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UV Laser Ablation of Electronically Conductive Polymers

by

Leon S. Van Dyke, Charles J. Brumlik, Zengi Yu, George J. Collins
and Charles R. Martin

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Department of Chemistry
Colorado State University
Ft. Collins, CO 80523



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UV Laser Ablation Of Electronically Conductive Polymers

Leon S. Van Dyke[†], Charles J. Brumlik, and Charles R.
Martin^{*}

Department of Chemistry
Colorado State University
Fort Collins, CO 80523

Zengi Yu and George J. Collins

Department of Electrical Engineering
Colorado State University
Fort Collins, CO 80523

^{*} To Whom Correspondence Should Be Addressed

[†]Present address: GE Plastics, Noryl Ave, Selkirk, NY 12158

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ABSTRACT

The UV laser ablation of thin polypyrrole and polyaniline films coated on an insulating substrate is described. UV laser ablation is used to pattern the conductive polymer coating; patterns with submillimeter features are easily obtained with edge resolution on the order of a few microns.



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INTRODUCTION

There is increasing interest in applying the concepts and methods of microlithography to electronically-conductive polymers (1-9). For example, patterns of such polymers on insulating substrates have been prepared using conventional lithographic processes involving photoresists (1-4). Alternatively, patterns of conductive polymers have been made via photochemical polymerization on masked semiconductors; however, this technique is limited to photoconductive substrates (6-8). Only one method for patterning of conductive polymers on an insulating substrate, without the use of photoresists, has been described; this method entailed using scanning electrochemical microscopy to do spatially-resolved polymerization of polyaniline (9).

We have recently developed a new technique, based on UV laser ablation, by which conductive polymers can be patterned without the use of photoresists. This process involves coating an insulating substrate with a thin conductive polymer film. The conductive polymer-coated substrate is then exposed to pulsed UV laser radiation through a mask. The irradiated portion of the electronically conductive polymer film is ablated from the surface exposing the substrate insulating polymer; since the portions of the surface that receive the UV photons is

determined by the pattern in the mask, an image of the mask is ablated into the conductive polymer film. We show in this paper that this laser ablation procedure can be used to pattern thin polypyrrole and polyaniline films.

EXPERIMENTAL

Materials and Instrumentation. Poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) film (10 mil thick, Dupont) was used as the substrate for the thin conductive polymer films. Pyrrole and aniline (Aldrich) were distilled under nitrogen prior to use. All other reagents were used as received. A Lumonics HyperEX400 XeCl excimer laser was used as the light source. This is a pulsed laser with a wavelength of 308 nm, a pulse width of 35 ns, and a maximum average power of 20 W. The laser beam was converged through a laser-grade UV-quartz condenser lens to yield fluences of between 0.1 and 1.5 J cm⁻² per pulse. An electroformed molybdenum contact mask (Towne Labs Inc. Somerville, N.J.) was used as a mask; this mask is 25 μm thick with 50 μm diameter holes at 500 μm intervals. Scanning electron micrographs (SEMs) were obtained using a Phillips 505 scanning electron microscope with a LaB₆ filament. Samples were sputter-coated with ca. 200 Å of gold, using a Technics Hummer I, prior to SEM analysis. .

Coating FEP with polypyrrole and polyaniline films. Prior to coating the FEP films with conductive polymer, the

surface-derivatization procedure developed by McCarthy was used to carboxylate the FEP surface (10). This was done to improve adhesion between the FEP surface and the conductive polymer over-coat. We have shown that conductive polymer films are strongly adherent to the carboxylated FEP surface (11). The carboxylated FEP was coated with conductive polymer by synthesizing the polymer in the presence of the FEP film. We and others have shown that the nascent conductive polymer preferentially nucleates and grows on the polymeric surface (11-13). As a result, the FEP surface becomes coated with a thin conductive polymer film.

