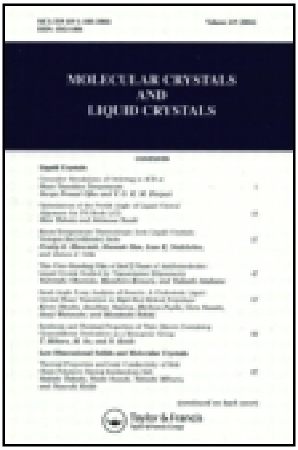

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Vacuum-Deposited Thin Films of α-Oligothiophenes Characterized by Optical Evanscent Wave Spectroscopy

Harald Knobloch [a] , Wolfgang Knoll [a] , Denis Fichou [b] & Hiroyuki Sasabe [c]

[a] Max-Planck Institut für Polymerforschung, Ackermannweg 10, Mainz, Germany

[b] Laboratoire des Matériaux Moléculaire, CNRS, ER 241-2, Rue Henry Dunant, 94320, Thiais, France

[c] Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN) 2-1, Hirosawa, Wako-shi, Saitama, 351-01, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Harald Knobloch , Wolfgang Knoll , Denis Fichou & Hiroyuki Sasabe (1994): Vacuum-Deposited Thin Films of α-Oligothiophenes Characterized by Optical Evanscent Wave Spectroscopy, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 252:1, 269-276

To link to this article: http://dx.doi.org/10.1080/10587259408038232

Mol. Cryst. Liq. Cryst. 1994, Vol. 252, pp. 269–276
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Printed in the United States of America

VACUUM-DEPOSITED THIN FILMS OF α-OLIGOTHIOPHENES CHARACTERIZED BY OPTICAL EVANSCENT WAVE SPECTROSCOPY

HARALD KNOBLOCH, WOLFGANG KNOLL
Max-Planck Institut für Polymerforschung, Ackermannweg 10, Mainz,
Germany

DENIS FICHOU
Laboratoire des Matériaux Moléculaire, CNRS, ER 241 - 2,
Rue Henry Dunant, 94320 Thiais, France

HIROYUKI SASABE
Frontier Research Program, The Institute of Physical and Chemical Research
(RIKEN), 2-1 Hirosawa, Wako-shi, Saitama 351-01, Japan

Abstract: We report on the generation of optical evanescent waves, namely waveguide modes and surface plasmons, in vacuum-deposited thin films of α-oligothiophenes. We characterized three different oligothiophenes: α-quaterthiophene (α-4T), α-sexithiophene (α-6T) and α-octithiophene (α-8T) concerning their optical properties. In addition to an accurate determination of the refractive index of thin films prepared from these molecules, the oberservation of evanescent waves in oligothiophene films indicates their high optical quality and therefore emphasizes their potential interest in integrated optics.

Keywords: oligothiphenes, thin films, evanescent wave spectroscopy, integrated optics, surface plasmons

INTRODUCTION

Optical Evanescent Wave Spectroscopy

Among the wide range of experimental techniques of thin film characterization light optical methods play an important role. Especially evanescent optical wave techniques proved to be a very useful tool to obtain information about the optical properties of thin film structures[1,2]. In this paper we report on the generation of surface plasmons and waveguide modes in thin films of α-oligothiophenes.

Surface plasmons (PSP for Plasmon Surface Polaritons) are electromagnetic waves, propagating along metal dielectric interfaces[3], with the field decaying exponentially into the metal and the dielectric, respectively[4]. Due to their dispersion behavior

$$k_{sp}^{0}=\frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m+\varepsilon_d}}. \qquad (1)$$

PSP are very sensitive on the dielectric constants at the metal-dielectric interface. In the case of an ultra thin film coating at the metal surface equation (1) has to be modified by[5]

$$k_{sp}^{1}=k_{sp}^{0}+\Delta k_{sp}^{c}(\varepsilon_c,d_c) \qquad (2)$$

with the dispersion being a function of the dielectric constant ε_c and the thickness d_c of the coating, too.

