Self-assembled organic supramolecular thin films for nonlinear optics

Ali N. Rashid *, Peter Gunter

Nonlinear Optics Laboratory, Institute of Quantum Electronics, Swiss Federal Institute of Technology, ETH-Hönggerberg, CH-8093 Zürich, Switzerland

Abstract

We analyze the issues that must be considered on the road towards a practical fabrication method for organic nonlinear optical thin films. The advantages and disadvantages of the most useful techniques for producing nonlinear optical thin films are reviewed. We describe a promising molecular beam deposition techniques that has been developed in our laboratory for the growth of ordered supramolecular self-assembled thin films that are nonlinear optically active and maintain their polar order for large thicknesses.
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

The flexibility of molecular engineering makes systems based on acentric supramolecular assemblies of organic conjugated molecules very interesting for a multitude of information-processing and photonic applications such as high speed electro-optic modulation, optical switches, terahertz wave generation, holographic storage, anisotropic charge-transport, self-assembled molecular nanowires, or nonlinear waveguides for integrated frequency conversion systems using low power semi-conductor lasers. The main characteristics of the desired organic thin films for fre-

quency conversion and telecommunication applications are: (i) they must be noncentrosymmetric, and therefore show second-order nonlinear optical effects, (ii) their thickness must be of the order of one micrometer and able to support waveguiding, (iii) they must be homogenous and of good optical quality over large dimensions, of the order of centimeters.

Since molecules showing a second-order nonlinearity also tend to be dipolar, the electro-static force works against an oriented polar order and makes the problem of creating noncentrosymmetric molecular assemblies quite difficult. Although macroscopic assemblies of dipolar molecules have been successfully grown in the form of crystals [1–3], the problem of producing a large-area thin film that consists of a noncentrosymmetric supramolecular assembly of nonlinear optical molecules has proven to be an even more difficult problem to

---

* Corresponding author. Tel.: +41-1-633-6559; fax: +41-1-633-1056.
  E-mail address: arashid@iqe.phys.ethz.ch (A.N. Rashid).

tackle. In this work we want to focus on supra-molecular self-assembled structures for use in nonlinear optical applications, hence we will not discuss the solution that consists in including the nonlinear optical molecules in a polymer matrix (either as a guest-host system, or as side chains) and to electrically pole the polymer thin film to achieve noncentrosymmetric packing [4–6].

Excluding polymers, there are two possible approaches that allow dipolar molecules to self-assemble on a substrate to form a thin film: (1) epitaxy on a lattice-matched, noncentrosymmetric substrate, (2) self-assembly on other kinds of substrates.

Although homoepitaxy of a molecule on the lattice-matched surface of its own crystal has been shown to work [7–9], in order to be able to obtain a waveguiding film heteroepitaxy must be used. The need to find a noncentrosymmetric substrate precisely matched to the structure of the molecule one wants to deposit makes this technique very difficult to implement as a general tool for growing organic thin films.

Self-assembly of a noncentrosymmetric film on centrosymmetric or amorphous substrates requires a ''global symmetry breaking condition'' that avoids the formation of independently oriented thin-film growth at different positions on the substrate. Even if one uses molecules that spontaneously form noncentrosymmetric crystals and crystal growth is possible on a substrate, it will generally result in independent nucleation of crystals with different orientations at different positions on the substrate. Subsequent crystal growth will then result in a macroscopically amorphous assembly of nano- or microcrystals, and in large light-scattering losses in waveguides. The ''symmetry breaking condition'' mentioned above can be found, for example, in the substrate structuring used to orient liquid crystals, where it leads to an in-plane ordering of the molecules. For supramolecular structures consisting of small molecules, the one symmetry breaking condition that has been found most successful is the substrate itself, which breaks the symmetry along the direction normal to its surface. Most supramolecular noncentrosymmetric organic thin films have been obtained with this principle [10–12], which

then leads to molecules that tend to orient perpendicular to the substrate and to a polar order in the same direction. For supramolecular structures where the molecular axis is parallel to the substrate, some other symmetry breaking condition that instructs the molecules to align along one particular direction must exist. One possibility is found in Langmuir–Blodgett (LB) films, where the symmetry is broken by the dipping direction, and by the fact that molecules are pre-ordered on the water surface. LB Films with in-plane polar order have been demonstrated [13].

