirements, the fabrication process had to work with liquid solutions containing suspended solids, pattern areas at least 1.0 cm^2, work at low temperature, adapt to different polymer blends and work on variable substrates. This daunting list led to the decision to pursue a stamping technique.

The first stamping approach investigated was micromolding in capillaries (MiMIC). The process is summarized in Figure 6. A master is created using a photolithographic based process. Photos of masters created in SU-8 photoresist and silicon-on-insulator (SOI) are shown in Figure 7. From these masters, Polydimethylsiloxane (PDMS or silicone) molds are created by coating the master with liquid PDMS, allowing it to cure and removing it from the master. The PDMS is then cut into individual device molds exposing the sides of the pattern. These molds can be applied, pattern down, to the target substrate. The flexible PDMS creates a good bond to the clean substrate surface. Liquid polymer blend is then deposited along the exposed edge of the pattern where it infiltrates the capillaries. The pattern is allowed to dry and then the stamp is removed leaving the patterned polymer on the substrate.

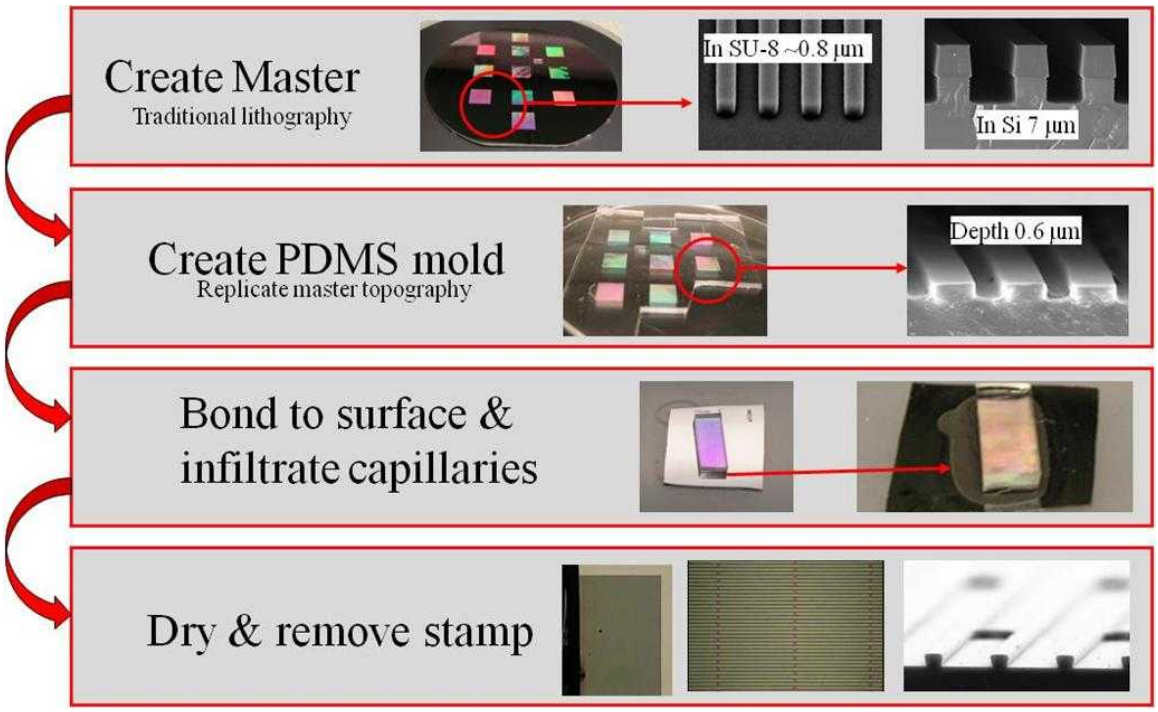


Figure 7. Summary of MiMIC stamping process

Initial trials were done with just the base polymer in solvent, DMF. Figure 8 shows a summary of this effort. Coverage of an 8x10 mm area was done with excellent pattern fidelity. There was some shrinkage of the pattern as compared to the PDMS mold; 14% in the vertical dimension and 20% in the lateral. This shrinkage will need to be accommodated in an updated master. This excellent initial result exhibits the potential of the approach; unfortunately, work with the full polymer blend has not been completely successful.

