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Microfabrication of electroluminescent polymer for devices construction

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ABSTRACT

We report on the femtosecond-laser micromachining of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) films. We study the influence of pulse energy and scanning speed on the microstructures produced on sample surface. The microstructures were analyzed using an optical microscope and the morphology of the polymer film was obtained by atomic force microscopy (AFM). It has been found that the surface roughness of the investigated films is significantly increased upon increasing energy pulses and velocity. Furthermore, we report a limit for ablation threshold on the produced line microstructures and its influence on the absorption spectrum. In the end, we investigated the conditions for produce a luminescent mechanism and succeed in fabricating a microstructured MEH-PPV device.

1. Introduction

Conjugated polymers are promising candidates for applications in light emitting devices [1,2], owing to some advantages they exhibit, such as, for instance, ease processability and flexibility [3]. Moreover, polymeric materials can be engineered to allow tuning their properties, for example electro-optic coefficient, nonlinear optical response and photosensitivity, aiming at a specific application [4]. In particular, poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) is a conjugated polymer with exceptional optical and electrical properties [5,6], being used in the development of several applications [1,7]. The strong two-photon absorption exhibited by MEH-PPV [8] has prompted new studies of its nonlinear optical properties, as well as its use for applications in photonics. In the last decade there has been a growth attention on methods to process materials for the development of devices. Femtosecond laser micromachining has prompted as a potential approach in this direction, enabling the production of several optical devices, from interferometers to waveguide couplers [9–16]. This technique presents several advantages when compared to other approaches, being a direct processing method, single-step and maskless [17–20].

In this paper, we have studied the microstructuring of MEH-PPV films by femtosecond laser micromachining, evaluating the changes induced by the laser irradiation on the optical properties of the sample. The influence of pulse energy and translation speed on MEH-PPV micromachining was determined by optical and atomic force microscopy. We determined the energy threshold for polymer removal, distinguishing the energy range for polymer removal from morphological changes. Once the proper fs-laser micromachining conditions were determined, we were able to apply such approach to fabricate a functional microstructured electroluminescent device, without disrupting the indium tin oxide layer used as the contact for the devices.

2. Experimental setup

The MEH-PPV was purchased from Sigma–Aldrich and used as received. The MEH-PPV, whose monomer molecular structure is shown in the inset of Fig. 1, was dissolved in chloroform (5 mg/ml), and cast on a teflon recipient over a glass substrate, yielding samples with thicknesses up to approximately 14 μm. The samples were stored at room temperature and protected from light to avoid photodegradation. The UV–vis absorption spectrum of the sample was measured using a spectrophotometer, and it is shown in Fig. 1 (blue line – left axis). As it can be seen, there is no absorption at 800 nm, wavelength used to perform the fs-laser microfabrication. The fluorescence of the sample, excited at 590 nm, is also displayed in Fig. 1 (black line – right axis).

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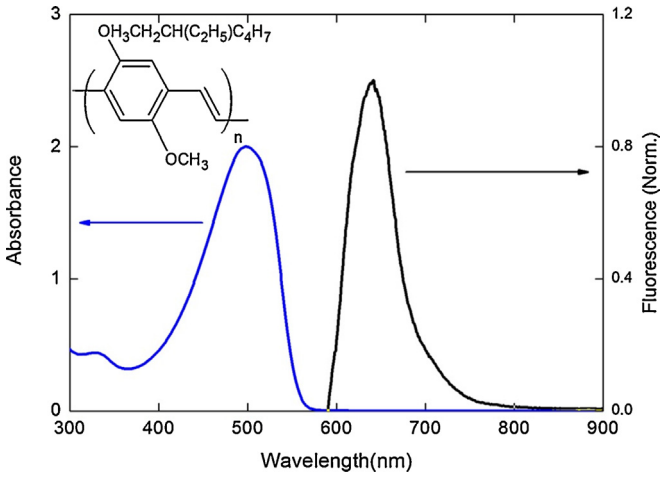

Fig. 1. UV–vis absorption (blue line – left axis) and fluorescence (black line – right axis) spectra of a MEH-PPV film. The inset shows the chemical structure of MEH-PPV. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

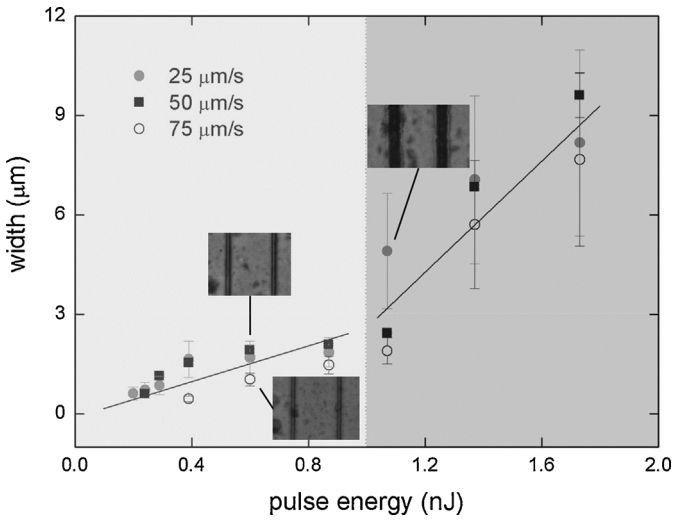

Fig. 2. Line thickness as a function of the pulse energy for different translation speeds. Morphological changes (light gray region) and ablation (dark gray region) regimes are specified. The pictures inset are examples of optical microscopic images used for evaluation.