Many attempts have been made to grow thin crystalline films of nonlinear optically active molecules [14–16]. While most of these techniques have the disadvantage that the films do not show large area order (in the cm range), three main techniques have been shown to produce thin films that are preferentially ordered over large dimensions: LB film deposition, Self-assembled monolayers from solution and molecular beam deposition, all of which have advantages and disadvantages. Solution based deposition is relatively easy to set up and has been intensively studied. Vapor phase deposition, on the other hand, while less developed offers the advantage of layer thickness control of organic thin films with very high chemical purity.

1.1. Langmuir–Blodgett films

The LB technique is the first technique that provided the chemist with the capability to construct ordered molecular assemblies. This technique consists of using amphiphilic molecules composed of a hydrophobic tail and a hydrophilic head group and allowing them to accumulate at the air/water interface. In this way a monolayer is formed. Repeating this process allows for the growth of multilayers to be accomplished. Among the advantages that the LB technique offers for the growth of anisotropic thin films are the possibility of easily changing the environmental parameters of a monolayer, the ease and variety in the design of nonlinear optical chromophores and the homogeneous thickness that can be achieved. Most films that have been grown adopted a centrosymmetric

head-to-head or tail-to-tail arrangement. However, this technique has recently been used to obtain noncentrosymmetric thin films with various chromophores, which have been found to display a herringbone arrangement [17–21], with the direction of the herringbone structure given by the dipping direction. The second harmonic intensity was found to depend on the square of the film thickness, showing the ordering obtained over several monolayers, and nonlinear optical waveguides using such films have been successfully demonstrated [22]. While this approach has been relatively successful in obtaining noncentrosymmetric thin films consisting of ~100 monolayers, the LB technique has the disadvantage that it is very time consuming and in many cases the structures are thermally unstable. This thermal instability has been attributed to the weak intermolecular forces within the layers.

1.2. Self-assembly of monolayers from solution

Self-assembled monolayers (SAM) and molecular self-assembly are an attractive alternative approach to second-order nonlinear optical (NLO) materials. This technique is based on the construction of covalently linked, intrinsically acentric superlattices containing molecular chromophoric subunits. SAMs are molecular assemblies that form spontaneously by the immersion of an appropriate substrate into a solution of an active surfactant in an organic solvent [12]. As a result one obtains films consisting of densely packed long chain organic molecules which are chemisorbed on inorganic substrates through a head group which has a specific affinity for the substrate. These materials offer greater net chromophoric alignment, greater number densities and greater stability and structural control than LB films. The general strategy is shown in Fig. 1. As a first step the substrate is thoroughly cleaned, washed and dried to produce a well-defined surface. In the second step the coupling layer is formed. This layer will provide the binding specificity of the NLO chromophore. The next step involves introduction of the chromophore layer. In the last step a capping layer is added to promote structural
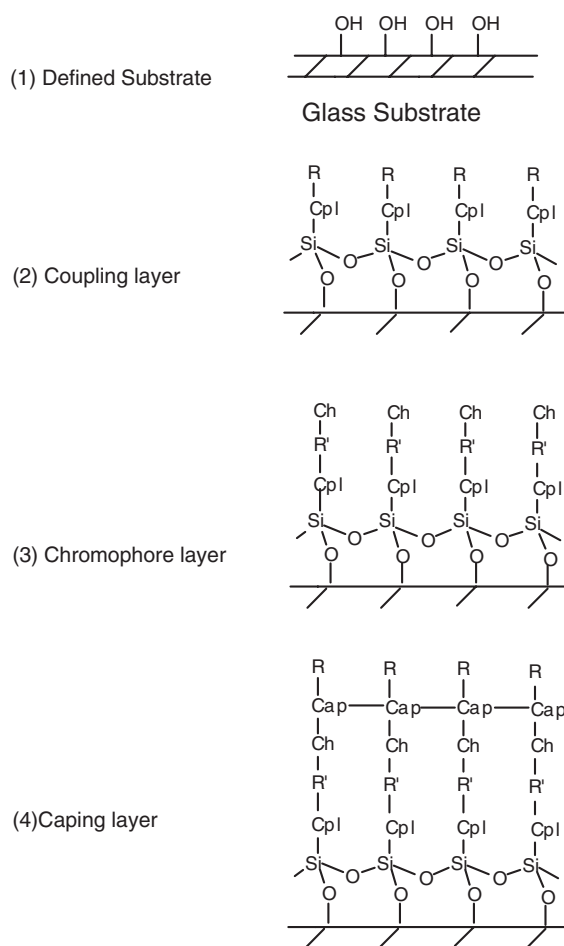

