

## 12<sup>TH</sup> MONTH REPORT

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- DEVELOPMENT OF ONE-DIMENSIONAL DIELECTRI-DIELECTRIC AND METAL-DIELECTRIC PHOTONIC BAND GAP FOR OPTICAL SWITCHING AND LIMITING APPLICATIONS.

Fourth Interim Report

(Contract Number: N62558-05-P-0456)

During the last part of the project, we investigated a newly synthesized bis-phenylazo derivative, namely bis-perfluoroalkylsulfonylamino-arylazomethylene-triphenyl-phosphorane (BAM-TPP). Azobenzenes constitute a class of conjugated organic materials that have received considerable attention for their reversible photochromism and remarkable second order nonlinear optical (NLO) properties. These photochemical/physical properties, combined with the ability of varying their chemical structure with the wavelength of the incident light, make azobenzenes particularly attractive candidates for applications like optical data storage, optical switching and liquid crystals technology. Specifically, some azobenzenes may intercurr a photoisomerization from a *cis*- to a *trans*- configuration under UV illumination, and viceversa. The two configurations correspond to different values of optical absorbance, thus being interesting for optical switching applications.

Thin films of BAM-TPP in polymethylmethacrylate (PMMA) matrix were prepared. The powder of BAM-TPP was dispersed into a polymeric matrix of PMMA and some films were prepared. Previously, two different solutions were prepared using chloroform (CHCl<sub>3</sub>) with the concentration values of  $4.6 \cdot 10^{-5}$  M and  $1.6 \cdot 10^{-4}$  M, respectively. The obtained solutions were then stirred for 24 hours. PMMA (99.9%, from Aldrich) was used as a photochemically inert host polymer. It was added to the initial solutions of BAM-TPP and CHCl<sub>3</sub>. Two different set of films were prepared with a concentration by weight of 0.35 %, being the only difference the molarity of the initial solution. The mixtures of PMMA and BAM-TPP were stirred for 48 hours at room temperature. The deposition of the polymeric films was realized by casting of the obtained PMMA and BAM-TPP mixture in to Petry dishes (fused silica). The complete removal of the solvent was obtained after an annealing process of one hours at 90°. Film thicknesses were measured with a surface profilometer and found to be in the range between 30 and 60 µm. The transmittance spectra of both solutions and films were recorded in the visible-NIR range by a standard spectrophotometric technique.

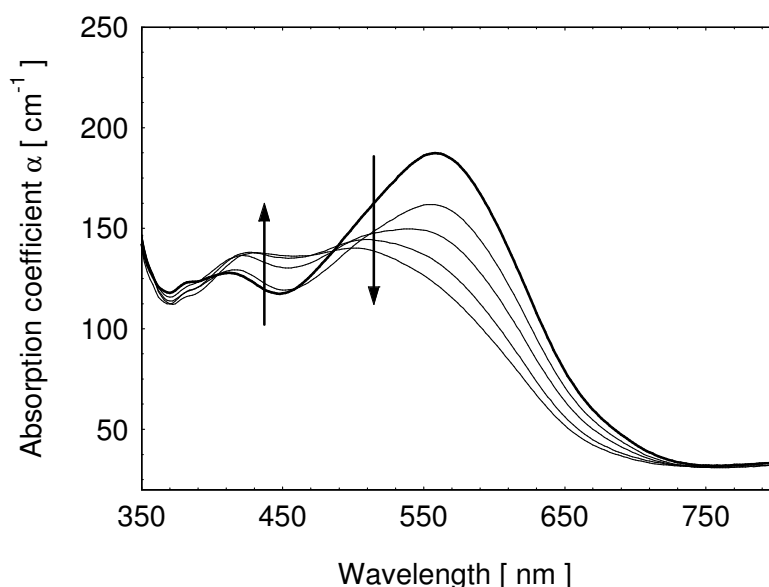
# Report Documentation Page

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1. REPORT DATE <b>10 OCT 2006</b>		2. REPORT TYPE <b>N/A</b>		3. DATES COVERED <b>-</b>	
4. TITLE AND SUBTITLE <b>Development of One-Dimensional Dielectric and Metal-Dielectric Photonic Band Gap for Optical Switching and Limiting Applications</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Dr. Maria Cristina Larciprete Via Michelangelo Schipa 4 00179 Roma Italy</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>SAR</b>	18. NUMBER OF PAGES <b>7</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