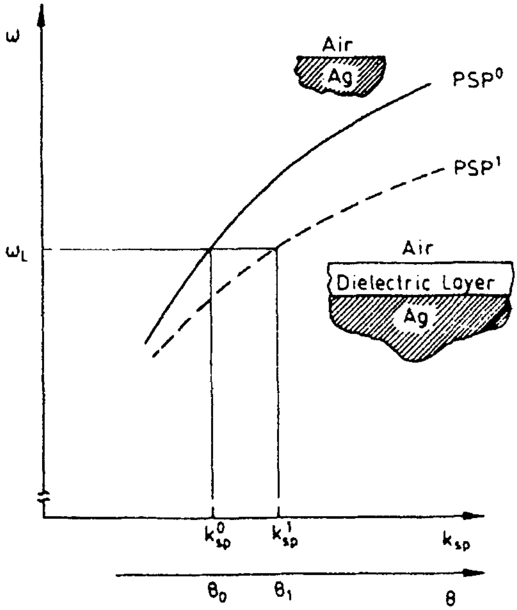


FIGURE 1 Dispersion relation of PSP at a metal/air (PSP^0, full line) and at a metal/coating/air interface (PSP^1, broken line).

As the wavevector k_{sp} is larger than that of an incident light beam, for the excitation of PSP it is nescessary to use a coupling arrangement, such as, for example a prism in the so-called Kretschmann configuration[6] (see Fig. 2). When the condition

$$k_x=\frac{\omega}{c}n_p\sin\Phi=k_{sp}^{1} \qquad (3)$$

is fulfilled PSP are excited and propagate along the metal-air-interface. As the excitation of PSP reduces the intensity of the reflected beam, a very narrow dip in the reflectivity-curve can be observed at the resonance angle Θ_i. This resonance angle, with eqation (2), is a function of the optical constants (ε_c, d_c) of a thin film coating at the metal-dielectric-interface.

In the case of optical waveguide modes, the light propagates inside the thin film. These modes can be excited, if the light travelling inside the film is totally reflected at the boundaries to the surrounding media and fulfills the well-known mode equation[7]

$$k_z d_c + \beta_0 + \beta_1 = m\pi \tag{4}$$

with k_z being the k-vector perpendicular to the plane of the film, β_i the phase shifts at the film boundaries an m the mode number. As the β_i strongly depend on the refractive indices of the film and the surrounding media, optical waveguide modes are highly sensitive on these parameters and therefore allow to characterize a thin film structure due to its optical properties.

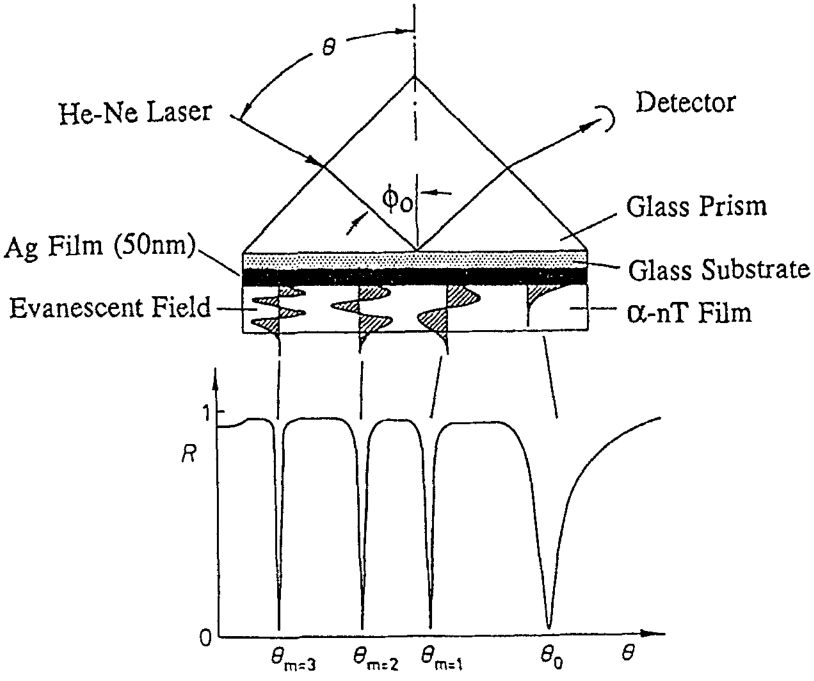


FIGURE 2 Set-up for the excitation of evanescent waves in thin films. PSP are excited at the angle Θ_0, waveguide modes at the angles Θ_m.

