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short report

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Abstract

Spectroscopic ellipsometry detected changes in refractive index for films of either polycarbonate, poly(1-vinylimidazole) or poly(2-vinyl-4,6-diamino-1,3,5-triazine-co-styrene) on silicon wafers when 4-nitrotoluene entered the films. The changes in refractive index were much more than adequate ($\Delta n > 0.003$) for use in an explosives sensor based on a Mach Zender interferometer. In the case of the poly(1-vinylimidazole) and the poly(2-vinyl-4,6-diamino-1,3,5-triazine-co-styrene) the refractive index changed after only 4 seconds exposure to a saturated atmosphere of 4-nitrotoluene vapor. These results suggest we can build a very sensitive, fast detector for TNT based explosives.

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Introduction

In the early 20th century the U. S. has faced numerous military and homeland security threats. One pernicious problem has been how to detect explosive devices, particularly improvised explosive devices. This is the objective of our research.

Figure 1. Schematic of a Mach Zender interferometer consisting of a polymeric waveguide with two optical paths. The laser beam enters from the left and leaves to the right

Our approach is to use a polymeric waveguide in the form of a Mach Zender interferometer, figure 1, as a sensitive, selective detector of the volatile components of explosives. The laser beam enters from the left and is split into two beams, one traveling the upper path, while the other travels the lower path. The optical path length for light is the physical path length times the refractive index of the medium. If the two optical path lengths are exactly the same, then the two beams will be in phase when they recombine, constructively interfere and give a high amplitude output. If the optical paths differ by $\lambda/2$ then the two beams will be out of phase and they will destructively interfere to give a low amplitude output.

To use the Mach Zender interferometer as a sensor, the polymer will be one that specifically absorbs the volatile components of an explosive. One leg of the Mach Zender interferometer will be exposed to the environment so that it can absorb any analyte in the gas phase, while the other leg will be encapsulated so as to not be able to absorb the analyte. The head space above TNT filled land mines contains 0.35 to 9.7 pg/mL 1,3-dinitrobenzene and 0.28 to 1.4 pg/mL 2,4-dinitrotoluene. 4-Nitrotoluene is also present and since we had this on our shelf, we chose to use 4-nitrotoluene as our analyte. When the analyte enters the polymer there will be an increase in the refractive index for one leg of the interferometer, causing a phase lag in the laser light traveling through that leg, relative to the other leg. When the beams are recombined this phase lag would result destructive interference and the intensity of the light leaving the interferometer would decrease. If the device used a He-Ne laser (λ = 632.8 nm) and the interferometer had a path length of 100 microns, then we would require a change in refractive index of only 0.003 to go from highest output amplitude (constructive interference) to zero amplitude (destructive interference).

In this first report we describe results that confirm our ability to see adequately large changes in refractive index. We also report new polymers directed at solving the problem of specificity.

Experimental

Materials. All reagents and solvents were purchased from Aldrich or from Fischer Scientific, unless otherwise noted. 2-Vinyl-4,6-diamino-1,3,5-triazine (VDAT) was purchased from TCI. Poly(1-vinylimidazole) was purchased from SelectiveTechnologies Inc.. Flint, MI.

Synthesis of poly(2-vinyl-4,6-diamino-1,3,5-triazine-co-styrene) (PVDAT-co-PS). PVDAT-co-PS was prepared using a free radical polymerization of VDAT and styrene as described by Chen and Sun. The VDAT content was 20 mole percent and the reaction was run at 80°C in DMSO using AIBN as the initiator to give a random copolymer.

