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NONLINEAR OPTICAL PROPERTIES OF ORGANIC AND POLYMERIC
THIN FILM MATERIALS OF POTENTIAL FOR MICROGRAVITY PROCESSING STUDIES

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ABSTRACT

In this paper, we will take a closer look at the state of the art of polydiacetylene, and metal-free phthalocyanine films, in view of the microgravity impact on their optical properties, their nonlinear optical properties and their potential advantages for integrated optics. These materials have many attractive features with regard to their use in integrated optical circuits and optical switching. Thin films of these materials processed in microgravity environment show enhanced optical quality and better molecular alignment than those processed in unit gravity. Our studies of these materials indicate that microgravity can play a major role in integrated optics technology.

Polydiacetylene films are produced by UV irradiation of monomer solution through an optical window. This novel technique of forming polydiacetylene thin films has been modified for constructing sophisticated micro-structure integrated optical patterns using a pre-programmed UV-laser beam. Wave guiding through these thin films by the prism coupler technique has been demonstrated. The third order nonlinear parameters of these films have been evaluated.

Metal-free phthalocyanine films of good optical quality are processed in our laboratories by vapor deposition technique. Initial studies on these films indicate that they have excellent chemical, laser, and environmental stability. They have large nonlinear optical parameters and show intrinsic optical bistability. This bistability is essential for optical logic gates and optical switching applications. Waveguiding and device making investigations of these materials are underway.

KEY WORDS

Nonlinear Optics, Bistability, Microgravity, Thin Films, Z-scan.

INTRODUCTION

In the recent years there has been tremendous interest in the field of nonlinear optics (NLO) and optical materials. Important applications such as optical switching, optical communication, and optical computing all require devices containing materials that possess large and fast nonlinear optical responses. NASA's two main interests in NLO research are that NLO materials could be of use for laser communications with satellites deployed in space, and that microgravity environment could significantly optimize the NLO properties of growing optical materials in space. This might will lead eventually, to devices with superior properties to those currently produced on earth.

In these studies, polydiacetylene (PDAMNA), prepared from a diacetylene derivative of 2-methyl-4-nitroaniline and metal-free phthalocyanine (PC) were chosen as two candidates for our investigation because of their potential for microgravity studies and for possible use in nonlinear optical devices. Both PDAMNA and PC films have been processed in space and were proven to benefit from the microgravity environment. Polydiacetylenes have large off-resonant third-order nonlinearities and sub-picosecond response times.¹⁻³ The large nonlinearity in polydiacetylenes has been attributed to delocalization of the π -electrons along the polymer backbone.⁴ Also, phthalocyanines have a two-dimensional π -electron system and show promise for nonlinear optical devices because of their outstanding nonlinear optical properties, excellent chemical and thermal stability against heating and photo-irradiation, and also because of their semiconducting behavior.^{5,6}

In section I, we will briefly discuss the polydiacetylene measurements, and follow it by the phthalocyanine results in section II.

I. PHOTO-DEPOSITED POLYDIACETYLENE FILMS

I.1 Film preparation

Thin polydiacetylene (PDAMNA) films can be obtained from dilute solution (3-4mg/mL) of DMNA in 1,2-dichloroethane by irradiation over a 2-day period with a UV light at 366 nm from a 15-watt lamp through a transparent window which serves as the substrate.^{7,8} These films show superior optical quality than those generally obtained via solid-state polymerization.⁹ The absorption spectrum of the PDAMNA film on quartz substrate exhibits a strong absorption in the wavelength range of 200 to 300 nm. The absorption decreases nearly monotonically in the visible region. The film is essentially transparent above 700 nm. It shows good adhesion to the substrate and has a high damage threshold at 1064 nm $> 0.4 \text{ Gw/cm}^2$.

