Charge transport under illumination in mesoporous continuous films.

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ABSTRACT.

Recent developments in the preparation of surfactant-templated mesostructured sol-gel silica materials have extended the morphology from the originally discovered powders, with particle sizes on the order of microns, to mesoporous continuous thin films. These films could find applications in membrane-based separations, selective catalysis and sensors. Particularly, sodium dodecyl sulfate (SDS)- templated sol-gel films formed by the rapid dip-coating sol-gel method possess highly ordered lamellar phase structure. The interest in the potential applications of these films and the introduction of new properties lead to the research of their chemical modifications. The improvement of their photorefractive response requires a knowledge of the microscopic processes as the charge transport mechanism. The photoconductivity technique provides information about that mechanism, and it allows measuring the transport parameters. Mesoporous continuous films were prepared by the dip-coating method on glass substrates. The films were doped with SDS, carbazole (SiK) and dispersed red one (DR1) at 1:20:20 molar concentration. Photoconductivity studies were done on them at different illumination wavelengths in order to know the transport mechanism and surfactant influence. The electric field versus current density plot shows a linear behavior, i.e. an ohmic response. The conductivity slope dependence with the polarization time shows a gaussian behavior. And there is an exponential decay from the absorption coefficient with the accumulated polarization time. Interpretation of these results is presented and the obtained charge transport parameters are reported.

Key word: Mesoporous films, thin films, photoconductivity, sol-gel., dip-coating.

INTRODUCTION.

Mesostructured mesoporous silica films are a new class of material that use surfactants to template or provide ordered structure to the amorphous silica matrix. The mesostructure types that have been observed show hexagonal, cubic, and lamellar phase structures. Dip coating in conjunction with surfactant-templating has been applied to the production of continuous, macroscopic films as thin as ~0.1 μm that contain long-range mesostructural order[1]. Since1990, the potential applications to optical information processing and holographic image storage have been studied by photorefractive response[2,3]. In the past five years organic materials have emerged as an important new class of photorefractive media[4,5,6]. There is a considerable interest in the development of photorefractive polymers owing to their large nonlinearities, low dielectric constant, structural flexibility and low cost. To be photorefractive, polymers have to exhibit photosensitivity, photoconductivity and electro-optic effect. The polymeric matrix itself supports charge transport. The most commonly used charge transporting groups are carbazole units. We prepared sol-gel thin films by fast dip-coating with a second-order chromophore (disperse red one DR1) and a charge transporting molecule (carbazole).

Then, the alignment of the nonlinear optical side groups in the sol-gel polymer films was achieved by single-point corona poling technique using a sharp metallic needle as electrode.

Photoconductivity studies on these films give information about charge transport mechanism. It provides a fundamental part to get a detailed knowledge on microscopic process. Therefore the material properties will be improved in photorefractive applications. This was possible through a structure control on these films.

Molecules and polymer chains, when incorporated into the films can be expected to line up these layered structures. This feature may allow electron transport from one end of the film to the other if the electron transferring species are densely aligned in the planes across the entire length of the film.

EXPERIMENTAL.

SDS-templated sol-gel silica films posses a highly ordered lamellar-phase structure. It was combined with carbazole groups (SiK) and dispersed red one (DR1).

The sol was prepared by refluxing TEOS (Aldrich), ethanol, water and HCl (molar ratio: 0.14: 0.52: 0.13: 3x10^{-3}) at 60 ^{0}C for 90 min. This forms the stock solution[1,7], designed to minimize the siloxane condensation rate. The hydrolysis was performed under acidic conditions with tetrahydrofuran (THF) as a common solvent. The molar concentration was defined as: DR1: SDS: SiK = [1:20:20]. Typically 0.1 ml of water, 0.4 ml of 0.07 N HCl, 15.7 ml of ethanol and 17 ml of THF were added to 3.3 ml of the stock solution. The sol was stirred for three days at room temperature.

The films were drawn with the equipment described previously that uses hydraulic motion to produce a steady and vibration-free withdrawal of the substrate from the sol[8]. Glass substrates (9 cm x 1 cm x 1 mm) were cleaned with Nochromix (Godax Laboratories Inc.) and then rinsed with and stored in deionized water prior to use. These substrates were connected, through a ribbon, to a weighted float in a cylindrical water tank whose drainage was controlled by a flow valve. On top of the sol reservoir a transparent Pyrex cover was placed to reduce the air current and to slow the evaporation rate. Convection-free drying was critical to obtaining high optical quality films. The films were withdrawn at a speed of 5 cm/min.

The structure of the final films was characterized with X-ray diffraction (XRD) patterns. Then, the film was cut and polished to get a small sample, whose dimensions were 0.6 cm x 0.5 cm.