As mentioned earlier, agglomeration of the suspended solids led to problematic inconsistencies of the polymer blend. These agglomerations also created problems for the MiMIC process. Capillary openings of approximately 1 µm width quickly became plugged as the suspended solids entered the channels. Figure 9 shows one example of the effective filtering of the polymer blend by the capillaries. Where the edge of the mold was located, there is a transition region. SEM inspection reveals that this area contains the suspended solids. Clearly, the material has agglomerated. Past this transition, in the interior of the device, the patterning is excellent but only consists of the base polymer.

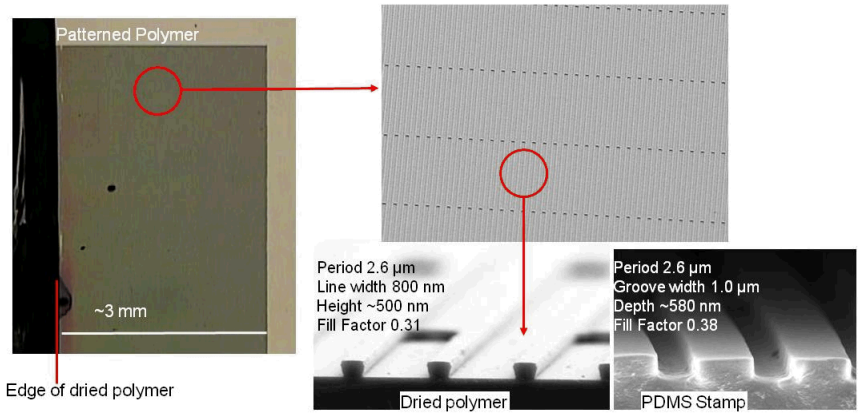


Figure 8. Results of MiMIC process with base polymer.

SDS was added to the MWNT in a water based solution and was successfully patterned using the MiMIC approach. Unfortunately, a method for dispersing the TiO_2 without adversely effecting the material response has not been identified. Work on the MiMIC process continues with efforts to more fully understand the use and control of the liquid precursors for TiO_2 precipitation.

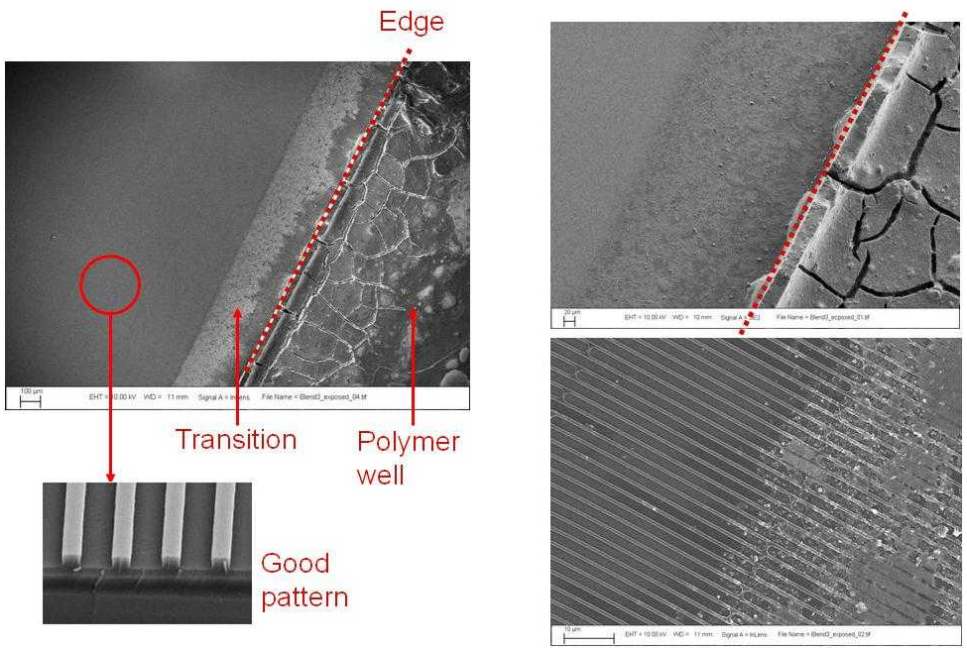


Figure 9. MiMIC process using full polymer blend exhibits filtering of suspended solids.

