ELSEVIER

Optical Materials 12 (1999) 345–350

OPTICAL Materials

Film thickness measurement and linear dichroism of organic thin films prepared by molecular beam deposition at oblique incidence

Bert Müller [a,b,*], Matthias Jäger [b], Ye Tao [b], Armin Kündig [b], Chengzhi Cai [b], Christian Bosshard [b], Peter Günter [b]

[a] *Swiss Federal Laboratories for Materials Testing and Research, CH-8600 Dübendorf, Switzerland*
[b] *Nonlinear Optics Laboratory, Institute of Quantum Electronics, ETH Zürich, CH-8093 Zürich, Switzerland*

Abstract

Linear dichroism – the in-plane optical anisotropy – is observed for organic thin films grown on fused silica and glass substrates. The films made of [4-pyrid-4-yl-ethynyl-benzoic acid] and [4-trans-2-(pyrid-4-yl-vinyl) benzoic acid] are deposited from an angle of about 30° with respect to the surface normal under ultra-high vacuum conditions. The film thickness measurements by alpha-step, atomic force microscopy in tapping mode, and in situ ellipsometry as well as transmission spectra are discussed in detail. Moreover, the optical constants of these novel materials are determined using ellipsometry and transmission spectroscopy. The remarkable optical asymmetry is found in the ultra-violet transmission spectra and attributed to oriented molecules which are connected by hydrogen bonds. © 1999 Elsevier Science B.V. All rights reserved.

PACS: 81.15 Ef; 68.55 Jk; 78.20 Ci
Keywords: Linear dichroism; Molecular beam deposition; Oblique incidence; Nonlinear optics; Organic molecules; Thickness measurement

---

Organic thin films with an acentric order hold promise for different linear and nonlinear optical applications [1]. Their fabrication under well-defined, ultra-high vacuum conditions, however, is believed to be difficult. In particular, for second order effects, dipolar molecules have to be aligned noncentrosymmetrically.

Molecular beam deposition (MBD) is a well-known growth technique with essential advantages. The growth conditions result in film structures with abrupt interfaces due to the moderate substrate temperatures, whereby the films themselves are extremely pure. The growth can be easily monitored by surface sensitive methods. Therefore, it is of interest to realize anisotropic thin film structures by MBD. From inorganic materials, we know that oblique incidence of the molecular beam can lead to structural, magnetic, and optical anisotropies [2]. There is no doubt that oblique-incidence MBD works equally well for organic materials and should also result in anisotropic thin film properties. But according to our knowledge, it is not yet done. Most probably, the thin films are unstable due to the weak interaction at the

---

[*] Corresponding author. Tel.: +41-1-633-6190; fax: +41-1-633-1120; e-mail: mueller@biocomp.mat.ethz.ch

PII: S0925-3467(99)00065-8

Fig. 1. Molecular structure of (a) PVBA, and (b) PEBA.

film-substrate interface and within the organic thin film. In order to align the organic molecules and to stabilize them, we have developed noncentrosymmetric molecules with a special feature. They are connected to each other by strong hydrogen bonds in a head-to-tail fashion giving rise to linear polymeric structures. Such polymers can be sublimated in vacuum. Here, the H-bonds are broken while the molecules themselves remain intact. At the substrate surface, the molecules re-assemble and the H-bonds between the molecules are formed again. In this communication, we demonstrate that such organic molecules deposited by MBD at oblique incidence can form anisotropic thin films which are quite stable. Their optical properties depend on the growth conditions (substrate temperature, deposition rate, film thickness, angle of incidence of the molecular beam). That means, it is a kinetically driven phenomenon, and the final state is not the thermodynamic equilibrium.

For the preparation of the anisotropic organic thin films, we have designed and synthesized two materials ([4-pyrid-4-yl-ethynyl-benzoic acid] – PEBA and [4-trans-2-(pyrid-4-yl-vinyl) benzoic acid] – PVBA). Their molecular structure is given in Fig. 1(a) and (b), respectively. Both noncentrosymmetric, organic molecules are characterized by a pyridyl ring on one end and an acidic group on the other end. The different ends form a strong intermolecular hydrogen bond. The hydrogen bonding is verified by solid state ^{15}N-NMR spectroscopy [3]. The thermal stability of PVBA, which is also an indication for the strong intermolecular interaction due to H-bonding, is shown in Fig. 2 by differential scanning calorimetry. PVBA decomposes and melts at 350°C. PEBA is almost as stable as PVBA. It melts at 300°C. That means, both materials have a high thermal stability with

