

# Surface modification and structuring of electrical conducting and isolating polyaniline films

T. Lippert\*, F. Raimondi, J. Wambach, J. Wei, A. Wokaun

Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

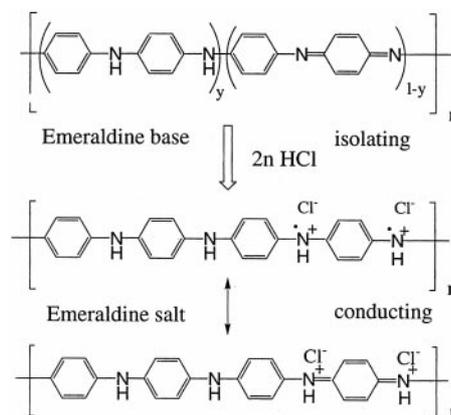
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**Abstract.** Laser ablation of polyaniline in its conducting and isolating form revealed very similar ablation properties upon irradiation at 308 nm. Both types of polymer film can be structured with high resolution at high fluences. The ablation craters have sharp contours and no debris contaminates the surrounding area. At low fluences the creation of cone structures is observed. X-ray photoelectron spectroscopy reveals the carbonization of the surface upon laser ablation. As preferred decomposition sites the imine groups in doped and undoped polyaniline are identified.

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Polyaniline (PAN) belongs to a group of conducting polymers that has been the subject of many studies in the last years [1]. PAN can be prepared in three different oxidation states: fully reduced leucoemeraldine, half-oxidized emeraldine base (EB) (shown in Fig. 1) and fully oxidized pernigraniline base [2]. The emeraldine base can be transformed into a conducting state upon doping with protonic acids, such as HCl (shown in Fig. 1) to yield the emeraldine salt (ES) [3]. These polymers exhibit a wide range of electronic, optical, magnetic, and mechanical properties that suggest a wide variety of possible applications. There are two applications we want to discuss in more detail.

Polymers with conjugated  $\pi$ -systems, such as polyaniline [4], are used as membranes to separate gas mixtures. PAN can be prepared in stable thin films, which can be fabricated into gas separation membranes or films. It has also been reported that carbonization of polymer films, such as polyimide, can increase the separation ability of membranes [5]. It is also known that it is possible to create a conducting carbon layer on polyimide upon laser irradiation [6]. One goal of this study was to test whether it is also possible to carbonize the surface of PAN films upon laser irradiation at 308 nm.



**Fig. 1.** Chemical structure of the undoped polyaniline (emeraldine base) and its doped form (emeraldine base salt)

The possibility of manufacturing thin conducting polymer films led to the development of all-organic active electronic devices, such as light-emitting diodes [7], thin film field-effect transistors [8], or Schottky-barrier devices [9]. Lithographic patterns of conducting polymers have been obtained by a few different approaches [10, 11], but the availability of powerful lasers has made it technically feasible to structure electrically conducting polymers directly with high resolution [12, 13]. This might be done in two different ways: either by structuring the undoped, isolating material and doping the structured film, or by directly structuring the doped conducting films.

We have studied the ablation parameters of both conducting and isolating polyaniline films to decide whether one material is preferable for structuring.

## 1 Experimental

The emeraldine base (EB), EB salt and the films were prepared according to the described procedures [4]. For irradiation an XeCl-excimer laser (Lambda Physik Compex 205) emitting at 308 nm was used. XPS spectra were recorded

\*Corresponding author. (Fax: +41-56/310-2199, E-mail: lippert@psi.ch)

with an ESCALAB 220I XL (VG Scientific) photoelectron spectrometer, using non-monochromatized Mg  $K_{\alpha}$  radiation at a source power of 300 W. The depths of the ablated craters were measured with a surface profiler (Dektak 8000). The quality of the structures obtained was controlled with a scanning electron microscope (SEM, Topcon ABT-60). The UV reflection spectra were recorded on a Perkin Elmer  $\lambda 19$  instrument, equipped with an integrating sphere.