I.2 Microgravity's Role

Recent experiments to investigate the effect of unit gravity on the optical quality of polydiacetylene films were performed by changing the optical window orientation with respect to the gravity downward direction. The orientation of the optical window is defined by the outward direction of its unit vector normal to the surface. Three experiments were performed. In the first, the chamber window was pointing upward (opposite to the gravitational field direction) and the UV-lamp was on the top. In the second, the window was pointing downward (same direction as unit gravity) and the UV-lamp was underneath it. In the third, the window was pointing sideways (Figures 1 a,b,c) respectively. The UV light was made to shine for an equal interval of time of ~ 20 hours in each of the orientations above. Waveguiding was achieved through these films by the end-fire coupling technique using He-Ne laser at 632.8 nm. The scattering from the three films were recorded and digitized by a CDD camera as shown in Figures 1 d,e,f. These scattering data indicate that the heating induced by the UV irradiation produces convection in the solution. The collision between insoluble polymer particles due to convection causes these particles to stick to each other and form clusters. The convection force causes those clusters to stick to the substrate and become part of the film. In the first experiment, because the formed clusters are slightly heavy and tend to deposit in the base of the chamber, only a few were able to reach the substrate at the top. Consequently fewer scattering centers are observed. In the second experiment, where the substrate is at the bottom of the chamber all the formed clusters settled down and were embedded into the film. Consequently, the scattering centers are comparably much larger in number. In the third experiment, the number of scattering centers is somewhat in between the first two experiments. These set of experiments demonstrated that unit gravity induced convection caused the formation of clusters that end up embedded into the film as scattering centers. This leads to films with inferior quality and of less use for optical devices.

Recently, microgravity mission experiment (STS 69) to photo-deposit polydiacetylene films demonstrated that superb quality films might be obtained in microgravity environment.

I.3 Nonlinear Optical Studies of Polydiacetylene

Polydiacetylene films showed a subpicosecond response of less than 120 fs using 850 nm femtosecond laser. The third order nonlinearity measured by the Four wave mixing technique at 532 nm using a 10 Hz pulsed Nd:YAG laser was estimated to be of the order of 10^{-8} esu. The large value of $\chi^{(3)}$ is attributed to resonance enhancement caused by the operating wavelength.

More rigorous studies to estimate the real and imaginary terms of the third order nonlinear susceptibility of polydiacetylene films were done using the Z-scan technique and He-Ne laser at 632.8 nm. A set of normalized Z-scan curves of the transmission with and without aperture as a function of z from the focal plane at different laser powers are shown in Figs. 2&3. The transmission curves with finite aperture are characterized by prefocal peaks followed by postfocal valleys for all laser power range of 5 to 30 mw. This implies that the nonlinear refractive index of polydiacetylene at 633 nm wavelength is of negative lensing nature. It is also observed that the area under the prefocal peak, for each power, is larger than that of the postfocal valley for all powers below and up to 25 mw. This asymmetry about $z=0$ of the peak to valley areas indicates the presence of a single photon saturation of absorption in the system. As the laser power increases beyond 25 mw, the postfocal valley becomes more prominent. This phenomenon is strongly reminiscent of a two-photon absorption(TPA) that takes place at the power level of 30 mw (Fig. 2f).

The dispersive (real part) third order nonlinear susceptibility ($\chi_R^{(3)}$) was evaluated at power levels between 5 and 25 mw of the He-Ne laser. The formula used to estimate $\chi_R^{(3)}$ from the finite aperture data is¹⁰

$$\chi_R^{(3)} = 2 n_0^2 \epsilon_0 c \gamma \quad (1)$$

where c is the speed of light (m/s), n_0 the linear refractive index of the film, and γ is the nonlinear refraction coefficient which is defined as¹⁰

$$\gamma = (\lambda/2\pi L_e I)(\Delta T/0.406[1-s]^{0.25}) \quad (2)$$

where ΔT is the peak-to-valley normalized transmittance, $L_e = (1 - \exp(-\alpha L))/\alpha$; α the linear absorption coefficient of the film of thickness L , I is the beam intensity at the focus, and s is the linear transmission of the aperture, measured to be 0.14. The $\chi_R^{(3)}$ values showed a linear increase from $-(2.07 \pm 0.2) \times 10^{-10}$ esu at 5.9×10^6 w/m² to $-(6.62 \pm 0.6) \times 10^{-11}$ esu at 2.9×10^7 w/m².