Optical absorption spectra were taken with a Milton Roy 3000 array Spectrophotometer. The sample was maintained in a 10^{-5} Torr vacuum cryostat at room temperature in order to avoid humidity. Silver electrodes were painted on the sample, previously. In order to measure photocurrents on the films, they were illuminated with an Oriel 79309 10-mW He-Ne laser. Currents were measured with a 642 Keithley electrometer connected in series with the voltage power supply. The applied electrostatic field E was parallel to the thin film. Light intensity was measured at the sample position with a Spectra Physics 404 power meter[9]. DR1 molecules were orientated under Corona electric field poling at 120 C as function of time, and the field was taken away once the sample reached room temperature.

RESULTS

Absorption spectra evolution as a function of the polarization time is illustrated in Fig. 1. A clear decrease is observed when the polarization time increases. The absorption coefficient, compared with the initial one, changes continuously until saturation level is reached after 60 minutes of polarization as it is depicted in Fig. 2.

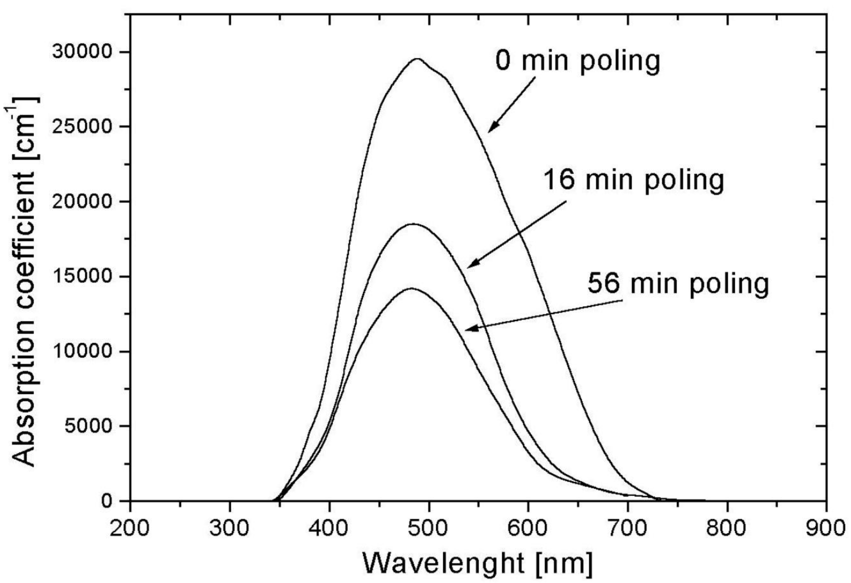

Fig. 1 Absorption coefficient evolution with poling time

This behavior is due to polarization saturation that follows the Langevin-Debye equation. Data satisfactorily fit this equation, as Fig. 2 shows (black line). Absorption diminished because the initial DR1 dipoles have a random orientation in the film plane. And due to the electric Corona Field, applied perpendicular to this plane, the molecules are orientated in the same direction.

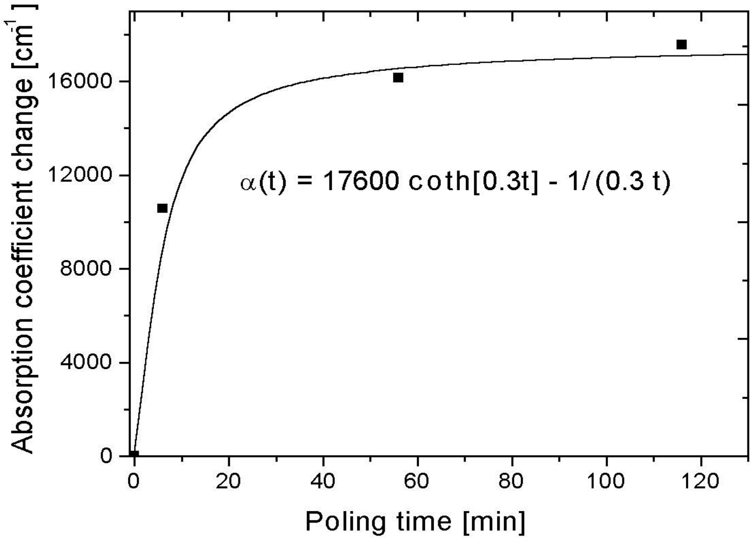

Fig. 2 Absorption change with poling time

The electric field from the light reaching the sample during absorption measurements (that is contained in the film plane) sees less transversal dipoles as they become oriented, that is why the absorption diminishes with the poling time increment. Therefore, each carbazole molecule presents a smaller absorption cross section to incoming photons, and absorption diminishes.

Photoconductivity results are shown in Fig. 3. A straight line was easily fitted to the data. This indicates an ohmic behavior.