Several alternatives to the MiMIC process have been investigated including air-brushed stamps, rigid stamping and infiltrated masters. The air-brushed stamps used a nitrogen gun to spray the polymer blend onto a PDMS stamp. The stamp was then applied to a substrate with a layer of partially cured optical adhesive. Example results are shown in Figure 10. This method suffered from non-uniform pattern replication and grating heights that did not fulfill the

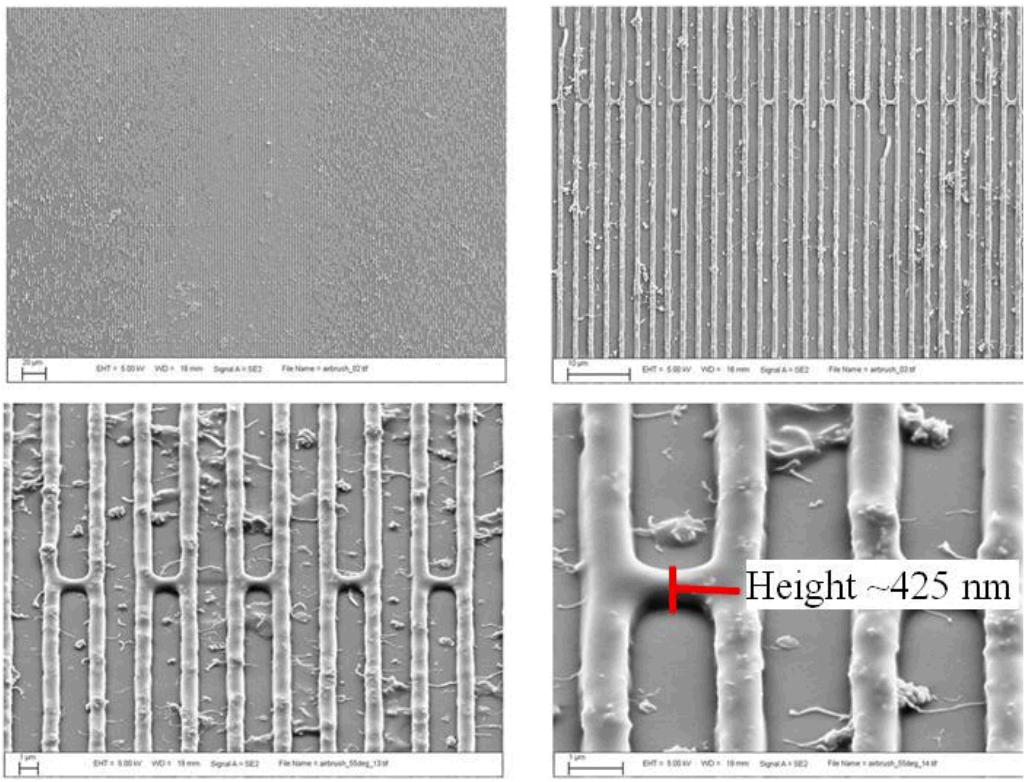


Figure 10. SEM inspection of air-brushed stamp gratings. Upper left shows inconsistency of pattern replication while higher magnification reveals height of gratings as well as evidence of agglomerated solids.