Fig. 1. Schematic representation of the SAM technique. A well defined substrate is successively immersed in various solutions containing the coupling agent (Cpl), the chromophore (Ch), and the capping agent (Cap).

stability. A test of concept synthetic approach to multiplayer NLO materials has been carried out and recently the method has been used to produce robust, densely packed thin films with high nonlinearities and further extended to produce multi-layered films with high nonlinear optical properties [23–25]. The major disadvantage afflicting this technique comes from it being a solution-based technique were side reactions and many molecule interaction can interfere with the deposition process. In addition the rates at which films are grown with this technique are relatively slow for practical uses.

1.3. Molecular beam deposition

Organic molecular beam deposition (OMBD) is a technique that consists in the evaporation of molecules onto a thermally stabilized substrate under high or ultra high vacuum (UHV) condition. This technique is interesting because it has many advantages over the solution based techniques previously mentioned, such as greatly reduced contamination in the UHV environment, a solvent free environment, superior control over growth parameters, and reasonable growth rates. In addition, mask-designed microstructures, such as strip waveguides and integrated hetero-layered structures, can be easily fabricated using this technique.

Organic thin films can be grown, as mentioned before, by epitaxy on a lattice-matched substrate. Such an organic molecular beam epitaxy (OMBE) procedure needs lattice-matched growth conditions and good film-substrate interactions for the achievement of single domain crystalline organic thin films that are required for nonlinear optical applications [26]. This is a major problem with OMBE. In the past the epitaxial growth of selected classes of organic compounds has been demonstrated [27–30], but ordered growth on inorganic substrates could not be achieved due to the incompatibility of lattice parameters and the weak forces between the substrate and the organic films. Because of these difficulties with OMBE, it is very interesting to investigate other possibilities for OMBD that do not require a lattice-matched substrate and epitaxial growth.

In this work, we will show, for the first time to our knowledge, that an almost perfect molecular ordering can be achieved and maintained over thicknesses of the order of 1 μm by vapor deposition of organic molecules on an amorphous glass substrate.

2. Experimental

The growth of organic thin films was carried out by vapor deposition of the material on cleaned amorphous glass substrates. In this technique a molecular beam is formed by evaporating the material of interest in an effusion cell positioned laterally to the substrate. This beam then propagates in the vacuum chamber so that the molecules approach the target without intermolecular interactions. The material was purified by recrystallization and it was subsequently placed in a molybdenum boat in a 10^{-6} Torr vacuum, the substrate was kept at room temperature, the thickness of the films was monitored by a quartz microbalance and determined by ellipsometry and the growth was carried out at a deposition rate of about 5 Å/s. The amorphous glass substrates were cleaned by immersing them in an ultrasonic bath of acetone for 5 min and then in an ethanol bath for 5 min. The substrates were then immersed in a piranha solution (H_2SO_4:30% H_2O_2, 70:30 v/v) and left in it for an hour at 80 °C (warning: piranha solution reacts violently with organic materials), they were then rinsed with deionized water and dried under vacuum at a temperature of 100 °C for 1 h. Semi-empirical calculations with AM1 parametrization, were carried out using the MO-PAC program as implemented in the Ceriuss suit of programs in order to determine the optimized structure of the molecule and its nonlinear optical properties.