The open aperture data, to evaluate the imaginary part of the third order nonlinearity ($\chi_I^{(3)}$), showed a little dip at the peak of the saturation curve at 5 mw power. As illustrated in (Fig. 3), the dip increased in depth as the laser power increased. This phenomenon is again a strong distinctive mark of a two-photon absorption effect taking place at the focus. The TPA effect has previously been observed in polydiacetylene and in poly(4-BCMU) gels^{11,12,13} at 1064 nm, as well as at shorter wavelengths.

At power levels beyond 25 mw, the TPA mechanism dominates the process, and the whole curve reverses its sign as shown in Fig.3f. The imaginary part of the third order nonlinear susceptibility ($\chi_I^{(3)}$) of the polydiacetylene film can then be expressed as

$$\chi_I^{(3)} = \chi_{sat}^{(3)} + \chi_{2ph}^{(3)} \quad (3)$$

where $\chi_{sat}^{(3)}$ and $\chi_{2ph}^{(3)}$ represent saturation of single photon and a two photon absorption, respectively. The conventional rule to evaluate $\chi_I^{(3)}$ from the open aperture transmittance data is to evaluate the fitting parameter β (nonlinear absorption coefficient) that achieves the best fit to the experimental data using the formula¹⁰

$$T(z, S=1) = \sum_{m=0}^{\infty} m_{m0} [-q(z)]^m / (m+1)^{3/2} \quad (4)$$

where $q = \beta I [L_e / (1 + z^2/z_0^2)]$, z_0 is the diffraction length $= \pi w_0^2 / \lambda$, λ is wavelength, and w_0 is the beam radius at the focus. To adopt equation (3) to estimate both $\chi_{\text{sat}}^{(3)}$ and $\chi_{2\text{ph}}^{(3)}$, which are present simultaneously in our sample, we follow the derivations in reference-10, by replacing both β and q by

$$\beta = \beta_1 + \beta_2 \quad (5)$$

where β_1 and β_2 are the nonlinear absorption coefficients for the saturation of single photon and two photon absorption respectively, and

$$q(z, r, t) = q_1(z, r, t) + q_2(z, r, t) \quad (6)$$

where $q_{1,2} = \beta_{1,2} I [L_e / (1 + z^2/z_0^2)]$. The transmittance function in terms of the sample position z can then be expressed as

$$T(z, S=1) = \sum_{m=0}^{\infty} \{[-q_1(z) - q_2(z)]^m\} / (m+1)^{3/2} \quad (7)$$

Both β_1 and β_2 also serve as fitting parameters and can be deduced by fitting the transmitted data with open aperture (dashed lines) to equation (6) (solid lines) as shown in Fig.3. The imaginary terms of the third order nonlinear susceptibility associated with saturation of absorption ($\chi_{\text{sat}}^{(3)}$), and with two photon absorption ($\chi_{2\text{ph}}^{(3)}$) can then be estimated from β_1 and β_2 , respectively, as follows¹¹

$$\chi_i^{(3)} = n_0^2 \epsilon_0 c^2 \beta / \omega \quad (8)$$

where $\chi_i^{(3)}$ stands for both $\chi_{\text{sat}}^{(3)}$ and $\chi_{2\text{ph}}^{(3)}$, and β represents β_1 and β_2 .