A 3% solution of polycarbonate was made using 0.93 g polycarbonate beads and 29.18 g cyclohexanone. The solution was heated and then shaken using the wrist-action shaker in

order to ensure that the polycarbonate completely dissolved. A 2.8% solution of 4-nitrotoluene was made using 0.74 g 4-ntirololene and 25.43 g cyclohexanone. From the 3% solution of polycarbonate and 2.8% solution of 4-nitrotoluene six different solutions were made. Each solution contained a different percentage of 4-nitrotoluene by weight (0%, 5.8%, 11.0%, 14.8%, 20.3%, 25.2%). Each solution weighed approximately 1.76g. Films were made of each solution on silicon wafers using a spin coater set at 2900 rpm for 120 seconds. The films were allowed to dry at room temperature overnight. Films that were made from the solutions that contained the lower amounts of 4-nitrotoluene had a blue color, while the films containing higher amounts of 4-nitrotoluene had a brown tint.

A two or three weight percent solution of poly(1-vinylimidazole) was spin coated onto silicon wafers by first spinning at 200 rpm for 15 s, followed by spinning at 500 rpm for another 15 s, then at 1000 rpm for 20 s, 2000 rpm for 20 s and finally at 3000 rpm for 20 s. The films were further dried at 70°C for one hour.

A three weight percent solution of PVDAT-co-PS in DMF was spin coated onto silicon wafers by first spinning at 200 rpm for 15 s, followed by spinning at 500 rpm for another 15 s, then at 1000 rpm for 20 s, 2000 rpm for 20 s and finally at 3000 rpm for 20 s. The films were further dried at 70°C for one hour.

Instrumentation.
The refractive index for the polymer films was determined using a J. A. Woollem Co. variable angle spectroscopic ellipsometer. For each film values of ψ and δ were determined for wavelengths from 300 to 1,000 nm at angles of 60, 65, 70, 75 and 80°. The data was fit to a model having a polymer film on a silicon wafer. The curve of n(λ) was constrained to a Cauchy model. The result was curves of n(λ) and k(λ).

Results and Discussion
Our first task was to determine whether polymer films containing 4-nitrotoluene would show an adequate change in refractive index (Δn > 0.003). In figure 2 are plots of refractive index as a function of wavelength for polycarbonate films with and without added 4-nitrotoluene. The curve with added 4-nitrotoluene has a higher refractive index than the one with no 4-nitrotoluene. Through most of the spectral range the difference in refractive index was about 0.02, a factor of six greater than what is required to get a signal in the waveguide.

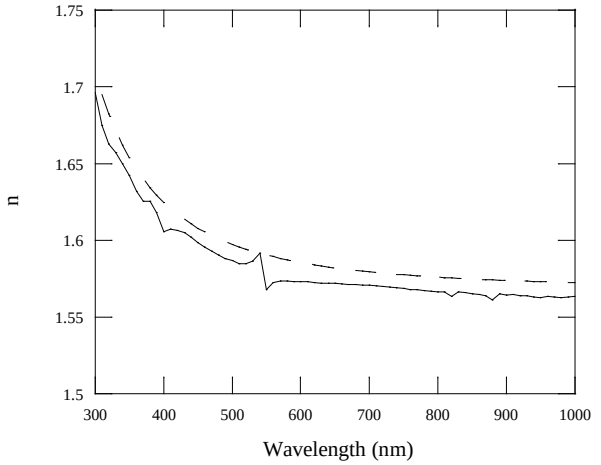
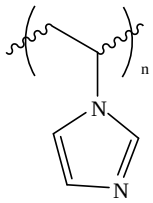


Figure 2. Plots of refractive index (n) as a function of wavelength for polymer carbonate films with no 4-nitrotoluene (solid curve) and with 4-nitrotoluene (dashed curve).

Our next task was to find new polymers with high affinity for the nitroaromatic molecules that are components of the vapor above explosives containing TNT. Since nitroaromatics are electron poor, we sought polymers with electron-rich functional groups or with functional groups that can hydrogen bond with the nitro groups. Our first candidate was poly(1-vinylimidazole) having electron-rich imidazole groups. A film was exposed to 4-nitrotoluene for only 4 seconds. The plots in figure 3 show a very large increase in refractive index after exposure. This suggests we could build a sensor with a fast response (seconds) and is very sensitive to nitroaromatic vapors.