## 2 Results and discussion

To get a rough idea about the absorptivity of the blackish PAN films, the reflectivity of the films was measured with an integrating sphere. Both films, doped and undoped PAN, exhibit nearly the same low ( $\approx 4\%$ ) reflectivity (roughly comparable to transmission) at 308 nm, suggesting that laser treatment and structuring should be possible. In Fig. 2 the ablation plots (etch rate vs.  $\ln$  fluence) for doped and undoped PAN are shown. Both polymers exhibit a similar behavior in these plots. The first five points of each curve were used to calculate the threshold fluence,  $F_{th}$ , and the effective absorption coefficient,  $\alpha_{eff}$ , according to (1):

$$d = \frac{1}{\alpha_{eff}} \ln \left( \frac{F}{F_{th}} \right) \quad (1)$$

$d$  is the etch rate and  $F$  the applied fluence. The ablation parameters are also comparable for both types of PAN:

PAN undoped:  $F_{th} = 32 \text{ mJ cm}^{-2}$  and  $\alpha_{eff} = 46\,000 \text{ cm}^{-1}$ .

PAN doped:  $F_{th} = 52 \text{ mJ cm}^{-2}$  and  $\alpha_{eff} = 42\,000 \text{ cm}^{-1}$ .

In Fig. 3 the SEM pictures of the irradiated undoped PAN are shown. The picture at the top shows a detailed view of the bottom of one ablation crater. At this low fluence ( $47 \text{ mJ cm}^{-2}$ ) the well-known ‘cone’ structures are observed. It has been suggested that these are due to the shielding effects of particles with different absorptivity and ablation threshold at the top of the cones [14]. The micrograph in Fig. 3 (bottom) shows the crater of a stretched film irradiated with 10 pulses at  $5.1 \text{ J cm}^{-2}$ . The scratch marks are due to measurements with the profilometer. The crater has sharp contours with no debris surrounding the etched area. Very similar results are obtained for doped PAN, suggesting that both kind of film can be structured directly by laser ablation to obtain high-resolution patterns.

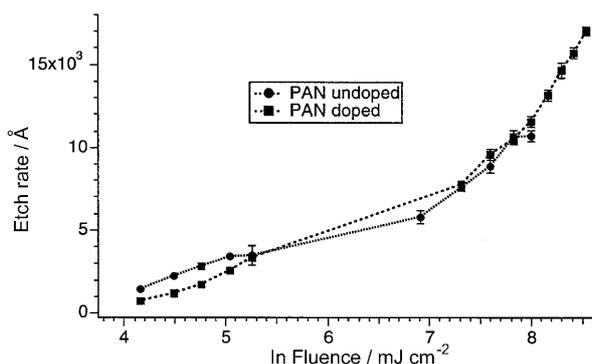


Fig. 2. Etch depth as a function of the logarithm of laser fluence for doped and undoped polyaniline

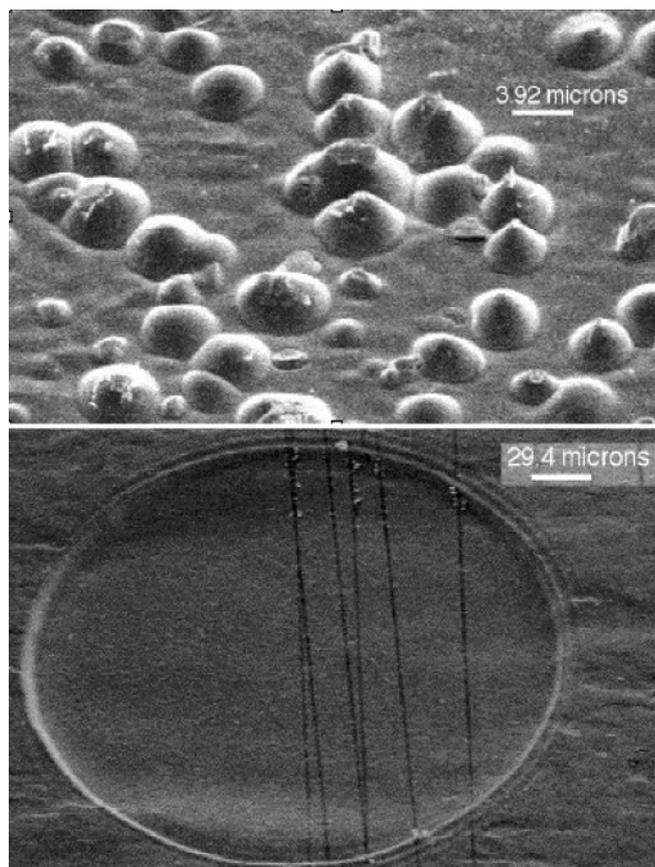
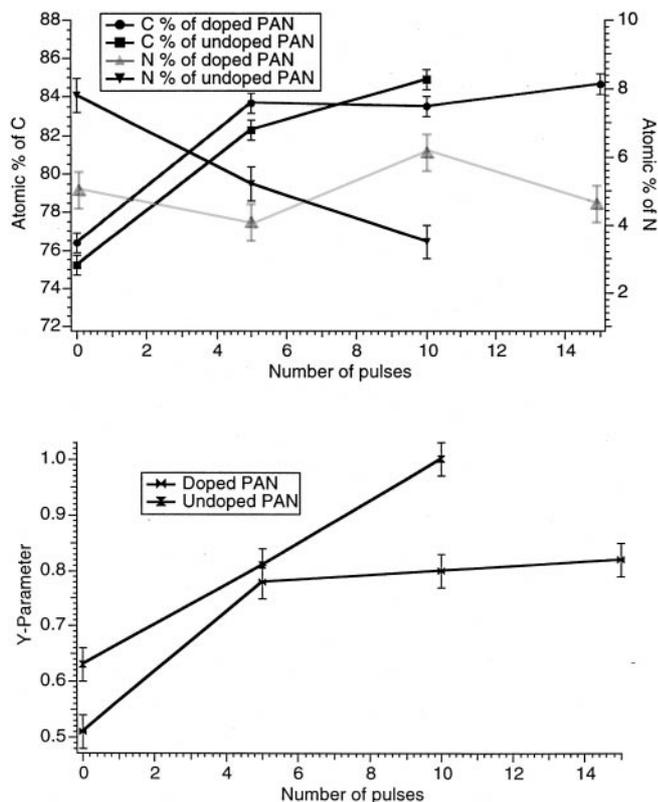