Thin MEH-PPV films were also prepared on Indium Tin Oxide (ITO) coated glass substrates, which is commonly used as transparent conductor in the optoelectronic devices [21]. In this case, the MEH-PPV film (~300 nm) was obtained by spin coating the substrate with a chloroform solution, with concentration of 4 mg/ml.

The samples were micromachined using an extended-cavity Ti:Sapphire laser oscillator, centered at 800 nm operating at a repetition rate of 5.2 MHz, that produces pulses with energy up to 100 nJ and duration of 50 fs. The beam was focused on the sample surface by a 40× (0.67-NA) microscope objective. More details about the system can be found elsewhere [22]. The sample was moved at a constant speed with respect to the laser beam, using a computer-controlled xyz stage. The pulse energy and scanning speed was varied to determine the optimal parameters for MEH-PPV microfabrication. Structures were also fabricated using a micromachining setup based on a pair of scanning mirrors. In this case, a lens with focal length of 20-cm was used instead of the microscope objective. Such system was used to produce the electroluminescent device with MEH-PPV.

3. Results and discussion

The influence of pulse energy and scanning speed on the features of the fs-laser micromachining was analyzed by optical microscopy, as illustrated in the images shown in the inset of Fig. 2. Groups of lines (1.5 mm long and spaced by 20 μm) were micromachined on the MEH-PPV film surface using different pulse energies (from 0.2 to 2 nJ) and scanning speeds (25, 50 and 75 μm/s). The threshold energy to observe changes on the sample was determined to be 0.2 nJ. Fig. 2 shows the dependence of the line width on the pulse energy; when the pulse energy varies from 0.2 to 1.8 nJ, the width of the lines range from 0.6 to 10 μm. Besides, shaper micromachined lines are obtained as the scanning speed increases. Fig. 2 reveals distinct behaviors for the micromaching processes of MEH-PPV. For pulse energies below 1.0 nJ, a small slope is observed for the line width on the pulse energy. Above 1.0 nJ, however, the width of the micromachined structures grows with the energy in a more pronounced manner (higher slope). This indicates that the interaction of fs-laser pulses with the polymer follows two regimes: (i) morphological changes which occur for low energies [23–25] and (ii) ablation of material that takes places when high pulse energy is used [26].

The distinct regimes of fs-laser micromachining of MEH-PPV were confirmed by atomic force microscopy, obtained for a set lines fabricated with pulse energies ranging from 0.6 to 1.1 nJ and scanning speeds of 25, 50 and 75 μm/s. Fig. 3 shows two representative atomic force micrographs of lines micromachined with at 25 μm/s and with pulse energies of 0.6 nJ (a) and 1.1 nJ (b). Such results show that for low pulse energies (below 1 nJ), the effect of the irradiation is to produce a bulge on the surface of the polymeric sample (morphological change). In the micrography displayed in Fig. 3a, the bulge height is approximately 0.7 μm. For energies higher than 1 nJ, on the other hand, removal of material occurs on the sample's surface (ablation). The depth of the valley presented in Fig. 3b is of about 6 μm.

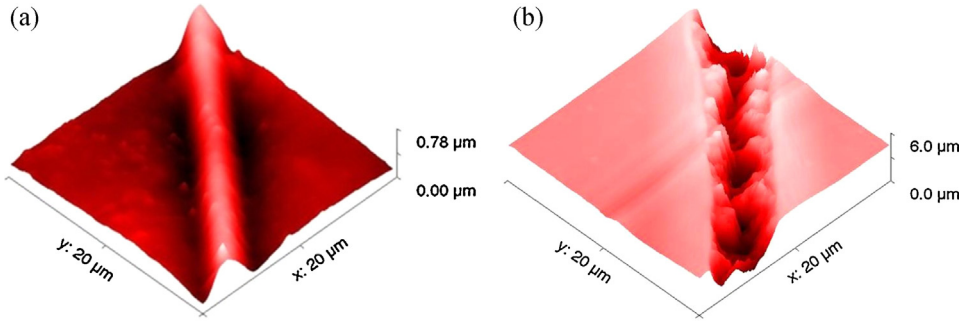

Fig. 3. Atomic force micrographs of MEH–PPV films microstructured with 0.6 nJ (a) and 1.1 nJ (b), using a scanning speed of 25 μm/s.