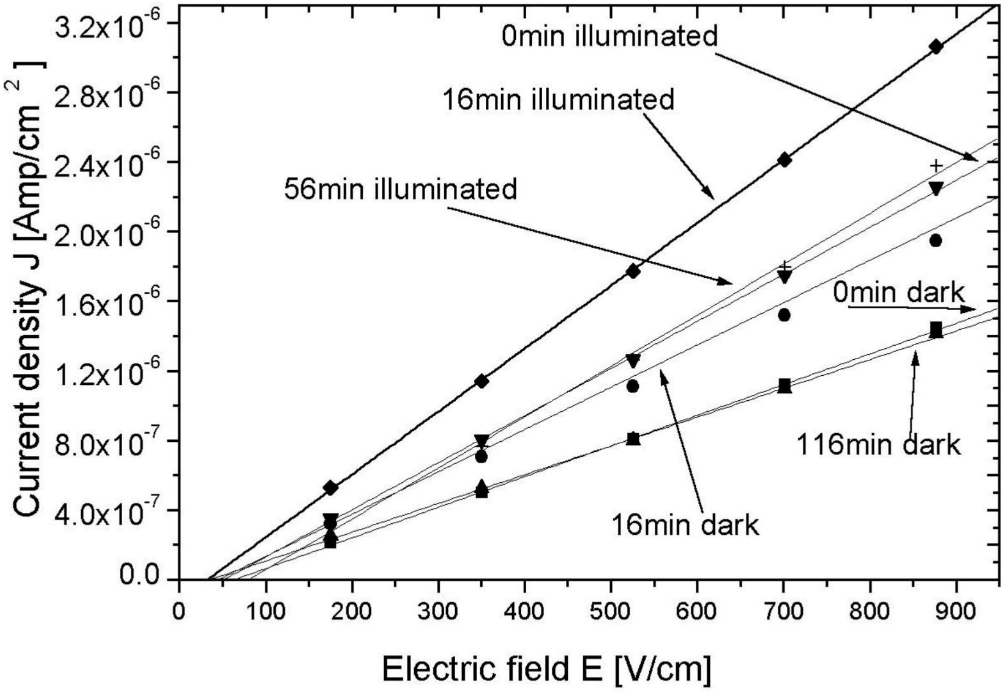

Fig. 3 Dark and illuminated current curves for different poling times

Charge transport in insulating materials is given by[9]:

$$j=e\phi l_0 \alpha I/h\nu +(en_0\mu +e\phi \mu \tau \alpha I/h\nu)E \qquad (1)$$

The first term is the photovoltaic effect transport, the second one is the dark conductivity $\sigma = en_0\mu$, and the third one is the photoconductivity itself. In this equation, I is the light intensity with energy $h\nu$, ϕ is the quantum efficiency for exciting a free carrier, μ is the charge mobility, E is applied electric field, α the absorption coefficient τ is the half life of the excited carriers, n_0 is the carrier density that produces dark conductivity and l_0 is the mean free path. With this equation, by measuring I, the dark conductivity and the conductivity under illumination, and fitting the data by the least squares method, as it is shown in Fig. 3, the ϕ l_0 and ϕ μ τ parameters are obtained. They are reported in table 1. Their magnitudes are similar to those obtained in photorefractive crystals[9].

DR1 with carbazole			KnbO$_3$:Fe	
t (min)	$\phi\ l_0$ (cm x10^{-11})	$\phi\mu\tau$ (cm^2/V x10^{-11})	$\phi\ l_0$ (cm x10^{-11})	$\phi\mu\tau$ (cm^2/V x10^{-11})
0	-6.627	0.230	850	23.38
6	-8.288	0.151	-	-
16	-3.870	0.457	-	-
56	-20.970	0.218	-	-
116	-19.540	0.157	-	-

Table 1. Transport parameters

As shown in Fig. 3, conductivity increases with poling time until a maximum is reached, and then it decreases. This is better shown in Fig. 4, which illustrates the slope change from photoconductivity results. As it is observed, there is an optimal polarization time of approximately 35 min. that produces the maximum conductivity response for both, dark conductivity and photoconductivity. We have observed the same result several times. By considering the arguments from Takimoto et al.[10], working on films with oligo-p-phenylene sulfide, on which they observed that carriers were more easily transported perpendicular to the molecular chain axis than along that axis, we can explain the photoconductivity increment with poling. According to these authors, when the molecules are oriented perpendicular to the film plane, the charge clouds from the π electrons in the molecules, are closer so they have a better chance to hope from one molecule to another, therefore increasing the photoconductivity. We should state that there no clear explanation to why there is an optimal poling time. More experiments are being conducted to clarify this point.