requirement of 1 μm. The pattern replication could be improved with the addition of a release agent on the stamp or better wetting to the substrate. Increasing the height is more difficult and no clear strategy for addressing this issue has been identified. The rigid stamping used a mold patterned in glass via reactive ion etching. This rigid mold was used to press the polymer blend into the pattern. This pattern is then lifted off the initial substrate using a second substrate with a thin, spin-coated, layer of optical adhesive, see Figure 11. While the pattern fidelity is still suspect, this process has produced gratings exhibiting a small, but measurable, polarization signature. Unfortunately, SEM inspection revealed that the grating pattern was only in the topmost layer of polymer with a large unpatterned layer underneath. This result helped identify the difficulty with the colloidal mixture. At the scale of the grating, the shear forces simply did not allow the rigid stamp to properly pattern the material. Finally, we have attempted to form gratings by using the masters from the MIMiC process and infiltrating them with the polymer blend and have had initial success with SOI masters.

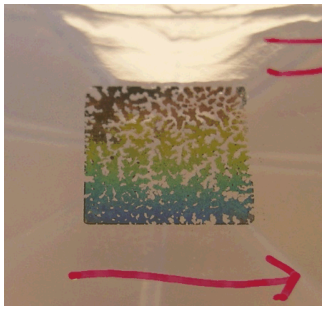


Figure 11. Grating fabricated using rigid stamp. The pattern fidelity is not uniform across the 1 cm^2 field. The rainbow appearance is due to diffraction of visible light by the grating.

While the infiltration of SOI gratings does not easily lend itself to a mass production process, it provides a useful alternative vehicle for demonstrating the sensitivity of the polymer blend to HF. SOI wafers with a silicon thickness of 10 μm have been used and exhibit a strong polarization signature even before the addition of the polymer blend. Testing with infiltrated polymer has just begun, but initial results are promising.

4. OPTICAL CHARACTERIZATION

As the work on the fabrication development proceeded, a laboratory system was constructed to characterize the polarization response of the optical devices. Figure 12 shows the basic measurement system. A laser with a wavelength of 3.39 μm is used to illuminate the device under test (DUT) with a linearly polarized input. The orientation of this input polarization is rotated using a halfwave plate. As the halfwave plate is rotated through θ degrees, the linear polarization rotates by 2θ degrees. The illuminating laser is chopped so that the output of the cooled HgCdTe detectors can be routed to lock-in amplifiers to reject spurious noise.