We performed transmission second harmonic generation (SHG) experiments where the transmitted, p-polarized SHG signals were measured as the substrate was rotated from normal incidence (0°) to grazing incidence (~90°) for both polarization of the incident fundamental light. We used 7 ns long optical pulses from a Q-switched Nd:YAG laser at a wavelength of 1064 nm. Blank glass substrates showed no measurable nonlinear response under the same excitation conditions.

3. Results and discussions

We believe that the best way to overcome the individual disadvantages of the various techniques mentioned above is to combine their main principles into new ideas. Using the advantages that each individual technique has to offer could compensate for the disadvantages of the other. In this vein, experiments have been conducted that combine the molecular design principles used in the LB

and SAM techniques so as to preferentially orient the molecules perpendicular to the substrate surface with the OMBD in order to have better control of the growth process of the thin films. These experiments in fact showed that growth of preferentially oriented organic thin films on amorphous inorganic substrates by OMBD is indeed possible.

The first issue that had to be tackled is the structural incompatibility of most organic molecules with the inorganic substrates discussed previously. A preferential unidirectional orientation of the chromophores has been obtained perpendicular to the surface of an amorphous substrate. In this approach, use is made of the natural symmetry breaking features of the substrate surface. The thin films are based on a hydrazone derivative named 5-bromo-5′-formyl-2, 2′-bithiophene 4-nitrophenyl hydrazone (BITINPH) similar to other hydrazone derivatives developed for second order nonlinear optics [31]. The structure is shown in Fig. 2(a). In the solid state, it shows relatively high nonlinearities, as observed by the Kurtz powder test. The molecules are designed with two hydrogen-bonding sites (Fig. 2(a)), which we believe to be involved in the out of plane ordering mechanism (Fig. 2(b)). One site corresponds to the oxygen on the nitro group that acts as hydrogen bond acceptor and the other site corresponds to the NH group that acts as the hydrogen bond donor. The nitro group site allows the molecules to interact with hydroxyl groups on the substrate surface via an O–H⋯O hydrogen bond. The molecule thus orients itself out of the plane of the substrate. The other site (NH) serves as an interaction site with the nitro groups of other molecules via an N–H⋯O hydrogen bond, thus forming a pseudo polymer chain that extends out of the substrate plane. The fact that one hydrogen-bonding site can only act as a donor and the other can only act as an acceptor guarantees that the molecules will build an oriented "polymer" chain. By designing the organic molecule so that one end posses a hydrogen bond acceptor and the other a hydrogen bond donor, one ensures that the ordering that will take place is unidirectional.

