CHEMISTRY LETTERS, pp. 469-472, 1986.

GENERATION OF ORGANIC CONDUCTING PATTERNS ON SEMICONDUCTORS BY PHOTOELECTROCHEMICAL POLYMERIZATION OF PYRROLE

Mitsutoshi OKANO,* Kiminori ITOH, Akira FUJISHIMA,
and Kenichi HONDA†

Department of Synthetic Chemistry, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113
†Division of Molecular Engineering, Kyoto University,
Sakyo-ku, Kyoto 606

Photoelectrochemical polymerization of pyrrole occurs at irradiated areas of semiconducting electrodes in aqueous solution of pyrrole. Organic conducting polypyrrole patterns were formed on semiconductors by area-selective irradiation of the semiconductor electrodes. The deposition rate was 0.5-0.7 μm per 100 mC. The conductivity of the deposited polypyrrole film was ca. 1 S cm^{-1}.

Pattern generation for integrated circuits and printed wirings is usually accomplished with multistep photoresist techniques. In order to reduce the number of processing steps, alternative techniques, including laser chemical vapor deposition1) and laser enhanced electroplating,2) have been investigated. The authors report here a new resistless technique for pattern generation utilizing the photo-generated holes in the valence band of semiconductors to polymerize organic conducting polymers; the authors3) and M. Kitayama et al4) have recently reported orally the generation of polypyrrole patterns on semiconductors. Because the values of conductivity of those polymers are recently approaching those of metals, they are interesting materials as nonmetallic conductors.5) Since the conducting polymers are organic materials, they have several merits, e.g. stability in acidic or oxidative atmosphere, abundance of source materials and flexibility. Moreover, few problems arise after use as they can be incinerated.

Photoelectrochemical polymerization, i.e. polymerization of monomers on an irradiated semiconductor electrode, was performed in a conventional three electrode system. Since stable and transparent substrate electrodes are more favorable for the basic investigations, n-TiO_2 electrode was employed as the working electrode for the most experiment; Si and GaAs are important as they are used in the semiconductor industry, however, they are not stable under irradiation. The n-TiO_2 electrodes (1000-2000 Å in thickness) were prepared by depositing TiO_2 onto SnO_2-coated glass plates by spray pyrolysis technique.6) Polypyrrole was employed as an organic conducting polymer. Anodic polymerizations were carried out in aqueous solutions containing pyrrole and sodium sulfate. The potential of the substrate electrode was controlled against a saturated calomel electrode (SCE) using a potentiostat and a potential sweeper. A 500 W xenon lamp was used as a light source. The conductivity of organic conducting polymer films was measured by the four point probe method and the thickness by the talistep method.

Pyrrole is polymerized on a platinum electrode at electrode potentials more positive than +0.6 V vs. SCE in an aqueous solution.7) However, this polymerization occurs with less bias on illuminated semiconductors, owing to the photosensitized electrolysis. Under irradiation, an anodic current was observed at potentials of the TiO_2 electrode more positive than -0.6 V vs. SCE; the anodic current means the oxidative polymerization of pyrrole, while no anodic current was observed up to +1.5 V vs. SCE in the dark (Fig. 1). However, at potentials more positive than +1.5 V vs. SCE an anodic current was observed owing to either defects of the semiconductor or tunneling of electrons through the very thin space charge layer. These results suggest that the photoelectrochemical polymerization takes place selectively at the irradiated areas on the TiO_2 when the potential is set between -0.6 V and +1.5 V vs. SCE. When the surface of n-TiO_2 was completely covered with polypyrrole film, the anodic current was observed at potentials more positive than ca. +0.6 V vs. SCE, indicating that the contact between the n-TiO_2 and polypyrrole was nearly ohmic.