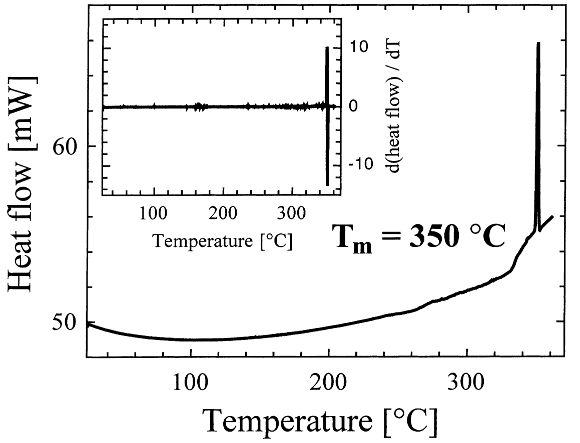

Fig. 2. Differential scanning calorimetry measurement of PVBA. The heating rate of the 4.29 mg PVBA was 5 K/min. Inset: Differentiated curve to emphasize the phase transition.

respect to many other nonlinear active organic materials, which are used e.g. for Langmuir–Blodgett films.

PVBA and PEBA were sublimated at a source temperature of about 220°C resulting in a deposition rate of 1 µm/h (1 monolayer per second) which is a typical rate for molecular beam epitaxy. Both materials were deposited on different transparent substrates (fused silica, glass, and sapphire) and differently prepared Si and Au surfaces under ultra-high vacuum conditions (base pressure during deposition 6×10^{-9} mbar). Before heating to 120°C for 30 min in vacuum, the substrates were cleaned by acetone and ethanol. The films with thicknesses ranging from 10 to 2000 nm were grown at substrate temperatures between −190°C and 175°C and a deposition rate between 0.05 and 0.5 nm/s. Temperatures were measured by thermocouples. The deposition rate was controlled by a quartz microbalance stabilized at 30°C and calibrated by the different in situ and ex situ film thickness measurement techniques, see below. The experimental set-up for deposition, basically an ultra-high vacuum chamber equipped with commercial low temperature effusion sources, is described elsewhere [4].

Besides the thermal stability, the mechanical stability of the organic thin films is a prerequisite for different characterization methods and many applications. Organic materials are known to be fragile. Therefore, a tip of an alpha-step (stylus depth measurement) can modify or even destroy organic thin films. Measurements can become unreliable. Certain organic materials, however, are mechanically stable enough to be characterized by an alpha-step. We have measured the film thickness at a shadow edge of PVBA and PEBA thin films for several times and different positions using the alpha-step Tencor 200. We have found within statistical error bars identical values. Only films prepared at a grazing incidence molecular beam, which were extremely rough, are too fragile for this kind of thickness measurement. In order to verify the film thickness measurement by the alpha-step, we have performed atomic force microscopy experiments. Here, the strength of interactions between tip and sample is drastically reduced. One can take advantage of different detection modes which are classified according to kind and strength of interactions between tip and sample. An AFM image at shadow edge obtained in the tapping mode (TopoMetrix, Explorer with TrueMetrix scanner), where the interactions are very low, is represented in Fig. 3. The image with a length and width of 100 µm shows on the left the film surface (bright) and on the right, the substrate surface (dark). The film thickness is measured using the bearing ratio: number of data above height level h divided by total number of data. The film thickness which is equal to the step height, corresponds to the difference in the height level at