Fig. 3. SEM micrographs of irradiated undoped polyaniline; top: bottom of ablation crater, 200 pulses at  $47 \text{ mJ cm}^{-2}$ ; bottom: 10 pulses at  $5.1 \text{ J cm}^{-2}$

To test whether surface carbonization of PAN can be achieved small spot XPS analysis ( $150 \mu\text{m}$  square) was used. Both films revealed a relatively high oxygen content, probably due to both oxidation of the polymer and water adsorption upon storage [15]. This is supported by the fast decrease of the oxygen content upon laser irradiation (the adsorbed water is removed) while the oxidized carbon content, as measured by high binding energy components in the C 1s peak, remains constant. The N 1s peaks were analyzed in detail, fitting the experimental data with components corresponding to neutral and protonated amine and imine groups [16]. Thus the Y-parameter, which appears in Fig. 1 and Fig. 4 (bottom) and equals the ratio of the amine species to the sum of the amine and imine species, can be obtained. Both films showed an increase of carbon and a decrease of nitrogen upon irradiation. This is shown for irradiation with  $1 \text{ J cm}^{-2}$  in Fig. 4 (top). The carbon content on the surface (analysis depth  $\approx 20 \text{ nm}$ ) increases for both films to around 85% (untreated around 75%). The decrease in the N content is less pronounced, especially in the case of doped PAN, but is nevertheless observable. The change in the Y-parameter is shown in Fig. 4 (bottom). In the case of the undoped PAN the ratio reaches unity with 10 pulses, suggesting total decomposition of those molecular moieties containing the imine groups. Decomposition at the imine functional group is certainly one step, probably even the first step, of decomposition upon UV laser irradiation at 308 nm. In the case of the doped PAN a slower increase of the Y ratio is observed, and the value levels off at around 0.8. This could be due to the higher stability of the ionic imine



**Fig. 4.** *Top:* change in the carbon and nitrogen atomic ratio of doped and undoped polyaniline films. Irradiation with  $1 \text{ J cm}^{-2}$ . *Bottom:* change in the Y-ratio, defined as the ratio [imine species/(imine + amine species)], upon irradiation with  $1 \text{ J cm}^{-2}$ .

groups (compared with the neutral species), or to the creation of other imine species upon irradiation, possibly through oxidation of the amine species. The analysis of the Cl  $2p$  peak suggests at least two different chemical environments for the chloride ions present in the doped polymer. Pronounced changes are observed upon laser irradiation, which will be studied in more detail in the future.

The first tests with laser-irradiated carbonized gas separation membranes showed slight improvements of the gas separation properties.

### 3 Conclusions

Laser ablation of doped, conducting and undoped isolating polyaniline revealed very similar ablation properties upon irradiation at 308 nm. Both types of polymer film can be structured with high resolution at high fluences. The ablation craters have sharp contours and no debris contaminates the surrounding area. At low fluences the creation of cone structures is observed. X-ray photoelectron spectroscopy reveals the carbonization of the surface upon laser ablation. The imine groups in doped and undoped polyaniline are identified as preferred decomposition sites.

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