A polypyrrole pattern was formed on the n-TiO_2 electrode with irradiation of the electrode through a lens and a mask (Fig. 2-b). The electrode potential was set at +0.5 V vs. SCE in order to avoid the ordinary electrochemical polymerization of pyrrole mentioned above, which may occur on a deposited polypyrrole film at potentials more positive than +0.6 V vs. SCE. Figure 2-a shows a picture of the polypyrrole pattern after passing ca. 50 mC per 1 cm^2 of irradiated area. The smallest line width obtained on Fig. 2-a was 0.2 mm. Though it is not clear on the picture, the gaps between the lines narrower than 0.5 mm were covered with very thin polypyrrole film. The relatively low resolution may come from the fact that polypyrrole grows not only vertically to the substrate electrode surface but towards every direction, and hence the lines of polypyrrole became wider as poly-

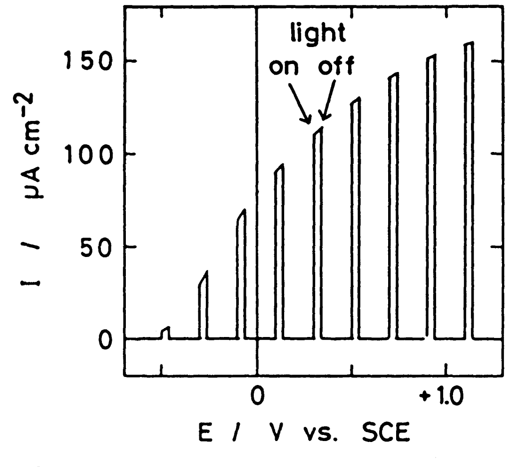
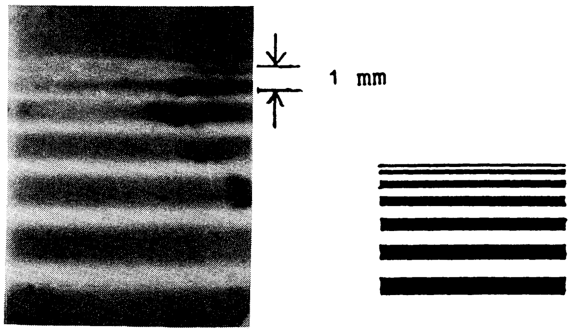


Fig. 1. Current-voltage characteristics for polymerization of pyrrole on an n-TiO_2 semiconductor electrode under irradiation and in the dark.



(a) pattern (b) mask

Fig. 2. (a)Picture of a photoelectrochemically formed pattern on an n-TiO_2 electrode(black part in (a) is polypyrrole). (b)the mask pattern employed.

pyrrole grew. However, taking account of the diffusion length (Ld) of photogenerated holes (Ld = ca. 100 Å)8) and the growth mechanism of the polypyrrole film, twice the thickness of the film (1000-2000 Å) plus 2 x 100 Å is thought to be the limit width of narrow patterns; this estimated value of resolution is much smaller than that observed in the experiment. Therefore, the authors believe that an improvement in their optical system will give much more fine patterns.

Photoelectrochemically polymerized polypyrrole films were removed from the n-TiO_2 electrodes, and their conductivities were measured in air by means of the four point probe method. Thickness measured by the talistep method was used for the calculation of conductivities. Typical conductivity (as grown, in the doped state) was ca. 1 S cm^{-1}. Ordinary electrochemical polymerization of pyrrole on a conducting SnO_2 electrode, from a solution of the same composition, gave a film with conductivity of ca. 100 S cm^{-1}. With the above experimental conditions, photoelectrochemically polymerized films grew with a rate of 0.5-0.7 μm per 100 mC, which is much larger than the rate for electrochemical polymerization, 0.2 μm per 100 mC. These results suggest that the photoelectrochemically polymerized films were coarse, compared with the electrochemically polymerized films. Thus, the relatively low conductivity of photoelectrochemically polymerized films is partly due to the coarseness of the films. The difference in the polymerization mechanism of the films should be taken into account for full explanation.

The doping and undoping characteristics of polypyrrole films on n-TiO_2 electrodes were studied by cyclic voltammetry. Anodic and cathodic currents in a cyclic voltammogram for polypyrrole films are known to be due to the incorporation of anions into the film and the release of the anions from the film, respectively.9) Since the cyclic voltammogram for the polypyrrole film on the n-TiO_2 showed an anodic and a cathodic currents, accompanying the color changes of the film, it is clear that the polypyrrole film on the n-TiO_2 can be doped and undoped. Also this result suggests nearly ohmic contact between n-TiO_2 and polypyrrole. The anodic current under irradiation was larger than that in the dark, owing to the photo-sensitized electrolysis. The polypyrrole coated n-TiO_2 electrode was kept at the potential of -0.5 V vs. SCE for 30 min in order to obtain an undoped film. The cathodic current gradually decreased and became less than 50 μA after 30 min. The conductivity of the undoped film was 5 x 10^{-4} S cm^{-1}. Thus, it is proved that polypyrrole patterns of different conductivities can be obtained on semiconductors.