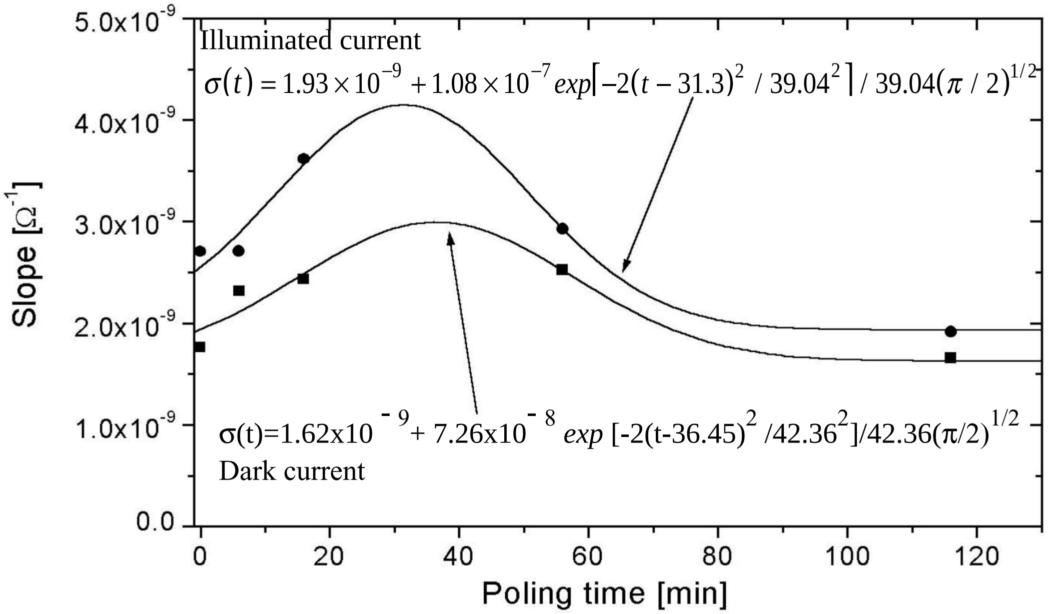

Fig. 4 Slope of lines in Fig. 3, as a function of the poling time

CONCLUSIONS

Photoconductivity on mesoporous sol-gel films doped with DR1 and SiK is poling sensitive. Conductivity parameters are comparable to those of photorefractive crystals. Absorption change with poling can be well fitted with a Langevin-Debye equation. Increased in conductivity with poling can be explained by considering the increase in π electrons hopping when the molecules are oriented perpendicular to the plane of the film. There is an optimal poling whose origin is under study.

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REFERENCES

1. M. H. Huang, B. S. Dunn, and J. I. Zink. In Situ Luminescence Probing of the Chemical and Structural Changes during Formation of Dip-Coated Lamellar Phase Sodium Dodecyl Sulfate Sol-Gel Thin Films . *J. Am. Chem. Soc.*, **122**, pp. 3739-3745, 2000.
2. Photorefractive materials. MRS Bull. 1994, XIX, No. 3.
3. F. Chaput, D. Riehl, J. P. Boilot, K. Cargnelli, M. Canva, Y. Levy, and A, Brun. New Nonlinear Sol-Gel Films Exhibiting Photorefractive . *Chem. Mater.*, **8**, pp. 312-314, 1996.
4. K. Sutter, P. J. Guenter, Photorefractive gratings in the organic crystal 2-cyclooctykamino-5-nitropyridine doped with 7, 7, 8, 8-tetracyanoquinodimethane . Opt. Soc. Am. B7, **12,** pp. 2274-2278, 1990.
5. W. E. Moerner, S. M. Silence, Polymeric photorefractive materials . *Chem. Rev.*, **94**, pp. 127-55, 1994.
6. B. Kippelen, K. Sandalphon, K. Meerholz, B. Volodin, S. R. Lyon, A. B. Padias, H. K. Hall Jr., N. Peyghambarian, Photorefractive and photoisomerization in azo-dye-doped polymers . *Mater. Res. Soc. Symp. Proc.* **328,** pp. 577-82, 1994.
7. C. J. Brinker et al. *In Access in Nanoporous Materials*; Pinnavaia, T. J., Thorpe, M. F., p. 123. Eds. Plenum: New York, 1995; .
8. F. Nishida, J. M. McKierman, B. Dunn, J. I. Zink, C. J.,; Brinker, A. J. Hurd, *J Am. Cer. Soc.* **1995**, 78, 1640.
9. J. Garcia M., M. A. Mondragon, J. M. Hernandez A., J. L. Maldonado R.. Photocurrent determination of charge transport parameters in $KNbO_3:Fe^{3+}$. *Optical Materials,* **3,** pp. 61-64, 1994
10. A. Takimoto, H. Wakemoto, H. Ogawa, "Molecular orientation and anisotropic photoconduction of evaporated oligo-p-phenilene sulfide films", Jpn. Appl. Phys., **32**, pp. 971-978, 1993.

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