Thin films grown with this methods do not require a periodic order in the substrate, which
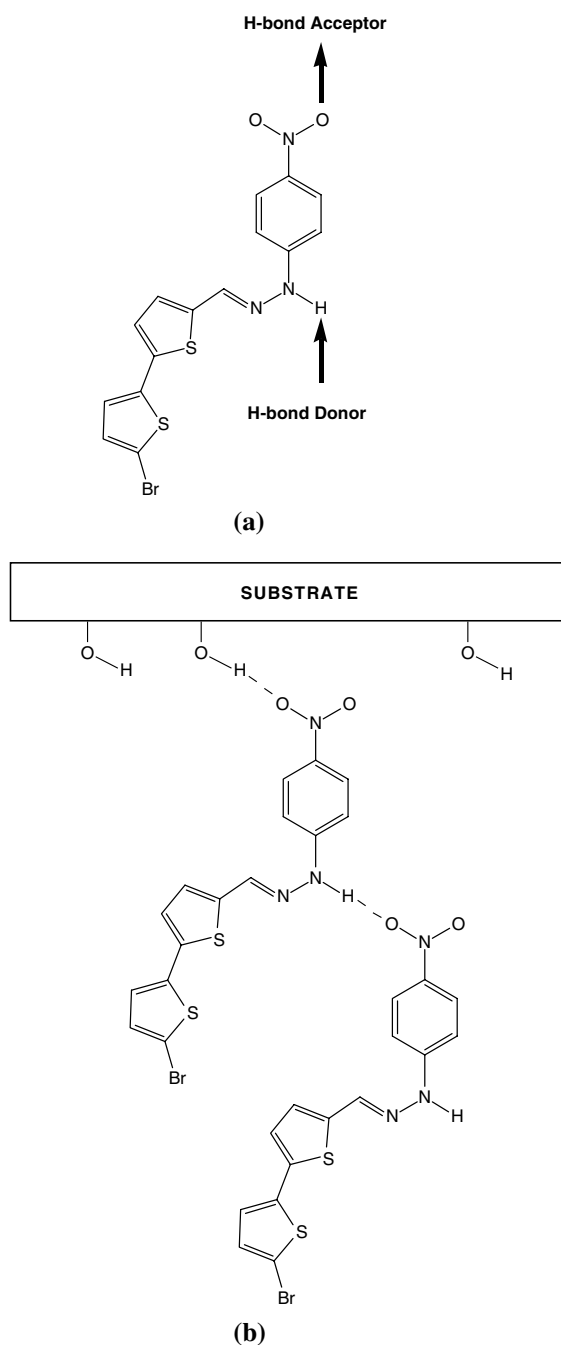
(a)

(b)

Fig. 2. (a) Chemical structure of BITINPH. (b) Model for out of plane alignment.

makes them compatible with many different substrates, overcoming in this way the restrictions on
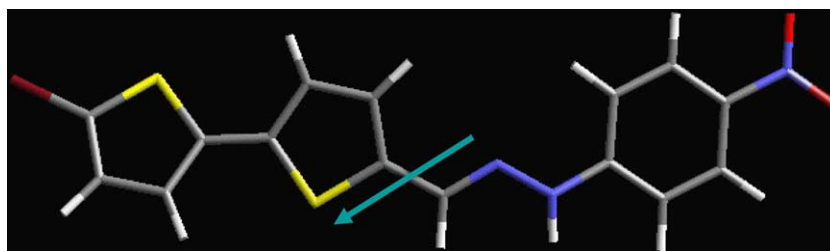
Fig. 3. MOPAC optimized structure of BITINPH.

the choice of substrate imposed by lattice matching.

Fig. 3 shows the optimized structure of the BITINPH with the dipole moment superimposed on the structure. Table 1 shows the calculated tensor elements of the molecular hyperpolarizability. This table shows that there is only one major component of the tensor that contributes to the second-order properties of this molecule. These results show that the molecule can be thought of as a one-dimensional rod like molecule.

The Polarized absorption spectra which were measured using s- and p-polarized light at different incidence angles were measured and from these spectra, the dichroic ratio, defined as (Ap−As)/(Ap+As), can be determined (Table 2). Here Ap and As are the absorptions due to p-polarized and s-polarized light respectively. A difference in absorption for p- and s-polarized light indicates a different projection of the molecular properties unto the directions of the optical electric field corresponding to s- and p-polarization [32,33]. Table 2 shows the dichroic ratio calculated from the polarized absorption spectra of an approximately 150 nm thick BITINPH thin film at four different incidence angles. The dichroic ratio is seen to increase when moving away from normal incidence to larger angles, corresponding to a situation where the electric field of the light acquires a component perpendicular to the substrate. These results demonstrate that the axis of largest optical

polarizability is oriented perpendicular to the substrate, corresponding to a molecular tendency for orientation normal to the film plane.