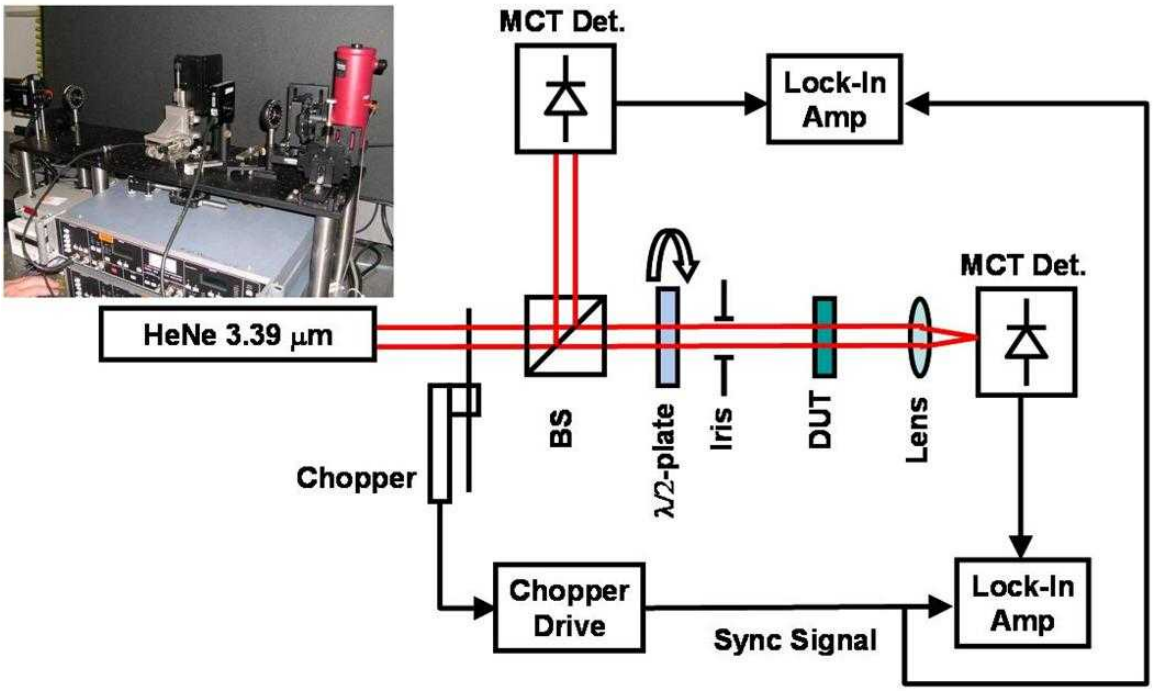


Figure 12. Schematic of test arrangement for measuring polarization response of optical devices.

Figure 13 shows a preliminary result from an infiltrated SOI grating exhibiting a strong polarization signature before exposure to HF as well as a significant change in this signal after exposure. The exposure here was done in the vapor phase by placing the device in the headspace above an HF solution with an exposure time of 15 minutes and an approximate HF concentration of 100 ppm.

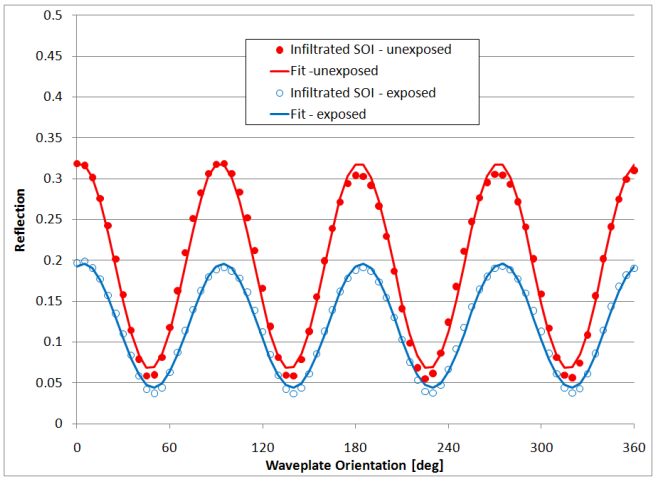


Figure 13. Response of SOI grating infiltrated with polymer blend to HF exposure.

5. SYSTEM MODELING

The last major area of investigation was the development of a system, or engineering, model. The intent was to provide a model that could translate material conductivity (and its change with exposure to HF) into a measured optical response. There are several steps between conductivity and optical response including:

- Translation of conductivity to optical parameters (complex refractive index) via the Drude model
- The use of the complex refractive index in conjunction with grating parameters to simulate a device response using rigorous coupled wave analysis (RCWA)
- Modeling the optical interrogation system and incorporating the device responses

The Drude model is shown in Equation 1. Since the material will be used in the mid-wave infrared (MWIR) spectral region, the Drude model is a good approximation. Note, there are two unknowns, n and k, in this single equation. To reduce the uncertainty, published values of n for similar materials are available in the published literature and limited ellipsometry measurements have been done on sample polymer films. It is expected that the addition of the TiO_2 will change the aggregate index of the material (most likely an increase of n) and as optical measurements are made, these changes will be better understood. Additionally, the composition within the fabricated gratings may differ from the original blend as demonstrated in dramatic fashion by the MiMIC results shown earlier.

$$nk = \frac{\sigma}{4\pi\omega\varepsilon_o} \tag{1}$$

The second step of the system model is the use of the complex refractive index with the geometrical parameters of the grating to determine the response of the individual optical device. This modeling work was done extensively to quantify the material and device requirements. Now the model can be used to translate measured material responses into device performance.

Finally, optical design software can be used to model the signals actually measured by an optical interrogation system. Non-sequential raytracing has been used to simulate the outputs of a simplified polarimetric imager. Figure 14 shows the basic arrangement. Four individual imagers with polarization optics in front provide the four Stokes parameters to characterize the polarization content of the imaged scene. The scene consists of a device and a control polarizer and the four imagers capture a total intensity image (Stokes parameter S0), horizontally polarized image (S1), 45 degree polarized image (S2) and circularly polarized image (S3, imager with two polarization components in front).