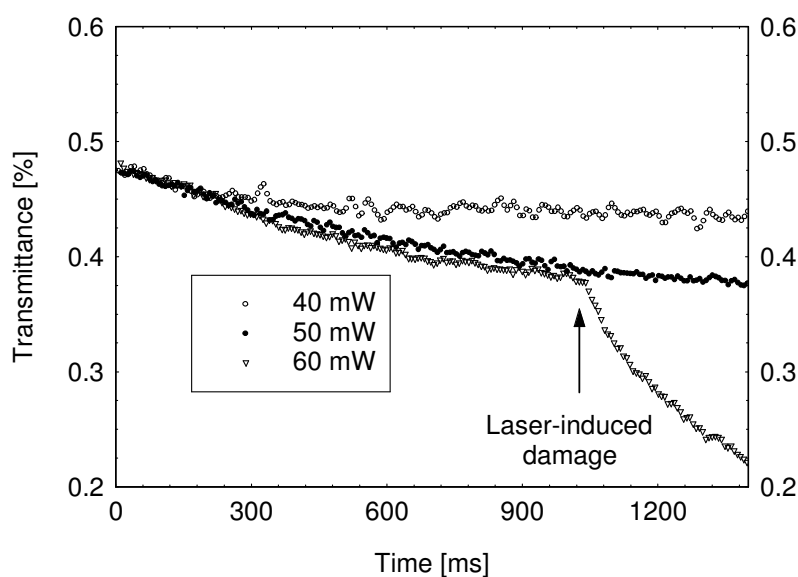
The films (thickness,  $d < 60 \mu\text{m}$ ) were exposed to UV light with variable intensity in order to stimulate the photochromic reaction of BAM-TPP. The resulting absorption changes of the BAM-TPP/PMMA films were investigated by spectrophotometry. The absorption spectra reveal that BAM-TPP molecules in PMMA undergo photoisomerization with resulting decrease of absorbance in the range 500-700 nm.



**Figure 1.** Variations of the absorption coefficient,  $\alpha$ , for a film of BAM-TPP in PMMA [film thickness values:  $53.7 \mu\text{m}$ ]. The thick solid line represents the film spectrum before UV exposure, while other lines stand for spectra taken every 10-sec of UV exposure. The arrow head indicates the verse of spectral variations following the increase of UV dose.

The UV dose was increased with consecutive exposures, each having a duration of 10 sec. A spectrophotometer was employed to analyze the film transmittance after each UV exposure. The absorption spectra of films at normal incidence with increasing UV light dose are reported in Figure 1.

The induced variation of absorbance and the position of the initially strong absorption peak in the visible region is particularly attractive for optical switching and limiting applications. We, therefore, investigated the effects induced by back photo-isomerization under illumination of a laser beam in the visible range. The transmittance at 514 nm through the samples was measured under increasing laser power. The experimental setup consists of a CW Argon laser, lenses to focus the light onto the sample, a photodiode to measure the transmitted signal and a 500 MHz digital oscilloscope to monitor the time evolution of the transmitted signal. The high initial absorbance in the visible, in fact, can be restored via visible light exposure, thus the films of BAM-TPP in the UV- activated *cis* form can act as passive, self-activated limiters of visible light beams.



**Figure 2.** Laser self-induced reduction of the transmitted signal as a function of time at  $\lambda=514$  nm for film b under different CW power: 40 mW (o), 50 mW (●) and 60 mW ( $\nabla$ ).