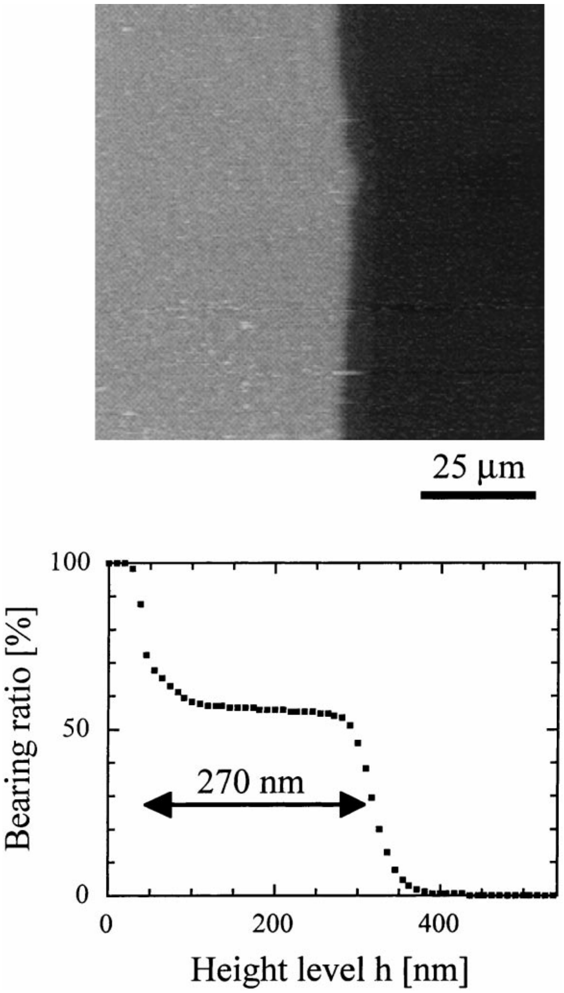

Fig. 3. Film thickness measurement using atomic force microscopy.

the half of the steps in the bearing ratio as indicated in Fig. 3. In the case of an almost ideal two level system, one can also use the histogram of the gray levels which exhibits two peaks. Their distance corresponds to the film thickness. Note, the scanning range has to be large enough that the shape of the step edge does not play any role. Therefore, in addition to the 100 μm scanning range, we have used a 50 μm range which leads to a value just slightly reduced. Because the values from the alpha-step and the AFM are identical, we can conclude that PVBA and PEBA are mechanically quite stable.

For film thickness measurement, however, both methods mentioned above have disadvantages. They are local methods and cannot be used as in situ tool during deposition. Since electron diffraction leads to surface damages especially for the isolating substrates, ellipsometry – an optical method, seems to be appropriate for film thickness measurements. Of course, ellipsometry has also limitations. It is restricted to substrate materials with high reflectivity and flat surfaces. The optical constants have to be known or must be fitted [5].

An example of an in situ measurement using the ellipsometer SE 401 (manufacturer SENTEC GmbH Berlin, Germany) at a wavelength of 670 nm is shown in Fig. 4. The sensitivity of the instrument is demonstrated for a PVBA film grown on an oxidized Si(0 0 1) substrate. After the growth of 40 nm we increased the substrate temperature until PVBA started to desorb. Just 0.7 nm remained on the surface due to the better bonding to the substrate. Although there is a considerable scattering of the data after $t = 80$ min, the average value corresponds exactly to monolayer coverage. Furthermore, using Auger electron spectroscopy we have detected the nitrogen of the PVBA monolayer [6]. Thus, the monolayer sensitivity of the ellipsometer SE 401 is verified. The optical constants of that new material, i.e. the refractive index $n = 1.825$ and the extinction coefficient $\kappa = 0$, are fitted using the Δ–Ψ plot obtained during deposition as well as assuming $n = 1.462$, $\kappa = 0$ for the 8 nm oxide film and $n = 3.68$, $\kappa = 0.018$ for the semi-infinite silicon substrate (cp. lower part of Fig. 4). The same values are found for desorption.