Poly(1-vinylimidazole)

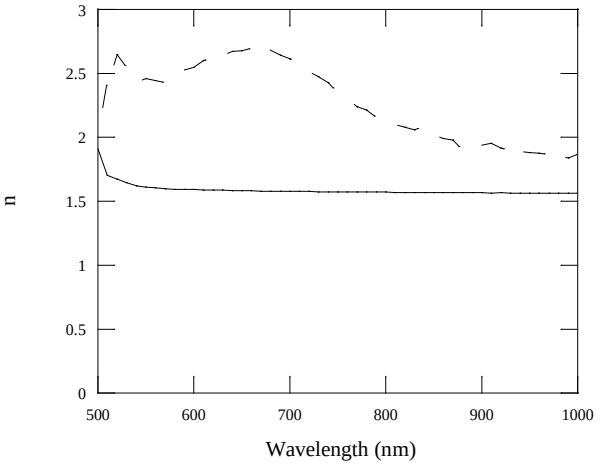
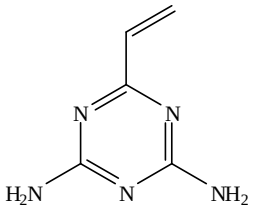


Figure 3. The change in refractive index of a polyvinylimidazole polymer film before (solid curve) and after (dashed curve) a four second exposure to a saturated vapor of 4-nitrotoluene.



2-vinyl-4,6-diamino-1,3,5-triazine (VDAT)

Poly(2-vinyl-4,6-diamino-1,3,5-tria-zine-co-styrene) (PVDAT-co-PS) was prepared using a free radical polymerization giving a random copolymer of styrene and 2-vinyl-4,6-diamino-1,3,5-triazine (VDAT). We expected the VDAT group would have a strong affinity for 4-nitrotoluene due to hydrogen bonding between the amino group on the polymer chain and the nitro groups. In the random copolymer used here the VDAT content was 20 mole percent. The plots in figure 4 show that this copolymer also responded very quickly to a saturated atmosphere of 4-nitrotoluene. After only four seconds exposure there was a measurable increase in refractive index. The increase was not as great of the case for poly(1-vinylimidazole). Perhaps this was because there are relatively fewer triazine functional groups in PVDAT-co-PS than imidazole groups in poly(1-vinylimidazole).

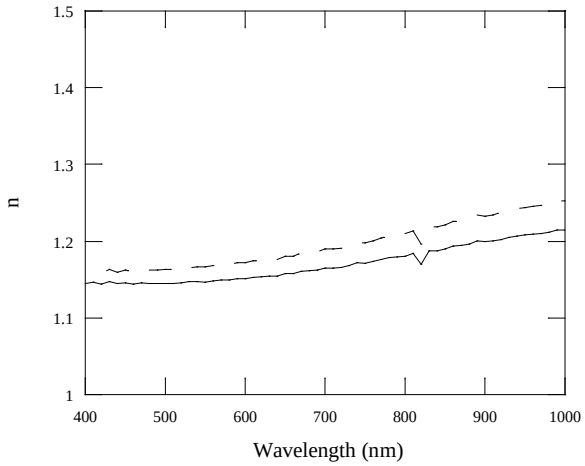


Figure 4. The change in refractive index of a PVDAT-co-PS film before (solid curve) and after (dashed curve) a four second exposure to a saturated vapor of 4-nitrotoluene.

Conclusions

We have shown that when 4-nitrotoluene enters polymer films the refractive index increases by an amount more that sufficient for detection by a sensor based on a Mach Zender interferometer. Furthermore the response can be fast, on a timescale of seconds. This is a very encouraging first step. However in order to realize a working sensor we must demonstrate that the absorption, leading to a refractive index change, is specific to the desired analyte and not to any other volatile organic specious that would raise the refractive index. To this end we look to building on the affinity of nitroaromatic species to electron rich functional groups. We will also use a molecular imprinting approach to further enhance specificity.

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