The time evolution of transmitted signal for different power of the incident light, is reported in Figure 2. For incident power up to 30 mW, the transmittance fairly corresponds to its linear value (50%) and it isn't reduced by the Argon light. When the power is increased to 40 mW, the absorption of the films is increasing and some effects of transmission reduction arise. At 50 mW the transmittance is further reduced to 37%, while an additional power increase, 60 mW, results in sample damaging. The observed behaviour is ascribed to a mechanism of back-isomerization which restores the initial high absorption value at  $\lambda=514$  nm. A further confirm is obtained when the same measurements are repeated on a thinner sample (29.5  $\mu\text{m}$ ). Due to the smaller thickness and, therefore, lower amount of BAM-TPP in this second film, the initial slope of the absorption peak was slightly reduced by UV exposure. At the same time, the transmittance variation measurements did not show any absorption increase, nor damage, up to 100 mW of incident Argon power at the wavelength of investigation. The linear absorption was not much affected by UV, therefore the film slightly responds to the power of the Argon laser beam, meanwhile the lower absorption value at this wavelength is responsible for the absence of laser damaging. Since the value of linear absorption at the investigated wavelength depends on the concentration of the active molecules, the obtained results indicate that, by choosing the appropriate concentration of BAM-TPP in the film, it is possible to get a suitable mechanism of self-switching at a wavelength falling within the visible range.

The investigated mechanism of photo-isomerization is suitable for self-switching applications at a wavelength falling within the visible range.

## FINAL REPORT

This project was based on the study one-dimensional (1D) Photonic Band Gap (PBG) structures for nonlinear optical applications as optical switchers and limiters. This studied started during within the support of the European Research Office, contract nr. N62558-03-M-0021 and is based on a collaboration between the principal investigator, Dr. Michael Scalora (Redstone Arsenal, Huntsville, AL (USA)).

During the first three months we investigated some devices based on a dielectric-dielectric PBG, composed of zinc selenide (ZnSe) and magnesium fluoride (MgF<sub>2</sub>) alternating layers, deposited on to a silicon sublayer. Thanks to the particular design of the substrate, a temperature increase can be electrically applied to the multilayer stack by means of the underlying heater. The well known thermo-optical effect is then responsible for refractive index variation, and hence for variations of the optical thickness of a layer. The proposed structure allows the optical switching of the reflected beam when a voltage is applied and, therefore, the sample temperature increases. We performed the spectral measurements under different voltage applied and, therefore, temperature increase. The multilayer stacks, realized by thermal evaporation, were designed so to get a reflection spectrum presenting a deep tuned at 628 nm. At a fixed incidence angle, and for  $\Delta T=0^{\circ}\text{C}$  the reflectance value for a fixed wavelength is low. When a heating is applied to the stack, the sample temperature is increased, the induced temperature increase is responsible for changes in the layers refractive index and, as a result, the reflectance spectra of the structure is shifted while the corresponding reflected signal at the same wavelength is increased with respect to its initial value. The maximum obtained spectral variation is a 7 nm shift of the photonic band edge for 90 V, corresponding to a maximum applied current of 2.5 mA for each heater. At a fixed wavelength close to the band edge, the proposed structure may allow the optical switching of the reflected beam when heating is activated. In this way we demonstrate theoretically and experimentally that the use of a high thermo-optical nonlinearity in a multilayer stack combined with an appropriate electrical circuit structure, gives rise to strong spectral shifts that can be tuned with an applied voltage. These results highlight the potential capabilities that active multilayer structures offer for optical switching applications [<sup>1</sup>].

Following to these measurements, some metallo-dielectric (MD) multilayer structures compose by silver (Ag) and zinc selenide (ZnSe) were designed and realized. The main idea was to realize a multilayer stack that reflects every wavelength incident upon it, while absorbing specific wavelengths. Here, the metal absorption together with the interference phenomena arising from the layers interfaces allow to eliminate a selected wavelength from the reflectance spectrum of the stack. Depending on the specific requirements, one or more wavelengths which are critical for both

active and passive protection can be chosen to be missing in the transmittance or reflectance spectrum. In the present case, we chose 532 nm, i.e. the second harmonic of Nd:YAG laser. Since ZnSe is a nonlinear material, a spectral variation can be obtained via the variation of the optical path in the ZnSe layers by thermo-optical effect. In this configuration the device can work as a switcher in reflectance mode, which is can be activated by heating. As a result, the reflectance deep can be shifted by changing the layers optical thickness. As a consequence, at the selected wavelength, the linear reflectance value drops down, while the transmission value is also zero all over the visible spectral range due to the presence of the mirror represented by the first bulky silver layer. This particular behaviour can be useful to realize a sensor with optical output, due to the obtainable sharpness of the gap.