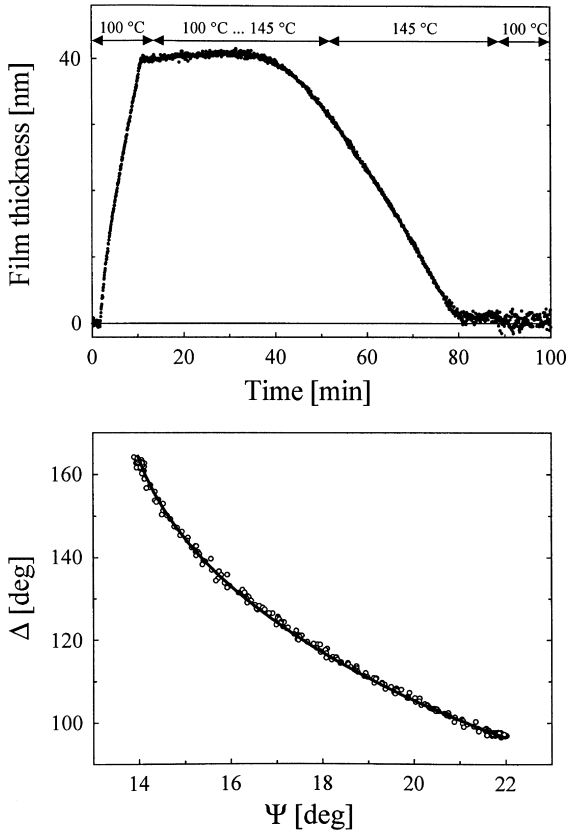

Fig. 4. Ellipsometric film thickness measurement (upper part). Fit of the optical constants using the $\Delta - \Psi$ plot (lower part).

Unfortunately, ellipsometry in reflection mode does not work for rough and for transparent samples. Here, transmission measurements can be helpful. Besides the film thickness, UV–VIS–IR transmission measurements offer a way to obtain the optical constants, i.e. the refractive index and the absorption coefficient. Fig. 5 shows these measurements for a series of PVBA films with various thicknesses grown on glass substrates at a substrate temperature of 30°C and a deposition rate of 0.08 nm/s. (The transmission measurements were performed by a Spectrophotometer Lambda 9 (Perkin-Elmer).) For very thin films (90 nm), there is just one peak at about 400 nm. For a thickness of 360 nm, however, one finds shoulders at 400 and 500 nm and peaks at 700 and 1300 nm. These characteristic features are Fabry–Perot fringes, a result of internal multiple reflections

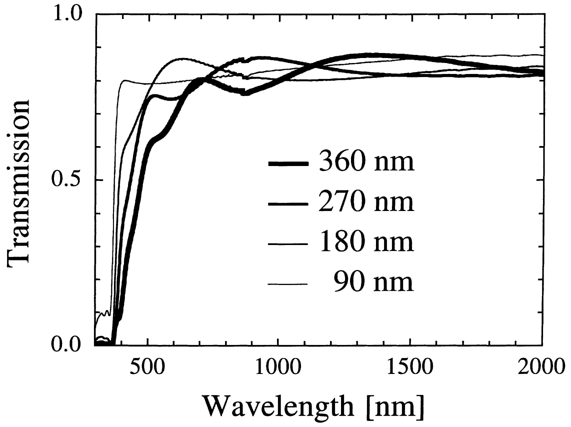

Fig. 5. Fabry–Perot fringes of UV–VIS–IR transmission spectra of PVBA films with various thicknesses grown on glass substrates using unpolarized light.

within the PVBA film. The period of these oscillations depends on the optical path length within the film. Their amplitude is determined by the refractive indices of the different layers. Therefore, the Fabry–Perot fringes can be used to evaluate the film thickness and the refractive index of unknown film materials by a computer code. Scattering effects, however, make a quantitative analysis difficult. The derived values for the film thickness were 10–20% smaller than found by alpha-step, AFM, and ellipsometer. With the knowledge of the film thickness, the refractive indices of these new materials can be calculated with higher precision. For that purpose, the transmission curves were fitted taking into account both the internal multiple reflections and the dispersion of the refractive index. The latter is calculated using the Kramers–Kronig relation. In agreement with the ellipsometric measurements, the refractive indices of PVBA and PEBA were found to be 1.8 at a wavelength of 670 nm.

But more important, below a wavelength of 400 nm the transmission spectra exhibit a remarkable anisotropy. Changing the angle of the polarizer in front of the sample, the transmission of the UV-light shows a sinusoidal behavior. Depending on wavelength, the maximum is within the plane of incidence of the molecular beam and the minimum perpendicular to the plane of incidence or vice versa. Such an optical in-plane anisotropy is called linear dichroism [7]. It is defined as the difference in the absorbance parallel and perpendicular to the molecular axis and characteristic for the molecular structure and the interactions of the molecules. Fig. 6 shows the relative linear dichroism, that is the linear dichroism divided by its average value, as a function of wavelength. The three curves correspond to PEBA films of different thickness grown on fused silica under almost identical conditions (substrate temperature 100°C, deposition rate 0.06 nm/s for the 90 and 180 nm films and 0.09 nm/s for the 270 nm film, respectively). The main peak for the two thinner films is found at 341 nm, whereby the main peak for the 270 nm film is shifted to 347 nm. This shift is not yet understood. It may be caused by the higher deposition rate. For PVBA, the peak is found at a wavelength of about 370 nm. Our preliminary results do not show any difference in position and amplitude of the main peak between deposition on fused silica and glass substrates. The main peak seems to be characteristic for the organic material. It should be mentioned that the scattering of the data within the characteristic peak is significantly reduced.