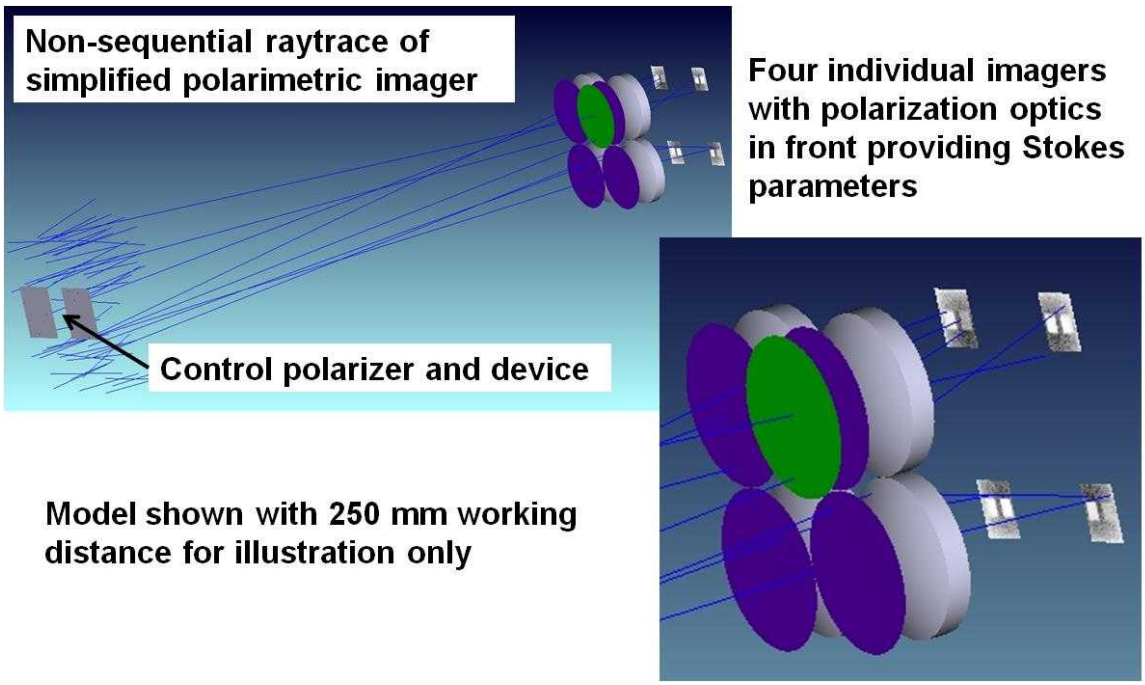


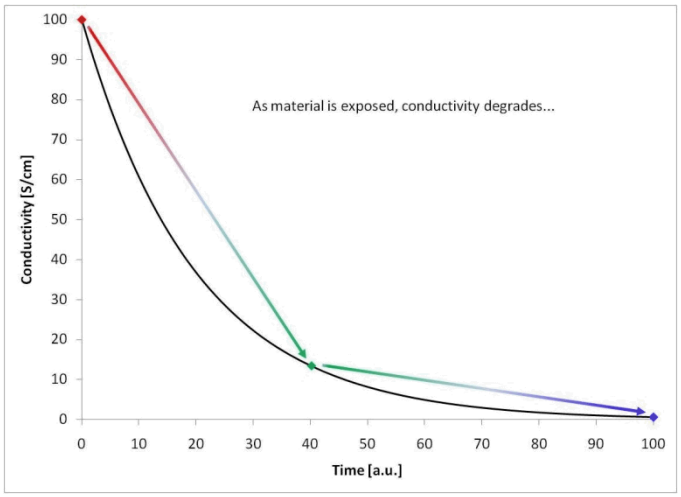
Figure 14. Optical model of polarimetric imaging of device and control polarizer.

