Organic electro-optic thin films by simultaneous vacuum deposition and laser-assisted poling

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Received May 23, 2011; revised June 17, 2011; accepted June 23, 2011; posted June 27, 2011 (Doc. ID 148111); published July 22, 2011

Organic materials with a high second-order optical nonlinearity have an important application for the next generation of computing, telecommunications, and other industries. Because of a high electro-optic coefficient and low dielectric constant, N-benzyl-2-methyl-4-nitroaniline (BNA) single crystals have been grown and their optical properties have been extensively studied. In this Letter, a poled BNA thin film material was prepared through simultaneous vacuum evaporation and laser-assisted electrical poling. The linear electro-optic coefficients of BNA were measured by a Young’s two-slit interference electro-optic measurement method. The dependence of the resulting electro-optic properties on optical power was explored. Enhancement induced by laser illumination was demonstrated. The BNA thin film can exhibit an n_{31} value comparable to that of BNA single crystals. © 2011 Optical Society of America

OCIS codes: 190.4710, 310.6860, 160.2100.

Organic electro-optic (EO) materials with large optical nonlinearities are mainly divided into two classes: poled polymers and organic crystals. For poled polymers, ancentric order (and thus EO activity) is induced by electric field poling (or by laser-assisted electric field poling) near the glass transition temperature of the material [1]. In this work, the same principle is extended to thin films of vacuum deposited organic EO crystals. Compared to poled EO polymers, organic EO crystals can have several advantages. For example, the loading density (concentration) of the nonlinear optic (NLO) molecules in the EO polymer is usually limited to about 30% (although higher values can be achieved for certain classes of poled polymers and dendrimers [1]), while EO crystals are composed entirely of NLO molecules. The orientational alignment of NLO molecules in poled EO polymers is thermodynamically unstable and is subject to relaxation over time, although the rate of such relaxation can be greatly reduced in a more rigid polymer matrix [1]. In contrast, the alignment of NLO molecules in a crystal is thermodynamically stable with no gradual relaxation below the melting temperature of the material. EO crystals can also have much better photostability than poled EO polymers [2]. Bulk organic EO crystals can be grown from solution and melt; however, most optical waveguide devices require thin films of EO material instead of bulk crystals. Crystalline thin films of organic EO materials have been grown in waveguide channels and specially structured templates, but often the crystal orientation obtained in these methods is not ideal for the operation of the device. In this Letter, a novel method of fabricating organic EO films is presented by utilizing direct-laser-assisted electric field poling during vacuum deposition. Benzyl-2-methyl-4-nitroaniline (BNA) thin films are simultaneously deposited and poled, and the polycrystalline BNA thin films of small angle domains are achieved. The enhanced EO effects of laser-assisted electrical poling of BNA are evaluated by using the Young’s two-slit interferometry. The results show that the high EO coefficient of N-BNA [3] thin films is comparable to those of bulk single crystals of the same material.

BNA is one of the NLO materials that can be grown into noncentrosymmetric crystals. This property has made this material useful in generating strong terahertz waves and thus it could also be useful in high-speed EO devices. Previously, BNA crystals were grown by slow cooling of melt with the presence of a crystal seed.

BNA was synthesized following the process of [4]. BNA has a strong absorption in the wavelength range of 400 to 500 nm [5]. BNA is a crystalline powder and has a melting point of 105 °C at normal atmospheric pressure [2]. The melt BNA can be evaporated in a thermal heater under vacuum and be deposited on substrates to form a polycrystalline thin film.

In our poling experiment, the substrates with coplanar Ti electrodes of two slits [6] of typically 5 μm wide were prepared lithographically on glass wafers. The procedure of simultaneous evaporation of EO thin film and laser-assisted electrical poling is shown in Fig. 1. An electric poling field was applied to the laser-illuminated sample when EO material was thermally evaporated onto the sample. The heated EO material was deposited on a

Fig. 1. (Color online) Schematic of the simultaneous EO material deposition and laser-assisted electrical poling of a two-slit sample.

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substrate at 5 x 10⁻⁶ Torr. The substrate with coplanar electrodes was mounted on a sample platform and kept at 40 °C with a substrate heater. The poling electric field across the slit was supplied by a DC source. The DC poling field promoted alignment of the polar NLO molecules in the direction of the poling field. A polarized CW laser beam (λ = 473 nm) passed through the glass vacuum chamber to illuminate the two slits in which the orientation of BNA molecules was desired. The incident laser was normal to the surface and the polarization of the light was parallel to the slits. This arrangement permitted the optical energy to be transferred more efficiently to molecules that lay perpendicular to the poling field in order to provide them with additional energy to rotate in the poling field.

BNA powder in a thermal evaporation source was heated at a rate of 10 °C/min. The evaporation temperature was kept at the optimal deposition temperature of 98 °C for 30 min with laser illumination and poling field applied. The thickness of evaporated BNA film was about 400 nm. The pump laser beam (λ = 473 nm) with linear polarization parallel to the slits (perpendicular to the electric poling field) was used to illuminate the two slits during deposition. After the required thickness of the film was obtained and deposition was stopped, the laser and substrate heater were turned off at the same time, and the electric poling field was kept on for an additional 90 min period.