We realized some preliminary samples in order to get a deep at 532 nm. A reduced number of layers was employed, at the expense of the contrast between maximum and minimum achievable values of reflectance. The samples were characterized by spectrophotometry in the range between 400 and 1100 nm. The contrast between high and low reflection is only ~20%. This effect is linked to the low number of layers, but can be adjusted depending on the requirements. Also the angle behaviour was investigated, and the reflectance spectra were measured at different incidence angles and it was found that the spectra is stable with increasing incidence angle. This is due to the fact that the operational wavelength is absorbed by the thick silver layer, in stead of being reflected via interference effects. Up to now, the investigated structures operate in reflectance mode, even though suitable applications and consequent geometrical arrangements allow to work in transmission mode. It's worth to note that all the presented device offers advantages and new opportunities of applications as an optical switch for eye protection when the light is reflected (i.e. telescopes or periscopes) and dichroic mirrors.

During the second six months of the project, the contractor has devoted much attention to some organic molecules, in order to get polymeric films with nonlinear optical properties.

First of all, metallo-phtalocyanines have bee investigated. This class of molecules present very attractive properties for nonlinear optical applications of both second and third order. Their strong nonlinear optical properties are related to the systems of delocalized  $\pi$ -electrons typical of their macrocyclic core, while the central position (M) offers the possibility to host a metal ion, whose nature has influence on the optical properties. The presence of a heavy atom, as a metal, has the effect to increase the optical nonlinearities. Due to their low solubility, aggregation in solution and in the solid state drastically limit their use. Therefore, it is still an open task to investigate the effect of concentration on both linear and nonlinear optical absorption, with regard to both solution and solid state.

We investigated Zinc-phthalocyanine in toluene solutions at increasing concentration. In order to evaluate the effect of increasing concentration, we prepared solutions with different solvents (toluene and three-chloroethane) and increasing concentration. Linear optical measurements performed by spectroscopic analysis show the best conditions for the realization of poly(methyl methacrylate) films. The characterization of the linear optical absorption was carried out via spectroscopic measurements in a quartz cuvette, 1 mm thick, thus evidencing the two absorption bands which are characteristics of these molecules, i.e. the B-band in the UV and the Q-band in the visible range. Afterwards, poly(methyl methacrylate) (PMMA) was employed as a photochemically inert host polymer. It was added to the initial solutions of PC and solvent, and the resulting mix was stirred for some hours. The films were then prepared by casting in to Petry dishes (fused silica) of the obtained solution. The solvent was completely removed by annealing at 90° for 1 h. The ratio by weight of the compound to the host polymer was varied between 0,004% to 0,15%, while all samples show a low degree of aggregation. The thickness of the prepared films was measured to be in the range of 50-80 μm with a surface profilometer.

The measurements of nonlinear transmission were carried out using a ns Nd:Yag laser (532 nm) and we found a nonlinear response for the two highest concentrations in weight (0,083% and 0,15%). The experimental data were fitted using a nonlinear absorption coefficients  $\beta$  of 29 and 43 cm/GW, respectively [2].

Finally, a newly synthesized bis-phenylazo derivative, namely bis-perfluoroalkylsulfonylamino-arylazomethylene-triphenyl-phosphorane (BAM-TPP) was investigated. Azobenzenes constitute a class of conjugated organic materials that have received considerable attention for their reversible photochromism and remarkable second order nonlinear optical (NLO) properties. These photochemical/physical properties, combined with the ability of varying their chemical structure, make azobenzenes particularly attractive candidates for applications like optical data storage, optical switching and liquid crystals technology. Thin films of BAM-TPP in polymethylmethacrylate (PMMA) matrix were prepared. The films (thickness,  $d < 60 \mu\text{m}$ ) were exposed to UV-vis light with variable intensity in order to stimulate the photochromic reaction of BAM-TPP. The resulting absorption changes of the BAM-TPP/PMMA films were investigated by spectrophotometry. The absorption spectra revealed that BAM-TPP molecules in PMMA undergo photoisomerization with resulting decrease of absorbance in the range 500-700 nm. Finally, the time response of film transmittance at 514 nm under increasing CW light intensity was recorded, showing that the reverse photochromic process brings the absorbance back to its pristine value. The obtained films thus proved to be suitable for fast optical switching applications [3].

The contractor highlights that the research activity described here is developed thanks to the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. This report is intended only for the internal management use of the contractor and the U.S. Government.

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