The values of $\chi_{\text{sat}}^{(3)}$ and $\chi_{2\text{ph}}^{(3)}$ were estimated for different intensities of the He-Ne laser. The $\chi_{\text{sat}}^{(3)}$ values increased, nearly monotonically with intensity, from $-(1.9 \pm 0.2) \times 10^{-11}$ esu to $-(6.5 \pm 0.6) \times 10^{-12}$ esu, while $\chi_{2\text{ph}}^{(3)}$ values suffered an initial decrease, followed by a nearly linear increase with intensity from $(1.5 \pm 0.1) \times 10^{-12}$ esu to $(6.2 \pm 0.6) \times 10^{-12}$ esu. The initial decrease of $\chi_{2\text{ph}}^{(3)}$ with intensity might be attributed to a poor theoretical fit at relatively low intensity.

The two photon amplitudes are measured as the depth of each dip from the peak of the theoretical fit to equation (2), using β_1 values. The normalized two photon amplitudes were found to have a linear dependence with the quadratic intensity as expected.

In conclusion, the z-scan technique demonstrated for the first time the presence of two-photon absorption along with the saturation of a single photon in polydiacetylene (PDAMNA). The experimental results also demonstrated that an intensity level beyond 3×10^7 W/m² causes permanent photo-oxidation (bleaching) to the polydiacetylene film, where its optical characteristics change drastically.

II. VAPOR-DEPOSITED PHTHALOCYANINE FILMS

II.1 Film Preparation

Metal-free phthalocyanine was purchased from Eastman Kodak Company and processed without further purification. A high optical quality set of metal-free phthalocyanine films of different thickness, ranging from 40-800 nm, were prepared by vapor deposition onto 0.6 inch quartz disks at 10^{-6} Torr. The source and substrate temperatures were 300 °C and 5 °C, respectively. The He-Ne laser at 632.8 nm is strongly absorbed by Metal-free phthalocyanine films. The absorption spectrum in the visible region shows a strong absorption peak at 626 nm.

II.2 Microgravity's Role

The processing of phthalocyanines in space was demonstrated by the deposition of films by physical vapor transport in microgravity of copper phthalocyanine (CuPc) by 3M company.^{12,13} Analyses of these films revealed that microgravity