Like in the case of surface plasmons, optical waveguide modes can only be excited, when

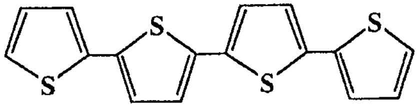
$$k_x = \frac{\omega}{c} n_p \sin\Phi = k_{wg} \tag{5}$$

the wavevectors of the incident light and the wavevector of the propagating mode are matched e.g. by using a prism (see Fig. 2).
Like in the case of PSP, the excitation of optical waveguide modes reduces the reflectivity, and they can be observed as a sharp dip in the reflectivity-curve.

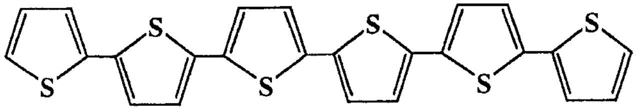
Therefore, in the case of optical waveguide measurement, as well as for PSP, the reflectivity is recorded as a function of the incident angle by rotating the prism with the thin film structure at its base.

Materials

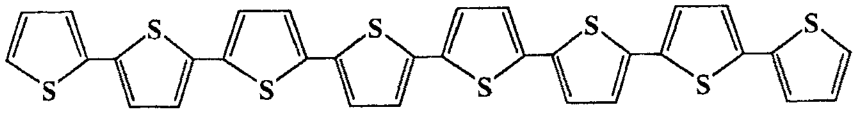
Vacuum-deposition of long linear α-oligothiophenes α-nT (n = 4 - 8) yields highly homogeneous thin solid films with specific electrical and optical properties[8]. In recent time it was shown, that these new organic materials have potential applications in various fields of technology such as microelectronics and all-optical information technology[8-10], but so far, only few information about structure and morphology of these films is available.



α-4T



α-6T



α-8T

FIGURE 3 Molecular structure of the α-oligothiophenes: α-quaterthiophene (α-4T), α-sexithiophene (α-6T) and α-octithiophene (α-8T)

α-4T, α-6T and α-8T are synthesized by coupling methods according to known procedures[11] and succesively purified by recrystallisation and sublimation before thin film preparation. Thin films of these materials were prepared by evaporation of the powdered oligomeres under reduced pressure (10^{-4}Pa). The evaporation rate was typically 1 - 2 $^{nm}/_{sec}$, the obtained thicknesses were in the range of 20 nm to 1.1 μm.

During deposition, the substrates (BK 7 glass slides, covered with a 50 nm thick sliver film for evanescent wave excitation) were positioned about 10 cm above the source and consequently were heated up to temperatures around 100°C.

In this configuration, we obtained films of homogeneous thickness throughout the sample with only 5% derivation from edge to center, the average surface roughness was as below 3 nm (Dektak α-stepper).

The film morphology is a crystalline network of inter-connected linear segments with an average diameter of 30 nm and an average length of 120 nm. As the size of the crystallits is far smaller than that of the wavelength of light, the obtained films were of high optical quality.