The measurement of second-order nonlinear optical susceptibilities $[d_{ijk} = \chi^{(2)}_{ijk}(-2\omega, \omega, \omega)/2d_{ijk}]$, gives further confirmation of the molecules orientation while providing additional details on the degree of molecular ordering. Fig. 4 shows the transmitted p-polarized SHG for both p- and s-polarized excitation light at 1064 nm. No strong azimuthal orientation was observed within the substrate plane in these experiments. This indicates that the films posses uniaxial symmetry about the substrate normal [34–36]. We define this direction as the 1-direction, and assume rotational symmetry around it, so that the only nonvanishing nonlinear optical coefficients that describe the deposited film are d_{111} and $d_{133} = d_{313} = d_{122}$ (we assume Kleinmann symmetry) [37]. The effective nonlinear optical coefficient whose square ampli-

Table 2
Dichroic-ratio calculated from the polarized absorption spectra of an approximately 150 nm thick BITINPH thin film at three different incidence angles

Incidence angle (deg)	Dichroic-ratio
0	0
60	0.05
50	0.13
40	0.17

Table 1
MOPAC calculated hyperpolarizability tensor elements

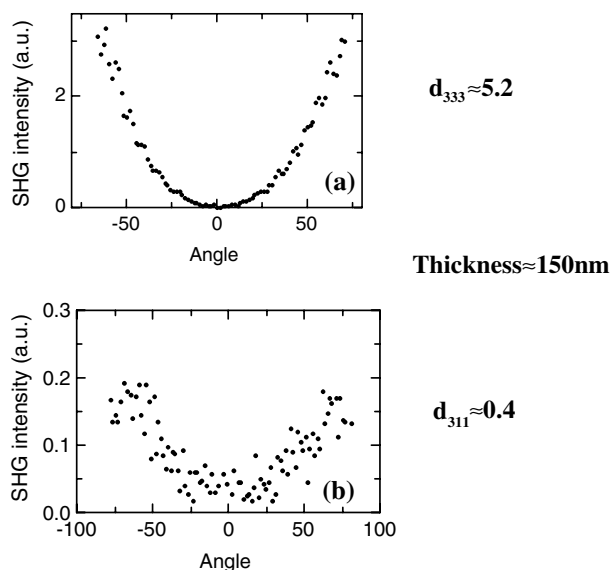| β_{XXX}	β_{XYY}	β_{XZZ}	β_{YYY}	β_{YXX}	β_{YZZ}	β_{ZZZ}	β_{ZXX}	β_{ZYY}
2463	14	1	12	114	1	1	44	1

Fig. 4. (a) Transmitted p-polarized SH intensity at 532 nm as a function of the angle of incidence of an (a) s- and (b) p-polarized beam.

tude gives the efficiency of the SHG process is then given by

$$p \rightarrow p : d_{\text{eff}}(b) = d_{111} \cos^3(b) + 3d_{133} \cos(b) \sin^2(b) \tag{1}$$

$$s \rightarrow p : d_{\text{eff}}(b) = d_{122} \cos(b) \tag{2}$$

The flatness of the data near normal incidence in the p-p measurement of Fig. 4(a) is an indication that the contribution from d_{133} is quite small, a fact that is confirmed by the s-p measurement which explicitly determines d_{133} (Fig. 4(b)). The value the of nonlinear optical coefficient d_{111} can be determined by calibrating the SHG intensities from the films with the intensities measured from a reference quartz crystal, which has a nonlinear optical coefficient $d_{111} = 0.3$ pm/V. In this way a value of d_{111} of 5.2 ± 0.2 pm/V and d_{133} of 0.4 ± 0.2 pm/V was obtained for films with thickness of approximately 100 and 800 nm. The second harmonic intensity was measured at various points on the same film in order to evaluate the homogeneity of the films. The films had dimensions of about 3 cm × 3 cm and the second harmonic intensity varied only to within less than 15% indicating a high homogeneity of the film. An additional important

observation is that the second harmonic intensity increased quadratically with film thickness up to a thickness of 800 nm, this fact confirms the regularity and the thickness-independence of the non-centrosymmetric order. This also shows that the symmetry-selective self-assembly process initiated by the substrate, becomes independent from the substrate, and is determined only by the molecular arrangement as the film grows.

