In-plane alignment of noncentrosymmetric molecules by oblique-incidence molecular beam deposition

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

Chengzhi Cai, Armin Kündig, Ye Tao, Martin Bösch, Matthias Jäger, Christian Bosshard, and Peter Günter
Nonlinear Optics Laboratory, Institute of Quantum Electronics, ETH Zürich, CH-8093 Zürich, Switzerland

(Received 9 October 1998; accepted for publication 30 March 1999)

The preferential orientation of noncentrosymmetric, organic molecules with intermolecular bonding is realized by means of oblique-incidence molecular beam deposition. The in-plane anisotropy in the optical properties of the thin films is shown by transmission spectra of ultraviolet light. Second-harmonic generation measurements demonstrate the preferential orientation of the molecules aligned in-plane. In addition, the dependence of the second-harmonic light intensity on the film thickness reveals the dominance of bulk effects with respect to surface contributions. Therefore, this molecular alignment technique is a promising method to produce stable thin films for applications in linear and nonlinear optics. *© 1999 American Institute of Physics.*
[S0003-6951(99)04221-7]

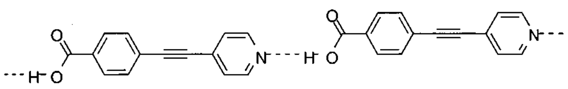
The breaking of symmetry in condensed-matter systems is responsible for many physical phenomena, including optical second-harmonic generation (SHG); the frequency doubling of light.[1] For surfaces and interfaces, the symmetry is broken by definition, and second-harmonic light can be observed. Bulk materials, however, exhibit SHG only if noncentrosymmetric constituents have a noncentrosymmetric order. For optically active organic thin films, this is achieved, e.g., by the use of the Langmuir–Blodgett (LB) technique.[2] Here, amphiphilic molecules comprising a hydrophilic head—the chromophore—and a hydrophobic tail are aligned at the air–water interface, and the resulting ordered monolayer is transferred to the desired substrate. For a practical use of the noncentrosymmetric monolayer, one has to build up a structure of many individual monolayers. Although this has been realized for several optically active molecules, the LB technique is often time consuming and the structures are sometimes thermally unstable. The low thermal stability may arise from the fairly small intermolecular forces within the layers. The stability of the ordered structures may be significantly improved if the molecules are aligned in-plane and connect to each other by chemical bonding.

In this letter, we report that nonlinear optically active thin films can be produced by oblique-incidence deposition of organic molecules, which are connected in a head-to-tail fashion via hydrogen bonds. It is well know from some inorganic systems that oblique incidence of the molecular beam results in growth anisotropies. These anisotropies which include the structural, magnetic, and optical properties of the thin films have been verified by different techniques.[3] Here, we show the growth anisotropy by transmission measurements of ultraviolet (UV) light. But more important, using SHG we demonstrate that the organic molecules are in-plane aligned, so that the heads of the molecules are directed on average.

The molecular structure of the two noncentrosymmetric, organic molecules ([4-pyrid-4-yl-ethynyl-benzoic acid]–PEBA and [4-trans-2-(pyrid-4-yl-vinyl) benzoic acid]–PVBA), we have designed and synthesized, is given in Fig. 1. Both molecules are characterized by a pyridyl and carboxylic group giving rise to strong intermolecular hydrogen bonding verified for the sublimated powders by solid state ^{15}N-NMR spectroscopy.[4] A consequence of this are the rather high melting points of PEBA (300 °C) and PVBA (350 °C) measured by differential scanning calorimetry.[5] Hence, this class of materials is thermally very stable which is a prerequisite for any application.

The organic molecules are sublimated from molecular beam effusion sources at a temperature of 220 °C under ultrahigh vacuum conditions (6×10^{-9} mbar). At this temperature the hydrogen bonds are meant to be broken while the molecules themselves are intact.[6] The incident molecular beam had an angle of about 30° with respect to the surface normal. This rather small angle guarantees the thickness ho-

(a) [4-pyrid-4-yl-ethynyl-benzoic acid] - **PEBA**



(b) [4-trans-2-(pyrid-4-yl-vinyl) benzoic acid] - **PVBA**

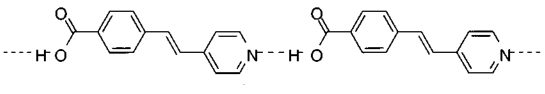


FIG. 1. Molecular structure of (a) PEBA and (b) PVBA.