Surprisingly, the amplitude of the linear dichroism strongly depends on the film thickness. It is considerably larger for the thicker films. From second harmonic generation, we know that the molecules are preferentially oriented parallel to the

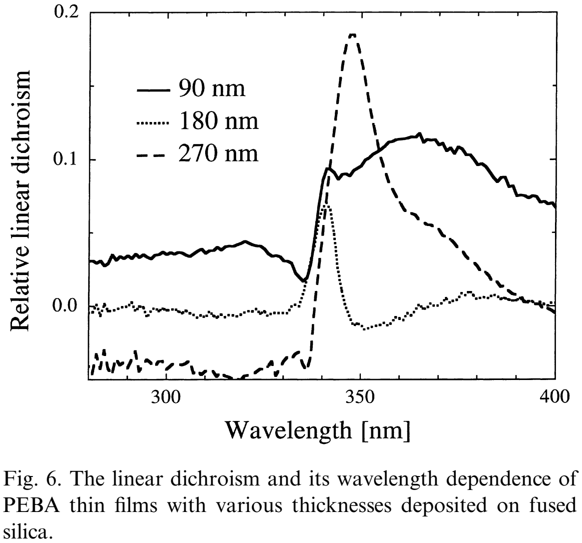

Fig. 6. The linear dichroism and its wavelength dependence of PEBA thin films with various thicknesses deposited on fused silica.

plane of incidence of the molecular beam [3]. Therefore, the main peak is attributed to the long axis of the aligned PEBA molecules. Indeed, the linear dichroism is an additional proof for the preferential orientation of the organic molecules with strong bonding deposited by oblique-incidence molecular beam deposition. Hence, oblique-incidence MBD opens up the possibility to tailor the optical properties of thin film structures for a great variety of applications.

In summary, we have shown that oblique-incidence MBD is an appropriate technique to produce organic thin film structures with anisotropic properties. It is not restricted to special substrates. There is free choice for the in-plane orientation of the molecules. The film thickness can be monitored and precisely controlled from the micrometer range down to the atomic scale. The systematic improvement of the growth parameter and the successful search for organic molecules with desired properties should result in potential devices for different optical applications. Such devices which are based on thin films can be easily implemented into electronic and optoelectronic circuits.

We would like to thank M. Ehrensperger for performing the DSC measurement. Financial support of the Swiss Priority Program "Optique II" is gratefully acknowledged.

References

[1] Ch. Bosshard, K. Sutter, Ph. Prêtre, J. Hulliger, M. Flörsheimer, P. Kaatz, P. Günter, Organic Nonlinear Optical Materials, Gordon and Breach Basel, 1995, in: F. Kajzar, J.D. Swalen (Eds.), Organic Thin Films for Waveguiding in Nonlinear Optics, Gordon and Breach, Amsterdam, 1996.

[2] Y. Park, E.E. Fullerton, S.D. Bader, Appl. Phys. Lett. 66 (1995) 2140; L. Jorritsma, Growth Anisotropies in Cu(0 0 1) Homoepitaxy, Wormgoor B.V. Almelo Netherlands, 1997; Y. Takeda, T. Motohiro, T Hioki, S. Noda, J. Vac. Sci. Technol. B 16 (1998) 7.

[3] C. Cai, M. Bösch, Y. Tao, B. Müller, Z. Gan, A. Kündig, C. Bosshard, I. Liakatas, M. Jäger, P. Günter, J. Am. Chem. Soc. 120 (1998) 8563.

[4] R. Schlesser, Diss. No. 11456 ETH Zürich, 1996.

[5] H.G. Tompkins, A User's Guide to Ellipsometry, Academic Press, Boston, 1993.

[6] C. Cai, Y. Tao, B. Müller, unpublished.

[7] A. Rodger, B. Nordén, Circular Dichroism and Linear Dichroism, Oxford University Press, Oxford, New York, Tokyo, 1997.