The ratio between the experimentally determined values of d_{111} and d_{133} is quite large (≈ 13) when compared to, e.g., poled electro-optic polymers where the ratio between these coefficients is near 3 indicating that the preferential molecular orientation is only a small trend riding on an essentially random orientational distribution. This large ratio measured for our films is an indication that the nonlinear optical properties of our films are not given by just a small preferential orientation, but are indeed determined by a much more regular molecular arrangement. Specifically, the average orientation of the axis of electronic delocalization of the individual molecules (corresponding to the largest diagonal molecular hyperpolarizeability) must be perpendicular to the substrate with only a small statistical variance.

This is the first time to our knowledge that such a good noncentrosymmetric molecular orientation is obtained over macroscopic film thicknesses and large surface areas by vapor deposition of a single molecular species on an amorphous substrate. Inducing the noncentrosymmetric order by using selective hydrogen bonding to the substrate and between the molecules leads to a much better molecular ordering than with the technique described in [13], which requires control of the molecular beam direction relative to the substrate. Because the present technique combines the advantages of the solution based techniques with those of the vapor deposition techniques a much simpler and faster way for the growth of order thin films is obtained.

4. Conclusions

Several methods to produce homogenous nonlinear optical organic thin films have been reviewed. The methods based on the OMBD technique, once applied to high-nonlinearity molecules offer many advantages over solution-based techniques (like purity, high control of film thickness, and a high density of chromophres). We have shown a simple and efficient new method to produce supramolecular self-assembled thin films with well-defined polar ordering perpendicular to the substrate surface. This method combines the advantages of solution base techniques with the advantages offered by vapor deposition techniques thus providing a much simpler and faster way for the growth of order thin films.

The resulting films are homogenous over a large area, and a regular, molecular ordering can be maintained over a large thickness of the order of 1 μm. The fact that the films were grown on amorphous glass substrates circumvents the need for surface epitaxy. The quality of the films and the simplicity of the fabrication method make this novel technique very attractive for the fabrication of nonlinear optical waveguides for frequency conversion or electro-optic modulation. Despite the relatively low nonlinearity ($d_{111} = 5$ pm/V) that has been obtained in this first demonstration, the high degree of molecular ordering and the fact that

the films consist of only one component make them potentially very interesting when compared to present candidates for organic electro-optic modulators, poled polymers. The higher degree of order and tighter molecular packing in our films should also lead to a better photostability when compared to amorphous systems with embedded chromophores.

A further detailed investigation of the mechanism that leads to the molecular ordering as well as optimization of the growth conditions is being performed. Since the ordering in these films can be maintained over large thicknesses, a study of the waveguiding properties of these films is also planned. This may lead to a new generation of organic waveguides for frequency conversion and electro-optic modulation.

Acknowledgements

References

[1] M.S. Wong, C. Bosshard, P. Günter, Ferroelectrics 202 (1991) 51.
[2] C. Serbutoviez, C. Bosshard, G. Knöpfle, P. Wyss, P. Pretre, P. Günter, K. Schenk, E. Solari, G. Chapuis, Chem. Mater. 7 (1995) 1198.
[3] R. Masse, M. Bagieu-Bucher, J. Pecaut, J.P. Levy, J. Zyss, Nonlinear Opt. 5 (1993) 413.
[4] K.D. Singer, J.E. Sohn, S.J. Lalama, Appl. Phys. Lett. 49 (1986) 248.
[5] C. Ye, N. Minami, T.J. Marks, J. Yang, G.k. Wong, Macromolecules 21 (1988) 2901.
[6] Z. Peng, L. Yu, Macromolecules 27 (1998) 2638.
[7] T. Gotoh, S. Fukuda, T. Yamashiki, Nonlinear optics, in: S. Miyata (Ed.), Proceedings of the Fifth Toyota Conference on Nonlinear Optical Materials, Aichi-ken, Japan, 6–9 October 1991, Elsevier, Amsterdam, 1992, p. 219.
[8] R. Schlesser, T. Dietrich, Z. Sitar, F. Gitmans, A. Kündig, L. Eng, B. Munch, P. Günter, J. Appl. Phys. 78 (1995) 494.
[9] S.R. Forrest, Chem. Rev. 97 (1995) 1793.
[10] G.J. Ashwell, J. Mater. Chem. 9 (1999) 1991.