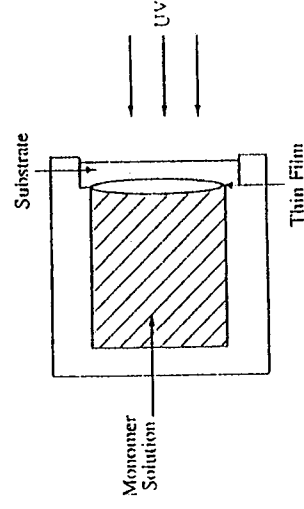
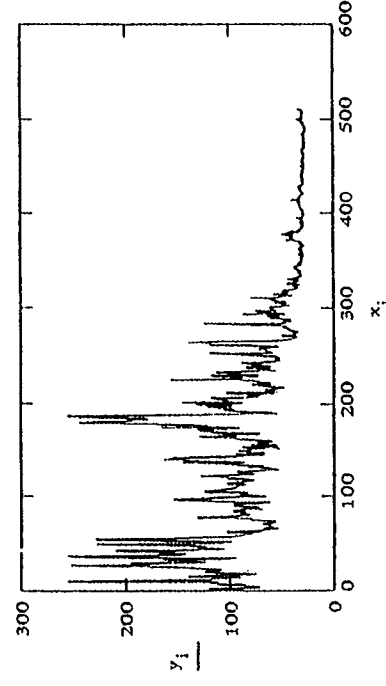
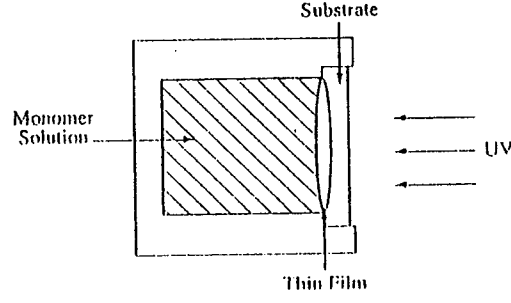
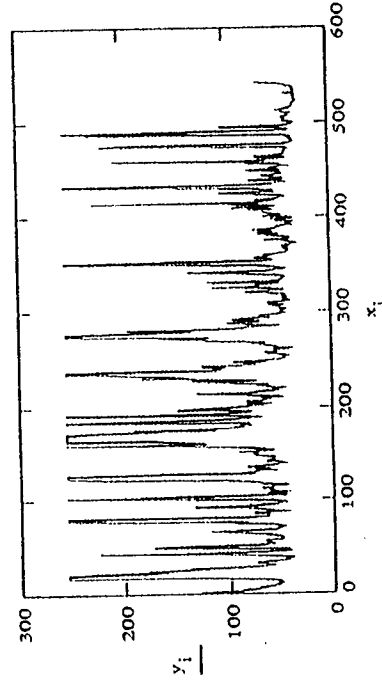
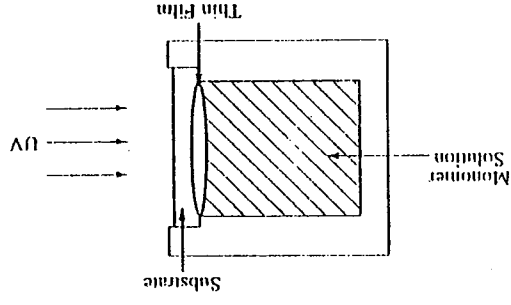
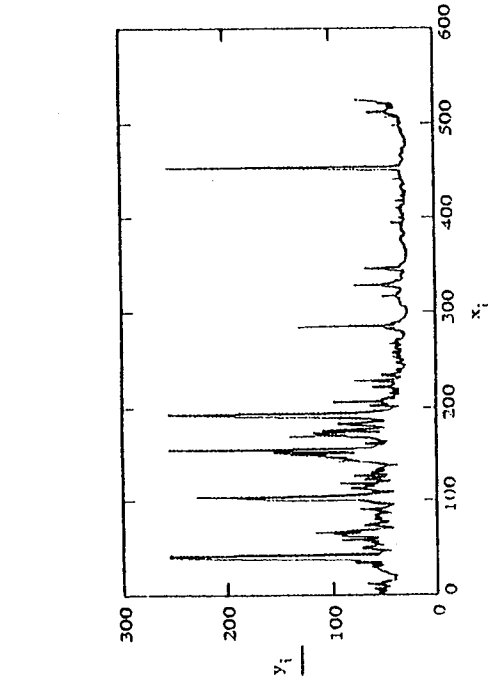


Fig. 1. (a,b,c) show the different orientations of the cell containing the monomer with respect to the downward gravitational field. (d,e,f) show the corresponding scattering centers for cell orientations a,b,c respectively, as seen by a CDD camera on the top of the film. The light is coupled through the film by end fire couplings.