Figure 3 shows the current-time relationship of the anodic current of photoelectrochemical polymerization. The electrode potential was set at +0.5 V vs. SCE. When the electrode was irradiated from the n-TiO_2 side (A), initially a photocurrent of 215 μA cm^{-2} was obtained. The current, however,

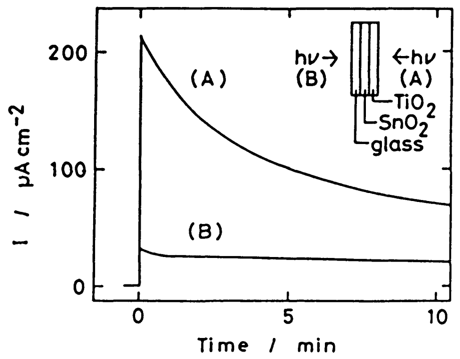


Fig. 3. Current-time relationship of anodic photocurrent for the photoelectrochemical polymerization; irradiation from the n-TiO_2 side (A) and from the glass side (B).

gradually decreased with time, and became one third the initial value after 10 min. A polypyrrole film of 0.3 μm in thickness was obtained in 5 min; the deposition rate was 0.6 μm per 100 mC. When the electrode was irradiated from the back side of the electrode (B), i.e. the glass side, an anodic current was smaller and its decay was slower compared with the former case (A). Probably the main reason for the current decrease is the absorption of light by the deposited polypyrrole film, preventing the light from reaching the n-TiO_2.

In acetonitrile, contrary to the above experiments, the photoelectrochemical polymerization of pyrrole on TiO_2, ZnO and α-Fe_2O_3 was unsuccessful. A possible explanation of this is as follows. In acetonitrile, pyrrole molecules react directly with the photo-generated holes in the valence band of the semiconductor. The holes oxidize pyrrole molecules so strongly that pyrrole molecules do not get polymerized but decomposed. In water on the other hand, either the holes are trapped at surface states which are known to exist on n-TiO_2 in water,10) or they react with water molecules directly to produce hydroxy radicals and the radicals react with pyrrole molecules. In both cases, the oxidizing force of photo-generated holes gets moderated first, and then oxidizes pyrrole molecules to polymerize them. Further investigation is under way.

In summary, organic conducting patterns are formed on semiconductors by means of the photoelectrochemical polymerization of pyrrole in aqueous solutions. The photoelectrochemically formed polypyrrole films can be doped to the conducting state and undoped to the insulating state electrochemically. Thus, polypyrrole patterns of different conductivities can be obtained.

We appreciate Mr. Eiji Kikuchi for his technical assistance in the preparation of semiconductors by the spray pyrolysis method.

References

1) S. D. Allen and A. B. Tringubo, J. Appl. Phys., <u>54</u>, 1641(1983).
2) R. J. von Gutfeld, E. E. Tynan, R. L. Melcher, and S. E. Blum, Appl. Phys. Lett., 35, 651(1979).
3) K. Itoh, M. Okano, A. Fujishima, and K. Honda, Abstract of the autumn meeting of the Electrochemical Society of Japan, 1985, Yokohama, p.138.
4) M. Kitayama and H. Yoneyama, Abstract of the autumn meeting of the Electrochemical Society of Japan, 1985, Yokohama, p.180.
5) M. Ogasawara, K. Funahashi, and I. Iwata, Mol. Cryst. Liq. Cryst., 118, 159 (1985).
6) K. Itoh and J. O'M Bockris, J. Electrochem. Soc., 131, 1266(1984).
7) S. Asavapiriyanont, G. K. Chandler, G. A. Gunawardena, and D. Pletcher, J. Electroanal. Chem., 177, 229(1984).
8) P. Salvador, J. Phys. Chem., 89, 3863(1985).
9) E. M. Genies, G. Bidan, and A. J. Diaz, J. Electroanal. Chem., 149, 101(1983).
10) Y. Aikawa, T. Sagara, and M. Sukigara, Abstract of The Fifth International Conference on Photochemical Conversion and Storage of Solar Energy, 1984, Osaka, pp.55-56.

(Received December 28, 1985)