Figure 2 is a scanning electron microscopy (SEM) image that shows the poled BNA thin film around one slit. It is clear from the image that the BNA crystal domains in the slit are well aligned along the electric field direction.

EO coefficients of direct-laser-assisted poling BNA were measured utilizing the Young’s two-slit interference method. The details of this method can be found in [6]. Both EO coefficients r₃₃ and r₁₃ can be independently measured using different polarization of the incident beam.

Laser-assisted electrically poled samples of BNA thin films were made at a poling field of 5 V/μm. The EO coefficient r₃₃ of the laser-assisted poling BNA thin films is shown in Fig. 3(a). r₃₃ initially increased with laser power. However, for a laser intensity beyond 1.6 mW/cm², r₃₃ began to decrease and became smaller as the power was increased further. This decrease could be caused by increased photocurrent through the BNA thin film. The relationship of measured r₃₃ at the 1550 nm measurement wavelength and laser power in BNA thin films is similar to the relationship between r₃₃ and laser-assisted poling power in EO polymers [1]. Figure 3(b) shows the relationship between the ratio r₃₃/r₁₃ and laser intensity. The ratio is an indicator of the degree of the alignment of NLO molecules, and when the r₃₃ reached its peak value, the ratio of r₃₃/r₁₃ also reached its peak, meaning the BNA molecules were optimally aligned. Results in Fig. 3 clearly show the strong effect of laser illumination on the alignment of BNA. At the optimal laser power intensity, the laser illumination produced a threefold increase of r₃₃.

Based on the theory of macroscopic EO effect of aligned second-order NLO molecules, the EO coefficients are written, respectively, [1,7]

\[ r_{33} = N \beta_{zzz}(\omega) \langle \cos^3 \theta \rangle g(\omega) \]  

and

\[ r_{13} = N \beta_{zxx}(\omega) \langle \cos \theta \sin^2 \theta \rangle g(\omega), \]

where N represents the total number density of nonlinear chromophores, \( \beta_{zzz}(\omega) \) is the molecular first hyperpolarizability of the chromophore, and \( g(\omega) \) is a local field correction factor. The noncentrosymmetric order parameter, \( \langle \cos^3 \theta \rangle \), represents the average degree of order of BNA molecules induced by the externally applied poling field, in which \( \theta \) is the angle between the dipole axis of the molecule and the electric poling field. As the laser
power increases, both higher $r_{33}$ and higher ratio of $r_{33}/r_{13}$ are achieved, which means that the average angle $\theta$ was decreased due to better alignment of BNA molecules. When laser power was increased further, both $r_{33}$ and the ratio of $r_{33}/r_{13}$ start to decrease. The ratio of $r_{33}/r_{13}$ is proportional to $\langle \cos^3 \theta \rangle / \langle \cos \theta \sin^2 \theta \rangle$ and independent of chromophore number density $N$. This indicates that the loss of alignment order rather than a decrease of chromophores number density $N$ due to photodegradation took place at high laser power. The randomization at high laser power could be because the molecules already aligned parallel to the poling field absorbed enough energy to overcome the potential of the poling field, leading to an increased photocurrent observed at high laser power. The peak of the ratio between EO coefficients $r_{33}$ and $r_{13}$ is 12.1 at a typical laser power intensity of 1.6 mW/cm². This corresponds to an average angle of 16° of BNA molecules in the polycrystalline thin films. The high 12.1-fold ratio of $r_{33}$ and $r_{13}$ may also be explained by effective reduction in lattice dimensionality induced by strong chromophore-chromophore electrostatic interactions inside polycrystalline grains because symmetry reduction from three-dimensional to one-dimensional (1D) results in a fivefold increase in acentric order [7], and BNA is known to crystallize with 1D symmetry. Single crystal BNA has been found to have near zero $d_{311}$ [5], which corresponds to the ratio of $r_{33}/r_{13}$ being nearly infinite. The results also show that BNA thin film made with laser-assisted alignment has a comparable EO coefficient $r_{33}$ of 43 ± 5 pm/V to the BNA single crystal grown from melt, which has an $r_{33}$ of 45 ± 6 pm/V at a wavelength of 1064 nm [5].

In summary, by applying an in-plane electric field using coplanar electrodes fabricated on the substrate and a laser beam with its wavelength in the absorption band of the BNA and polarized perpendicular to the poling field, BNA molecules deposited on the substrate through thermal evaporation can be aligned to form a polycrystalline thin film of small angle domains. A threefold increase in EO coefficient is observed with the laser illumination. BNA thin films fabricated with laser-assisted poling exhibit an $r_{33}$ value comparable to that of BNA single crystals. There exists an optimal value of the laser power, indicating the laser produces competing processes that respectively enhance and reduce the alignment of BNA molecules.

This research has been partially supported by the National Nature Science Foundations (NSF) of the United States (Grant Nos. ECS-0437920, NSF-DMR-0092380, DMR-0120967); National Nature Science Foundations of China (NSFC) (Grant Nos. 60790711, 61 040 064); Shaanxi Province Science Technology International Cooperation Funds of China (2011KW-03); and Fundamental Research Funds for the Central Universities, China.

References