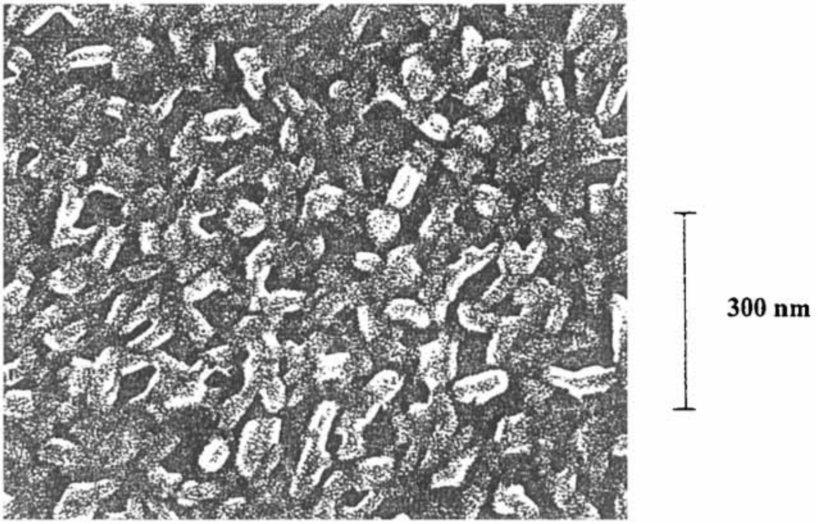


FIGURE 4 Surface morphology of a vacuum-deposited α-6T thin film of 78 nm thickness as observed by SEM.

RESULTS AND DISCUSSION

Figures 5 (a), (b) show typical reflectivity curves for α-6T films of different thickness. In the case of very thin films, only PSP can be excited (Fig. 5 (a)), whereas for an increased thickness also waveguide modes can be generated (Fig. 5 (b)). The measurements were performed with a Helium-Neon laser (λ = 632.8 nm) in TE-(transverse electric) and TM-polarisation (transverse magnetic) for optical waveguide modes. Due to their polarization properties, PSP can only be excited by TM-polarized light[4].