With all of these portions of the model in place, the effect of exposure can be translated into a temporally changing optical signal as shown in Figure 15. In Figure 15a, the conductivity is shown to be decreasing with time. Figure 15b shows how the transmission response of the optical device changes in a corresponding fashion. The S1 image of the device and polarizer are shown in Figure 15c. Notice how the image of the polarizer does not change but the polymer based device does. In this way, the accumulated exposure experienced by the device can be determined.

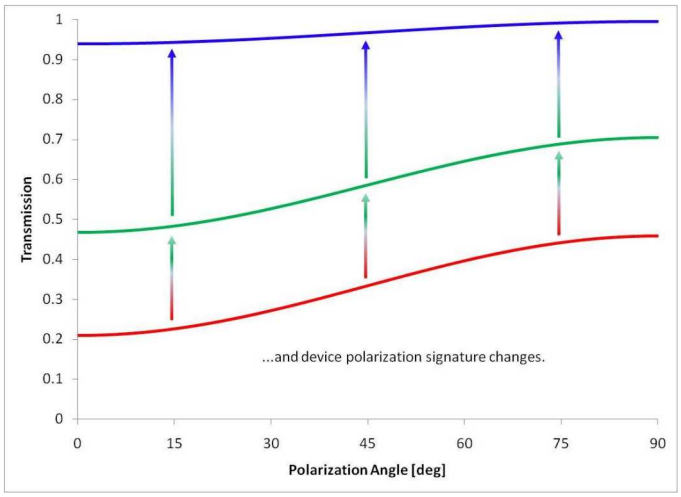
6. CONCLUSIONS AND FUTURE WORK

Continuing development will see an emphasis on producing optical devices that can be demonstrated in an illustrative environment. The first task to be addressed is the optical measurement of device sensitivity to HF. Devices have been fabricated and are currently being characterized for use in this experiment. Continued development of device fabrication processes will proceed in parallel with efforts to better disperse the MWNT within the polymer blend and control the precipitation of TiO_2. There are many parameters that can be changed as part of this effort including solvent choice, blend preparation technique, blend deposition during device fabrication and solids loading. The fabrication development will also strive to improve device uniformity, scale and signal level.

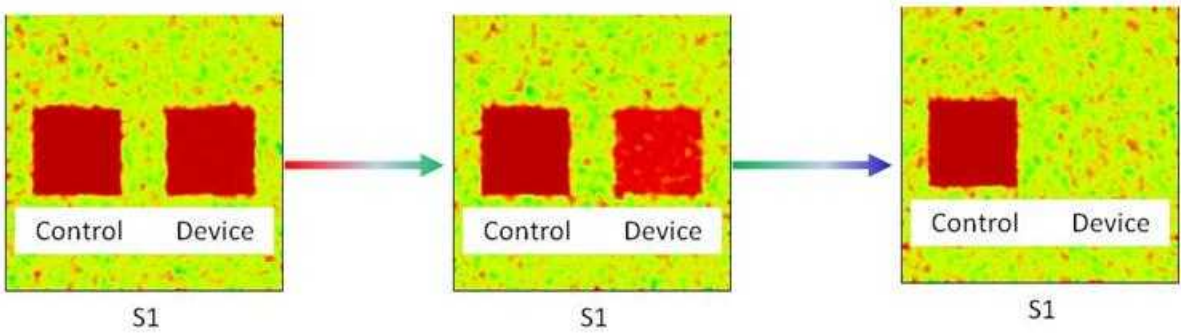
These remaining tasks will seek to replace the simulated portions of the system model with empirical results and provide guidance for the design of a demonstration system. As devices are fabricated and measured, the assumptions made in the system model, e.g. translation of material response to device response, can be refined to more closely approximate actual performance. The insight provided by this iterative improvement in the model will help guide the construction of an imaging based experiment that more closely resembles the concept of operation for these devices.



(a)



(b)



(c)

Figure 1. Outputs from system model (a) change of material during exposure (b) device response with respect to input polarization (c) changes in S1 image from imaging polarimeter.

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