[11] T.J. Marks, M.A. Ratner, Angew. Chem. Int. Ed. Engl. 34 (1995) 155.

[12] A. Ulman, Chem. Rev. 96 (1996) 1533.

[13] G. Decher, B. Tieke, C. Bosshard, P. Günter, J. Chem. Soc. Chem. Commun. 133 (1998) 933.

[14] L. Zhou, M. Thakur, J. Mater. Res. 13 (1998) 13.

[15] M. Baldo, M. Deutsch, P.E. Burrows, H. Gossenberger, M. Gerstenberg, V. Ban, S. Forrest, Adv. Mater. 10 (1998) 1505.

[16] S. Gauvin, J. Zyss, J. Cryst. Growth 166 (1996) 507.

[17] G. Decher, B. Tieke, C. Bosshard, P. Günter, J. Chem. Soc. Chem Commun. 189 (1988) 933.

[18] C. Bosshard, G. Decher, B. Tieke, P. Günter, Poc. SPIE-Int. Soc. Opt. Eng. 141 (1988) 1017.

[19] G. Decher, B. Tieke, C. Bosshard, P. Günter, Ferroelectrics 91 (1989) 193.

[20] H. Nakahara, W. Liang, H. Kimura, T. Wada, H. Sasabe, J. Opt. Soc. Am. B 15 (1999) 458.

[21] W. Liang, H. Nakahara, H. Kimura, T. Wada, H. Sasabe, Thin Solid Films 423 (1998) 327.

[22] C. Bossard, M. Florsheimer, M. Küpfer, P. Günter, Opt. Commun. 85 (1991) 247.

[23] D. Li, M.A. Ratner, T.J. Marks, C. Zhang, J. Yang, G.K. Wong, J. Am. Chem. Soc. 112 (1990) 7389.

[24] A. Facchetti, M.E. van der Boom, A. Abbotto, L. Beverina, T.J. Marks, G.A. Pagani, Langmuir 17 (2001) 5939.

[25] M.E. van der Boom, A.G. Richter, J.E. Malinsky, P.A. Lee, N.R. Armstrong, P. Dutta, T.J. Marks, Chem. Mater. 13 (2001) 15.

[26] R. Schlesser, T. Dietrich, Z. Sitar, F. Gitmas, A. Kundig, L. Eng, B. Munch, P. Günter, J. Appl. Phys. 78 (1995) 4943.

[27] M. Mobus, N. Karl, T. Kobayashi, J. Cryst. Growth 116 (1992) 495.

[28] C.D. Englund, G.E. Collins, T.J. Schuerlein, N.R. Armstrong, Langmuir 10 (1994) 2748.

[29] E.I. Haskal, F.F. So, P.E. Burrows, S.R. Forrest, Appl. Phys. Lett. 60 (1992) 3223.

[30] Y. Ito, M. Hikita, T. Kimura, Jpn. J. Appl. Phys. 29 (1990) 1128.

[31] C. Serbutoviez, G. Knopfle, P. Gunter, E. Solari, G. Chapuis, Chem. Mater. 7 (1995) 1198.

[32] A. Rodger, B. Norden, Circular Dichroism and Linear Dichroism, Oxford Univ. Press, Oxford, 1997.

[33] L.V. Natarajan, F.M. Stein, R.E. Blankeship, R. Chang, Chem. Phys. Lett. 95 (1983) 525.

[34] H.E. Kaatz, G. Sceller, M.T. Putvinski, M.L. Schilling, W.L. Wilson, C.E.D. Chidsey, Science 254 (1991) 1485.

[35] T.J. Marks, M.A. Ratner, Angew. Chem. Int. Ed. Engl. 34 (1995) 155.

[36] D. Li, B.I. Swanson, J.M. Robinson, M.A. Hoffbauer, J. Am. Chem. Soc. 115 (1993) 6975.

[37] D.A. Kleinman, Phys. Rev. 126 (1962) 1977.