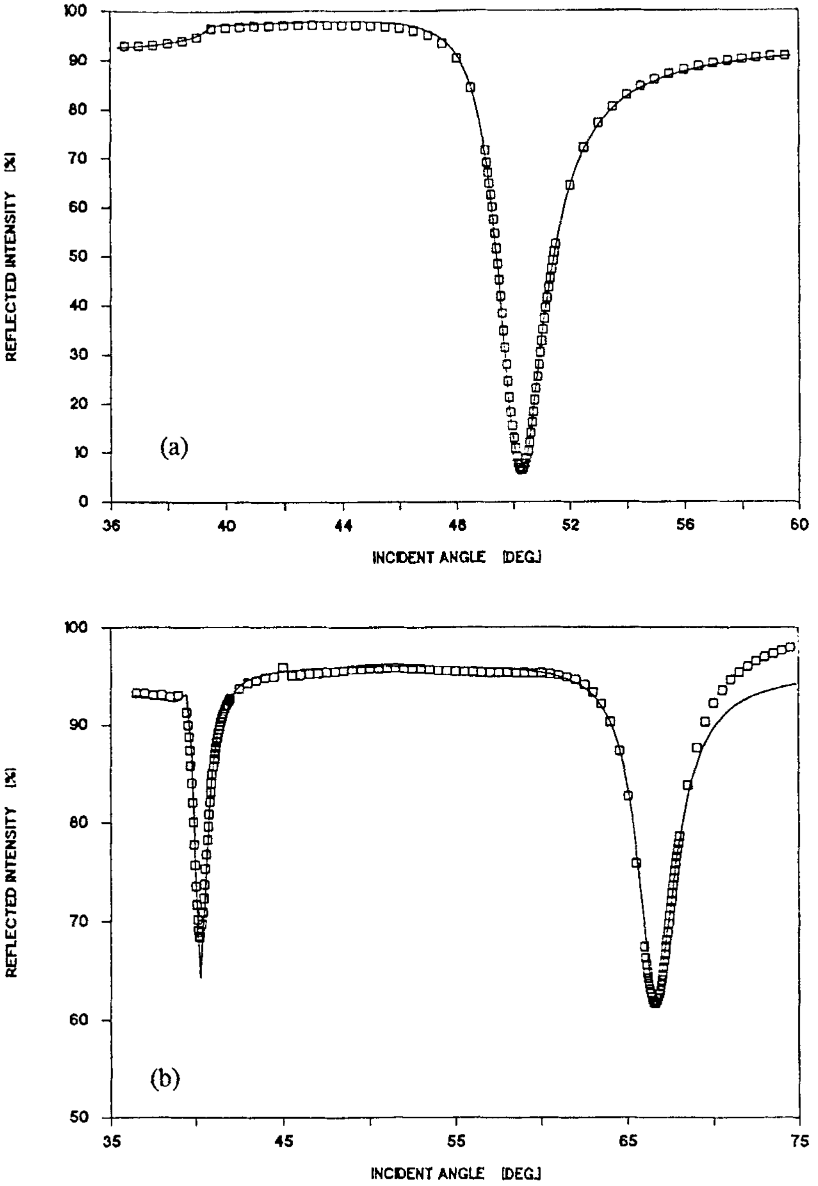


FIGURE 5 Reflectivity R versus the angle of incidence Θ_i of TM polarized laser light ($\lambda = 632.8$ nm). For a thin film of α-6T (24 nm) only PSP can be excited (a). In the case of a thicker film of α-6T (1.12 μm) two waveguide modes (b) can be generated in the film.

The experimental points (square points) in fig. 5 are compared with calculations (full lines) done by fresnel formalism[12] which allows an accurate determination of refractive index and film thickness. A good fit is obtained for every sample and the various parameters are listed in TABLE I. For the first time it can be shown that the refractive index n of α-oligothiophene films linearly increases with the oligomer length from α-4T to α-8T. In this range of chainlength, there seems to be no leveling off for the refractive index, resulting in values as high as n = 1.965 for α-6T and even n = 2.076 for α-8T.

TABLE 1 Results of evanescent wave spectroscopy on α-oligothiophenes. The values for the real part of the refractive index n_r were obtained by comparing the measured reflectivity with fresnel calculations, the film thickness d_f was confirmed by using an α-stepper.

Oligomer	**d_f [nm]**	**Θ_i [deg.]**	**Wave**	**n_r (632.8nm)**
α-4T	35	57.4	PSP	1.857
	91	41.2	WG	1.853
α-6T	24	50.2	PSP	1.965
	78	44.6	WG	1.966
	1128	40.0	WG	1.950
		66.6		
α-8T	66	39.5	WG	2.076

Although a weak chain length dependence of α-nT films has already been reported by Zhao et al[13], their values are much lower (e.g. n = 1.623 for α-6T) than ours, probably because of a lower density of their films. As a matter of fact, in the case of the α-6T our values correspond quite well to those reported recently as measured by inteference method[14].

The narrow dips of the resonance, with the reflectivity going down to values below 10%, indicates the high optical quality of these films. However for thicker films, the resonances become broader and the minimum reflectivity is not as deep as in the thin films. This phenomena can be explained by refering to the imaginary part of the refractive index. Since the laser wavelength we used to generate the evanescent waves is far from any absorption band[15], we can expect the imaginary part κ_i of the refractive index

$$n = n_r + i\,\kappa_i \tag{6}$$

of α-nT films to be zero. That was indeed the case for the thin film samples, whereas for samples of increased film thickness the calculated values for κ_i are slightly increased, resulting from an enhanced surface roughness in thicker films.

The most remarkable point in our measurements are the high values of refractive indices obtained in our measurements, especially that for α-8T. Normally it is quite unusal for organics to have such a high refractive index out of any absorption band. They are originated to a combination of two effects: the long π-conjugated system (electronic factors) and the high film crystallinity and density (morphology factors). This is typically for the α-8T, the longest unsubstituted oligothiophene so far. Therefore, in contrast to 3-alkylated polythiophene films, whose porosity results in low refractive indices in the range of 1.5 - 1.7, evaporated films of unsubstituted oligomers fulfill both, electronic and structural requirements to affort films of high optical quality.

ACKNOWLEDGEMENTS

The authors thank Dr. Taiji Furuno for performing the SEM measurements as well as Dr. Horst Orendi and Dr. Reinald Lawall for fruitful discussions.

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