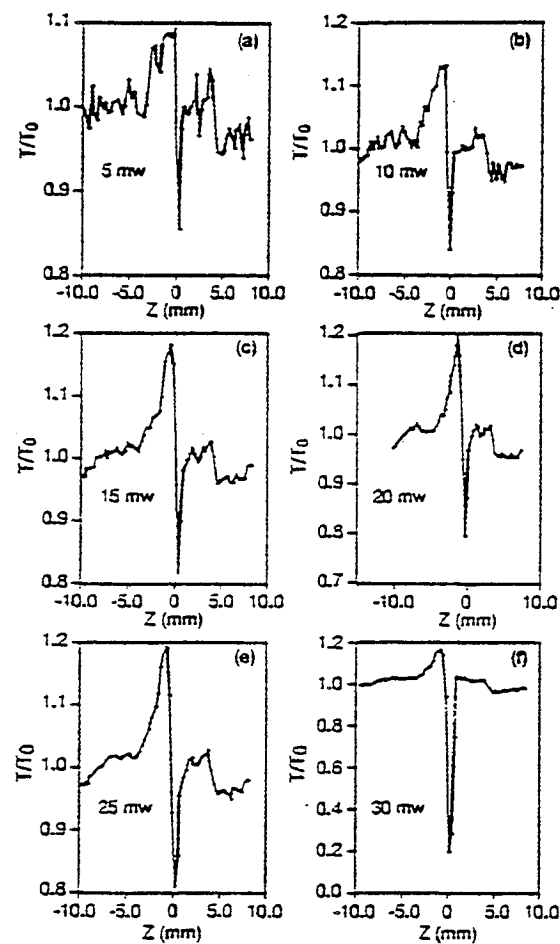


Fig.2. the Z-scan data with finite aperture at different powers of He-Ne laser. The data are representative of a negative lensing effect, and of prominent saturation effect at power levels below 30 mw.

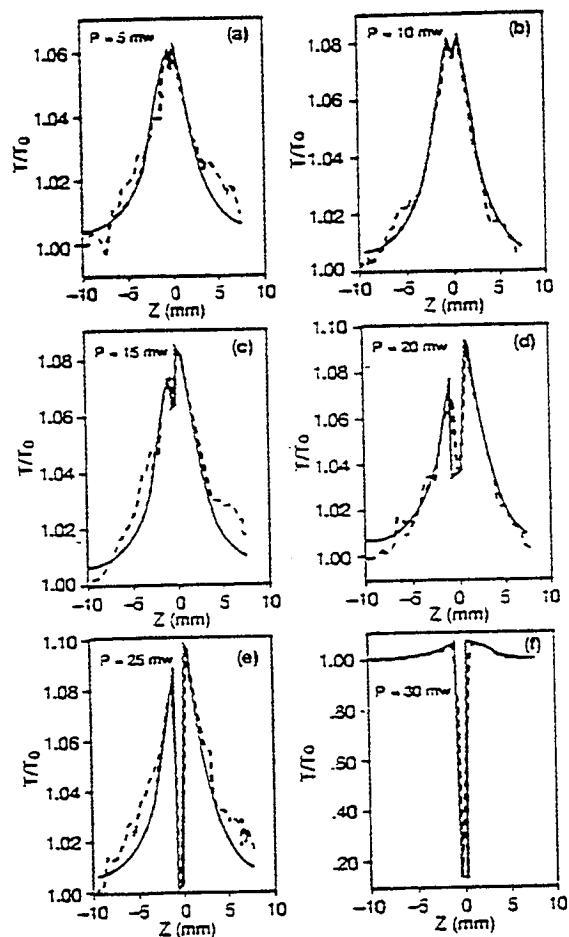


Fig.3. the Z-scan data with open aperture at different powers of He-Ne laser. The dashed lines represent the experimental data. The solid lines represent the theoretical fits.