The polymerization solution for polypyrrole was prepared by mixing equal volumes of an aqueous solution that was 0.1 M in pyrrole and an aqueous solution that was 0.2 M in FeCl_3 and 0.2 M in sodium tosylate. The carboxylated FEP film was immersed in this solution and the polymerization was allowed to proceed for 5 minutes. The polypyrrole-coated FEP was then removed from the polymerization solution and rinsed with deionized water. The polymerization solution for polyaniline was prepared by mixing equal volumes of a solution that was 0.25 M in ammonium persulfate with a solution that was 0.5 M in aniline; the solvent was 1 M aqueous HCl . The carboxylated FEP was immersed in this solution and the polymerization was allowed to proceed for 10 minutes. After polymerization the film was rinsed with

deionized water. The thicknesses of the resulting conductive polymer films were estimated from scanning electron micrographs of cross-sections of the composite membranes.

RESULTS AND DISCUSSION

Figure 1 shows UV-visible absorption spectra for the carboxylated FEP substrate (A) and for the same material after coating with polyaniline (B) and polypyrrole (C). Polyaniline and polypyrrole absorb strongly throughout the UV and visible portions of the electromagnetic spectrum; this accounts for the enhanced absorbance seen in spectra A and B. Indeed, the spectra in Figure 1 do not effectively illustrate the strength of the conductive polymer absorbance, relative to the FEP substrate, because the substrate is over three orders of magnitude thicker than the conductive polymer films. Electron micrographic data (e.g. Figures 2 through 4) suggest that the polypyrrole films used in these studies were ca. 100 nm in thickness, whereas the polyaniline films were ca. 20 to 30 nm-thick.

It is difficult to prepare thicker polyaniline films via the polymerization method used here. We have found in this and related work (11) that the polyaniline deposit becomes powdery and poorly adherent after a ca. 30 nm film is laid down. Evidence for this powdery layer can be seen in the micrograph shown in Figure 3. In contrast,

polypyrrole is much more cohesive and thicker films of this polymer can be deposited.

Figure 2 shows a scanning electron micrograph of the surface of the polyaniline-coated FEP after irradiation, through the mask, with a single 1.5 J cm^{-2} laser pulse. The polyaniline has been ablated away in a pattern corresponding to the holes in the mask. Figure 3 shows a higher magnification image of a single ablated spot. The ablated area is somewhat larger than the $50 \text{ }\mu\text{m}$ hole in the mask. This is undoubtedly the result of thermal damage to the polymer surrounding the irradiated spot (14). The wavelength used here, 308 nm , is in the region where a crossover between photo and thermal ablation typically occurs (14). Cleaner ablation of other polymers has been obtained by using shorter wavelengths and shorter laser pulses (15). The use of shorter pulses and shorter wavelengths would undoubtedly minimize thermal damage in the polymers investigated here.

Figure 4 shows a scanning electron micrograph of the surface of polypyrrole-coated FEP after irradiation, through the mask, with a 1.0 J cm^{-2} laser pulse. Again, the irradiated portion of the conductive polymer coating was ablated away. The edge resolution of the ablated polypyrrole (Figure 4) is somewhat poorer than that of the ablated polyaniline (Figure 3). This is undoubtedly related

to the difference in film thickness because thicker polypyrrole films showed even poorer edge resolution. This inverse dependence of edge resolution on film thickness is characteristic of thermal ablation processes (14).

We have also investigated the effect of UV photon fluence on this laser ablation process; the process is extremely sensitive to photon fluence. Irradiation of a polypyrrole film of 100 nm thickness with ten pulses at 0.1 J cm^{-2} per pulse produced no ablation (as evidenced by SEM analysis). In contrast, complete removal of the irradiated portion of the film occurred upon application of a single pulse with an energy density of 0.5 J cm^{-2} , or higher. The minimum UV photon fluence required to produce ablation in a single pulse was found to be ca. 0.3 J cm^{-2} , for the polypyrrole films investigated here.