[a)] Present address: ETH-BWB, Wagistr. 23, CH-8952 Schlieren, Switzerland. Electronic mail: mueller@biocomp.mat.ethz.ch

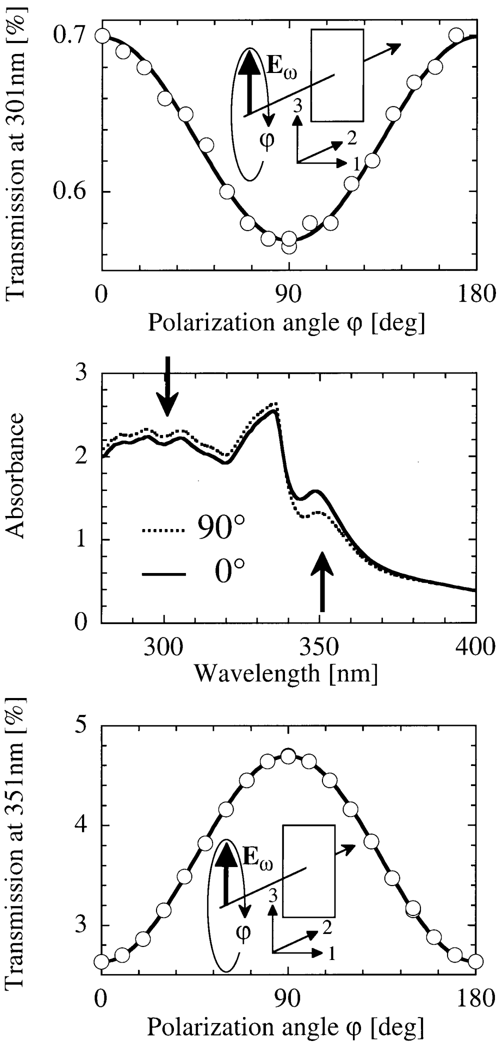


FIG. 2. Transmission measurements of UV light for a 270-nm-thick PEBA film on fused silica (Suprasil®) deposited at a substrate temperature of 100 °C and a deposition rate of 5.5 nm/min. The upper and lower images represent the transmission vs polarization angle at a wavelength of 301 and 351 nm, respectively, following perfectly a sine and shifted to each other by 90°. The central part shows the anisotropy of the absorbance.

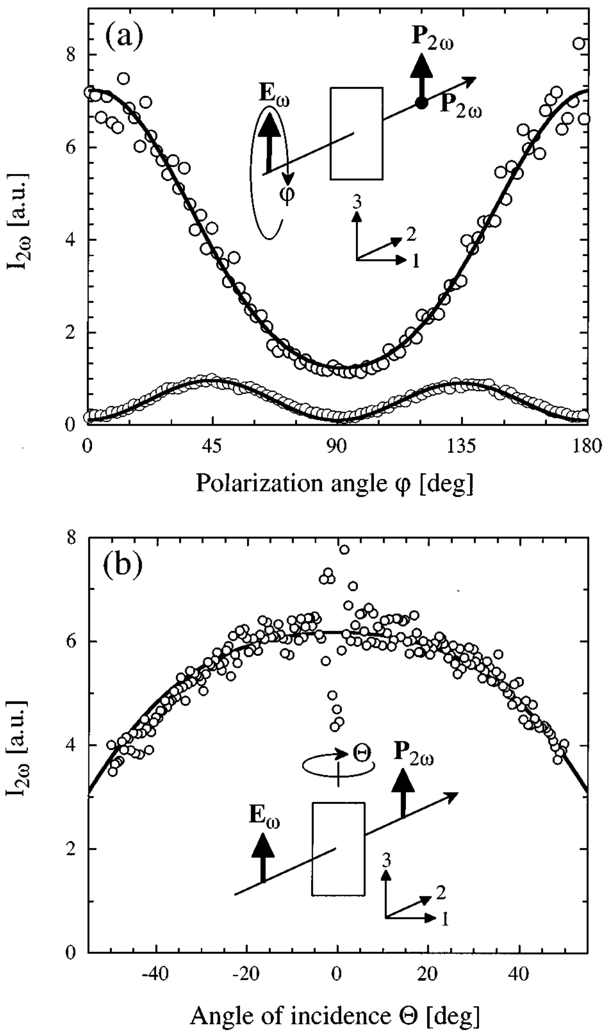


FIG. 3. SHG intensity as a function of the polarization angle and the angle of incidence. The PEBA thin film with a thickness of 180 nm was deposited on fused silica at a substrate temperature of 100 °C and a deposition rate of 5 nm/min.