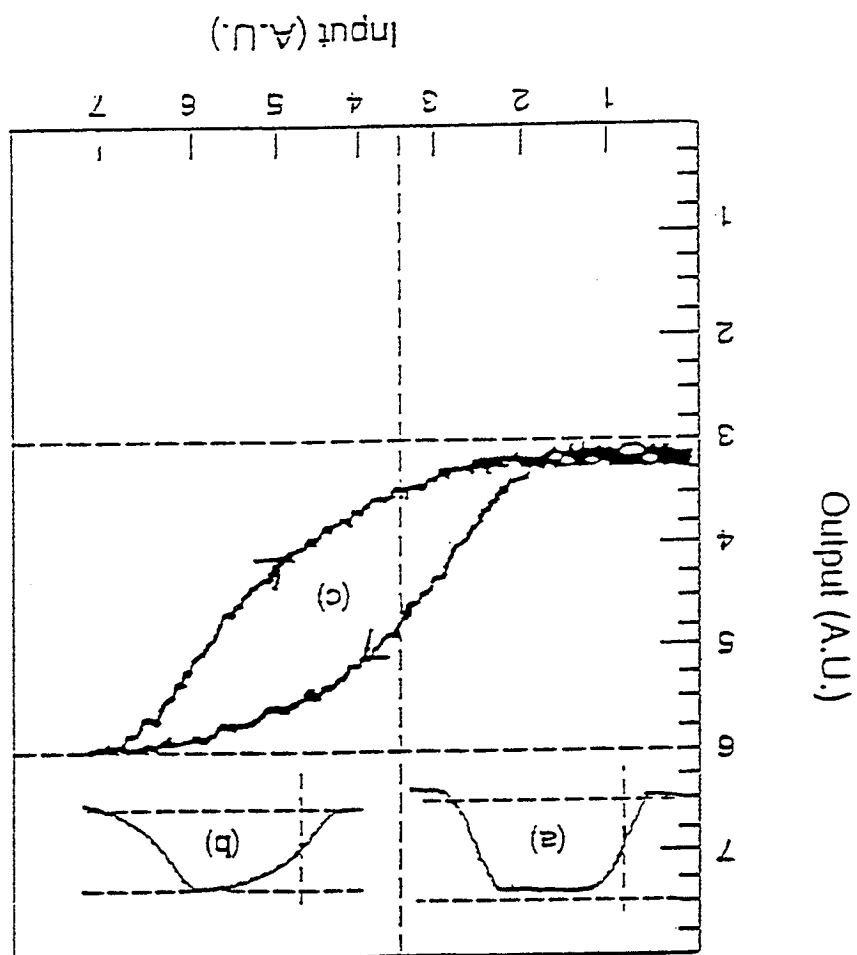


Fig. 4. (a) and (b) are the input and transmitted pulses, respectively, from a chopped cw He-Ne laser at 632.8 nm passing through a metal-free phthalocyanine film of 833 nm thickness. (c) Bistability switching, constructed from (b) above.

grown films are highly uniaxially oriented than earth-grown films and consisted prominently of crystalline domains of a previously unknown polymorphic form of CuPc. The microstructure of the film grown in microgravity is more dense and of much better molecular alignment than its counterpart grown in unite gravity

II.3 Nonlinear Studies of Metal-Free Phthalocyanine films

The results of several optical measurements of metal-free phthalocyanine films made at room temperature using a He-Ne laser at 632.8 nm are presented. For the first time to our knowledge, we report observation of intrinsic optical bistability in a vapor deposited metal-free phthalocyanine film. The temporal transmission of the film, its saturation intensity, and its absorption cross section are also measured.

Two separate experiments were performed to monitor transmission and bistability. In both experiments a lens of 5-cm focal length was used to focus the beam to $\sim 10 \mu\text{m}$ diameter. A second lens was used to collect all the transmitted light on a fast photodiode which was connected to a digital storage oscilloscope and a PC computer. The film was mounted to a translation stage. In the first experiment, a cw He-Ne laser at a fixed input power of $\sim 30 \text{ mw}$ was focused on a 230 nm thick film. The temporal increase in transmission was very slow and reached saturation within ~ 12 hours. Fitting the transmission data to a single exponential gave a rise time of ~ 2.2 hours to reach a steady state.

The slowly temporal transmission effect in the film can be explained by the following sequence:

1. The initial low transmission of the beam through the film can be attributed to a strong absorption of the beam which generates free electrons and holes.
2. These free charges relax to excitonic states⁵ and release their excess energy in the form of heat to the system at the focal point.
3. The very long temporal variations in transmission indicate that the thermal diffusivity in the film is quite small. This conclusion is derived from the fact that the thermal diffusivity η is¹⁴

$$\eta = w^2 / 8 t_c \quad (9)$$

where t_c is the time to reach steady state, and w is the beam waist. Using the rise time of 2.2 hours, obtained above, and the beam waist of $\sim 10 \mu\text{m}$, the thermal diffusivity of the phthalocyanine film was estimated to be of the order of $\sim 1.6 \times 10^{-11} \text{ cm}^2/\text{s}$.