CONCLUSIONS

We have shown that laser ablation can be used to do microlithography in thin polypyrrole and polyaniline films on FEP surfaces. Preliminary studies with various other conducting polymers, including poly(3-methylthiophene) and poly(N-methylpyrrole), have shown that these materials can also be ablated using this method. Because the highly-doped forms of all electronically conductive polymers are highly absorbing, this method should prove to be applicable to a broad range of materials of this type. Furthermore, it is

now well known that the polymerization method described here can be used to grow thin films of conductive polymers on a variety of polymeric substrates including polycarbonate (16), nylon (12,17), and polyester (12,17). The laser ablation method should be applicable to any of these substrates, provided the substrate is transparent (or very weakly absorbing) at the wavelength of light used.

Finally, the coating of insulating substrates with conductive polymers, such as polypyrrole and polyaniline, and then the subsequent electrodeposition of copper onto the conductive polymer precoat has recently been described (18,19). The method by which the conductive polymer precoat was applied resulted in the formation of a conductive coating over the entire insulating substrate (12,19). The UV laser ablation method described here could be used for patterning this conductive polymer precoat. The patterned conductive polymer could then be coated with copper to form circuits and electronic devices.

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FIGURE CAPTIONS

Figure 1. UV-Visible absorption spectra of: A) Carboxylated FEP film. B) Polyaniline-coated carboxylated FEP film. C) Polypyrrole-coated carboxylated FEP film.

Figure 2. Scanning electron micrograph (SEM) of polyaniline-coated FEP after irradiation with a 1.5 J/cm^2 laser pulse through the contact mask.

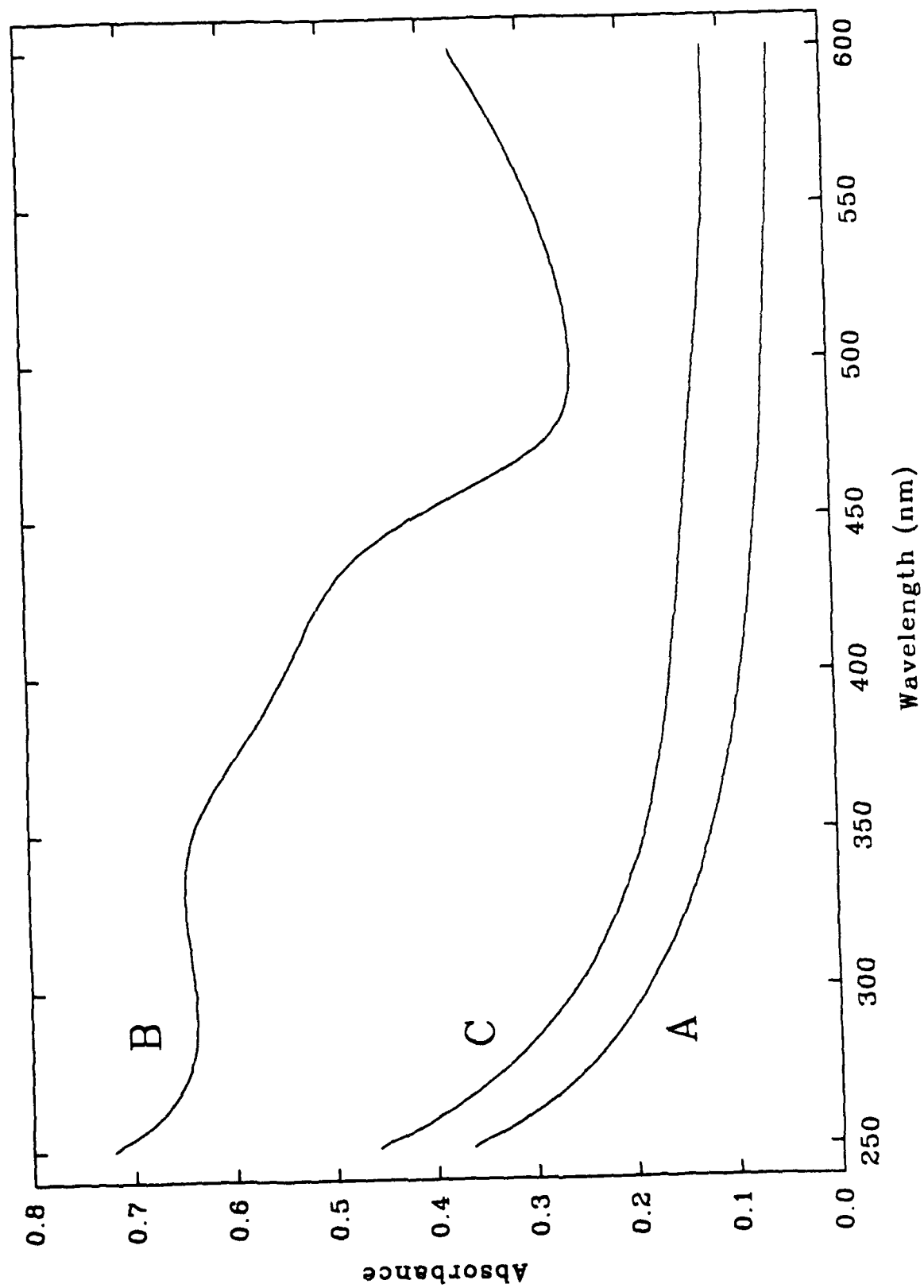
Figure 3. SEM as per Figure 2 but higher magnification.