mogeneity, it results, however, in anisotropic optical film properties. This in-plane optical anisotropy, i.e., the linear dichroism,[7] is demonstrated by typical UV spectra in Fig. 2. The transmission of the 270-nm-thick PEBA film grown on fused silica (Suprasil®) at a substrate temperature of 100 °C with a deposition rate of 5.5 nm/min has been measured *ex situ* by a Spectrophotometer (Lambda 9–Perkin-Elmer). While for wavelengths between 280 and 338 nm the absorbance is higher when the polarizer is perpendicular to the plane of incidence of the molecular beam, for wavelengths above 338 nm the absorbance becomes higher parallel to the incident beam. The polarization dependencies of the transmission always show the well-known sinusoidal behavior, but at the neutral point of 338 nm the phase shifts by 90° indicating excitations parallel and perpendicular to the molecules. Two characteristic curves (301 and 351 nm) are given in Fig. 2. This optical anisotropy reveals the preferential alignment of the molecules within the plane of incidence. Due to the geometry of the deposition experiment that only induces an anisotropy within the plane of incidence, it is plausible that the net orientation of the long axis of the molecules is parallel to the plane of incidence. This reflection of the symmetry is backed by the observation that the main peak at 350 nm does not change its position by the replacement of fused silica by glass or sapphire substrates. The exchange of the organic material, however, PVBA instead of PEBA, shifts the peak to a wavelength of 373 nm.[6] This means that the main peak is characteristic for the organic material and may be attributed to the long axis polarized transition.

Light transmission is independent of the polarity of the aligned molecules. SHG, on the other hand, is a nonlinear method and sensitive to the macroscopic charge transfer which is the average of the charge transfer within the individual molecules. Therefore, using SHG one can detect structural anisotropies due to the preferential orientation of the molecules. We have observed strong polarization dependent second-harmonic light by the use of a B.M.I. Nd:YAG laser (wavelength 1064 nm, pulse duration 25 ns, repetition rate 30 Hz) in transmission mode (Fig. 3). The maximum of intensity $I_{2\omega}$ is found when the polarizers are parallel to the plane of incidence of the molecular beam. As expected from the transmission measurements, the in-plane component of the effective charge transfer has its maximum in direction 3,

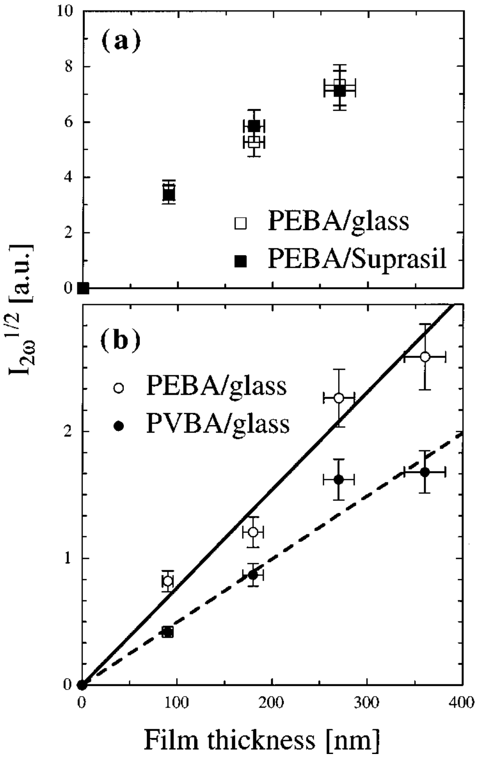


FIG. 4. Variation of the square root of the SHG intensity with the film thickness. (a) PEBA on glass an fused silica grown at a substrate temperature of 100 °C and a deposition rate of (4±1) nm/min; (b) PEBA and PVBA on glass deposited at a substrate temperature of 30 °C and a rate of (4±1) nm/min.

along the long axis of the molecules. The related nonlinear optical coefficient $d_{333}=(0.8\pm 0.1)$ pm/V is determined using the standard Maker-fringe technique [calibration reference $d_{11}(\text{quartz})=0.3$ pm/V]. The refractive indices for fundamental and second-harmonic light are found to be 1.75 and 1.82, respectively.[5] The dependence of the SHG intensity on the angle of incidence Θ [Fig. 3(b)] shows that d_{333} has its maximum at $\Theta=0$. Therefore, the molecules are preferentially oriented *in-plane.* Hence, besides d_{333} only the coefficient $d_{311}=d_{131}=d_{113}$ is of significance. The ratio of the nonlinear optical coefficients $d_{333}/d_{311}=(2.8\pm 0.3)$ is derived from the data in Fig. 3(a). The nonlinearity of our samples is still low but it should be raised by the use of chromophores with stronger donor and acceptor substitutes or improved ordering by optimized growth conditions.