4. The build-up of the localized heating at the focus reduces the absorption level of He-Ne laser and causes saturation of absorption. This is in agreement with the results obtained from a separate experiment to measure the sample's absorption at elevated temperature from the room temperature, using a heated water bath. Such reduction in absorption allows more transmission to take place with time.

The change in the index of refraction, which is dominated by the thermo-optic effect, can be written to the first approximation as:

$$n = n_0 + (dn/dT) \Delta T \quad (10)$$

where n_0 is the linear refractive index, dn/dT is the change in the refractive index with temperature, and ΔT is the change in temperature. The thermal heating in the system is due to absorption of light energy and governed by the heat diffusion as mentioned earlier. St. John et al.¹⁴ derived the formula for the modulation of the refractive index for a 10 ms pulse which is applicable for a cw beam, as:

$$n(r,t) = n_0 + (dn/dT) (P_0 \alpha_0 / \kappa) \{ \ln(1 + t/t_c) - (2r^2/w^2)[t/(t + t_c)] \} \quad (11)$$

where P_0 is the input power (a constant), κ is the thermal conductivity, and α_0 is the linear absorption. Equation (3) indicates that the nonlinearity in the system continues to grow with time.¹⁴

In the second experiment the laser beam at 632.8 nm was chopped at different frequencies ranging between 100 to 750 Hz. The experiment was performed on a film of 833 nm thickness. The film was mounted on a micrometer stage at the focus of the lens. Initially, the film was translated transversely by a micrometer stage away from the laser beam and the input square pulse was recorded by a Hewlett Packard (hp) digitizing oscilloscope model 54120B and a hp plotter model 7470A (Fig.4a). Later, the sample was placed again at its original position at the focus. The transmitted pulse was then sensed by the same detector and recorded (Fig.4b). The same procedure was repeated for the range of frequencies mentioned above. The asymmetrical shape of the transmitted pulses indicated the presence of intrinsic bistability in metal-free phthalocyanine. A typical and clear bistable switching is shown in figure 4c, which is constructed from the transmitted pulse in figure 4b. This bistable switching was recorded for the entire frequency range used in this study. Combining of the switching power of $\sim .33 \mu\text{w}$ per pulse and a pulse duration of 1.37 ms recovery time yields a very low switching energy of $\sim 0.45 \text{ nJ}$.

The saturation of absorption in the 230 nm thick film was also investigated at the same He-Ne laser frequency. Figure 3 illustrates the experimental data of absorption of a 230 nm thick film and the theoretical fitting using a Bloch-type saturable absorption with negligible scattering losses¹⁵

$$\alpha(I)L = [\alpha_0 L / (1 + I/I_s)] \quad (12)$$

where I_s the threshold power of the saturation, L is the thickness of the sample, and α_0 is the linear absorption coefficient. The saturation intensity, estimated from the theoretical fitting, is $\sim 20.0 \times 10^3 \text{ W/cm}^2$.

Modeling phthalocyanine as a three level system, a molecule in the ground state at saturation absorbs light at a rate

$$1/\tau = \sigma_0 I_s / h\nu \quad (13)$$

where τ is the decay time of the excited triplet state, I_s the saturation intensity, σ_0 is the absorption cross section of the ground state, and $h\nu$ is the energy of the incident photon. From the measurements of the fall time of 1.0756 ms at 245 Hz in figure 2b, the absorption cross section was estimated¹⁶ to be on the order of $\sim 2.4 \times 10^{-17} \text{ cm}^2$.

III. CONCLUSION:

Microgravity research on processing materials in space opens a great opportunity for the generation of a new and unique class of materials of enhanced optical properties. These materials are strongly believed to be of great potential for the manufacturing of the future optical computing and optical communication integrated circuits.

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