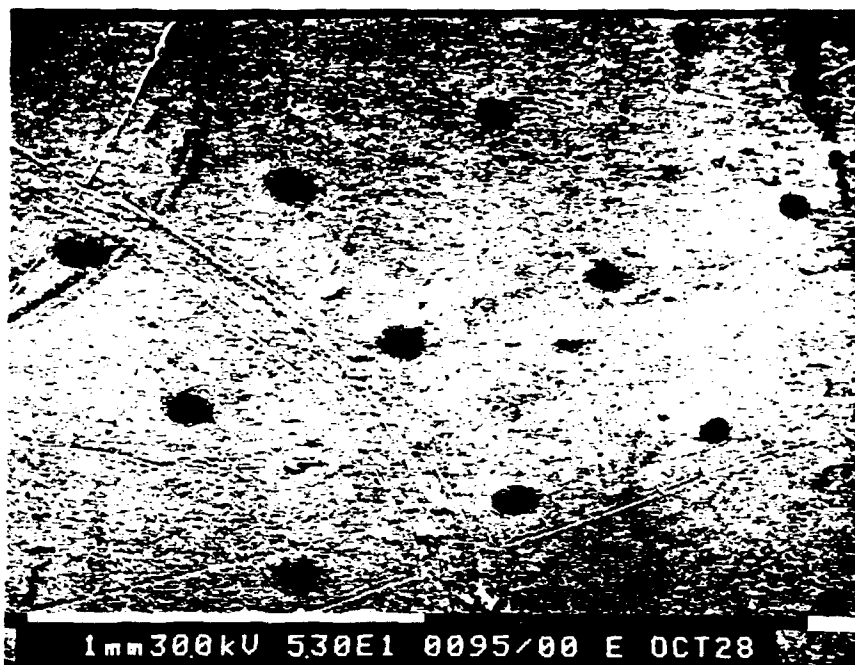
Figure 4. SEM of polypyrrole-coated FEP after irradiation with a 1.0 J/cm^2 laser pulse through the mask.