Because the nonlinearity is quite small, one may come to the conclusion that the second-harmonic light is only generated at the interfaces. A significant contribution of the interfaces of the organic film to the SHG intensity, however, is excluded since the peak intensity of the SHG signal increases quadratically with the film thickness as shown in Fig. 4. The film thickness was measured *in* and *ex situ* by ellipsometry, atomic force microscopy, and alpha-step.[5] In the upper part of Fig. 4 we compare PEBA films grown under identical conditions on fused silica and simple glass substrates whereby in the lower part the different organic molecules are deposited on glass substrates. Due to the geometry chosen for this experiment (both polarizers parallel to the plane of incidence, the slope of the curves corresponds to the nonlinear coefficient d_{333}. In agreement with the former analysis, we have found $d_{333}(\text{PEBA})=(0.77\pm 0.05)$ pm/V and $d_{333}(\text{PVBA})=(0.50\pm 0.03)$ pm/V.

The alignment of the molecules due to external fields or due to a groovelike substrate morphology is ruled out by the following experiments. In a first experiment, the sample was rotated by 180° after deposition of half the film thickness. Due to the induced sign reversal of the nonlinearity, the SHG signal was reduced by a factor of 20. At both ends, where the sample was shadowed by the holder, the film has only half thickness, and we have found the expected SHG intensity. In a second experiment, the substrate was cut into four pieces rotated to each other by 90° and fixed at the holder before deposition. We found an anisotropy of the films measured by transmission and SHG, which was only given by the deposition geometry and not by the substrate orientation. In addition, we have performed preliminary deposition experiments in a different MBE chamber where the angle of incidence of the molecular beam was varied from 10° via 20° to 30° with respect to the surface normal. Here, both the linear dichroism as well as SHG intensity increases considerably. Therefore, we conclude the oblique incidence of the molecular beam is the key element for the fabrication of ordered thin films by the present method. It opens up the possibility to choose the direction of the in-plane alignment of the organic molecules by *in situ* substrate rotation.

In conclusion, we have demonstrated that oblique-incidence molecular beam deposition can result in anisotropic thin films with a preferential orientation of the molecules even on amorphous substrates. Due to the intermolecular hydrogen bonding the organic films are stable enough for potential applications in linear and nonlinear optics.

Financial support of the Swiss Priority Program, ''Optique II'' is gratefully acknowledged.

[1] N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin, New York, 1965); Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).
[2] G. Roberts, *Langmuir-Blodgett Films* (Plenum, New York, 1990); A. Ulman, *Ultrathin Organic Films from Langmuir–Blodgett to Self-Assembly* (Academic, Boston, 1991); C. Bosshard, K. Sutter, P. Prêtre, J. Hulliger, M. Flörsheimer, P. Kaatz, and P. Günter, *Organic Nonlinear Optical Materials* (Gordon and Breach, Basel, 1995); J. Zyss, *Molecular Nonlinear Optics Materials, Physics, and Devices* (Academic, San Diego, 1994); V. Mizrahi, G. I. Stegeman, and W. Knoll, Chem. Phys. Lett. **156**, 392 (1989); K. Kajikawa, H. Takezoe, and A. Fukuda, *ibid.* **205**, 225 (1993).
[3] Y. Park, E. E. Fullerton, and S. D. Bader, Appl. Phys. Lett. **66**, 2140 (1995); L. Jorritsma, *Growth Anisotropies in Cu(001) Homoepitaxy* (Wormgoor, Almelo, Netherlands, 1997); Y. Takeda, T. Motohiro, T. Hioki, and S. Noda, J. Vac. Sci. Technol. B **16**, 7 (1998).
[4] C. Cai, M. Bösch, Y. Tao, B. Müller, Z. Gan, A. Kündig, C. Bosshard, I. Liakatas, M. Jäger, and P. Günter, J. Am. Chem. Soc. **120**, 8563 (1998).
[5] B. Müller, M. Jäger, Y. Tao, A. Kündig, C. Cai, C. Bosshard, and P. Günter, Opt. Mater. **12**, 345 (1999).
[6] B. Müller, C. Cai, M. Bösch, M. Jäger, C. Bosshard, P. Günter, J. V. Barth, J. Weckesser, and K. Kern, Thin Solid Films **343–344**, 168 (1999).
[7] A. Rodger and B. Nordén, *Circular Dichroism and Linear Dichroism* (Oxford University Press, Oxford, 1997).