REFERENCES

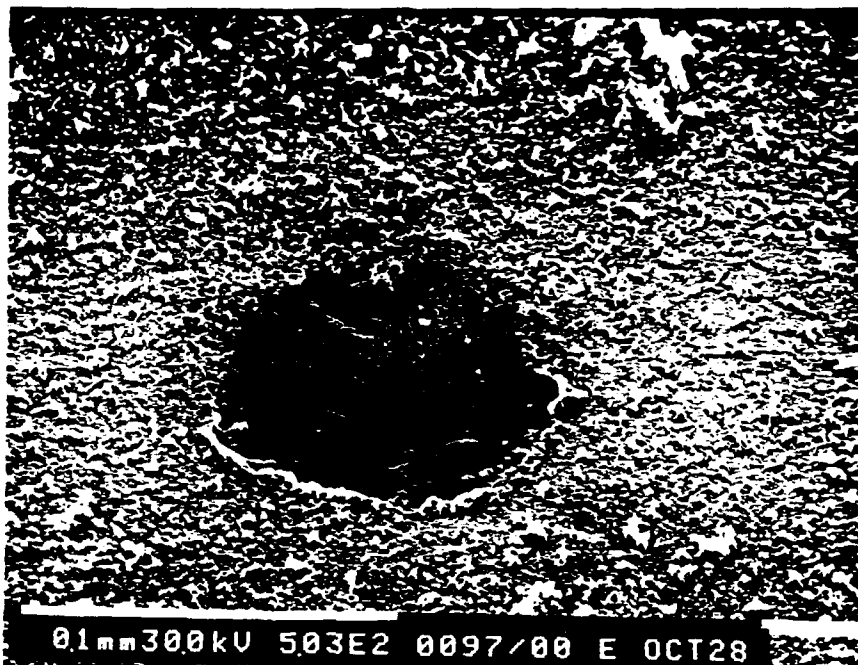
- (1) Kern, J. M.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1989**, 657.
- (2) Bargon, J.; Behnck, W.; Weidenbruck, T. *Synth. Met.* **1991**, 41-43, 1111.
- (3) Nannini, A.; Serra, G. *J. Mol. Elect.* **1990**, 6, 81.
- (4) Kobel, W.; Kiess, H.; Egli, M. *Synth. Met.* **1988**, 22, 265.
- (5) Hikita, M.; Niwa, O.; Sugita, A.; Tamamura, T. *Jpn. J. Appl. Phys.* **1985**, 24, L79.
- (6) Okano, M.; Itoh, K.; Fujishima, A.; Honda, K. *Chem. Lett.* **1986**, 469.
- (7) Yoneyama, H.; Kawai, K.; Kuwabata, S. *J. Electrochem. Soc.* **1988**, 135, 1699.
- (8) Okano, M.; Kikuchi, E.; Itoh, K.; Fujishima, a. *J. Electrochem. Soc.* **1988**, 135, 1641.
- (9) Wu, Yee-M.; Fan, Fu-R. F.; Bard, A. J. *J. Electrochem. Soc.* **1989**, 136(3), 885-886.
- (10) Shoichet, M. S.; McCarthy, T. J. *Macromolecules* **1991**, 24, 982.
- (11) Van Dyke, L. S.; Brumlik, C. J.; Liang, W.; Lei, J. T.; Martin, C. R.; Yu, Z.; Li, L.; Collins, G. J. **1992**; in preparation.
- (12) Gregory, R. V.; Kimbrell, W. C.; Kuhn, H. H. *Synth. Met.* **1989**, 28, C823-C835.
- (13) Martin, C. R.; Van Dyke, L. S.; Cai, Z.; Liang, W. *J. Am. Chem. Soc.* **1990**, 112(24), 8976-8977.
- (14) Srinivasan, R.; Braren, B. *Chem. Rev.* **1989**, 89, 1303.
- (15) Kuper, S.; Stuke, M. *Appl. Phys. Lett.* **1989**, 54, 4.
- (16) Cai, Z.; Lei, J.; Liang, W.; Menon, V.; Martin, C. *R. Chem. Mater.* **1991**, 3(5), 960-967.

- (17) Gregory, R. V.; Kimbrell, W. C.; Kuhn, H. H. *Int. SAMPE Electron. Conf.* **1989**, 3, 570-577; (Electron. Mater. Processes).
- (18) Gottesfeld, S.; Uribe, R. A.; Armes, S. P. J. *Electrochem. Soc.* **1992**, 139, L14.
- (19) Huang, wS.; White, J. R.; Angelopoulos, M.; Park, J. M. *Mol. Cryst. Liq. Cryst.* **1990**, 189, 227.





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